

This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

SO₃H-containing functional carbon materials: Synthesis, structure, and acid catalysis

Jyoti Konwar, Lakhya; Mäki-Arvela, Päivi; Mikkola, Jyri-Pekka

Published in:
Chemical Reviews

DOI:
[10.1021/acs.chemrev.9b00199](https://doi.org/10.1021/acs.chemrev.9b00199)

Published: 01/01/2019

Document Version
Accepted author manuscript

Document License
All rights reserved

[Link to publication](#)

Please cite the original version:

Jyoti Konwar, L., Mäki-Arvela, P., & Mikkola, J.-P. (2019). SO₃H-containing functional carbon materials: Synthesis, structure, and acid catalysis. *Chemical Reviews*, 119(22), 11576–11630.
<https://doi.org/10.1021/acs.chemrev.9b00199>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

A comprehensive review on SO₃H containing functional carbon materials: synthesis, structure and acid catalysis

Lakhya Jyoti Konwar^{†*}, Päivi Mäki-Arvela[‡], Jyri-Pekka Mikkola^{†‡}

[†]Technical chemistry, Department of Chemistry, Chemical-Biological Centre, Umeå University, SE-901 87 Umeå, Sweden

[‡]Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Åbo-Turku, FI-20500, Finland

*Corresponding author email: - lakhya07@gamil.com, lakhya.konwar@umu.se

CONTENTS

Abstract

1. Introduction

2. -SO₃H Containing functional carbon materials

2.1. Structure of sulfonated carbons

2.2. Surface chemistry and bulk composition of sulfonated carbons

3. Carbon supports or precursors

3.1. Semi-carbonized materials

3.2. Activated carbons

3.3. Ordered mesoporous carbons

3.4. Nanostructured carbons

3.5. Silica-carbon nanocomposites

3.6. N-doped carbons and carbon nitride

4. Sulfonation methods

4.1. In-situ functionalization approach

4.1.1. Simultaneous sulfonation and carbonization with H₂SO₄

4.1.2. Simultaneous sulfonation and carbonization with organosulfonic acids

4.1.3. Other in-situ sulfonation methods

4.2. Post-grafting functionalization approach

4.2.1. Concentrated H₂SO₄ and fuming H₂SO₄

4.2.2. Sulfonation with ClSO₃H

4.2.3. Aryldiazonium sulfonates (4-benzene-diazoniumsulfonate)

4.2.4. Other sulfonating reagents

5. Catalytic applications

5.1. Esterification reactions

5.2. Acetalization and etherification reactions

5.3. Transesterification reactions

5.4. Hydrolysis and hydration

5.4.1. Hydrolysis of polysaccharides

5.4.2. Hydrolysis of carboxylic acid esters

5.4.3. Hydration

5.5. Dehydration and ring opening of monosaccharides

5.6. C-C bond forming reactions

5.7. Other industrially relevant reactions

6. Activation and deactivation

6.1. Deactivation and regeneration in alcoholic media

6.2. Deactivation and regeneration in hydrothermal and solvothermal environments

6.3. Other modes of deactivation and regeneration

7. Conclusions and future outlook

Author Information

Corresponding Authors

Notes

Biographies

Acknowledgments

References

ABSTRACT

The ‘sulfonated carbons’ are a new class of metal free solid protonic acids characterized by their unique carbon structure and Brønsted acidity ($-H_0 = 8-11$) *on par* to conc. H_2SO_4 . These carbon materials covalently functionalized with SO_3H groups via C- $PhSO_3H$ or C- SO_3H linkages can act as versatile water tolerant solid acids. Due to their low production costs, unique surface chemistry, high chemical and thermal stability as well as tailorable pore structures they are regarded as potential substitutes to liquid H_2SO_4 . Catalysis, in particular biomass and large molecule catalysis

is one of the important areas in which acidic carbons have demonstrated exceptional activity and selectivity, outperforming traditional solid acid catalysts (cation-exchange resins, sulfated oxides, and acidic zeolites). In this review we address developments in the different types SO₃H and PhSO₃H functionalized acidic carbon materials, their structure, active sites and surface properties, applications in catalysis, as well as activation and deactivation characteristics covering important literature since 2004. In particular, we aim to provide a systematic discussion on the specific merits and demerits of such materials obtained from different carbon precursors and functionalization methods which directly influence the structure-stability-acidic properties and catalytic performances.

1. INTRODUCTION

Acids are an important class of chemical species (pH<7) characterized by their unique ability to either donate H⁺ ions (Brønsted acid) or to form a covalent bond with an electron pair (Lewis acid). Mineral acids such as H₂SO₄, HNO₃, HCl, H₃PO₄ etc. have diverse applications in numerous industrial and chemical processes including mineral processing, fertilizer production, detergent manufacturing, as catalysts, electrolytes and industrial cleaning agents. On the contrary, organic acids such as acetic acid, ascorbic acid, lactic acid and so forth are primarily used by food and pharmaceutical industries. With an annual production close to 290 million tonnes, H₂SO₄ remains by far the most important industrial chemical produced. In fact, H₂SO₄ production capacity has been viewed as an indicator of a nation's industrial strength by many economists.¹⁻² The main consumers of H₂SO₄ are the chemical and fertilizer manufacturing industries followed by oil refineries, metal processing and fiber and pulping industries. Due to its low cost, H₂SO₄ has been widely used in chemical and metallurgic industries for various reactions and treatments (also as a catalyst) such as nitration, sulfonation, esterification and alkylation of organics as well as electrolysis, electroplating (H⁺ conductor) and acid pickling of metals. In short, H₂SO₄ has a direct or indirect role in the production of almost all manufacturing goods that we use today. As a result of such widespread industrial use, large volumes of waste H₂SO₄ are also generated annually (ca. 15 million tonnes of H₂SO₄ are consumed annually as unrecyclable sulfates) which cause severe environmental hazards and disposal issues (neutralization generates large volumes of gypsums or highly concentrated ammonia wastewater). Although H₂SO₄ recovery is technically possible and even practiced at industrial scale, such processes tend to be extremely expensive due to use of

energy demanding distillation and regeneration processes and thus cannot be regarded as a solution in long term and in the spirit of green chemistry.¹⁻⁴ Perhaps, the biggest drawback upon use of these liquid acids is that they are employed as catalysts or co-catalysts in chemical processes which complicates the downstream product recovery as additional steps for separation, purification and detoxification become necessary to remove the unreacted acids from the products (e.g. biomass pretreatment during ethanol production).⁵ Accordingly, these limitations have stimulated the study of recyclable strong solid acids as eco-friendly and ‘green’ replacement for unrecyclable ‘liquid acids’ such as H₂SO₄. Inorganic solid oxide hybrids such as zeolites⁶, tungstophosphoric acid (H₃PW₁₂O₄₀.6H₂O), heterogenized heteropolyacids^{7,8}, WO₃ on metal oxides,⁹ sulfated metal oxides,¹⁰ as well as strongly acidic cation-exchangeable polymer resins (amberlite, amberlyst and dowex)¹¹ and perfluorosulfonated ionomers (nafion)¹² are some of the most extensively studied/used solid Brønsted acids and H⁺ conductors. However, with the exception of zeolites, the practical large scale application of such solid acids is limited by a number of issues including complex, expensive synthesis procedures, poor acid activity (typically much lower than that of sulfuric acid), operational stability and reusability. On the other hand, zeolites (e.g. H-ZSM-5) enjoy wide commercial success as catalysts in petroleum refining, gas conversion and related petrochemical industries.⁶

Until recently, a major obstacle to the progress of research in the field of solid acid catalysis has been the lack of an affordable material whose acid activity (strength, acid site concentration, H⁺ conductivity etc.), stability and cost is *on par* to that of liquid H₂SO₄. An ideal solid substitute for the applications considered for H₂SO₄ should possess several strong protonic or Brønsted acid sites with Hammett strengths less than or equal to that of H₂SO₄ ($H_0 \leq -11$) which are stable in H₂O and organic solvents, at elevated temperatures and pressures. Nevertheless, the perfluorosulfonated ionomers and SO₃H containing cation exchange polymer resins such as Amberlyst, Amberlite or Dowex exhibit acidic properties comparable to liquid H₂SO₄, albeit these materials tend to be expensive upon large scale use and suffer from issues related to thermal stability (T_{\max} 120-190 °C) and chemical stability, active site leaching and regeneration.

The SO₃H functionalized acidic carbon materials or ‘sulfonated carbons’ are a relatively new addition to the family of solid protonic acids, characterized by their low production cost and high Brønsted acidity ($H_0 \leq -11$) *on par* to conc. H₂SO₄. These materials have been recommended by many experts as ideal substitutes to liquid H₂SO₄ in applications including catalysis,

electrocatalysis, water treatment, CO₂ capture and energy storage, owing to features such as high chemical, mechanical and thermal stability, tailorable pore structure as well as surface chemistry.¹³⁻²³ Catalysis, in particular large-molecule and biomolecule catalysis is one of the most interesting areas in which sulfonated carbons have been demonstrated to outperform traditional homogeneous mineral acids and solid acid catalysts (zeolites, ion-exchange resins, sulfated metal oxides etc.).¹⁴⁻¹⁶

The use of heterogeneous, metal-free carbocatalysts in organic transformations as well electrochemical processes has rapidly progressed over the last decade as a part of our continuous effort towards realization of green and sustainable chemical processes, and also, in part as a result of diminishing supplies of rare earth and novel metals commonly used as catalysts in industrial processes. Carbon materials including nanostructured carbons, activated carbons, glassy carbon, ordered carbon materials and doped carbon materials have been identified as potential low-cost catalysts and/or electrocatalysts for many industrial processes.¹³ Among the different metal free carbocatalysts ‘sulfonated carbons (or sulfated carbons)’ are the most comprehensively studied carbocatalysts.¹³⁻²¹ Since their introduction in 2004 as solid acids by Hara and co-workers^{14-16,22}, these materials have gained considerable attention as alternative low-cost catalysts for various organic transformations.²² This can be recognized from the rapid growth in the number of articles and patents describing the preparation, characterization and applications of such SO₃H containing acidic carbon materials since 2004. These metal free carbocatalysts are generally prepared via sulfonation of incompletely carbonized organic matter or via semi-carbonization of organic/carbon matter in strong sulfonating agents like conc. H₂SO₄.^{14,15,22,23} A detailed discussion on the synthesis, structure and catalysis of sulfonated carbon materials are given in the sections below.

Although numerous review articles, chapters and books addressing the synthesis, properties and application of the traditional inorganic solid acids, sulfonic acid resins and metal free carbocatalysts can be found in literature,^{13,24,25,26,27,28} to date, a comprehensive review addressing ‘sulfonated carbons’ encompassing aspects of their synthesis, structure, surface chemistry, active sites activation/deactivation and applications in catalysis is missing. In particular, a systematic evaluation of the merits and demerits of such materials obtained from different carbon precursors and preparation methods which play a critical role in the structural and acidic properties have not been addressed. The aim of this review is to give a comprehensive account on the structure, active sites and catalysis of SO₃H functionalized carbon materials, highlighting the

influence of raw material and preparation routes on the surface, acidic characteristics, stability and activity of these materials.

2. -SO₃H CONTAINING FUNCTIONAL CARBON MATERIALS

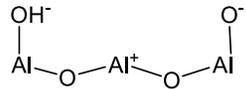
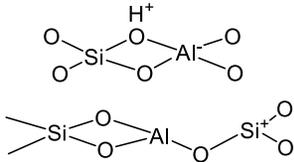
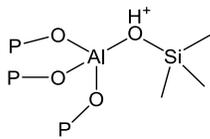
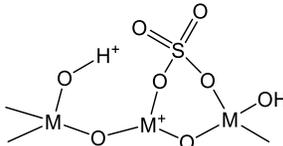
In general, these SO₃H containing acidic carbons are obtained by sulfonating amorphous carbon materials. Depending on the surface properties of the carbon precursor, it is possible to obtain a wide range of materials with different textural properties and degrees of SO₃H functionalization.¹⁴⁻¹⁶ Despite the fact that Hara and co-workers are credited to coin the term ‘*sulfonated carbons*’, in reality the existence of these SO₃H containing carbon materials can be traced far back.²⁹⁻³¹ In fact, the earliest account of such SO₃H functionalized carbon materials can be found in several patents published between 1960-2000.²⁹⁻³⁴ These patents describe a number of different processes for modification of carbon blacks yielding a product called sulfonated carbon black, wherein large quantities of sulfonic acid groups have been covalently attached to a carbon surface, thus rendering unique surface and acidic properties (most importantly enhanced hydrophilicity). The surface modification was achieved either by ‘*treating carbon black with (NH₄)₂SO₄/(NH₄)₂SO₃ and heating the resulting compound to a high temperature, sufficient to decompose the ammonium compounds*’ or by ‘*treating carbon blacks with gaseous SO₃, oleum or fuming H₂SO₄ under ambient conditions*’.²⁹⁻³¹ Similarly, sulfated carbons were also obtained by either ‘*reacting organic sulfite intermediates with carbon black and related carbonaceous materials*’ or ‘*by reacting carbon materials with diazonium salts containing SO₃H groups*’.³²⁻³⁴ Due to their enhanced hydrophilicity these materials were traditionally suggested as components in ink formulations, fillers, pigments in paper and related cellulosic products as well as H⁺ exchange materials.²⁹⁻³⁴

Nonetheless, Hara and co-workers were perhaps the first to identify these SO₃H modified carbons as versatile solid Brønsted acid catalysts.^{22,23} Such functionalized acidic carbons have been obtained from a wide variety of inexpensive carbon sources including natural organic carbon matter such as sugars, carbohydrates, cellulosic materials, lignin,^{14,15,22,23,35-37} peat, agro-wastes (e.g. husk, straw, seed cover, cow manure, corn cob),³⁸⁻⁴⁴ industrial waste carbons (oil-pitch, polycyclic aromatic compounds, petroleum coke, glycerol, char etc.)^{22,44-47} and commercial polymer resins^{48,49}. Similar acidic carbons have also been obtained by sulfonating more expensive carbon supports such as templated carbons (ordered mesoporous carbons, zeolite templated

carbons),⁵⁰⁻⁵⁴ commercial carbon supports (glassy carbon, active carbon, carbon foam and carbon fibers)^{22,53-55} as well as nanostructured carbons (graphene, graphene oxide, nanotubes and carbon dots)⁵⁶⁻⁶⁴. Sulfonation of carbon supports is typically achieved by reacting it with a sulfonating reagent such as concentrated H₂SO₄, fuming H₂SO₄, gaseous SO₃, ClSO₃H, *p*-toluenesulfonic acid or SO₃H containing aryl diazoniums to name a few.^{14,15,22,23,29-65} Sulfonated carbons have also been prepared by semi/incomplete carbonization of SO₃H acid containing macromolecules such as lignosulfonate and polystyrenesulfonic acid and polymer precursors like 4-hydroxybenzenesulfonic acid, hydroxyethylsulfonic acid and alike.⁶⁶⁻⁷¹ Lignosulfonate or lignosulfonate salts have also been converted to SO₃H acidic resins by phenol-formaldehyde type condensation reactions⁷²⁻⁷⁴. Sulfonated carbons have been typically investigated as alternative solid acid catalysts for industrially important organic reactions such as esterification, transesterification, hydrolysis, saccharification, acetylation, acetalization, alkylation, dehydration and related reactions in batch and as well as continuous flow reactors.^{14,15,22,23,29-71} Selected studies have also been conducted towards elucidating the reaction kinetics, mechanisms, as well as activation and deactivation of SO₃H sites.⁷⁵⁻⁸⁰ In addition, non-catalytic applications of these carbon materials have been demonstrated in the areas of water purification,¹⁷ CO₂ capture,¹⁸ reactive extraction,⁸¹ energy harvesting and storage¹⁹⁻²¹ and as components in ink formulations and composite materials.²⁹⁻³⁴

Irrespective of the rapid advancements in the field sulfonic acid functionalized carbon materials during the last 14 years, a generalized definition or classification for these acidic carbon materials is not yet available. As a result, all the carbon and semi-carbonized materials incorporating SO₃H sites are referred to as *sulfonated carbons* or *sulfated carbons*, irrespective of the differences in structure, textural and surface acidic properties. These differences can be usually traced to the variations in preparation methods and properties of carbon precursor (or support) used in the sulfonation step. The need of a separate classification system is also justified by the dissimilarities in the structure, surface chemistry and acidity of these materials with the traditional solid acids (Table 1).^{5-13,24-28,82-90}

Table 1. Composition and acidic properties of different solid acids

solid acid	chemical composition	acid sites	Hammett acidity ($-H_0$)	strength ($\Delta H^\circ_{adsNH_3}/kJ, mol^{-1}$)	stability		Ref.
					thermal ($^\circ C$) ^b	chemical	
alumina	Al ₂ O ₃		4.4~5.7	50-130	>2000	limited hydrothermal stability and poor chemical stability at low pH	82
alumosilicates e.g. silica-alumina, MCM-41, MCM-22, zeolites (H-Y, H-ZSM-5, H-beta etc.)	SiO ₂ -Al ₂ O ₃		4.4~5.7	~72-184	>1000	limited hydrothermal and chemical stability	82,89
silicoaluminophosphate (e.g. SAPO-18, SAPO-34)	SiO ₂ -AlPO ₄		4.4~5.7	113-136	~400	limited hydrothermal and chemical stability	84
tungstophosphoric acid	H ₃ [P(W ₃ O ₁₀) ₄]. xH ₂ O	H ₃ PO ₄	13.2	138-164	~95	hygroscopic, poor hydrothermal and chemical stability	85
sulfated metal oxides	SO ₄ ²⁻ -MO (MO=ZrO ₂ , TiO ₂ , SnO ₂ , Al ₂ O ₃ etc)		16	100-155	~400	good hydrothermal and chemical stability	10,87

WO ₃ on metal oxides	WO ₃ -MO (MO=ZrO ₂ , TiO ₂ , SnO ₂ etc)		14.6	150	~200	good hydrothermal and chemical stability	24,88
sulfonated silica	SiO ₂ -SO ₃ H			133-136	up to 250	poor hydrothermal and chemical stability	90
nafion	C ₇ HF ₁₃ O ₅ S·C ₂ F ₄		11-13	158	250-300	excellent hydrothermal and chemical stability	90
sulfonic resins (Amberlyst, Amberlite, Dowex)	C ₁₈ H ₁₈ O ₃ S		11-13	110-150	100-170	good hydrothermal and chemical stability	57,97
sulfonated carbon	Variable (C _a H _b O _c S _d)		8-11	50-220	up to 250	excellent hydrothermal and chemical stability	57

^bin inert (N₂) atmosphere

Thus, one of the objectives of this review is to introduce a simplified classification system for these acidic carbon materials on the basis of their structure, textural properties and preparation method (sulfonation). Sulfonated carbons may be defined as a new class of carbon materials covalently functionalized with SO_3H groups or sites, characterized by their distinct '*hydrophilic-oxyphilic*' properties and strong '*Brønsted acidity*' which is *on par* to that of the sulfonic acid resins and liquid H_2SO_4 . The basic structural unit of these materials can be approximated by a flexible amorphous carbon (or oxidized carbon) framework which has been covalently linked with several sulfonic (SO_3H) acid groups (Figure 1). The sulfonic groups are usually introduced onto the carbon framework structure via chemical modification or functionalization techniques in a step commonly referred to as 'sulfonation', whereupon the sulfonic group density varies in the range of (0.05-7.3 mmol/g), depending on the sulfonation method used and framework structure of the parent carbon support.^{14-16,22,23,29-81,91-96} These Brønsted acidic sulfated carbons may be subdivided into several categories on the basis of their textural and surface properties as outlined in Table 2 below. In fact, the nature of carbon support and the method of SO_3H functionalization have direct impact on the resulting material properties and cost.

Table 2. Overview of different types of SO₃H functionalized acidic carbons obtained by sulfonating different carbon supports

acidic carbon	carbon support (or precursor)	comments	properties					application
			specific surface area (m ² /g)	average pore size (nm)	acidity (mmol/g)		thermal stability (°C) ^b	
					SO ₃ H	total ^a		
non-porous sulfonated carbons	(a) hydrochars, biochar and partially carbonized materials or	<ul style="list-style-type: none"> ➤ low-cost precursors ➤ readily available ➤ low degree of polycondensation ➤ highly hydrophilic ➤ easily functionalized with H₂SO₄ by in-situ or post grafting methods 	<2	n.r	0.56-4.9	1.4-7.2	190-250	<ul style="list-style-type: none"> ➤ acid catalysis (hydrophilic reactants in both polar and apolar media)
macroporous sulfonated carbons	(b) polyaromatic compounds, natural organic matter, and waste materials partially carbonized materials		up to 120	>50				
mesoporous sulfonated carbons	ordered mesoporous carbons (templated and non-templated) and mesoporous activated carbons	<ul style="list-style-type: none"> ➤ moderate to very high cost precursors ➤ commercially available support ➤ rigid and hydrophobic amorphous carbon framework with high degree polycondensation 	75-1191	3.1-28.1	0.14-1.88	1.74-8.2	~250	<ul style="list-style-type: none"> ➤ acid catalysis (large hydrophilic or hydrophobic reactants in both polar and apolar media)

		<ul style="list-style-type: none"> ➤ very difficult to functionalize with H₂SO₄ 						
microporous sulfonated carbons	activated carbons and templated microporous carbons	<ul style="list-style-type: none"> ➤ high cost precursors ➤ commercially available ➤ rigid and hydrophobic amorphous carbon framework with high degree polycondensation ➤ very difficult to functionalize with H₂SO₄ 	800-2000	<2	0.5-1.1	0.8-5.4		
nanostructured sulfonated carbons	nanostructured carbon materials (nanotubes, graphene, graphene oxide and alike)	<ul style="list-style-type: none"> ➤ very high precursor cost ➤ limited commercial availability ➤ very rigid (sp² like) carbon framework ➤ often hydrophobic ➤ difficult to functionalize with H₂SO₄ 	215-500	n.r	0.68-2	0.67-2.85	~250	<ul style="list-style-type: none"> ➤ acid catalysis ➤ electrode fabrication ➤ proton conductor ➤ chemical sensing ➤ water treatment

^a SO₃H, carboxylic acid, lactone, phenol and carbonyl groups

^b in inert (N₂) atmosphere

n.r = not reported

These acidic (sulfonated) carbons retain the structure and textural properties of parent carbon/carbon support irrespective of the nature of sulfonation reagent or sulfonation reaction conditions which served as the foundation for the introduced classification system. Successful sulfonation of carbon materials is usually reflected in terms of changes in surface acidity, hydrophilicity and thermal properties. The sulfonated forms of carbon materials are typically characterized by an increased surface acidity, surface acidic strength and hydrophilicity resulting from the incorporation of additional sulfonic (SO_3H) acid groups. At the same time, the onset decomposition temperature (T_{onset}) of sulfonated counterparts shows a decline at 245-250 °C, resulting from the limited thermal stability of C-S bonds, this effect is especially noticeable for acidic sulfonated carbons based on thermally stable nanostructured and graphite like (sp^2) carbon supports.^{14-16,22,23,29-81,91-96} Nevertheless, the actual stability of sulfonic sites is also affected by the operational/process conditions (temperature, pressure, nature of reactants, presence of solvents and H_2O).⁷⁵⁻⁸⁰ The individual types of sulfonated carbons and their surface chemistry are discussed in detail in the Sections below.

2.1. STRUCTURE OF SULFONATED CARBONS

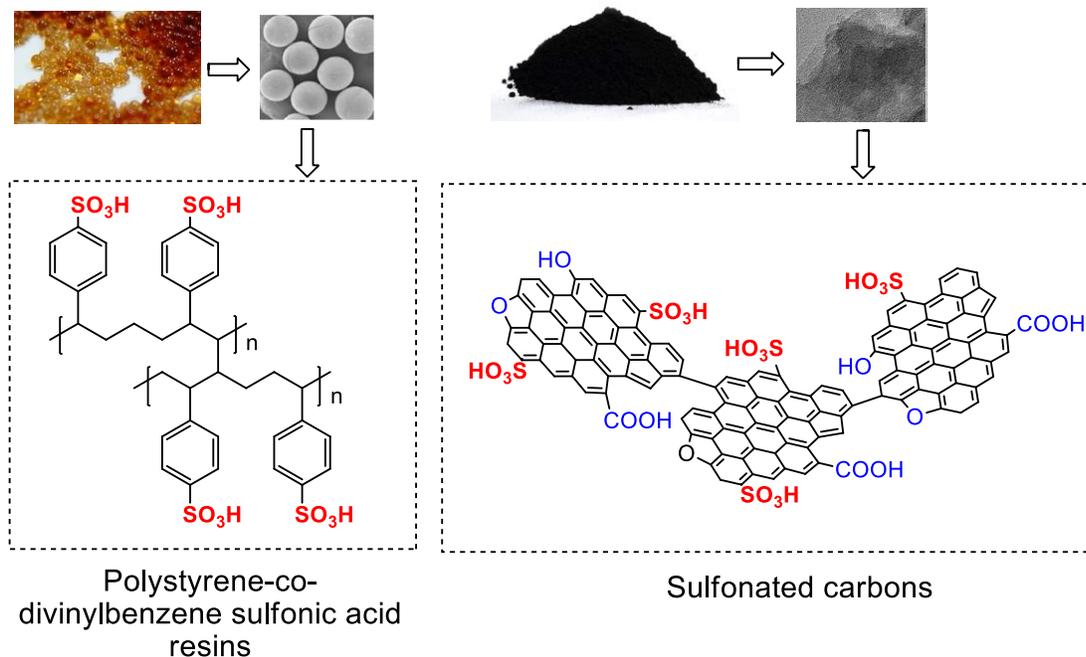


Figure 1. Structure of sulfonated carbons in comparison to polystyrene-co-divinylbenzene sulfonic acid resins.

Sulfonated carbon materials present distinct structural, physical and surface properties which renders them ideal, alternative low-cost solid acids for industrial applications. Structurally and chemically these acidic carbons are very different from inorganic solid acids due to their unique carbon framework (Table 1).^{14-16,22,23,29-81,91-96}

Among the known solid acids, the cation exchangeable *polystyrene-co-divinylbenzene sulfonic acid resins*^{11,26,97} are perhaps the most close chemical analogues of *sulfonated carbons*^{14-16,22,23,29-81,91-96} as both materials present an analogous chemical (elemental) composition and are made up of a flexible carbon based backbone that has been covalently linked to the strongly Brønsted acidic SO₃H sites (Figure 1). Nevertheless, in spite of their compositional similarities, sulfonated carbons present several advantages over the sulfonic acid resins including improved stability and low-cost. Most importantly, unlike the commercial sulfonic resins, it is possible to fine-tune the textural, acidic and hydrophilic properties of sulfonated carbons by adjusting the synthetic conditions and carbon support. The differences in the physico-chemical properties of the two classes of materials originate mainly from the difference in their carbon framework structure and surface chemistry. In case of sulfonic resins, the flexible polystyrene-co-divinylbenzene backbone results in a material with a nonporous/macroporous structure with a limited chemical, thermal (120-190 °C) and mechanical stability. In contrast, the chemically resistant and thermally inert hydrophobic amorphous carbon (sp² or sp²-sp³) core of sulfonated carbons gives rise to its superior material properties, such as higher thermal stability (up to 250 °C) and improved chemical and mechanical resistance. Furthermore, these acidic carbons retain the textural properties and surface defects of the parent carbon materials; therefore they incorporate large amounts of oxygen functionalities (OH, COOH and lactones) along with the SO₃H groups giving rise to the improved hydrophilic/oxyphilic properties (Figure 1). These oxygen functionalities may also be created upon oxidation of a carbon support by the strongly oxidizing sulfonating agents such as conc. H₂SO₄, oleum and gaseous SO₃.^{22,36,42,52-55,94,98} Such defects have generally been demonstrated to have a positive effect on the catalytic activity of these materials.¹⁴⁻¹⁶

2.2. SURFACE CHEMISTRY AND BULK COMPOSITION OF SULFONATED CARBONS

The structure, surface and textural properties of sulfonated carbons (or sulfated carbons) are influenced mainly by the chemical structure of the parent carbon support used in the sulfonation

step and the resulting acidic carbons typically retain all textural properties and defects of the support, irrespective of sulfonation reaction conditions.^{14-16,22,23,29-81,91-96,98-106} Most importantly, these SO₃H containing functional carbon materials can be manufactured from all forms of carbon allotropes with sp² (graphene, carbon nanotubes)⁵⁶⁻⁶⁴ and mixed sp²-sp³ hybridization (amorphous carbon, graphitic carbon)^{22,53-55} as well as nitrogen-doped carbons^{42,43}, carbon nitride¹⁰¹⁻¹⁰⁴ and incompletely carbonized materials^{14-16,22,23,66-75}. As a result, it is possible to obtain hydrophilic as well as hydrophobic acidic carbons with a wide range of surface SO₃H acidity (0.05-5.7 mmol/g), porosity (specific surface area ranging from ≤1-2000 m²/g) and carbon framework structures.^{14-16,22,23,29-81,91-96,98-106} Figure 2 shows some of the plausible chemical structures (framework) for sulfonated carbons derived from the different types of carbon supports. These acidic carbon materials, particularly those obtained from incompletely carbonized and defective carbon materials (hydrochars, hydrothermal carbons, oxidized carbons and chemically activated carbon), can adsorb or retain large amounts of hydrophilic molecules, including water, into the carbon bulk due to the presence of a large amount of oxygen functional groups (COOH, OH), in addition to the SO₃H groups bonded to the flexible carbon structure.^{42,66-73,74-80,91,93,96,107} Such incorporation enhances the adsorption and accessibility of hydrophilic reactants in solution to the active SO₃H sites (large hydrophilic surface area), which in turn boosts the catalytic performance of these materials in various organic transformations.

The catalytic activities of these carbon materials are reported to be equally dependent on the specific surface area and density of hydrophilic functional groups. In many instances, despite the lack of porosity (low specific surface area) in dry form and low concentration of active SO₃H sites, these materials are able to outperform mineral acids and commercial sulfonic resins owing to their unique surface-textural properties (e.g. those solid acids derived from hydrochars, hydrothermal carbons and semi-carbonized organic matter).^{14-16,22,23,66-73,74-80,91,93,96,107} It is also important to note that the sulfonation step has a direct impact on the surface acidity (sulfonic density, hydrophilicity) and to a lesser extent on the porosity of these carbon framework-based solid acids. In case of incompletely carbonized sulfonated carbon materials, a strong correlation has also been observed between the carbon surface structure and SO₃H density with the carbonization temperature before sulfonation.^{14-16,22,23,66-73,75-80} Also, different sulfonating agents possess different efficiencies (the efficiency is mainly affected by the chemical structure of the carbon precursor or support). For conventional, strong sulfonating agents such as conc. H₂SO₄,

oleum, gaseous SO_3 or ClSO_3H , it was observed that the non-rigid partially-carbonized materials (hydrochars, biochar and semi-carbonized organic matter) are much easier to be sulfonated in comparison to the more rigid and ordered graphite like sp^2 carbons (nanostructured carbons, templated carbons and activated carbon obtained at high temperatures).^{14-16,22,23,65-73,75-80,91-94} On the other hand, the ordered graphitic carbons are more effectively sulfonated by a reductive alkylation/arylation of sulfonic acid containing arylradicals.^{42,48-56,63,95,96,98,99,105,106} A detailed discussion on the different carbon supports and sulfonating reagents and their effects on material properties are presented in section 3 and section 4 below.

X-ray powder diffraction (XRD) and laser Raman microscopy conducted on different sulfonated carbons have confirmed that these materials exhibit a structure consistent with amorphous or disordered carbon materials.^{15,22,35-80} Irrespective of the method of production or carbon precursor used, the XRD patterns always exhibit two distinct diffraction peaks near 20° and 45° attributed to the graphitic (002) and (101) planes. Similarly, the Raman spectra of sulfated carbons always show the characteristic D (1350 cm^{-1} , A_{1g} D breathing mode) and G (1580 cm^{-1} , E_{2g} G mode) bands related to the aromatic carbon/graphene sheets in the carbon bulk. The small variations observed in the intensity of XRD peaks and I_D/I_G intensity ratios of Raman peaks are related to the structural order of the carbon material. Generally, sharper XRD peaks and low I_D/I_G ratios are observed for rigid or ordered carbon materials (active carbon, ordered carbons, graphene and related carbon materials obtained at high carbonization temperatures).^{15,22,35,82-110}

Organic elemental analysis, energy-dispersive X-ray spectroscopy (EDX) and Fourier-transform infrared spectroscopy (FTIR) studies on different sulfonated carbons have confirmed the significant variations observed upon the composition and surface chemistry of these materials. Typically, the acidic carbons derived from semi-carbonized materials such as those derived from biochars, hydrochar and hydrothermal carbons exhibit a highly functionalized surface structure with large O/C, S/C and H/C ratios.^{65-73,75-80,91-94} In contrast, those materials derived from more rigid carbons such as nanostructured carbons, activated carbon and template carbons treated at elevated temperatures ($\geq 700^\circ\text{C}$), exhibit a less functionalized carbon surface structure characterized by low O/C, S/C and H/C ratios.^{42,48-56,63,95,96,98,99,105,106}

In the case of post-sulfonation materials, the presence of sulfonic groups are confirmed by the appearance of the characteristic S=O symmetric (1033 cm^{-1} and 1008 cm^{-1}) and asymmetric

SO₂ (1175 cm⁻¹ and 1240 cm⁻¹) stretching bands in FT-IR. However, such analysis do not give any information on the nature of linkage between support and SO₃H groups.^{14-16,22,23,29-81,91-96,98-106} Typically, further confirmation on the presence of covalently bonded SO₃H and/or PhSO₃H sites on sulfonated carbons are usually based on X-ray photoelectron spectroscopy (XPS) and solid-state ¹³C CP/MAS-NMR studies. ¹³C CP/MAS-NMR particular is very useful analytical technique for characterizing the different C-SO₃H or Ar-SO₃H linkages with the carbon support.^{14-16,67,76-78} XPS conducted on these carbons have confirmed the presence of both acidic –SO₃H groups (S2p photoelectron peak at 168.5 eV corresponding to oxidized S species) and low-valent S species such as -S-, -SH, C-S (S2p photoelectron peak at 164 eV).^{14-16, 22,23,29-81} These low-valent S species are typically formed in small amounts during carbonization and/or sulfonation steps by the carbothermal reduction of SO₃H sites (Ar-SO₃H+C→Ar-SH+CO₂).^{42,66,67} Therefore, the oxidation state of S sites in acidic carbons should be carefully evaluated by XPS to confirm the presence of active SO₃H sites. Analogously, solid-state ¹³C CP/MAS-NMR studies conducted on the acidic carbon materials have confirmed the presence of C-SO₃H or C-PhSO₃H, as well as phenolic C-OH, and C-COOH bonds covalently linked to polycondensed amorphous carbon frameworks (the characteristic chemical shifts appear at 46, 140, 150 and 177 ppm), such studies also reveal a great deal of information regarding the degree of polycondensation as well as the presence of furanic residues in the carbon structure.^{15,22,71,67,91,92} The ¹³C CP/MAS-NMR is a very useful analytical tool for probing the stability and deactivation of SO₃H sites in acidic carbons. To summarize, these analytical and spectroscopic characterizations give valuable information on the structure and active sites of acidic carbons which is vital to gain insights into mechanisms of surface catalysis occurring in these new carbon materials.

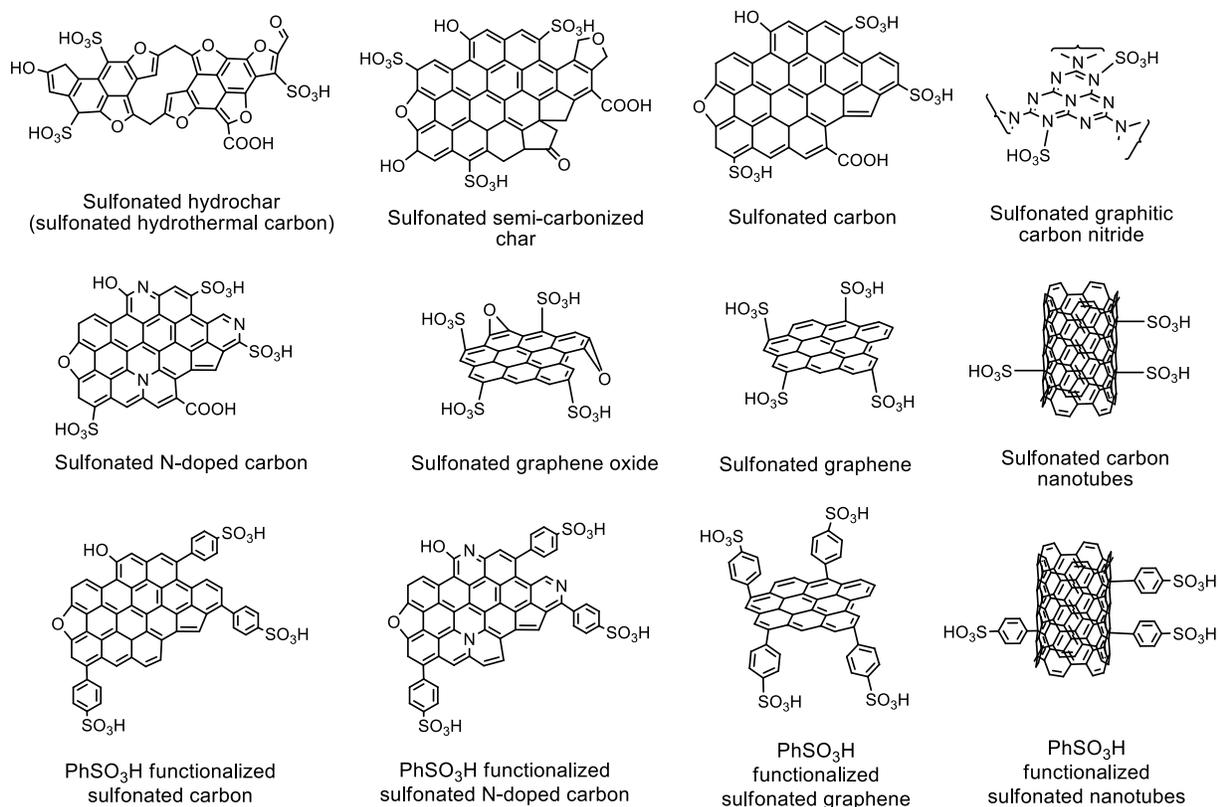


Figure 2. Plausible chemical structures (framework) for sulfonated carbons obtained from different carbon supports functionalized by SO₃H or PhSO₃H sites.

Acidic properties of these multifunctional acidic carbons have been extensively studied using a wide range of analytical techniques such as acid-base neutralization (Boehm) titrations, Hammett indicators tests, temperature programmed desorption (TPD), NH₃-temperature programmed desorption (NH₃-TPD), NH₃ chemisorption, NH₃ adsorption calorimetry, pyridine probe FTIR and thermogravimetric analysis (TGA).^{14-16,22,23,29-81,91-96,98-106} These methods have been used to characterize SO₃H functionalized carbon materials with sulfonic site densities ranging from 0.05-4.9 mmol g⁻¹. The acidic strength of carbons have been experimentally confirmed to be comparable to H₂SO₄ in the Hammett H_0 scale ($-H_0$ 8~12).^{14-16,22,23,29-81,91-96,98-107} Acid-base back titrations and NH₃-TPD studies have confirmed the presence of both weak and strong acid sites, whereupon the weak sites were attributed to COOH, phenolic OH and lactonic groups while the strong sites are characteristic for SO₃H groups. Similarly, microcalorimetric NH₃ adsorption

studies have revealed the presence of sites of different acid strength ($\Delta H_{ads} \sim 50-220, \text{ kJ.mol}^{-1}$)

¹⁾ which were attributed to the presence of Brønsted acidic COOH and SO₃H sites.⁵⁷ Nevertheless, it is also important to point out that temperature programmed techniques should be carefully used upon estimation of surface acidity of such carbon materials (preferably in the presence of MS detector), as the use of temperature programmed techniques such as NH₃-TPD and TGA for acidity

measurement easily lead to overestimation of acid site concentrations. The acidity values obtained by these methods are always higher than those based on NH₃ microcalorimetry and neutralization titrations.^{40,42,46,94,108} Such overestimation is related to the presence of volatile gases such as CO, CO₂, H₂O and SO_x which are released along with NH₃ upon the decomposition of surface functional groups from acidic carbons at temperatures >250 °C during TPD and TGA measurements.^{22,94} The acidic sites of selected sulfonated carbons (sulfonated active carbon and sulfonated graphene oxide) have also been studied by pyridine FTIR; interestingly, these studies have revealed the presence of both Brønsted (bands at 1633 cm⁻¹ and 1531 cm⁻¹) and Lewis sites (broad band at around 1460 cm⁻¹). The origin of Lewis sites was explained in terms of electron inductive effect of S=O double bonds of SO₃H sites similar to sulfated zirconia and sulfated silica materials.^{57,109} Nevertheless, this technique may be less practical for characterizing acidity of the highly functionalized hydrochars and semicarbonized material due to presence of overlapping background bands. Therefore it is our recommendation to use a combination of analytical or measurement techniques to accurately estimate the surface acidity and hydrophilicity of such sulfonated carbons.

3. CARBON SUPPORTS OR PRECURSORS

The development of heterogeneous, metal-free carbocatalysts for use in organic transformations and electrochemical processes has gained significant momentum in recent years, in part as a result of diminishing supplies of rare earth and noble metals commonly used as catalysts in industrial processes. Carbon materials including nanostructured carbons, activated carbons, glassy carbon, ordered carbons and doped carbon materials have been identified as potential low-cost catalysts and/or electrocatalysts for many industrially important reactions. The catalytic activity of these carbon materials have been attributed to the structural defects (e.g. surface oxides, heteroatom doping) and unique electronic properties that give rise to characteristic acid, base or redox sites.¹³

Acidic carbons containing SO₃H groups or sulfated carbons have gained considerable attention as alternative metal-free solid Brønsted acid catalysts for various organic transformations. In particular, during the last five years, an extensive amount of research effort has been directed towards understanding the synthesis, structure and catalysis (active sites, activation and deactivation) of these acidic carbons. These metal free acidic carbocatalysts have been

obtained from a wide range of carbon precursors and carbon support sources including commercial carbons, activated carbons, templated carbons, nanostructured carbons as well as inexpensive semi-carbonized materials derived from natural organic matter (biochar and hydrochar). This section gives a comprehensive account on the various carbon precursors or supports and their impact on the properties of sulfonated carbons produced. Brief comments for each carbon support with respect to its cost, availability, pore characteristics and their impact on the properties of acidic carbons are presented in Table 2.

3.1. SEMI-CARBONIZED MATERIALS

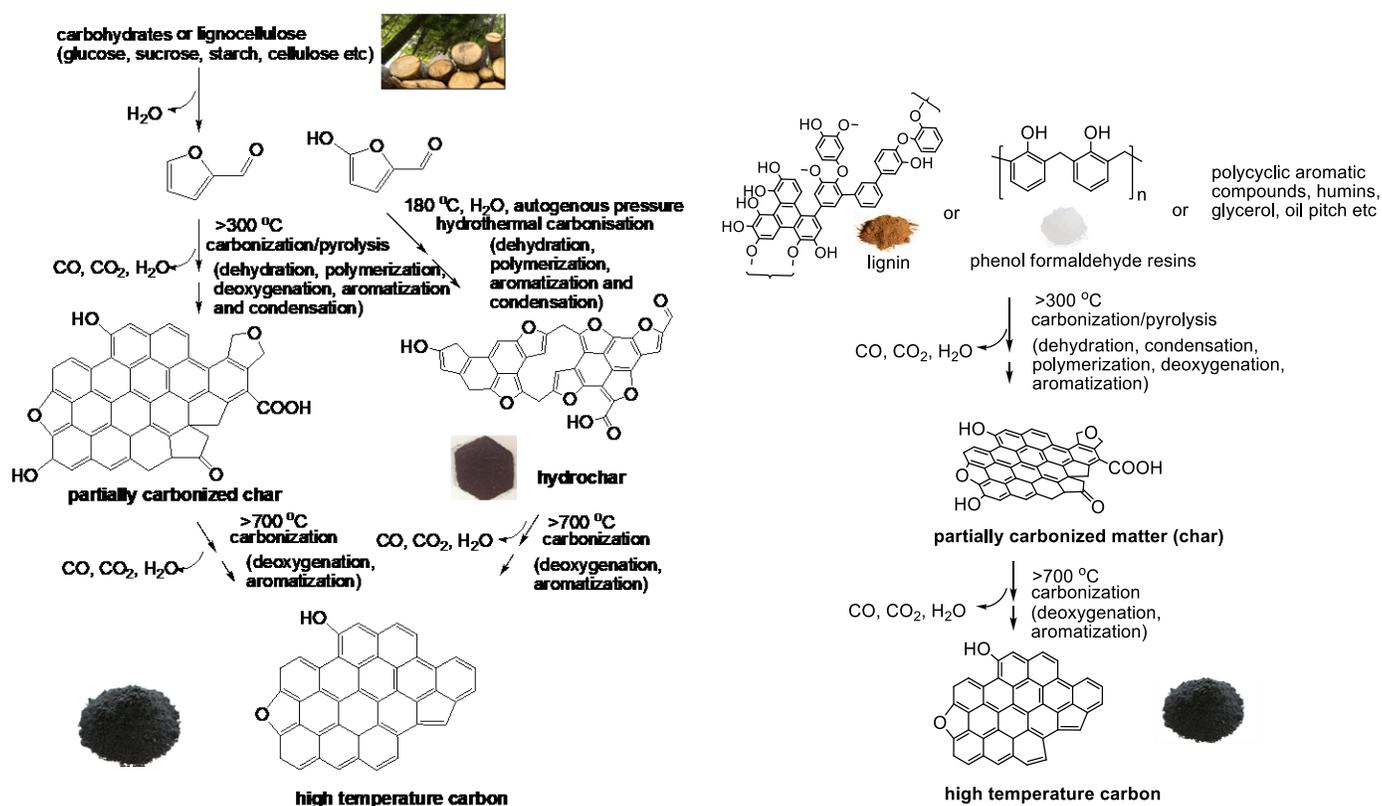


Figure 3. Plausible mechanisms for carbonization for different precursors.

Acidic carbons based on semi-carbonized materials are the most well-known and comprehensively studied class of sulfated carbon materials. Due to the ease of undergoing sulfonation and low material costs, semi-carbonized materials are regarded as the most promising precursors or supports for producing such materials. Furthermore, the acidic carbon materials obtained from such semi-carbonized carbon supports afford a high density of SO_3H sites.^{14-16,22,23}

Acidic carbons based on semi-carbonized materials are characterized by their distinct non-porous, highly functionalized amorphous or oxidized hydrophilic carbon structure (high O/C and H/C ratios) and low costs. These materials are typically obtained using inexpensive hydrochars (HC), biochars (BC) and related partially or semi-carbonized (PC) matter derived from natural, waste (lignocellulosic) or polymeric materials as the precursor (Figure 3).

The hydrochar based sulfonated materials or sulfonated hydrothermal carbons (SHCs) have been successfully obtained by reacting hydrochars derived from glucose,^{62,77,78,79,110,111} xylose,^{112,113} sucrose,¹¹⁴ cellulose,^{113,115} as well as natural organic matter such as lignin,^{113,116,117} wood meal,¹¹³ and macroalgae¹¹⁸ with a strong sulfonating agent (conc. H₂SO₄, fuming H₂SO₄ and chlorosulfonic acid). These SHCs have been demonstrated to exhibit SO₃H densities ranging between 0.57-1.58 mmol/g. A variation of this method was used by Nakhate *et al.*⁶² to obtain sulfonated graphene oxide monoliths by addition of small amounts of graphene oxide as a structure directing agent during hydrothermal carbonization of glucose.⁶² Alternatively, SHCs are obtained via one-step hydrothermal carbonization of organic molecules in the presence of organosulfates.^{65,69,70,71} Organosulfonic acids such as *p*-toluenesulfonic acid,^{65,119,120,121} hydroxyethylsulfonic acid,^{69,71,122,123} and sulfosalicylic acid¹²⁴ are some of the most commonly used sulfonating reagents, while biomolecules such as glucose,^{65,69,71,119,122,124} resorcinol,¹¹⁹ sucralose,¹²¹ citric acid,⁶⁹ acrylic acid,⁷¹ furfural,^{170,123} β -cyclodextrin,^{120,122} and lignin¹¹⁷ have been employed as the carbon source. These one-step SHCs also exhibit a non-porous surface structure but with enhanced SO₃H densities 0.7-2.1 mmol/g. In fact, using a modification of the above procedure, Shen *et al.*¹²⁵ produced a highly acidic carbon with SO₃H density of 3.1 mmol/g; obtained by subjecting the acidic hydrochar/resin like material (SO₃H density of 1.8 mmol/g) derived from hydrothermal reaction of glucose and 4-hydroxybenzenesulfonic acid to a 2nd round of sulfonation with at 98% H₂SO₄ at 170 °C.¹²⁵ Another variation of this method has been adapted for obtaining amphiphilic SHCs (SO₃H density of ~1.1 mmol/g). Starting from furfural and Na-dodecylbenzene sulfonate mixtures, these materials have been shown to exhibit enhanced activity and water tolerance upon transformation of bulky organic acids.⁷⁰ In spite of the lack of porosity resulting from a highly hydrogen bonded interconnected structure, these materials have demonstrated excellent catalytic activity and selectivity in various organic reactions; particularly upon biomass conversion (polysaccharide hydrolysis, fatty acid esterification, biodiesel production, sugar dehydrations and alike) and aqueous phase reactions. The unusually high activity

of SHCs were attributed to an enhanced adsorption of oxygenated reactants by hydrophilic surface functional groups and the unfolding of ultramicropores in polar reaction media (swelling).^{65-73,74-80,91,93,96,107,110-125} On the downside, the biggest drawbacks of these SHC are (a) the poor thermal (<200 °C) and hydrothermal stability which limit their applicability in high-temperature applications and (b) the highly hydrophilic surface and presence of low-oxidation state S species that are likely to contribute to the poisoning of catalytic sites through strong chemisorption of water, oxygenated molecules and metal impurities present in reactant streams.^{69,71,113,125,126}

Preparation of acidic carbons from partially or semi-carbonized (PC) materials and biochars (BC) is based on a multistep approach identical to the sulfonation of HCs.^{14-16,23} In this method, the acidic carbons are obtained by sulfonating PC materials or BC materials (carbonized at ≤ 600 °C) obtained from an inexpensive natural organic matter such as sugars, carbohydrates, glycerin, oil pitch, lignocelluloses, lignin, humins, deoiled press cakes, rice husk and related agro-wastes.^{14-16,23,35-37,39-44,47,91-94,127-132} Sulfonation is usually achieved by treating the carbon material with an excess of a strong sulfonating agent (usually conc. H₂SO₄ or fuming H₂SO₄), at elevated temperatures (150-200 °C), for extended periods of time (2-24 h) yielding acidic carbon materials with SO₃H densities up to 1.2 mmol/g.^{16,22,23} Nevertheless, many variations of the aforementioned processes have been developed over the years and adapted for obtaining highly acidic non-porous sulfonated carbons from semi-carbonized materials (SPC)^{14-16,22,23,35-37,39-44,47,91-94,127-132} and commercial biochar (SBC)^{46,94,133-138} derived from a natural organic matter and waste materials. Interestingly, the same method (partial carbonization-sulfonation) has been proven to be efficient even upon supporting sulfonated carbons on honeycomb monoliths (sulfonating semi-carbonized carbon coated monoliths obtained from a 65 wt.% sucrose solution via the dip-coating method). The monolithic carbocatalysts showed comparable catalytic performance with the powdered sulfated carbons and provided an interesting alternative to the conventional powdered acid catalysts.¹³⁹ Nevertheless, when compared to SHC, the SPC and SBC exhibit a more rigid, hydrophobic and thermally stable (~250 °C) carbon framework structure with a lower density of SO₃H (usually less than 1 mmol/g) and surface OH and COOH sites.

Non-porous acidic carbons have also been obtained in one-step in a non-hydrothermal process via incomplete carbonization of polycyclic aromatic compounds, glycerol, oil pitch and natural organic matter like lignin, cellulose in the presence of conc. H₂SO₄.^{22,45,140-142} While this process offers an advantage in obtaining carbon materials with a very high SO₃H density (up to

4.9 mmol/g) similar to the SHCs, the release of large volumes of acid gases (SO_2 and SO_3) during carbonization gives rise to safety and environmental hazards which renders the process impractical for large scale production.^{22,35,42,140-142} Recently, a greener built-in approach based on mild-carbonization of inexpensive water soluble sulfonated polymer salts (Na-lignosulfonate, Na-polystyrene or their mixtures) as dual carbon and sulfur (SO_3H) precursors was proposed. It was further demonstrated that by incorporating an ice-templating step before carbonization it was even possible to incorporate macro/mesoporosity into the acidic carbon structures.^{66,67} These materials presented highly stable SO_3H sites (0.32-1.24 mmol/g) with specific surface areas up to 120 m^2/g . Most importantly, these materials were demonstrated to be suitable for continuous flow applications.^{66,67}

Overall, in terms of catalysis the activity of SPC and SBC are comparable to their hydrothermal counterparts, exhibiting comparable activity in large molecule catalysis in polar media resulting from the presence of high density of surface oxygenates (large hydrophilic surface areas) and low degree of polycondensation in the carbon framework structures. Nevertheless, in spite of the drawbacks, these semi-carbonized sulfonated materials show high potential for industrial scale-up due to their low cost, ease of production and other cost benefits.

3.2. ACTIVATED CARBONS

Activated carbons are typically obtained from natural carbonaceous matter such as wood, bamboo or coal by physical activation or chemical activation. Mechanistically the process of obtaining activated carbons resembles pyrolysis/carbonization described above (Figure 3). Upon physical activation, the carbonized material is exposed to mild oxidants (CO_2 or steam) at temperatures 600–1200 °C which induce pore enlargement (activation), whereas in chemical activation the raw material is directly impregnated with activating agents (H_3PO_4 , NaOH , KOH , ZnCl_2 and alike) and carbonized at rather high temperatures (450–900 °C) to induce simultaneous carbonization/activation. Chemically activated carbons are almost identical to the amorphous carbons obtained by high temperature carbonization/pyrolysis of different natural or chemical precursors presenting a rigid, graphite like amorphous carbon structure with high degree of polycondensation. The only difference being the existence of a large number of defects/pores in the bulk particles created during activation/mild oxidation step (Figure 4). Activated carbons (AC) are well-known supports for a wide range of catalytic materials including noble metals (Pt, Pd and

Ru) owing to their high microporosity, chemical and thermal stability and commercial availability. They are also used in large scale as adsorbents for gases and as water purification media.¹³

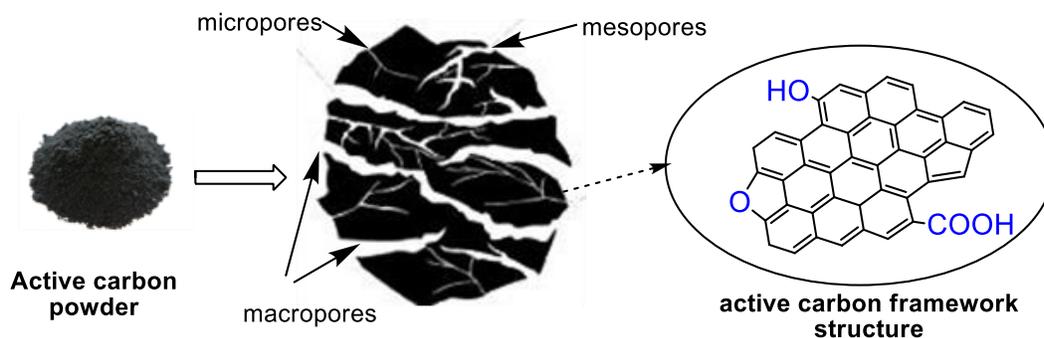


Figure 4. Chemical structure of activated carbons.

Due to their low cost, desirable textural properties and potential for undergoing sulfonation reactions, active carbons have been also studied as an alternative carbon support for obtaining sulfonated carbons by SO_3H functionalization. The incorporation of micro and/or mesoporosity into the structure of sulfonated carbons has been demonstrated to have a positive impact on the performance of these materials. Several studies have confirmed the potential of active carbons to form SO_3H functionalized porous carbocatalysts (specific surface area $\sim 119\text{-}1560\text{ m}^2/\text{g}$) by chemical grafting and demonstrated the positive effect of incorporating high porosity on the catalytic activity and selectivity of sulfated carbons.^{42,55,94,95,105,106,115} However, due to the presence of a hydrophobic and aromatized, rigid, graphite like (sp^2) core structures, sulfonation of these carbons materials by conventional conc. H_2SO_4 treatment is very difficult, particularly for graphitized active carbon and carbon materials obtained by high temperature CO_2 , steam and KOH activation.^{22,42,55,94,132,136} Successful sulfonation of ACs has been demonstrated only with strong sulfonating reagents such as fuming H_2SO_4 , gaseous SO_3 and $\text{ClSO}_3\text{H}/\text{H}_2\text{SO}_4$ mixtures, affording highly porous sulfonated active carbons (SAC).^{42,46,54,55,94,132} For example, using the aforementioned strong sulfonating reagents, chemically activated ACs (H_3PO_4 ,⁴² ZnCl_2 ,⁵⁵ KOH ,^{46,115}) as well as commercial mesoporous ACs obtained at low activation temperatures ($<700\text{ }^\circ\text{C}$) have been successfully functionalized with SO_3H sites to yield SACs. In fact, both Ellis *et al.*⁴⁶ and Hara *et al.*⁵⁵ individually observed a trend of decreasing SO_3H density and specific surface area of SACs upon increasing activation temperature for KOH and ZnCl_2 activated ACs derived from biochar (BC) and wood powder. This is in agreement with the reduced efficiency of strong

sulfonating agents towards aromatized, hydrophobic carbon structures. The use of stronger reagents and harsh sulfonation conditions also results in a partial collapse of the AC pore structure (particularly for carbons obtained at carbonization temperatures $<700\text{ }^{\circ}\text{C}$) and reduced activity. Also, the SACs materials obtained from ACs carbonized at temperatures $>700\text{ }^{\circ}\text{C}$ are susceptible to deactivation due to leaching of loosely bonded $-\text{SO}_3\text{H}$ groups (in the absence of electron-withdrawing COOH sites the $\text{C}(\text{sp}^3)\text{-SO}_3\text{H}$ in bonds are significantly weakened).^{42,46,55, 94,134-136} Most importantly, the SO_3H densities of the SACs obtained by aforementioned routes are typically lower than those of SHCs, SBC and SPCs. Nevertheless, due to their large specific surface area (high porosity), SACs based on high-temperature AC ($>700\text{ }^{\circ}\text{C}$) afford an improved catalytic activity (turnover frequency) and selectivity, particularly upon catalysis of large hydrophobic molecules (e.g. triglycerides and C16-C18 acids). The stability of the functionalized SO_3H sites is influenced by the process conditions and active carbon structure.^{42,46,55}

Recently, it has been demonstrated that sulfonation of ordered sp^2 like carbons is more efficient by chemical reduction with aryl diazoniumsulfonates (4-benzenediazoniumsulfonate) instead of conventional sulfonating agents.^{52,99} The method has several advantages including the use of mild, non-oxidative sulfonation conditions, low dosage of sulfonating agent, preservation of structure and textural properties of parent carbons and high stability of $-\text{PhSO}_3\text{H}$ sites (strongly bonded $\text{C}(\text{sp}^2)\text{-SO}_3\text{H}$ sites). Although initially developed for sulfonating nanostructured carbons (graphene, nanotubes, graphene oxide)^{56,57,63,109,143,144} and hard templated carbons (OMC, CMK) obtained at high carbonization temperatures,^{52,96,99,106,107} sulfonation with aryl diazoniumsulfonates has proven to be equally efficient upon sulfonating of ACs.^{42,95,105,106,145,146} The sulfonating agent, 4-benzenediazoniumsulfonate, is either freshly prepared by diazotization of sulfanilic acid or prepared *in-situ* by reaction of sulfanilic acid with isoamyl nitrate.^{42,56,160} The PhSO_3H containing SACs obtained by such a method are reported to exhibit SO_3H densities in the range of 0.64-1.42 mmol/g, being much higher than those SACs obtained with the strong sulfonating reagents. Most importantly, some of these materials demonstrate catalytic activity and stability which is *on par* to that of SO_3H functionalized ordered mesoporous carbons (OMC) resulting from the high PhSO_3H density and improved inter-particle diffusion and external mass transfer.^{42,95,105,106,145,146} In fact, using mesoporous AC as a carbon precursor and 4-benzenediazoniumsulfonate as a sulfonating agent, PhSO_3H functionalized (0.7-0.9 mmol/g)

mesoporous SACs with specific surface areas as high as 352-556 m²/g and large pore diameters up to 3.6-4.9 nm have been obtained.^{42,145-148}

Structurally the SACs retain the textural properties of the framework structure of the parent ACs; they usually exhibit a high thermal stability close to ~250 °C (comparable to the thermal stability of C-SO₃H or C-S bonds). The surface hydrophilicity and SO₃H density of AC derived acidic carbons are mainly depending on the activation conditions. In general, chemically activated carbons produce more hydrophilic SACs, in comparison to those obtained by physical activation and as such they are much easier to be sulfonated with H₂SO₄.^{22,42,55,145-148} In terms of catalysis, SACs are demonstrated as efficient catalysts upon converting large hydrophobic as well as hydrophilic molecules in liquid-phase reactions. Overall, these materials show potential for industrial scale-up, particularly within the biorefinery platform due to the commercial availability of ACs and noticeable cost-benefits in long-term operations.

3.3. ORDERED MESOPOROUS CARBONS

Ordered mesoporous carbons (OMCs) exhibiting highly desirable properties such as large specific surface areas, ordered mesopore structure and superior thermal and mechanical stability, have been extensively studied for applications in various fields including catalysis, electrocatalysis, energy storage, CO₂ capture, water purification and adsorption.¹⁴⁹⁻¹⁵¹ Typically, OMCs have been synthesized from hard-templating or soft-templating carbonization methods (Figure 5).

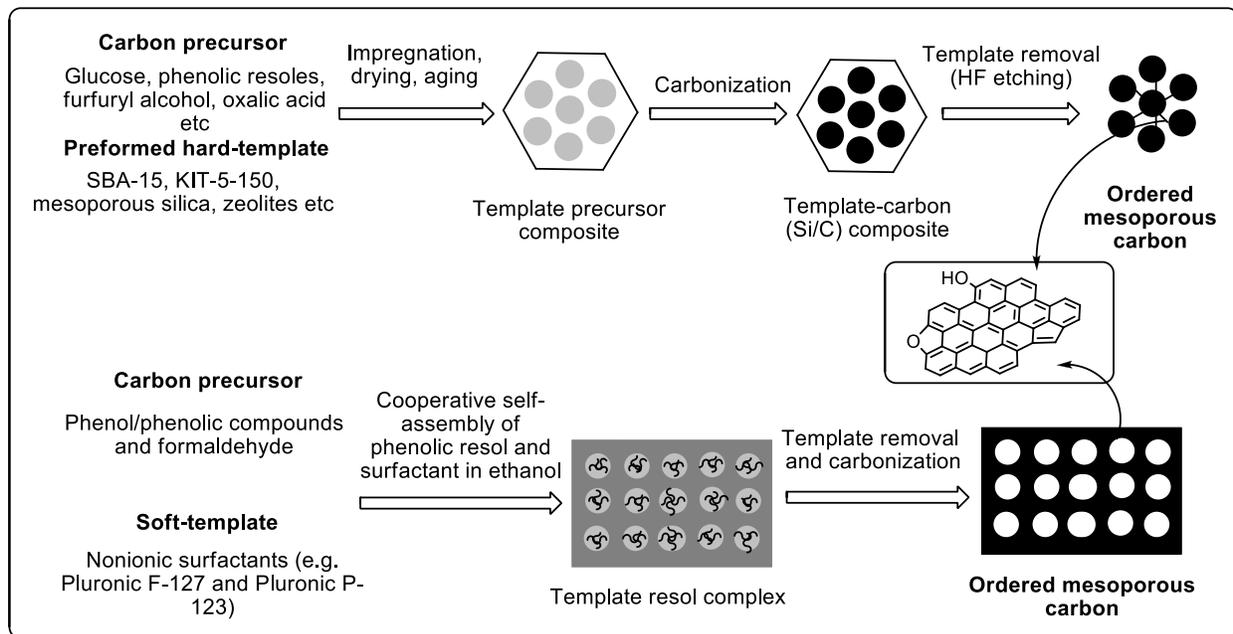


Figure 5. Schematic representation of the hard-template and soft-template approach for the synthesis of OMCs.

Owing to their large specific surface areas (up to $1800 \text{ m}^2/\text{g}$), large pore volumes (up to $2.5 \text{ cm}^3/\text{g}$), high thermal stability and potential for undergoing sulfonation reactions, OMCs have also been extensively investigated as supports to yield sulfonated ordered mesoporous carbon (SOMC).^{48-54,96,98,99,106-108,143,152-163} However, the preparation and removal of silica/inorganic templates upon the hard templating approach require multiple steps and inevitably bring severe environmental hazards from the use of HF. Soft-templated carbons have the advantage that herein one avoids the use of hazardous HF and achieves typically the same strength as in the case of hard-templated OMCs. Similarly to SACs, SOMCs can be obtained by either sulfonating the OMCs with (a) strong reagents like conc. H_2SO_4 , fuming H_2SO_4 , gaseous SO_3 , ClSO_3H and $\text{ClSO}_3\text{H}/\text{H}_2\text{SO}_4$ or (b) by chemical reduction with aryl diazoniumsulfonates (4-benzenediazoniumsulfonate) under mild conditions. Using the aforementioned process, a wide range OMCs were converted to SOMCs (sulfonated) including hard-templated OMCs (CMK-3, CMK-5, CKT, 3D0m and alike),^{48-54,96,98,99,106-108,143,152-157,159} soft-templated OMCs,^{48,49,160,161} and template free mesoporous carbons like Starbon™ 300.^{54,162,163} The SO_3H (active site) density of SOMCs was found to be greatly influenced by the sulfonating reagent and the framework structure of OMC similar to SACs. The presence of defective polycyclic aromatic rings (mixed sp^2/sp^3) and elevated reaction temperatures was found to be essential for obtaining

a highly SO₃H functionalized SOMC when using strong sulfonating reagents (conc. H₂SO₄, fuming H₂SO₄ and gaseous SO₃).^{22,48,49,51,53-55,96,98,152-155,162,163} In fact, several authors studied the influence of carbonization temperature (300-900 °C) on the functionalization of OMC materials with strong sulfonating reagents and found a direct correlation between the content of defective polycyclic aromatic groups and SO₃H density. When the carbonization temperature was raised beyond 400 °C, the content of polycyclic aromatic carbons in OMCs decreased which resulted in reduced sulfonation efficiency and a corresponding decrease in the SO₃H density; similar trends of SO₃H density have also been reported for SACs and SBCs.^{46,49,55,98,152} In contrast, 4-benzenediazoniumsulfonate and ClSO₃H were more effective upon sulfonating of OMCs with aromatized sp² like carbon framework structure obtained at carbonization temperatures >700 °C. Also, the PhSO₃H density in SOMCs increased with increasing carbonization temperatures.^{50,52,56,57,63,96,99,106-109,143,155-160}

Using the aforementioned grafting methods, highly stable (~250 °C), highly porous (specific surface areas 120-1175 m²/g and pore diameter 3.1-15 nm) and hydrophobic SOMCs with high SO₃H densities (up to 1.93 mmol/g) have been obtained from various templated and non-templated OMCs. For example, a highly ordered SOMCs with thin pore walls (~1.7 nm), large mesopores (3.77-9.77 nm), high PhSO₃H density (1.16-1.88 mmol/g) and specific surface areas (636-1175 m²/g) could be obtained using γ -Al₂O₃ templated OMCs obtained using phenolic resoles as carbon precursors and 4-benzenediazoniumsulfonate as the functionalizing reagent.^{106,159} Mesoporous silicon carbide derived OMCs presenting specific surface areas in the range of ~2800 m²/g, were also similarly sulfonated with 4-benzenediazoniumsulfonate or H₂SO₄ to obtain SOMC with acid densities up to 1.6 mmol/g.¹⁵⁵ In another work, three dimensionally ordered mesoporous (3DOM) carbon was obtained using larger zeolite particles with three-dimensionally ordered mesoporous as a hard template and furfuryl alcohol as a carbon precursor for OMC. Grafting OMC carbonized at 900 °C with 4-benzenediazoniumsulfonate, a SOMC with a very high specific surface area (1191 m²/g) and extremely large mesopores (28.1 nm) could be obtained. The amount of PhSO₃H was varied in the range of 0.14 to 1.31 mmol/g, depending on the mass ratio of sulfanilic acid (4-benzenediazoniumsulfonate) to OMC.¹⁰⁷ In fact, using similar hard templating procedures with microporous zeolite, Hara and co-workers^{50,156} even demonstrated the synthesis of sulfonated ordered microporous carbons with very high specific surface areas (800-2000 m²/g) and SO₃H densities (0.5-1.1 mmol/g) with ClSO₃H as a sulfonating reagent.^{50,156}

Soft templated OMC could be also similarly treated with different sulfonating reagents to produce SOMCs. For example, large pore (6.43-9.17 nm) SOMCs with high SO₃H densities (0.5-1.87 mmol/g) could be obtained by sulfonation of OMCs derived from carbonizing templated resol composites with conc. H₂SO₄ or 4-benzenediazoniumsulfonate. The composites were derived from cooperative self-assembly of phenolic resol in ethanolic solutions containing pluronic F127 as the soft template and resorcinol together with formaldehyde as the carbon precursors (Figure 5).^{48,49,160} Recently, a self-templated OMC derived from carbonizing calcium citrate at 700 °C was similarly treated with 4-benzenediazoniumsulfonate to obtain SOMC with large mesopores (6.8 nm), specific surface area of 639 m²/g and a very high degree of PhSO₃H functionalization (1.97 mmol/g).¹⁰⁸ Commercially available mesoporous carbon (e.g. Starbon 300) could also be identically treated with different sulfonating agents to yield sulfonated mesoporous carbons (4-15 nm).^{54,163}

In terms of catalytic performance, the SOMCs and sulfonated mesoporous carbons are reported to outperform the commercial sulfonic resins (Amberlyst, Dowex, Amberlite etc), SHC, SBC, SPC and SACs in various acid catalyzed reactions involving hydrophobic reactants resulting from the superior ordered large pore structure, high specific surface areas and high SO₃H/PhSO₃H densities. These materials present negligible inter-particle diffusion and external mass transfer limitations which improve reaction kinetics and catalyst stability upon catalysis of large molecules.^{48-54,96,98,99,106-108,143,152-163} However, due to the high costs, multistep synthetic procedures and environmental hazards associated with the production OMCs, the potential of SOMCs in industrial scale-up is somewhat limited.

3.4. NANOSTRUCTURED CARBONS

Due to their unique electronic and surface properties, nanostructured carbons have attracted a great deal of attention for application in areas such as microelectronics, energy harvesting and storage, bio-imaging and nanomedicine. Fabrication of carbon nanomaterials have been achieved via various top-down and bottom-up approaches (e.g. chemical vapor deposition, templated growth, physical and chemical exfoliation of graphite and so forth). An elaborate discussion on the different synthetic methodologies for the fabrication of carbon nanomaterials is beyond the scope of the current review. Nevertheless, due to their commercial availability and environmental acceptability, certain nanostructured carbon materials (nanofibers, nanotubes, nanodiamonds,

graphene and graphene oxide) have also attracted considerable attention as metal-free catalysts and/or catalyst supports in many catalytic and electro-catalytic processes.^{13,164,165} The reasons for the usually enhanced activities of nanostructured carbons are based on several characteristic of their carbon framework matrix including (a) defect-free sp² structures enabling delocalization of free electrons, (b) availability of free bonds on edges of the graphitic layers for saturation/functionalization of the with heteroatoms such as O, N and S, giving rise to the acidic/basic functionalities and (c) the inability of chemical species or reactant molecules (e.g. H₂, O₂, H₂O, alkanes and olefins) to form sub-surface species which limit complexity of the catalyzed reaction to two dimensions.^{164,165}

As such, nanostructured carbons such as nanofibers,^{19,20,61} nanotubes,^{58-60,64,100,143,144} nanodiamonds,^{166,167,169} as well as graphene (and graphene oxide)^{17,21,57,56,62,63,109,168-170} have also been functionalized with SO₃H or PhSO₃H sites to induce hydrophilicity and strong acidity required in various applications including catalysis. During post-functionalization, the acidic carbon materials retain the nanostructure of support which further enhances the performance of these materials. Similar to the SACs and SOMCs, thermal stability of these nanostructured acidic carbons is limited only by the stability of C-S bonds (~250 °C). In addition to their application as solid acids, these nanostructured acidic carbons have also been extensively studied as adsorbents in water and gas purification,^{17,18} as proton exchange membranes,^{19,20} and as a hole-extraction layer in high-performance polymeric solar cells²¹. Ideally, the nanostructured carbons are functionalized by chemical reduction with aryl diazoniumsulfonates (4-benzenediazoniumsulfonate) or by treatment with ClSO₃H under mild conditions producing highly stable carbocatalysts with a high density of covalently bonded SO₃H/PhSO₃H sites (up to 2 mmol/g).^{56,57,63,109,169,172} Concentrated and fuming H₂SO₄ are also demonstrated to be efficient sulfonating agents, but their use usually results in the formation of structurally deformed carbon materials with much lower density of SO₃H sites (up to 1.2 mmol/g).^{58,170,171} These nanostructured sulfonated carbocatalysts, particularly the sulfonated graphene/graphene oxides (SG) functionalized with PhSO₃H, are demonstrated to exhibit catalytic activity comparable to those of SACs and SOMCs, in various organic transformations including conversion of large biomolecules like carbohydrates, fatty acids and triglycerides.^{56,109,169} Recently, one-pot preparation of sulfonated graphene oxides with a SO₃H density up to 1.6 mmol/g was demonstrated from graphite using a modified ‘Tours’ method (oxidation with H₂SO₄/H₃PO₄). Most importantly, the materials also demonstrated high catalytic

activity and stability as an acid catalyst for dehydration of C6 sugars (fructose and glucose) at 120 °C.¹⁶⁸

Nevertheless, in spite of their promising materials properties and high catalytic activities, the application of nanostructured sulfonated carbons as acid catalysts in the industrial scale remains unlikely in near future as the material costs significantly outweigh their benefits.

3.5. SILICA-CARBON NANOCOMPOSITES

In addition to the conventional carbon supports described above, sulfonated carbons have been obtained from mesoporous silica-carbon composites/nanocomposites (MSiC).^{92,173-183} To obtain such hybrid support materials, carbon precursors (such as glucose, maltose, cellulose, chitosan, starch and 2,3-dihydroxynaphthalene) were initially loaded into the mesopores of the silica supports (SBA-15, K100, KIT-6 and mesocellular silica) and then subjected to partial carbonization.^{92,173-175} Alternatively, such materials are obtained by carbonizing a template-silica-precursor composite obtained by the solvent-evaporation-induced tri-constituent co-assembly method (Figure 6).^{179,180,181}

Subsequent sulfonation of these carbon loaded silica composites with fuming or conc. H₂SO₄ yields the mesoporous sulfonated silica-carbon composites (SMSiC).^{92,173-175} The silica (SiO₂) component of these composites introduces structural ordering as well as high mechanical and thermal stability while the mesostructure prevents aggregation of impregnated carbon precursors during carbonization resulting in materials with a uniform dispersion of acid sites. Typically, uniform carbon loadings between 15-44 wt% can be obtained (without loss of mesoporosity) which yield materials with SO₃H loadings in the range of 0.38 to 0.71 mmol/g, much lower than the pure carbon supports discussed above. Even so, these hybrid materials demonstrate high catalytic activity in hydrophobic acid-catalyzed reactions, comparable to the more acidic counterparts discussed above.^{92,173-175} To achieve higher SO₃H loadings, an alternative built-in approach can be applied using *p*-toluenesulfonic acid as a dual carbon and sulfur (SO₃H) precursor for loading with silica supports (SBA-15, fumed silica and hollow silica). Subsequent carbonization of these *p*-toluenesulfonic acid-silica hybrids at 250 °C in the presence of H₂SO₄ as an activating agent, yields materials with SO₃H densities in the range of 1-2.9 mmol/g.¹⁷⁶⁻¹⁷⁸

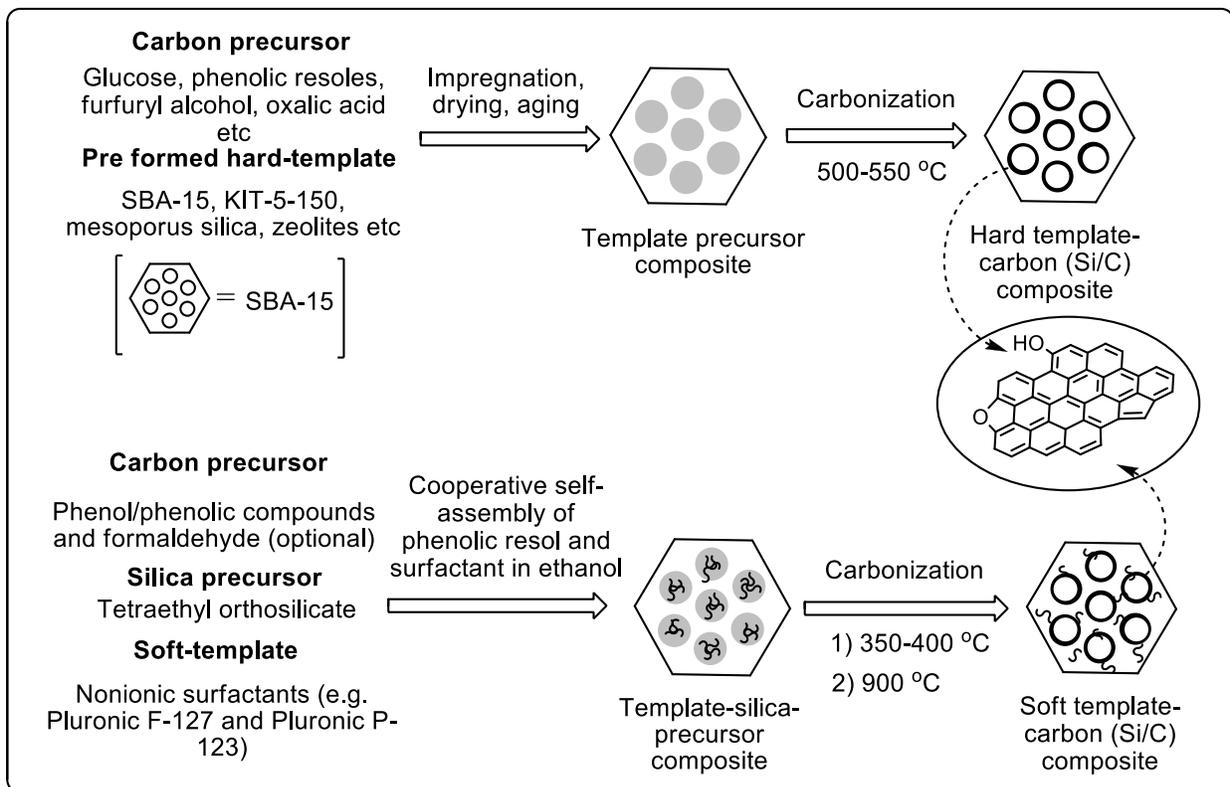


Figure 6. Schematic representations of hard-template and soft-template approaches for the synthesis of silica-carbon composites (MSiC).

Alternatively, the MSiCs are obtained by carbonizing template-silica-precursor composites obtained via a solvent-evaporation-induced tri-constituent, co-assembly method (Figure 6); using tetraethyl orthosilicate (TEOS) as a silica precursor, organic molecules like sucrose as the carbon precursor and a triblock copolymer, structure-directing amphiphilic surfactant like Pluronic F127 as a soft-template.¹⁷⁹⁻¹⁸¹ The process closely resembles the synthesis of soft-templated OMCs (Figure 5). In a variation of this method, MSiCs were obtained by a template carbonization strategy in which the organic template itself served as a sacrificial carbon source.¹⁸¹ In the synthetic protocol, TEOS was used as a silica precursor and amphiphilic poly(ethylene oxide)-b-polystyrene (PEO-b-PS) both as a structure-directing amphiphilic surfactant and a carbon source during solvent-evaporation-induced aggregating assembly.¹⁸¹ This alternative strategy has the advantage that it enables the synthesis of composites with more uniform mesopores and higher carbon loadings (up to 66 wt%) which upon sulfonation produce SMSiC material with enhanced SO₃H loadings. In fact, according to the literature data, a linear relationship

exists between the density of SO_3H site and carbon content of various SMSiCs.^{92,174-180} In addition to the aforementioned procedures, SMSiCs with high specific surface area ($779 \text{ m}^2/\text{g}$) and uniform mesopores of 2.6 nm have also been synthesized in an integrated approach by carbonizing a mixture of glucose (as the carbon source as well as a non-surfactant templating precursor), TEOS as a silica precursor, and H_2SO_4 as the sulfur (SO_3H) precursor.¹⁸² Most importantly, the sulfonated silica carbon nanocomposites demonstrated good catalytic activity upon tertiary butylation of phenol during multiple reaction cycles. In a recent work, similar sulfonated carbon/nano-metal oxide composites have also been obtained by replacing MSiC with nano- TiO_2 , nano- CeO_2 and nano- ZrO_2 during the starch impregnation step. Subsequent carbonization at $400 \text{ }^\circ\text{C}$ and sulfonation of these starch impregnated nano-metal oxides with H_2SO_4 at $160 \text{ }^\circ\text{C}$, yield SO_3H functionalized active carbocatalysts ($0.18\text{-}0.32 \text{ mmol/g}$).¹⁸³ In fact, using the generalized impregnation-carbonization-sulfonation route, several magnetically separable sulfonated carbons ($\text{Fe}_3\text{O}_4@\text{CSO}_3\text{H}$) were prepared, using Fe_3O_4 nanoparticles as an oxide support, glucose a carbon source and $\text{ClSO}_3\text{H}/\text{H}_2\text{SO}_4$ as a sulfonating reagent.^{148,184,185} Similarly, magnetic sulfonated carbons have also been obtained by sulfonating magnetic char derived from FeCl_3 soaked sawdust with conc. H_2SO_4 .¹⁸⁶ The magnetically separable sulfonated carbons were reported to exhibit a good catalytic activity upon transformation of biomass components such as carbohydrates, triglycerides and fatty acids.^{148,184-186} Sulfonated carbons have also been similarly loaded onto ceramic monoliths using the impregnation-carbonization-sulfonation route. Such honeycomb structured sulfonated carbon catalysts are of significant interest in industry as they can overcome the limitations of powdered carbon catalysts such as agglomeration and difficulty of filtration, due to the formation of fines upon slurry phase operations and the high pressure drops observed upon gas-phase operations.¹³⁹

Overall, these inorganic-organic hybrid materials demonstrate good catalytic performance as acid catalysts; they present advantages over conventional acidic carbons in terms of structural rigidity as well as mechanical and thermal stability. As such, the use of silica-carbon composites may be beneficial in terms of gas-phase operations in a fixed bed reactor. Nevertheless, the hydrothermal stability of sulfonated silica-carbon composites needs further investigation, as many of the reactions of interest are performed under harsh hydrothermal environments. Similarly, in case of magnetic sulfonated carbons, it is very difficult to ensure uniform carbon coatings over Fe_3O_4 particles and, as these oxides are known to demonstrate poor stability in acidic conditions,

Fe leaching may be unavoidable upon long term operations. Further studies are needed with regard to the operational stability in context of large scale applications.

3.6. N-DOPED CARBONS AND CARBON NITRIDE

Although N-doped carbons and carbon nitrides have been extensively studied as supports for transition and noble metal catalysts,¹³ only a handful of studies have been conducted investigating N-doped carbons and graphitic carbon nitrides as supports for the fabrication of SO₃H functionalized carbocatalysts.^{42,43,101-104} Generally, two primary strategies exist for the fabrication of N-doped carbons, which are post-treatment of carbons with nitrogen-donors and *in-situ* synthetic methods using nitrogen containing precursors (Figure 7).¹⁸⁷ Graphitic carbon nitrides are obtained similarly by thermal polymerization of highly nitrogen rich precursors like melamine, urea and dicyandiamide.¹⁰¹⁻¹⁰⁴

The sulfonated N-doped carbons reported so far have been based on the functionalization of N-doped amorphous carbons obtained upon incomplete carbonization of nitrogen-rich biomass/agro wastes such as de-oiled waste cakes,^{42,145-148,188} palm kernel shells¹⁸⁹ and cow manure.¹⁹⁰ The studies have shown that similar to the conventional carbon supports; N-doped carbons can be functionalized with both SO₃H and PhSO₃H groups (up to 0.9 mmol/g) by treating them either with strong sulfonating agents (conc. H₂SO₄ or fuming H₂SO₄)^{42,188,189} or by chemical reduction with aryl 4-benzenediazoniumsulfonate.^{42,145-148} Interestingly, in a recent work it was demonstrated that it is even possible to obtain sulfonated carbons in the form of Brønsted acidic ionic liquid functionalized N-doped microporous carbons by quaternary ammonization of the heterocyclic nitrogen sites on the doped carbon surface with 1,4-butane sultone, followed by an anion exchange with strong acids of H₂SO₄ or HSO₃CF₃.¹⁹⁰ The obtained hydrophobic carbon functionalized ionic liquids (NPC-[C₄N][SO₃CF₃] and NPC-[C₄N][SO₃H]) exhibited high concentration of acid sites (1.21-1-25 mmol/g) and microporosity (701-726 m²/g). Most importantly, the carbon supported ionic liquid, NPC-[C₄N][SO₃CF₃], gave rise to a catalytic activity comparable to its homogeneous counterpart upon fatty acid esterification, triglyceride transesterification and levulinic acid production from microcrystalline cellulose. Similarly, the PhSO₃H functionalized mesoporous N-doped carbons are also active catalysts upon transformation of biomolecules like fatty acid esterification, triglyceride transesterification and microcrystalline cellulose acetylation, owing to their favorable pore structure and PhSO₃H densities (0.7-0.9

mmol/g). N-doped sulfonated carbon nanotubes have also been obtained by boiling N-doped carbon nanotubes with 50% H₂SO₄.⁴³

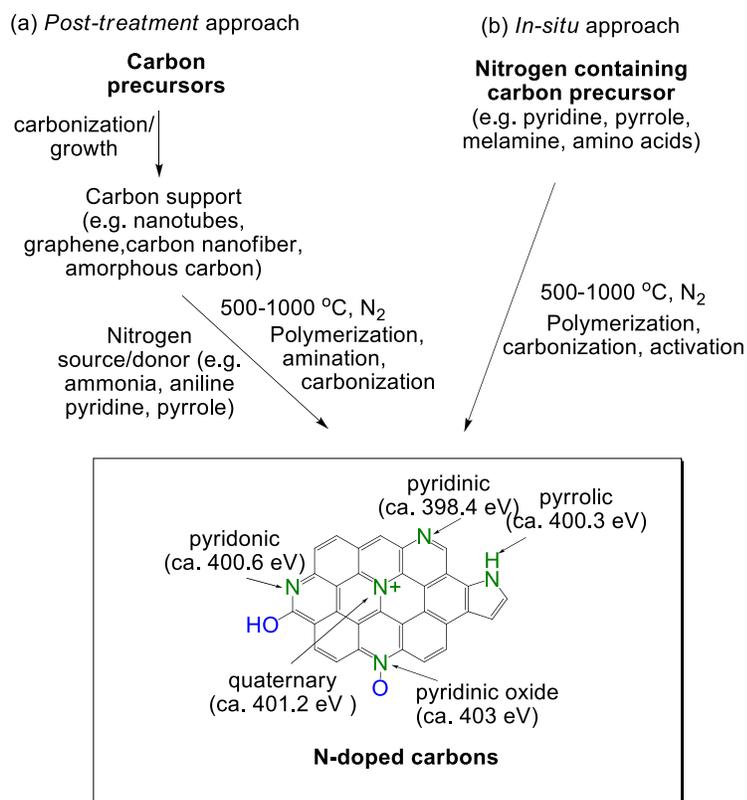


Figure 7. Schematic representation of the different approaches for obtaining nitrogen containing functional carbon materials (N-doped carbons).

The use of graphitic carbon nitride (g-CN) upon fabrication of SO₃H functionalized sulfonated carbon nitride was originally demonstrated by Varma and co-workers using ClSO₃H as the sulfonating reagent, at room temperature. Based on sulfur content of the ClSO₃H treated materials, the concentration of surface SO₃H sites was estimated to be ~5.47 mmol/g, amongst the highest values reported for sulfonated heterogeneous acid catalysts (including sulfonated carbons, sulfonated oxides and commercial sulfonic resins). Successful functionalization was clearly evident from the characteristic FTIR (1190, 1170, 1020 and 1040 cm⁻¹) as well as ¹³C NMR (140 ppm) and XPS signals (~168 eV).¹⁰²⁻¹⁰⁴ Recently, using a modification of the above synthetic procedure, a highly ordered mesoporous sulfonated graphitic carbon nitride was also obtained (SBA-15 was used as a hard temple).¹⁰¹ In terms of performance, these materials exhibited

remarkable activity as solid acids, outperforming the sulfated carbons discussed above. Unprecedented activity was demonstrated upon oleic acid esterification, at room temperature, and upon conversion of carbohydrates (xylose, fructose) into furanics (furfural, 5-hydroxymethylfurfural) and related value-added products (benzimidazoles, 2,5-diformylfuran, Levulinic acid, etc) under relatively mild conditions (100-150 °C).¹⁰¹⁻¹⁰⁴ The materials also demonstrated high catalytic activity upon synthesis of dihydropyrimidinone derivatives under mild and environmentally benign conditions (Biginelli reaction).¹⁰¹

N-doped carbons and carbon nitride based acidic carbons have demonstrated excellent catalytic activities as solid acids *on par* to that of the most active acidic carbons. Structural properties and thermal stability of such materials are mainly affected by the carbonization/activation conditions similar to the conventional (non-doped) acidic carbons. Moreover, such carbon supports can be easily fabricated from inexpensive natural or commercially available precursors using existing activation/carbonization strategies. The presence of N-doping in the carbon framework renders such materials particularly suitable for the synthesis of bifunctional metal catalysts via selective deposition of metal/metal precursors over these nitrogen sites.

4. SULFONATION METHODS

Sulfonation is the key step in the fabrication of sulfonated carbon materials as this step is directly responsible for covalent functionalization or grafting of SO₃H groups on the carbon framework of the supports/carbon precursors. Over the years a number of different functionalization techniques have been developed and optimized to attach SO₃H sites through C-S or C-C bonds. Nevertheless, the different sulfonation methods can be broadly divided into two groups' viz. (a) in-situ functionalization and (b) post-grafting functionalization approach as summarized in Figure 8. This step has a direct impact on the structure, surface chemistry, stability as well as cost of sulfonated carbon materials. With respect to the amount of starting carbon support, the yield (w/w) of sulfonated material is usually close to 100% for all ex-situ sulfonation routes and, less than 100% for in-situ functionalization methods. Brief comments for each sulfonation approach with respect to cost, environmental hazards, SO₃H density and stability reviewed in this section are presented in Table 3.

Table 3. Brief comments for each sulfonation approach with respect to cost, hazards, thermal and chemical stability of SO₃H sites

sulfonation method		sulfonation conditions			yield ^d	hazards and drawbacks	acidity (mmol/g)		stability of SO ₃ H sites		cost	
		T (°C)	time (h)	reagent ratio ^c			SO ₃ H	total ^e	thermal (°C) ^f	chemical (SO ₃ H leaching)	material ^g	operating ^h
in-situ functionalization	with conc. H ₂ SO ₄	250 (in N ₂)	15	10-20	upto 55	(++++) ➤ strong oxidizing acids ➤ release of acid gases (SO ₂ , SO ₃) ➤ H ₂ SO ₄ neutralization waste ➤ surface oxidation of support	0.74-7.3	1-7.3	<200	yes, especially under elevated temperature and pressure	219-538	moderate
	with organosulfonic acids	180 ^a	4-24	0.5-4	15-60	(++) ➤ strong oxidizing acids, ➤ H ₂ SO ₄ neutralization waste ➤ surface oxidation of support	0.12-2.4	up to ~4	<200	yes, especially under elevated temperature and pressure	210-510	low
	carbonization of sulfonated macromolecules	300-450 (in N ₂)	0.5-1	not required	30-50	(+) ➤ dilute acid waste	0.32-1.24	3-5	up to 250	stable (no leaching observed in 90 h fixed bed)	20-400	low

										operation at 55 °C)		
	spray pyrolysis with aq. H ₂ SO ₄ in the presence of M ₂ SO ₄ (M = Li, Na and K)	400-1000 (in N ₂)	cont ^b	aq. H ₂ SO ₄	upto 30	(+) ➤ H ₂ SO ₄ neutralization waste	0.08-1.12	1-7	200-250	operationa l stability not reported	370-420	low
post-grafting Functionalization	with H ₂ SO ₄ (conc. and fuming)	180-250 (in N ₂) or 150-180 ^a	15-24	15	70-100	(+++) ➤ strong oxidizing acids ➤ limited release of acid gases (SO ₂ , SO ₃) ➤ H ₂ SO ₄ neutralization waste ➤ surface oxidation of support	0.17-2	1.4-8.9	up to 250	SO ₃ H leaching in organic media	low (219-538)	moderate
	with ClSO ₃ H	0-25 (in air)	12	1-18	~100	(++) ➤ strong oxidizing acids, release of HCl, chlorinated solvents	0.5-5.47	2.5-8.2	up to 250	stable	807-2610	moderate
	with aryldiazonium sulfonates	0-80 (in air)	1-24	2-20		(+) ➤ dilute acid waste	0.14-2.57	0.62-3.96	up to 250	stable (no leaching observed in fixed-bed operation)	840-8000	low

										at 45-130 °C)		
	plasma sulfonation	20 °C (Plasma)	minutes	dil. H ₂ SO ₄ (0.1-1 M) 0.01 g/ml loading		(+) ➤ dilute acid waste	0.5-2.2	2.3-4.4	n.r	hydrothermal leaching (120-210 °C) of ca. 20% SO ₃ H sites	76-760	high

^ahydrothermal carbonization

^bcontinuous (7 ml/min)

^csulfonating agent/precursor (w/w) ratio

^dyield = (mass of sulfonated carbon/mass of carbon precursor) × 100%

^eSO₃H, carboxylic acid, lactone, phenol and carbonyl groups

^fin inert (N₂) atmosphere

^gapproximate cost of raw material (in USD, lowest price quoted from Merck and/or Fisher scientific) for the production of 1 kilogram of sulfonated carbon

^hqualitative estimate based on equipment/automation and waste treatment/management

n.r = not reported

4.1. IN-SITU FUNCTIONALIZATION APPROACH

In-situ sulfonation routes are based on a built-in approach in which both carbonization and sulfonation steps occur simultaneously. This approach offers several advantages over the post-grafting approach including reduced costs, reduced environmental hazards (in most cases), low energy requirements and a high degree of SO₃H functionalization. The different variations of *in-situ* sulfonation are discussed elaborately in the sub-sections below.

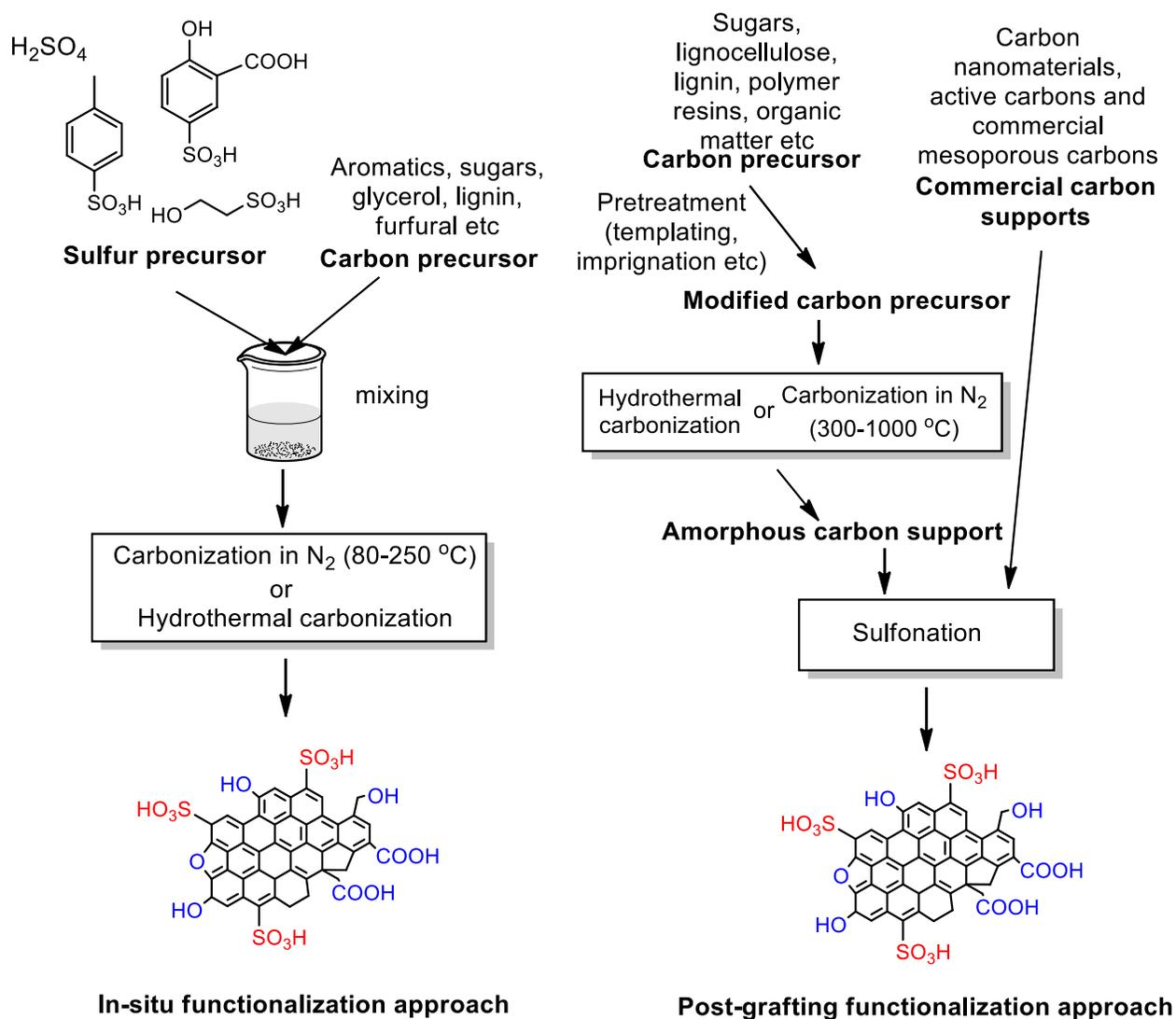
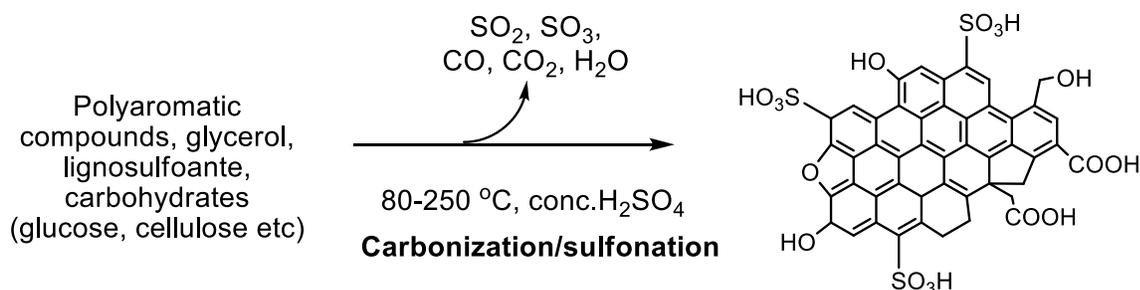


Figure 8. Summary of different methods for functionalizing carbon materials with SO₃H sites.

4.1.1. SIMULTANEOUS SULFONATION AND CARBONIZATION WITH H₂SO₄

Scheme 1. Schematic representation of the generalized approach for obtaining sulfonated carbons by simultaneous sulfonation and carbonization with H₂SO₄.



The direct treatment of carbonaceous matter with conc. H₂SO₄ (excess 10-20 fold by mass) at elevated temperatures, is a very effective technique to obtain SO₃H functionalized carbocatalysts.^{22,45,140-142} Hara and co-workers originally demonstrated the fabrication of sulfated carbons with SO₃H densities up to 4.9 mmol/g by directly heating polyaromatic compounds like naphthalene, perylene and coronene in the presence of conc. H₂SO₄, at 250 °C for 15 h.²² Using the same synthetic procedures, Mahdavi *et al.*¹⁴¹ obtained a carbon material with SO₃H densities up to 7.3 mmol/g from sucrose (heated with conc. H₂SO₄ at 250 °C) and a similar material with lower density of SO₃H groups (1.9 mmol/g) was also obtained treating glycerol pitch in a similar manner.^{45,191} While this route has proven to be advantageous when aiming at carbon materials with an extremely high SO₃H density (4.9-7.3 mmol/g), the environmental hazards and safety issues caused by the use of a large excess of H₂SO₄ (~10-20 times in excess of carbon source), release of large volumes of acid gases (SO₂ and SO₃) and neutralization wastes generated during carbonization and washing step renders the process impractical in large scale production.^{22,42} Nevertheless, it was demonstrated by Zhang *et al.*¹⁹², Mao *et al.*¹⁴² and Malina *et al.*¹⁹³ with carbohydrate precursors (starch, cotton and bamboo powder) that charring/carbonization and sulfonation could be induced under much milder conditions (80-180 °C) by heating with 80%-98% H₂SO₄, to yield SO₃H functionalized acidic carbocatalysts. Moreover, by subsequent sulfonation of the obtained materials with conc. H₂SO₄, high degree of SO₃H functionalization (1.13-1.87 mmol/g) could be achieved.^{142,192} Similarly, it was demonstrated in separate studies by Lee,³⁵ Liang *et al.*¹⁴⁰ and Chen *et al.*¹⁹⁴ that commercial lignosulfonate could also be effectively converted into SO₃H functionalized carbonaceous catalysts by heating with excess conc. H₂SO₄ under much milder conditions (120, 150 and 150-175 °C for 1 to 6 h). These materials also afforded reasonable

SO₃H densities of 0.92-1.4 mmol/g. Black liquor was also similarly treated at 200 °C for 12 h to produce an acidic carbon material with 0.74 mmol/g to 0.78 mmol/g of SO₃H sites.¹¹⁷ Mechanistically, it has been proposed that the reaction proceeds via an initial formation of sulfoaromatic hydrocarbons followed by incomplete carbonization (Scheme 1).²² The direct treatment of organic matter (e.g. glucose, de-oiled press cakes) with conc. H₂SO₄ under hydrothermal conditions (180 °C, 24 h) has also been reported to afford similar materials with high SO₃H densities.^{42,65}

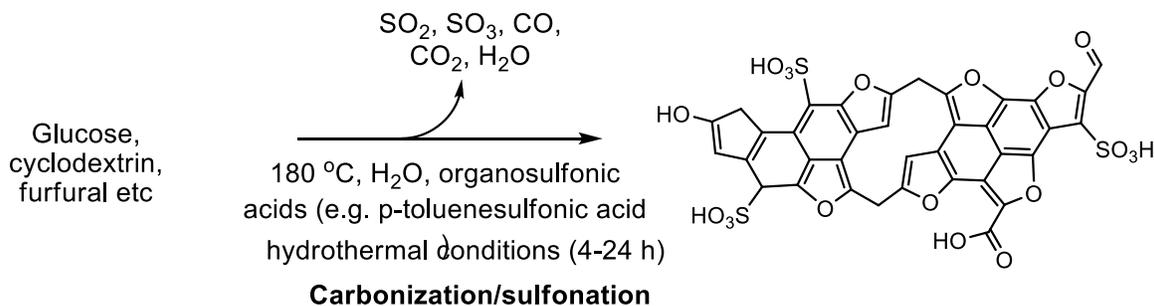
Although simultaneous sulfonation and carbonization with H₂SO₄ is an efficient and simple route to obtain acidic carbocatalysts with a high degree of SO₃H functionalization, these materials pose negligible porosity, high density of oxygen functional sites (1-7.3 mmol/g) and a poor thermal stability thus rendering them less efficient in case of applications in hydrophobic media and at high temperatures. Also, these carbons have a soft (less rigid) structure with low degree of polycondensation due to which some of the SO₃H functionalized aromatic fragments are easily leached out to the reaction media during liquid-phase reactions, particularly above 100 °C under solvothermal/hydrothermal conditions as well as when using hydrophobic organic reactants such as higher fatty acids and triglycerides.^{22,23}

4.1.2. SIMULTANEOUS SULFONATION AND CARBONIZATION WITH ORGANOSULFONIC ACIDS

Simultaneous sulfonation and carbonization of organic matter in the presence of organosulfates is another *in-situ* approach that also affords highly acidic SO₃H functionalized sulfonated carbons. However, unlike H₂SO₄, the use of organosulfate reagents requires hydrothermal reaction conditions in order to induce carbonization and prevent the evaporative escape of low-boiling organosulfates. In a typical synthetic procedure, the carbon precursor, organosulfate reagents and water are uniformly mixed and subjected to hydrothermal carbonization at 180 °C (4-24 h). The resulting carbon materials typically exhibit a hydrochar like carbon structure with a high degree of SO₃H functionalization (up to ~2.4 mmol/g). Organosulfonic acids such as *p*-toluenesulfonic acid^{65,119-121,196} and hydroxyethylsulfonic acid,^{69,71,122,123} have been the sulfonating reagents of choice in most studies, while in terms of carbon precursor, glucose has been the preferred choice due to its high solubility in water. Recently, a less hazardous non-volatile organic compound, sulfosalicylic acid was also identified

as an efficient sulfonating agent. It was demonstrated by Qi *et al.*¹²⁴ that carbon microspheres functionalized with SO₃H groups could be easily obtained by a simple hydrothermal treatment of a 2:1 (w/w) mixture of glucose and sulfosalicylic acid.¹²⁴ Analogously, sulfonated carbon microspheres with a specific surface area of ~138 m²/g were also obtained by the hydrothermal treatment of a mixture of glucose, citric acid and hydroxyethylsulfonic acid (10:5:1 w/w ratio), at 180 °C in 4 h. Meanwhile, Maneechakr *et al.*¹²² obtained sulfonated carbon microspheres with a specific surface area up to 162 m²/g and a high degree of SO₃H functionalization (1.82 mmol/g) by hydrothermally treating a 6:1 (w/w) mixture of hydroxyethylsulfonic and β-cyclodextrin at 180 °C in 4h. In addition, sulfonated carbons materials were also obtained upon treating 2:1 (w/w) furfural-hydroxyethylsulfonic acid and furfural-*p*-toluenesulfonic acid mixtures in an analogous manner.¹²³ Nevertheless, although no mechanism has been proposed to date, the reaction most likely proceeds by simultaneous formation of sulfoaromatic compounds and their hydrothermal carbonization with the carbon precursors (Scheme 2). It is also worth mentioning here that the microsphere sulfonated carbon carbons typically present larger specific surface areas (>128 m²/g) than the materials obtained by carbonizing in H₂SO₄ (Section 4.1.1).

Scheme 2. Schematic representation of the direct hydrothermal approach for obtaining sulfonated carbons by simultaneous sulfonation and carbonization with organosulfonic acids.



In an alternative approach, the carbon precursor is first uniformly mixed with the *p*-toluenesulfonic acid in the ratio 1:1-1:4 w/w, and directly heated in a sealed Teflon lined vessel at 180 °C. Using this approach, SO₃H functionalized acidic carbon has been obtained from glucose and β-cyclodextrin.^{65,120,121} A variation of this method was proposed by Wang *et al.*⁷⁰ who produced SO₃H functionalized amphiphilic carbons, by treating a mixture of N-dodecylbenzenesulfonate/H₂SO₄ and furfural at 180 °C for 24 h.⁷⁰ It is likely that even in the absence of water, the reaction follows a mechanism similar to the hydrothermal carbonization/sulfonation

as an adequate amount of H₂O is produced as a by-product from the dehydration of the carbon precursors.^{65,120,121} Nevertheless, the key difference of these materials produced in the absence of water with those obtained under hydrothermal conditions is their reduced porosity (specific surface area <40 m²/g).

Overall, simultaneous sulfonation and carbonization with organosulfonic acids offer several advantages in terms of environmental safety (no release of acid gases, lower dosage of sulfonating agents and milder conditions) and energy input. Even so, these carbon materials have drawbacks in terms of the high hydrophilicity resulting from the presence of a high density of oxygen functional sites (up to ~4 mmol/g) and poor thermal and operational stability (low degree of polycondensation in carbon framework) that make them less attractive when hydrophobic media and high temperatures are involved.

4.1.3. OTHER IN-SITU SULFONATION METHODS

Non-conventional, *in-situ* sulfonation techniques have also been developed, some of which are discussed below. For example, Konwar *et al.*^{66,67} obtained SO₃H functionalized (0.32-1.24 mmol/g) meso-macroporous acidic carbons via mild pyrolysis (350–450 °C) and ion/H⁺ exchanging ice-templated, water-soluble polyelectrolyte polymers i.e. Na-lignosulfonate/Na-polystyrene sulfonate (or their mixtures).^{66,67} In a related work, Duyckaerts and co-workers¹⁹⁷ produced mesoporous sulfonated carbons materials by one-step spray pyrolysis of an aqueous solution of sucrose as a carbon source, sulfuric acid as a sulfur source and Li₂SO₄/Na₂SO₄ as a structure directing agent, at 400-800 °C.¹⁹⁷ In their work, carbon materials with a specific surface area of 506 m²/g and mesopore size distribution between 2 and 8 nm were produced using Li₂SO₄ as the structure directing agent.¹⁹⁷

Mesoporous SMSiCs have also been synthesized in an *in-situ* approach using inexpensive glucose as the carbon source as well as a non-surfactant templating precursor, TEOS, as the silica precursor as well as H₂SO₄ as the sulfur (SO₃H) precursor.¹⁸² Direct carbonization of a mixture containing TEOS, glucose, H₂O and H₂SO₄ (in the mole ratio of ~1:0.385:4.8:0.88), in N₂ atmosphere at 300 °C also facilitated the direct transformation of the glucose moieties into hydrophobic carbon sheets bearing sulfonyl groups that are trapped in the stabilizing hydrophilic silica matrix, yielding the SMSiCs.¹⁸² Similarly, a bifunctional mesoporous SMSiCs

functionalized with SO₃H and Cl sites were synthesized by a modified solvent-evaporation-induced tri-constituent co-assembly with the addition of (3-mercaptopropyl)-trimethoxysilane as a sulfur precursor and sucralose as the Cl precursor during the composite synthesis. In order to obtain SO₃H sites, the cured MSiCs (200 °C, 15 h in N₂) composite was simply oxidized with H₂O₂.¹⁶¹ In other related works various SMSiCs with a high degree of SO₃H functionalization (1-2.9 mmol/g) were obtained by carbonizing *p*-toluenesulfonic acid impregnated with mesoporous silica materials (SBA-15, fumed silica and hollow silica) at 250 °C, in the presence of H₂SO₄ as the activating agent.¹⁷⁶⁻¹⁷⁸

Some of the non-conventional, *in-situ* sulfonation approaches discussed above (direct pyrolysis of lignosulfonate and spray pyrolysis) show potential for large production of acidic carbons as they address several issues related to the conventional methods (eliminating use of conc. H₂SO₄, acid waste generation and release of large volumes of acid gases) without compromising the properties of the resulting materials. In fact, these materials are superior in terms of textural properties (pore size, surface area, etc.) and surface SO₃H acidity.^{66,67,197}

4.2. POST-GRAFTING FUNCTIONALIZATION APPROACH

Post-grafting approaches of functionalization are based on the treatment of carbonized materials (or carbon supports) with different sulfonating reagents to create covalently bonded SO₃H sites (Figure 8). The biggest advantage of the post-grafting approach is the preservation of the original mesostructure/nanostructure of carbon that makes it possible to obtain a wide range of materials with different (and tunable) textural properties, surface chemistry (hydrophobicity/hydrophilicity) and degree of SO₃H functionalizations. It is also important to highlight that in the *in-situ* approach, the oxidation state of sulfur species is significantly affected by the synthesis conditions as the SO₃H sites are susceptible to reduction. In many instances, both the SO₃H and low-valent S sites are found on the surface of carbon materials obtained via the *in-situ* functionalization approach.⁶⁶⁻⁶⁹ In fact, it was clearly shown that upon increase of carbonization/sulfonation temperature from 300 to 450 °C, almost 40% of the SO₃H sites were reduced to low-valent S species due to carbothermal reduction.⁶⁶⁻⁶⁸ The different variations in post-grafting sulfonation are discussed elaborately in the sub-sections below.

4.2.1. CONCENTRATED H₂SO₄ AND FUMING H₂SO₄

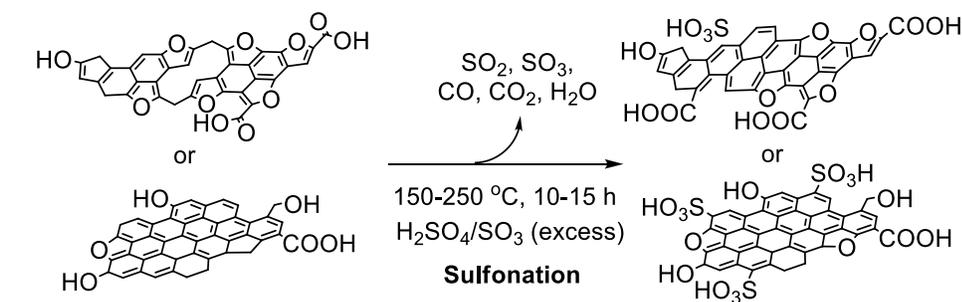
Sulfonation of carbon/carbonized materials with H₂SO₄ at elevated temperatures (~80-150 °C) is a well-known functionalization technique for creating covalently bonded SO₃H sites on carbon materials. Originally proposed by Hara and co-workers,^{23,14-16} several variations of the method have been developed over the past decade and comprehensively studied. Further, the synthesis routes were optimized for different types of carbon supports, including partially-carbonized materials, hydrochars/hydrothermal carbons, activated carbons, ordered carbon and carbon nanomaterials (Scheme 3).^{14-16,23,35-37,39-44,47,55,58,75-81,91-94,110-116,127-132, 94,133-138,188,189, 170-175}

The extent of sulfonation (expressed in terms of SO₃H density of the obtained product) is influenced by (a) strength of H₂SO₄, (b) temperature, (c) duration and (d) framework structure of the carbon support. In the original work by Hara *et al.*, SO₃H functionalized acidic carbocatalysts were obtained by sulfonating semi-carbonized (400 °C) natural sugars like glucose and sucrose at 150 °C for 15 h in N₂.²³ Their results indicated that the sulfonated carbon produced with fuming H₂SO₄ (15 wt% SO₃) acid resulted in the formation of a higher acid site density (2.5 mmol/g total and 1.2 mmol/g SO₃H density) than the material obtained with conc. H₂SO₄ (2.5 mmol/g total and 1.2 mmol/g SO₃H density). The usefulness of stronger fuming H₂SO₄ as a more efficient sulfonating agent was also documented in many other studies.^{16,46,55,93,98} The influence of the carbon precursor on the SO₃H density as such was studied by Lou *et al.*¹³¹ using four different carbohydrate precursors, namely D-glucose, cellulose, sucrose and starch upon catalyst preparation via the carbonization-sulfonation route. The authors observed that the SO₃H density decreased in the following order: starch-derived catalyst (1.83 mmol/g) > cellulose-derived catalyst (1.68 mmol/g) > sucrose-derived catalyst (1.59 mmol/g) > D-glucose-derived catalyst (1.48 mmol/g). In another study, a sulfonated carbon composite solid acid (P-C-SO₃H) with a three-fold higher SO₃H density than the sulfonated-carbons (2.42 mmol/g vs 0.82 mmol/g) was produced from glucose impregnated Amberlite XAD1180. The obtained composite material, a glucose impregnated polymer matrix (Amberlite XAD1180), was pyrolyzed (at 300 °C) followed by its sulfonation with conc. H₂SO₄, similar to the synthesis route of glucose based sulfonated carbon.²⁰⁰

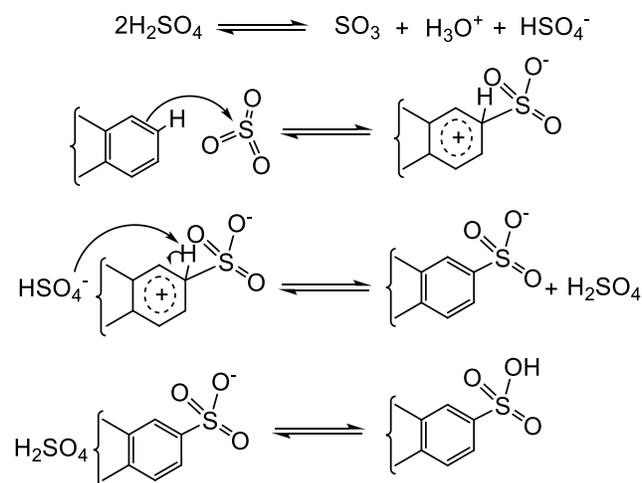
Sulfonation of sugar (glucose, xylose) derived hydrochars with conc. H₂SO₄ has been reported to yield similar materials with identical SO₃H densities in the range of 0.56-0.95 mmol/g.^{76-80,110-115} However, heating with H₂SO₄ simultaneously causes oxidation of hydrochar surface and creates additional carboxyl sites which significantly increased the density of oxygen

functional groups (by almost ~1.2-1.3 fold). Typically such materials present very high COOH densities 4.43-4.84 mmol/g a value almost ~4 times higher than in case of the catalysts obtained from pyrolyzed or semi-carbonized materials.^{22,76-80} In another work, sulfonation of hydrothermally treated (240 °C, 10 h) alkali lignin with conc. H₂SO₄ (at 180 °C for 12 h) afforded materials with higher SO₃H densities (1.2 mmol/g). The same authors also showed that by addition of 50% acrylic acid during the hydrothermal treatment, materials with two-fold enhanced COOH (2.88 mmol/g) and 1.2 fold enhanced SO₃H densities (1.53 mmol/g) were produced.¹¹⁶ Similarly, sulfonation of hydrothermally treated macroalgae produced sulfonated hydrochars with the concentration of SO₃H sites being around 0.953-1.62 mmol/g.¹¹⁸ The higher degree of SO₃H functionalization achieved over lignin and lignocellulose based hydrochars is most likely due to the presence of more aromatized carbon framework structure in comparison to the sugar based hydrochars.

Scheme 3. Schematic representations of the generalized (post-grafting) H₂SO₄ sulfonation approach for obtaining sulfonated carbon materials.



Sulfonation mechanism



Irrespective of the carbon structure, for both reagents (fuming or conc. H_2SO_4), sulfonation is believed to proceed via an electrophilic substitution mechanism ($\text{Ar-H} + \text{H}_2\text{SO}_4 \rightarrow \text{Ar-SO}_3\text{H} + \text{H}_2\text{O}$) (Scheme 3). Nevertheless, the actual functionalization process is accompanied by many side reactions such as oxidation, dehydration, condensation and cross-linking, etc. which significantly alters the structure and surface chemistry of carbon material/support.^{22,42,48,49,51,53-55,96,98,152-155,162,163} In fact, the graphene carboxylate groups formed on the carbon surface by the oxidation of the aromatic rings during sulfonation are responsible for stabilizing the C-S bonds of SO_3H sites on amorphous carbon bearing SO_3H groups.^{23,80}

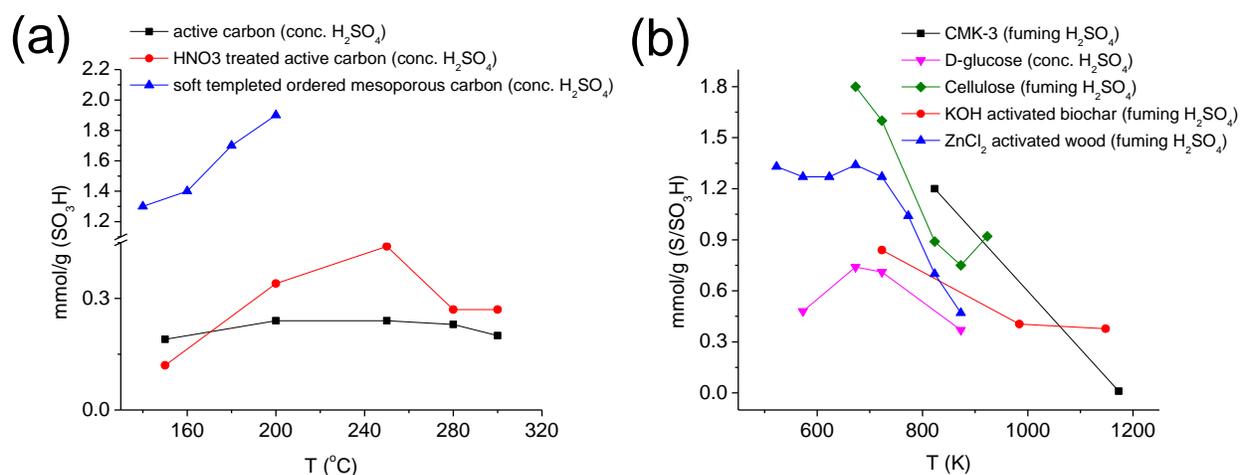


Figure 9. Effect of (a) sulfonation temperature (Compiled from Ref. 53,98) and (b) carbonization/pyrolysis temperature (Compiled from Ref.16,46,55,93,98) on density of SO_3H sites.

Studies on the influence of sulfonation time have shown ~15 h to be optimal to archive complete functionalization.^{22,48,49,51,53-55,110} In another study, Zhang *et al.*⁵³ found that by elevating the sulfonation temperature from 150 °C to 250 °C, it was possible to enhance the SO_3H density of the active carbon based acidic carbocatalysts by ~3 fold (keeping the pore structure intact), albeit a further increase in the sulfonation temperature resulted in a reduction of SO_3H density and collapse of the active carbon pore structure.⁵³ The reduced SO_3H densities and collapsed structure at higher sulfonation temperatures (higher than 250 °C), are attributed to thermal decomposition of the C- SO_3H moiety and carbon surface oxidation.^{53,98} Pre-oxidation of active carbon with HNO_3 was also found to be favorable in terms of enhancing the SO_3H densities.⁵³ Nevertheless, the optimal sulfonation temperature can vary significantly for different carbon supports; for example, 150 °C for semi-carbonized materials, 180 °C for ordered mesoporous carbon and 250 °C for

activated carbon and CMK-3, respectively.^{23,14-16,53,198} Figure 9(a) summarizes the trends in SO₃H density vs. sulfonation temperature for different carbon supports.

Alternatively, sulfonation can be carried out in a Teflon-sealed autoclave under hydrothermal conditions, which offers a safer and easier approach than the conventional approach.^{49,153,154,179} The presence of defective polycyclic aromatic rings (mixed sp²/sp³) within the carbon support and elevated reaction temperatures are necessary (150 °C or higher) to induce SO₃H functionalization (sulfonation) by H₂SO₄ (fuming and concentrated).^{22,48,49,51,53-55,96,98,152-155,162,163} In fact, independent studies conducted on the influence of the carbonization (or activation) temperature on sulfonation, for both concentrated and fuming H₂SO₄, revealed a trend of decreasing SO₃H density with increasing carbonization temperatures. This is consistent with the increased structural ordering and hydrophobicity of the materials obtained at elevated temperatures. In other words, increased carbonization temperatures reduce the amount of defective polycyclic aromatic rings and increase the sp² cross-linking of the carbon support (Figure 9(b)).^{16,46,55,93,98} A comparative study on sulfonation of hydrothermally treated cellulose and KOH activated hydrothermally treated cellulose with H₂SO₄ also produced identical results: the hydrochar derived materials exhibited ca. 5.5 times higher SO₃H density (0.953 mmol/g) than the KOH activated char (0.172 mmol/g).¹¹⁵

However, it is also important to highlight that such sulfonation is also accompanied by a significant loss in specific surface areas (up to ~709 m²/g) and, in case of porous carbon supports obtained at low activation/carbonization temperatures, even complete loss of porosity could be observed as a result of the oxidative effects of H₂SO₄ causing a collapse of the pore structure (Figure 10)⁵⁵. In some cases (for biochars), H₂SO₄ even acted as an activating agent creating porosity.⁹⁴ It is also important to note that the liquid phase sulfonation of mesoporous carbon supports with conc. H₂SO₄ or fuming H₂SO₄ will lead to a deterioration or even a severe collapse of the pore structure, while in some cases it was demonstrated to create porosity by activation/oxidation of the carbon precursor.^{16,46,55,93,98,94,136} Gas-phase sulfonation with 50% SO₃ in H₂SO₄ (60 °C for 48 h)⁹⁸ as well as SO₃ (room temperature for 6 days)^{94,136} were also investigated as alternative routes for functionalization. Nevertheless, the methods were found to be powerful in terms of obtaining a higher degree of SO₃H functionalization (~2-3 folds higher than concentrated H₂SO₄) and in terms of preserving the carbon pore-structures. Importantly, the

use of volatile and highly toxic acid gases makes gas-phase sulfonation ‘eco-unfriendly’ and impractical in large scale material fabrication.

As a summary, concentrated H_2SO_4 and fuming H_2SO_4 are the most versatile and inexpensive sulfonating reagents for efficient grafting of carbon surfaces with SO_3H sites. Moreover, their applicability is only limited by the reduced tendency to yield ordered (hydrophobic) carbon materials and harsh temperature requirements. It is also important to point out here that some of the sulfonated carbons obtained by liquid-phase H_2SO_4 (in particular those based on semi-carbonized materials presenting a low degree of polycondensation) are susceptible to deactivation by H_2O adsorption as well as leaching of SO_3H sites.^{22,42,46,55,75,94,134,136,200}

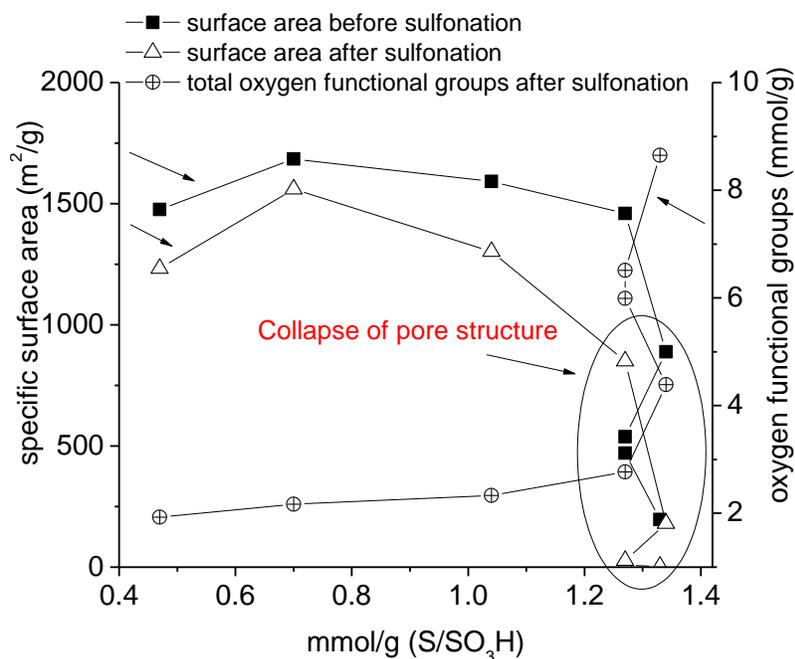


Figure 10. SO_3H density as a function of oxygen functional groups and specific surface areas before and after sulfonation with fuming H_2SO_4 (Compiled from Ref. 55).

4.2.2. SULFONATION WITH ClSO_3H

ClSO_3H is a much stronger sulfonating agent than fuming or conc. H_2SO_4 . Therefore, sulfonations with ClSO_3H are normally carried out at room temperature. Due to its aggressive nature, it has been the reagent of choice upon sulfonation of rigid carbon materials with high degree of polycondensation such as carbon nanomaterials, templated carbons, commercial carbon supports (starbon 300) and carbon nitrides.^{63,101-104,199}

In a typical synthetic procedure, the carbon support is dispersed in an excess of dichloromethane (dry) and stirred. In the next step, ClSO₃H is slowly added to the reaction mixture by a drop-wise addition and stirred for 12 h. The mass ratio between ClSO₃H to the carbon support varies in the range of ca. 1-18.^{101-104,199} Using ClSO₃H as the sulfonating reagent, Varma *et al.* obtained sulfonated carbon nitrides with ~5.47 mmol/g SO₃H sites, at room temperature.¹⁰¹⁻¹⁰⁴ Graphene,^{63,172} templated microporous carbons^{50,159} were also similarly functionalized with SO₃H groups by a ClSO₃H treatment. Even, hydrothermally obtained graphene oxide monoliths were also easily sulfonated with ClSO₃H, at room temperature (in 2 h), yielding sulfonated materials with a high density of SO₃H sites (1.96 mmol/g).⁶² The procedure was also efficient when sulfonating the hydrothermally coated carbon layers of Fe₃O₄ nanoparticles to afford magnetically separable SO₃H-C@Fe₃O₄ composites with a very high density of SO₃H groups (1.4 mmol/g).¹⁸⁵ Interestingly, ClSO₃H-H₂SO₄ mixtures (2:10 and 3:10 v/v) were shown to be a powerful sulfonating reagent mix under reflux conditions, producing a high degree of SO₃H functionalization over Starbons-300 (densities up to 2.3 mmol/g which is almost 2.1 times higher than the materials obtained with conc. H₂SO₄ under identical conditions). However, its use causes aggressive oxidation and collapse of the carbon structure, as evident from the ~2.5 fold increase in total acidity and ~50% reduction in porosity (specific surface area) observed for sulfonated Starbons-300.⁵⁴

Nevertheless, the low temperature liquid phase sulfonation with ClSO₃H offers a very attractive way to graft SO₃H through C-S bonds without affecting the textural and surface properties of carbon supports. ClSO₃H offers advantages in terms of its efficiency for a wide range of carbon supports (from highly ordered graphitic carbons to functionalized hydrothermal carbons): high degrees of sulfonation are achieved under mild process conditions and with lower reagent dosages. Although small quantities of HCl gas are released as a byproduct, it can be easily neutralized with alkali scrubbers. In terms of drawbacks, the use of ClSO₃H is limited by its sensitivity to moisture, the use of non-eco-friendly chlorinated solvents and reproducibility issues.⁶³

4.2.3. ARYLDIAZONIUM SULFONATES (4-BENZENE-DIAZONIUMSULFONATE)

Grafting/functionalization of carbon surfaces through electrochemical or chemical reduction of aryl diazoniums (Billups reaction) and alkyl halides (Billups-Birch reactions) is

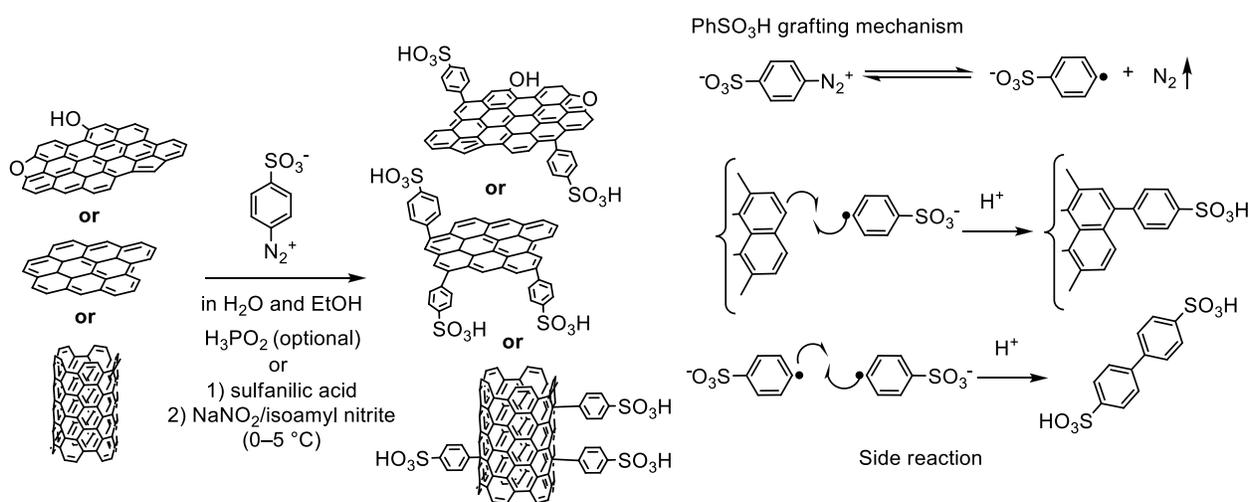
regarded as the one of most efficient routes to produce functional carbon materials.²⁰¹⁻²⁰⁴ These routes have been extensively studied upon functionalization of nanostructured carbons and carbon electrodes with different functional groups including NH₂, COOH, OH, CH₃, OCH₃, Cl, Br, SO₃H and so forth.²⁰¹⁻²⁰⁴ The reaction takes place in liquid phase under relatively mild conditions (0-4 °C or 80 °C), in both aprotic and in (dilute) aqueous acidic solutions and, therefore, the method is non-destructive in terms of textural properties of carbon precursors.

Billups reaction (grafting by chemical reduction of aryl diazoniums) has also been extensively used in the preparation of sulfonated carbons by reductive alkylation/arylation of aryl diazoniumsulfonates (4-benzenediazoniumsulfonate) with rigid/graphite like carbon supports (nanotubes, graphene, ordered mesoporous carbon and activated carbons) (Scheme 4). The sulfonating agent, 4-benzenediazoniumsulfonate, is either freshly prepared by diazotization of sulfanilic acid or prepared in-situ by reaction of sulfanilic acid with isoamyl nitrate or NaNO₂.^{42,52,56,57,61,63,95,96,99,105-109,143-148,157-160,203,205} This functionalization route has several advantages, including the use of non-oxidizing mild sulfonation conditions in liquid phase, low dosage of the sulfonating agent, preservation of the structure and textural properties of the parent carbons and high stability of the resulting -PhSO₃H sites (strongly bonded C(sp²)-SO₃H sites). In addition, the covalently attached benzenesulfonic acid groups are expected to provide an enhanced proton release ability due to the electron-withdrawal capability of aryl groups.^{108,205} As a consequence of the stronger acidity and higher degree of SO₃H functionalization is achieved and the high porosity of these materials results in higher catalytic activity than in the case of carbon-based acids sulfonated by conc. H₂SO₄.

Synthesis of highly ordered sulfonated mesoporous carbon catalysts with a high degree of PhSO₃H functionalization (1.7-1.95 mmol/g) and large specific surface areas (689-741 m²/g) has been reported by Feng *et al.*^{54,99}. The synthetic reaction procedures proceeds through sulfonation of SBA-15 templated ordered mesoporous carbons (obtained from furfuryl alcohol and carbonized at 900 °C) with 4-benzenediazoniumsulfonate in the presence of H₃PO₂ (Billups reaction).^{54,99} Using identical sulfonation procedures, CMK-5 and alumina templated carbons (C-AI-900, C-AII-900 and C-AIII-900) were also functionalization with high densities of PhSO₃H groups.^{106,158,159} Highly acidic sulfonated graphene materials were also produced using identical grafting procedures from both hydrazine hydrate and sodium borohydride reduced graphene oxides whereupon the PhSO₃H densities of the sulfonated materials were ~2 and 2.57 mmol/g,

respectively. The graphene oxide precursor was obtained by oxidative exfoliation of graphite by the ‘Hummers method’.^{17,56} Also in related studies, a mixture of sulfanilic acid and isoamyl nitrate (at 80 °C) was used as the sulfonating reagent (*in-situ* generation of 4-benzenediazoniumsulfonate radicals) to obtain PhSO₃H containing carbon nanofibers,⁶¹ carbon nanocages (CKT),¹⁵⁷ soft templated carbons,¹⁶⁰ hollow mesoporous carbons²⁰⁵ or carbon nanotubes^{61,144}. In another variation of the *in-situ* approach, PhSO₃H functionalized activated carbons were directly obtained by heating a mixture consisting of activated carbon, sulfanilic acid and NaOH (1:1-14:1 w/w in 150 ml water at 5-80 °C for 12 h) and the highest PhSO₃H density (0.72 mmol/g) was obtained when using sulfanilic acid to activated carbon ratio of 7:1 at 80 °C.⁹⁵ Commercial activated carbons,^{95,99,105,106,158} soft templated mesoporous carbon¹⁰⁸ and H₃PO₄ activated carbons^{42,145-148} were also similarly functionalized with 4-benzenediazoniumsulfonate to afford PhSO₃H functionalized activated carbons. In fact, Zhang *et al.*¹⁰⁸ obtained PhSO₃H densities up to 1.97 mmol/g for a self-templated, ordered mesoporous carbon material (carbonized at 700°C, pore diameter 11.5 nm) using the optimized sulfonation conditions described by Murnieks *et al.*⁹⁵. Use of higher sulfonation temperatures are reported to reduce functionalization efficiency due to evaporation/degradation of isoamyl nitrite and side reactions of aryl radicals.^{63,160,201-203}

Scheme 4. Schematic representation of the post-grafting sulfonation approach for obtaining sulfonated carbon materials through electrochemical or chemical reduction of aryl diazoniumsulfonates.



Irrespective of the carbon precursor, the presence of defect-free polycyclic aromatic rings (sp² like) within the carbon support, a low degree of sp² cross-linking (structural ordering), H₃PO₂ and

mild temperatures are necessary (80 °C or 0-4 °C) to induce a high degree of PhSO₃H functionalizations by the Billups reaction. Unlike conventional sulfonating reagents (H₂SO₄, ClSO₃H and SO₃), grafting of 4-benzenediazoniumsulfonate likely occurs through a free-radical process via a homolytic cleavage of the C-N bond, which is also dependent the reduction potential and conductivity of carbon support.^{63,201-203} In fact, a positive effect of carbonization/activation temperatures in terms of the PhSO₃H density was observed for alumina templated carbon¹⁵⁹ and H₃PO₄ activated mesoporous carbons¹⁴⁶; these observations are in agreement with the trend of increasing sp² character of the resulting carbon materials with increasing carbonization temperature (increasing content of sp² like polycyclic aromatic rings, Figure 11(a)).^{146,159}

Similar results were also obtained upon sulfonation of graphene oxide, graphene/reduced graphene oxide (mildly and aggressively reduced) as well as graphite with 4-benzenediazoniumsulfonate by Oger *et al.*⁶³ The authors observed ~2-2.5 fold higher PhSO₃H loadings for hydrazine reduced graphene oxide samples (1.21 and 1.79 mmol/g) in comparison to the non-reduced graphene oxides (0.55 and 0.7 mmol/g) which is consistent with the negative impact associated with the presence of surface oxygenated functional groups such as phenols, epoxides, carboxylic acids and ketones upon grafting with 4-benzenediazoniumsulfonate. The authors also observed that upon a more aggressive two-step reduction of graphene oxides, a sequential use of NaBH₄ and hydrazine resulted in almost defect-free, extensively restacked graphene sheets that were very difficult to sulfonate, similar to the case of native graphite (Figure 11(b)).⁶³ Interestingly, when H₃PO₂ was added as a reducing agent to accelerate the formation of aryl radicals, the reachable PhSO₃H loadings dropped to around 50% (0.80 mmol/g), suggesting that a high concentration of aryl radicals favors undesired pathways like aryl-aryl dimerization.⁶³ These results are in striking contrast to the results reported for activated carbon, whereupon 50% lower PhSO₃H loadings were obtained in the absence of H₃PO₂ as a reductant.¹⁴⁵ It is also interesting to note that the PhSO₃H groups attached to carbon are also susceptible to reduction upon extended exposure to strong reducing agents like H₃PO₂.⁴² Therefore, particular care must be taken to carefully control the reaction conditions and minimize side reactions upon such sulfonation in the presence of H₃PO₂.

Nevertheless, 4-benzenediazoniumsulfonate is effective non-oxidizing sulfonating reagent for controlled covalent grafting of carbon surfaces with PhSO₃H sites under mild conditions via the Billups reaction. This approach preserves the mesoporous channels of the parent material and

offers excellent control of the material properties (PhSO₃H density and surface area) by simple adjustment of the 4-benzenediazoniumsulfonate/carbon mass-ratio and the reaction temperature. This method addresses all major drawbacks and environmental hazards related to the use of conventional sulfonating reagents such as H₂SO₄, ClSO₃H and SO₃ (no release of acid gases SO₂, SO₃ and HCl as well as reduced wastewater generation). The only limitations of this sulfonation route are the higher cost of sulfanilic acid and bulky size of PhSO₃H moieties that significantly decreases the specific surface area (~400-550 m²/g) and pore volume (~30-35%) of the material.^{42,45,106,158,159} As such, 4-benzenediazoniumsulfonate is not the reagent of choice for functionalizing/sulfonating microporous carbons as grafting of bulky PhSO₃H moieties may result in the blockage of micropore channels.¹⁰⁶

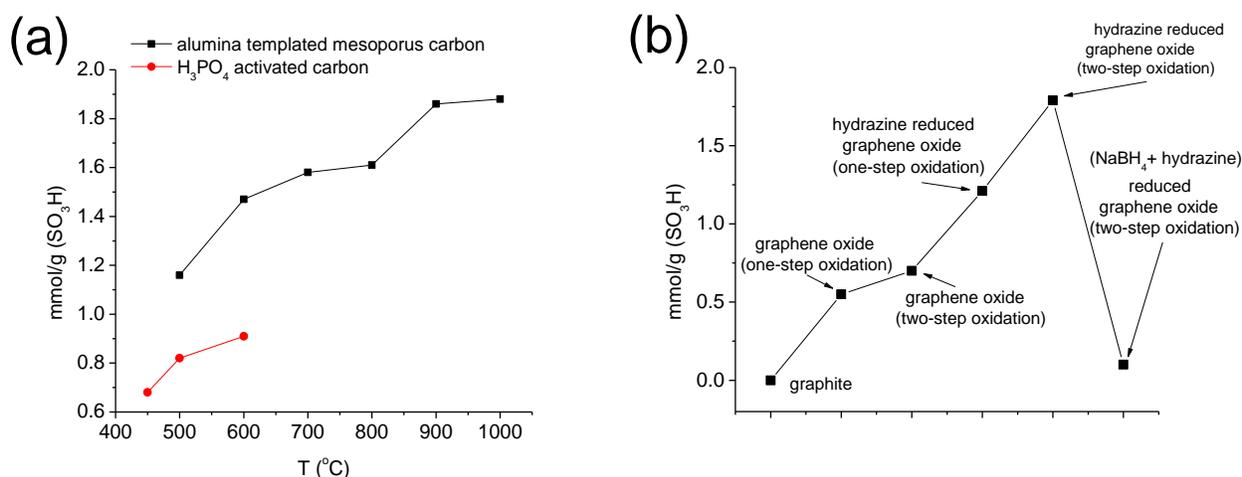


Figure 11. Influence of (a) carbonization/pyrolysis temperature (Compiled from Ref. 146,159) and (b) graphene structure (Compiled from Ref. 63) on the density of PhSO₃H sites.

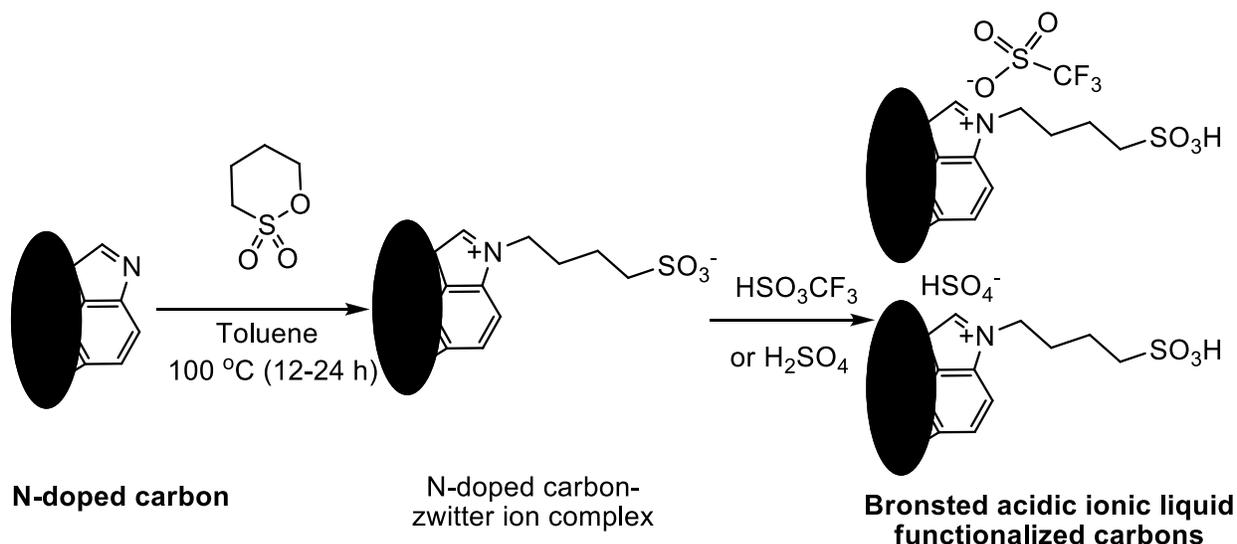
4.2.4. OTHER SULFONATING REAGENTS

In addition to the post-grafting approaches described above (Sections 4.2.1-4.2.3), also several other non-conventional approaches have been developed in recent years that will be discussed below.

For example, poly(*p*-styrenesulfonic acid) was demonstrated as a powerful non-oxidizing sulfonating reagent when grafting SO₃H onto surfaces of carbon nanofibres and carbon nanotubes. Using this approach, very high SO₃H densities of ca. 4.26-5.67 mmol/g was obtained without destroying the delicate surface structure via the free radical polymerization mechanism.¹⁴³ Ionic liquid-functionalization is another alternative grafting approach, in which the SO₃H sites are

functionalized as Brønsted acidic ionic liquids on the surface of N-doped carbons. Noshadi *et al.*¹⁹⁰ showed that by quaternary ammonization of the heterocyclic nitrogen sites (on the doped carbon surface with 1,4-butane sultone, followed by an anion exchange with strong acids of H₂SO₄ or HSO₃CF₃), it is possible to obtain highly hydrophobic ionic liquids functionalized carbons (NPC-[C₄N][SO₃CF₃] and NPC-[C₄N][SO₃H]) (Scheme 5).¹⁹⁰ Similarly, ionic liquids containing bifunctionality have also been obtained by reacting 1-(trimethoxypropyl silane)-3-methyl imidazoliumchloride, Na-exchanged sulfonated biochars followed by acidification with HCl,²⁰⁶ or by the simple wet-impregnation of ionic liquids on sulfonated carbons.²⁰⁷ In another study, Chang *et al.*²⁰⁸ created SO₃H sites on oxidized active carbon surface by amidation of 1-amino-2-naphthol-4-sulfonate with surface COOH groups; the material was applied as a selective solid-phase sorbent upon extraction of gold(III).²⁰⁸

Scheme 5. Schematic representation of the (post-grafting) sulfonation approach for obtaining Brønsted acidic ionic liquids functionalized carbon (adapted from Ref. 190).



In another recent work, a novel plasma-sulfonation process was introduced by Ishizaki and co-workers.²⁰⁹ Unlike conventional sulfonation, the plasma process induced a rapid (in minute scale), high degree of SO₃H functionalization from dilute H₂SO₄ in carbon black. The material SO₃H density was mainly influenced by the concentration of H₂SO₄ and the SO₃H density increased from 0.5 mmol/g to 2.2 mmol/g upon increasing the H₂SO₄ strength from 0.1 M to 1 M. A parallel increase in the density of oxygen functionality was also observed resulting from the

oxidation of carbon black. On the basis of active radicals produced during plasma discharge, the authors proposed a radical type reaction mechanism which was initiated by the following reactions: (1) generation of active SO_3 when H radicals reacted with H_2SO_4 , and (2) successive attack of active SO_3 groups aggressively on the surface of carbon black and formation of $-\text{HSO}_3$ on the surface. Furthermore, it was stated that the formation of $-\text{COOH}$ and phenolic $-\text{OH}$ can also occur simultaneously due to the presence of O and OH radicals.²⁰⁹

5. CATALYTIC APPLICATIONS

The $\text{SO}_3\text{H}/\text{PhSO}_3\text{H}$ -functionalized acidic carbons have demonstrated to have promising behaviors as alternative solid acids catalysts in various organic transformations including esterification, ester-exchange (transesterification), Beckmann rearrangement, acetalization, etherification, hydrolysis, dehydration and various C-C, C-N and C-O bond forming reactions such as alkylation, alkylation/hydroxylalkylation, cross-aldol condensation, Michael condensation, Knoevenagel condensation, amidation, reductive amination, oxidation and multicomponent organic reactions like the Biginelli reaction. Most importantly, due to their favorable surface-textural properties and strong Brønsted acidity, the resulting materials were useful upon liquid phase catalytic transformation of industrially important biomass and biomass-components into high value products such as fuels, additives and chemicals. For example, such solid acids have been applied upon esterification of fatty acids, trans-esterification of triglycerides, acetalization and etherification of glycerol, hydrolysis of polysaccharides (cellulose, hemicelluloses, inulin and starch), dehydration of monosaccharides and condensation/cross-condensation of renewable furanics. The catalytic performance and stability of sulfonated carbons are dependent on both the process conditions and the surface-textural properties of carbon used and, therefore, these properties were strongly influenced by the sulfonation route and carbon precursors.

5.1. ESTERIFICATION REACTIONS

Sulfonated carbons have been extensively studied as esterification catalysts (Scheme 6)^{14-16,22,23,35,36,40,42,43,45,51,54,55,57,58,60,62,65,69,70,75,77-79,93-95,99,102,105,106,110,112,117,118,129,133,139,140,145,153,154,155,159,160,170,171,174,178,186,212,213,205} and acetic acid esterification was, in fact, one of the earliest model reactions used to probe the acid activity of these versatile acidic carbons^{16,22,55,58,75,93,105,123,171,212,213,205}.

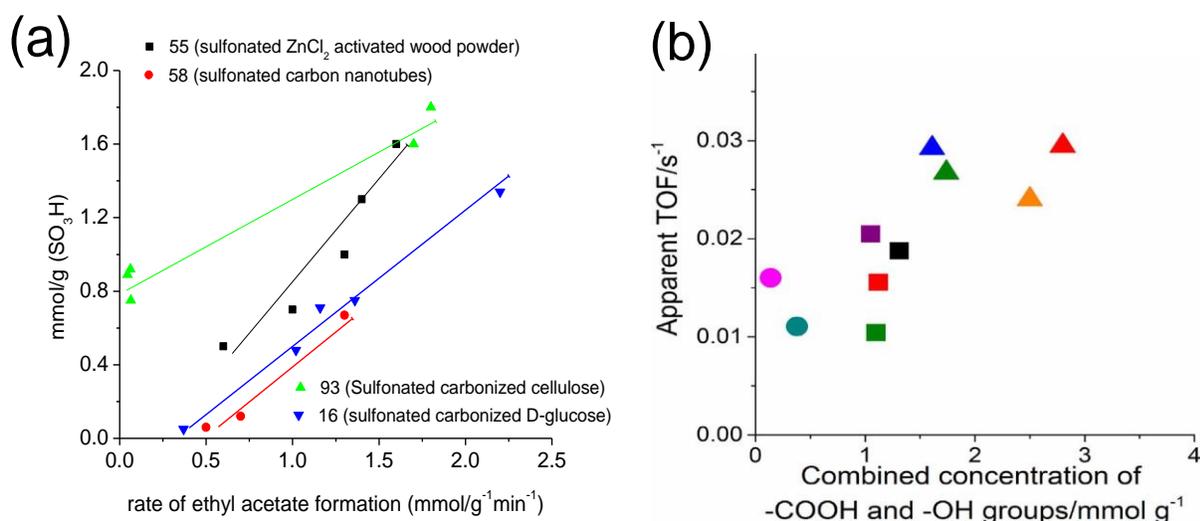
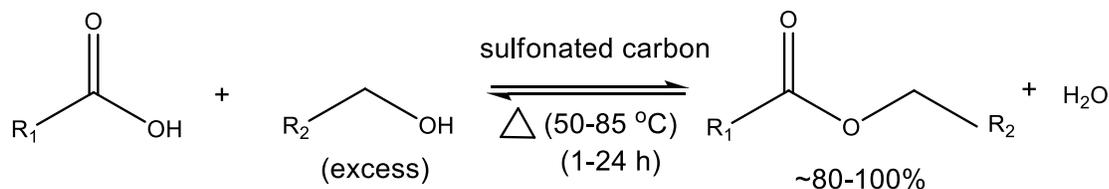


Figure 12. (a) Influence of SO₃H density on acetic acid esterification (rate of ethyl acetate formation) (Ref. 16,55,58,93) and (b) The concentration of additional oxygen-containing functional groups influences the rate (TOF) of levulinic acid esterification with ethanol. Reprinted with permission from Ref. 213. Copyright 2018 Elsevier.

From the different studies conducted upon acetic acid esterification with monohydric alcohols, we can draw certain conclusion based on the SO₃H densities in sulfonated carbon structures (semi carbonized materials, active carbon and nanotubes): It is clearly evident that the catalytic activity upon acetic acid esterification is dependent only on the acid concentration and independent of the specific surface area (pore-characteristics) and carbon structure (Figure 12). In other words, during the liquid phase esterification of acetic acid, these catalysts gave rise to an identical activity per site (turnover frequencies, TOF).^{16,55,57,58,93,105} The observed trends were explained in terms of (a) enhanced adsorption of hydrophilic acetic acid molecules onto the materials with a higher density of SO₃H sites and (b) the negligible mass-transfer limitations of small reactant molecules. The catalytic activity of acidic carbons (TOF) were identical to commercial sulfonic resins like Amberlyst-15.^{22,55,58,75,93,212,231} Esterification of acetic acid with glycerol also showed similar trends in terms of the reaction kinetics (initial rate) for sulfonated carbons, but to achieve high selectivities of the desired tri-esters, either a stoichiometric excess of acetic acid or continuous removal of H₂O was required.^{39,44} Alternatively, a 100% tri-ester selectivity has been achieved with acetic anhydride as the esterification/acetylation reagent.¹⁴⁶ Lactic acid esterification in liquid-phase also produced identical results where the initial rate of ethyl lactate formation increased linearly with the increasing density of surface acid sites,

irrespective of the catalyst structure or textural properties.⁵⁷ The unfolding (swelling) of carbon catalysts in polar liquid media also plays a crucial role in terms of their catalytic performance.⁷⁵ This is supported by the fact that during gas-phase operations, a significant drop in the esterification rate and longer induction periods were demanded for the sulfonated carbon in comparison to Nafion. On the contrary, upon liquid phase operations, the activity trend was reversed being consistent with the poor swelling of carbon materials in the gas phase.⁷⁵ Overall, these acidic carbocatalysts exhibited high activity and stability in both liquid and gas phase esterification of small C2-C3 organic acids.^{57,75}

Scheme 6. Reaction scheme upon esterification of carboxylic acids with alcohols.



Esterification of bulkier levulinic acid with sulfonated carbons gave rise to very different activity trends that were consistent with the collective impact of porosity, surface oxygen functional groups, (COOH and OH) and SO₃H density.^{35,205,213,214} For example, Ogino *et al.*²¹³ found a direct correlation between the total amount of surface -OH and COOH sites (non-catalytic) and TOF for sulfonated carbons, this being indicative of the promotional effects of surface oxygenates on the catalytic activity (Figure 12).²¹³ The observed trend was explained in terms of the enhanced adsorption of levulinic acid on the catalyst surface by strong hydrogen bonding interactions between the γ -keto group of levulinic acid and the presence of surface OH or COOH groups of carbon. In another work, PhSO₃H functionalized hollow mesoporous carbon spheres were demonstrated to be more active than the non-porous sulfonated carbons derived from semi-carbonized glucose and cellulose, as well as Amberlyst-15 and H₂SO₄. However, one should emphasize that the observed activity trend was based on the specific activities (TOF) calculated with respect to the total amount of acid sites as no information was given on the actual SO₃H or COOH and OH densities.²⁰⁵ Similar trends in terms of the total surface acidity dependent catalytic activity were also observed upon levulinic acid esterification with ethanol over sulfonated carbon nanotubes.⁶⁰ Thus, the catalytic performance of solid acids in the esterification reaction is not only related to the strength and amount of acid sites but also to the ability of solid acids to adsorb

different reactants (hydrophobicity and hydrophilicity).^{70,213,214} The influence of catalyst surface chemistry and diffusion limitations become more noticeable in case of esterification of bulky-hydrophobic reactants like hexanoic acid, caprylic acid, decanoic acid and long chain fatty acids (oleic, stearic and palmitic, see below).^{55,77-79,105,110,112,117,140,170} In fact, Wang and co-workers observed that a highly hydrophilic sulfonated hydrochar (Section 4.1.1) is less prone to esterify hydrophobic molecules (pivalic and phenylacetic acid), in comparison to an amphiphilic carbon catalyst bearing dodecyl benzene sulfonate sites. The authors attributed the superior activity of amphiphilic catalyst to its enhanced ability to selectively adsorb hydrophobic pivalic acid and phenylacetic acid.⁷⁰

A large number of studies were conducted upon esterification of long chain (C16-C18) fatty acids (oleic, stearic and palmitic acid) with methanol or ethanol, in order to highlight the catalytic potential of such acidic carbons in biofuel (biodiesel) production. Table 4 summarizes some of the important results on the esterification of fatty acids using the different acidic carbons including sulfonated hydrochars,^{77-79,110,112,117,140} semi-carbonized sulfonated carbons,^{23,36,43,45,94,99,129,139,186} sulfonated active carbons,^{42,94,95,105,133,145} sulfonated carbon nitride,¹⁰² sulfonated silica carbon composites^{178,174} and sulfonated, ordered mesoporous carbons^{51,54,106,153-155,159,160,174,178}.

Table 4. Catalytic activity of sulfonated carbons upon esterification of C16-C18 fatty acids

catalyst	description	pore size (nm)	specific surface area (m ² /g)	acidity (mmol/g)		T (°C)	MeOH/acid (mol/mol)	TOF (h ⁻¹)	stability/ no. of recycle	Ref.
				SO ₃ H	total ^a					
sulfonated semi-carbonized materials	SO ₃ H functionalized hydrochar	n.r	<1	1.30	4.2	64	20	29.2	unstable ^d /3	42
		n.r	4	0.59	5.43	85	10	127.2	unstable ^d /3	79
		n.r	2.2	0.57	7.2	55		15.48 ^c	n.r/n.r	110
	SO ₃ H functionalized sulfonated semi-carbonized glucose	n.r	2	0.7	1.4	80	10 ^b	220 ^c	n.r/n.r	23
		n.r	1	1.2	2.5	80	10 ^b	215 ^c	n.r/n.r	23
		n.r	4.13	1.5	-	80	10	191.4 ^c	n.r/n.r	36
		n.r	<5	3.4	-	80	10	101	n.r/n.r	153
	SO ₃ H functionalized sulfonated biochar	1.06	338	0.45±0.03	5.87	57	20	2.4 ^c	stable with heptane washing and drying/6-12	94
		1.05	242	0.61±0.03	5.57	57	20	9 ^c		94
		n.r	n.r	1.06	3.69	80	10	36.89 ^c	stable with hexane washing and drying/8	129
sulfonated active carbon	PhSO ₃ H functionalized mesoporous active carbon	0.24	318	1.42	1.74	65	57	44	n.r/n.r	106
		3.9	96	0.70	3.96	64	20	70.81	stable with drying/3-5	42
		4.8	483	0.84	3.62	64	20	104		42
		4	468	0.75	3.01	64	20	102.3		42
		n.r	556	0.73	2.426	80	21	51.5		42

	SO ₃ H functionalized mesoporous active carbon	4.1	690	0.30	2.01	64	20	26	unstable ^e /3	42
	SO ₃ H functionalized microporous activated carbon	1.10	1391	0.2±0.01	2.59	57	20	10.8 ^c	unstable ^e /6	94
		0.71	967	0.1±0.002	0.641	60	20	33.6 ^c		94
		1.11	1137	0.81±0.01	2.23	60	20	10.8 ^c		94
sulfonated ordered mesoporous carbons	PhSO ₃ H functionalized ordered mesoporous carbons	14.7	75	1.80	8.2	80	10	244 ^c	unstable ^e /2	54
		9.42	741	1.7±0.07	1.7±0.07	80	^x 10	105.8 ^c	stable with H ₂ O washing and drying/5	99
		2.83	354	1.49	2.55	65	57	109	n.r	106
		8.16	1118	1.86	n.r	65	57	128	stable with MeOH washing and drying/6	159
	SO ₃ H functionalized mesoporous carbon	3.9	807.8	2.3	n.r	80	10	144.15	stable with acetone washing and drying/5	153
sulfonated silica-carbon composites	SO ₃ H functionalized silica-carbon composites	10.5	530	0.39	2.9	n.r	n.r	31	stable with acetone washing and drying/4	174
		10.2	590	0.38	3	n.r	n.r	26		174
		28.8	520	0.35	3.9	n.r	n.r	31		174
sulfonated silica	benzenesulfonic acid	10.0	610	1.17±0.09	1.17±0.09	80	^x 10	52.4 ^c	unstable ^e /5	99

	functionalized SBA-15									
commercial sulfonic resin	amberlyst-15	0.31	43	5.03	5.03	65	57	15	unstable ^e /n.r	159
	nafion (NR50)	n.r	n.r	n.r	n.r	80	^x 10	14.6 ^c	n.r/n.r	99

^a*SO₃H, carboxylic acid, lactone, phenol and carbonyl groups*

^b*ethanol*

^c*TOF values were re-calculated in (h⁻¹) from the kinetic data in the articles in corresponding Ref.*

^d*derivatization and leaching of acid (SO₃H and COOH) sites*

^e*leaching of SO₃H sites*

n.r = not reported

The observed activity trend, sulfonated semi-carbonized > sulfonated ordered mesoporous carbons \geq sulfonated hydrochars > sulfonated mesoporous active carbon > sulfonated biochar = sulfonated wood activated carbon (microporous) = sulfonated silica-carbon composites > sulfonic resin, clearly shows that the catalytic activity upon C16-C18 fatty acid esterification is dependent on three main factors: (a) SO₃H density, (b) density of surface oxygenates (total acid density) and (c) porosity (specific surface area and pore size). The superior turnover frequencies (TOF) observed for non-porous sulfonated hydrothermal carbons and sulfonated, ordered mesoporous carbons further suggest that the total acid density (or density of surface oxygenates) has a more significant impact on the catalytic performance, in comparison to the porosity (Table 4). This unusual activity of the non-rigid sulfonated hydrochars (section 4.1.1 and section 4.1.2) as well as semi-carbonized sulfonated carbons (section 4.2.3) has been attributed to the swelling or unfolding of ultramicropores in highly polar reaction media like methanol or ethanol. The swelling/pore enlargement further enhances the adsorption of bulky hydrophilic fatty acid substrates onto the various hydrophilic surface sites (SO₃H, OH or COOH sites, Figure 13(a)). In fact, it has been experimentally demonstrated on the basis of H₂O adsorption (or H₂O adsorption-desorption) experiments that the hydrophilic surface areas of these materials are in the range of 220-535 m²/g and significantly higher than the dry form specific surface areas (<50 m²/g) obtained from N₂ adsorption-desorption isotherms. Moreover, the hydrophilic surface areas display a decreasing trend with respect to increasing carbonization temperature and in agreement with the hypothesis of removal of surface oxygenates at higher carbonization temperatures, Figure 13(b).^{77-79,216}

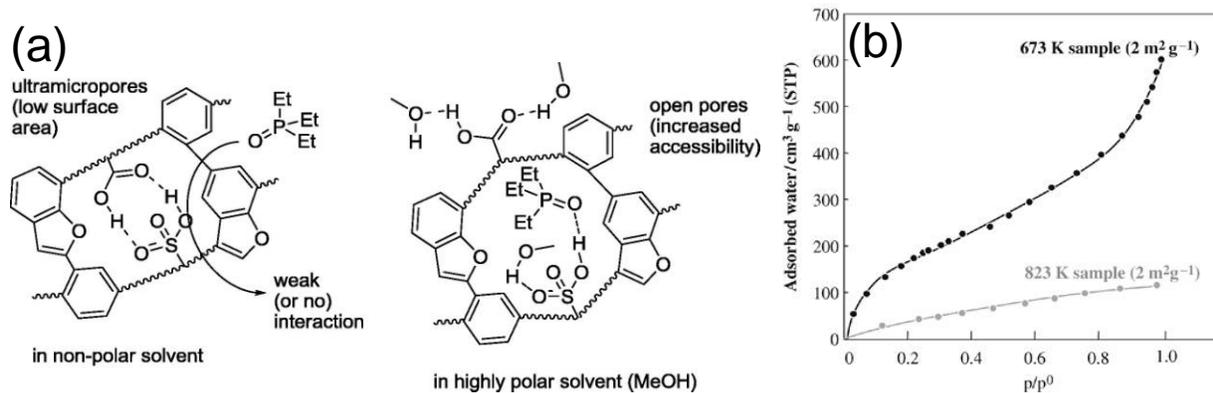


Figure 13. (a) Mechanism depicting the unfolding of ultramicropores of sulfonated semi-carbonized materials in a polar media that facilitate adsorption of bulky oxygenates. Reprinted with permission from Ref. 77. Copyright 2014 Elsevier and (b) of H₂O adsorption isotherms for

carbon based sulfonated solid acids prepared from D-glucose at different carbonization temperatures. Reprinted with permission from Ref. 216. Copyright 2007 John Wiley and Sons.

The adsorption-enhanced catalysis also accounts for the unusually high TOFs observed for chemically activated sulfonated carbons and sulfonated starbons-300A2 with lower specific surface areas but very high densities of surface oxygenates (higher total acidities) (Table 4).^{42,54} On the other hand, in terms of long term stability and reusability, the catalytic materials presenting larger mesopores and a hydrophobic, rigid carbon backbone, are advantageous as they are less susceptible to leaching of the sulfonated aromatic fragments (1 to 1.3 nm) and poisoning through chemisorptions of water and oxygenated molecules.^{14,15,51,54,75,106} Overall, large pore amorphous carbon catalysts demonstrating a good balance of SO₃H as well as surface COOH and OH sites are essential when aiming at performance (in terms of activity, selectivity and long term stability) upon esterification of large fatty acids.^{42,54,99,106,153,159}

Similarly, glycerol esterification with lauric and oleic acids using sulfonated mesoporous carbon and sulfonated hydrochar afforded improved activities and selectivities towards mono-glycerides; 70–80 % selectivities were reached at fatty acid conversion levels of 80–95%. In contrast, over acidic zeolites, mono-glyceride selectivities were in the range of 60-67% even at lower (~50%) conversion levels. The improved activity and selectivity were attributed to the unique combination of oxyphilic and surface sulfonic sites simultaneously promoting selective adsorption of glycerol and preventing adsorption of higher mono-glyceride and di-glycerides.²¹⁰ The sulfonated carbons were even shown to be good catalysts upon solid-phase esterification reactions, as confirmed by the high yield of cellulose acetate (77%) observed during solid-phase acetylation of cellulose with acetic anhydride (80 °C, acetic anhydride-to- anhydroglucose unit (AGU) mole ratio of 4.5–9). It was possible to control the yield and degree of substitution of esterified products by a simple adjustment of reaction conditions. Most importantly, after the reaction, it was possible to separate the esters soluble in acetone or dimethyl sulfoxide from the catalytic materials thus proving the recyclability of the catalyst.¹⁴⁸

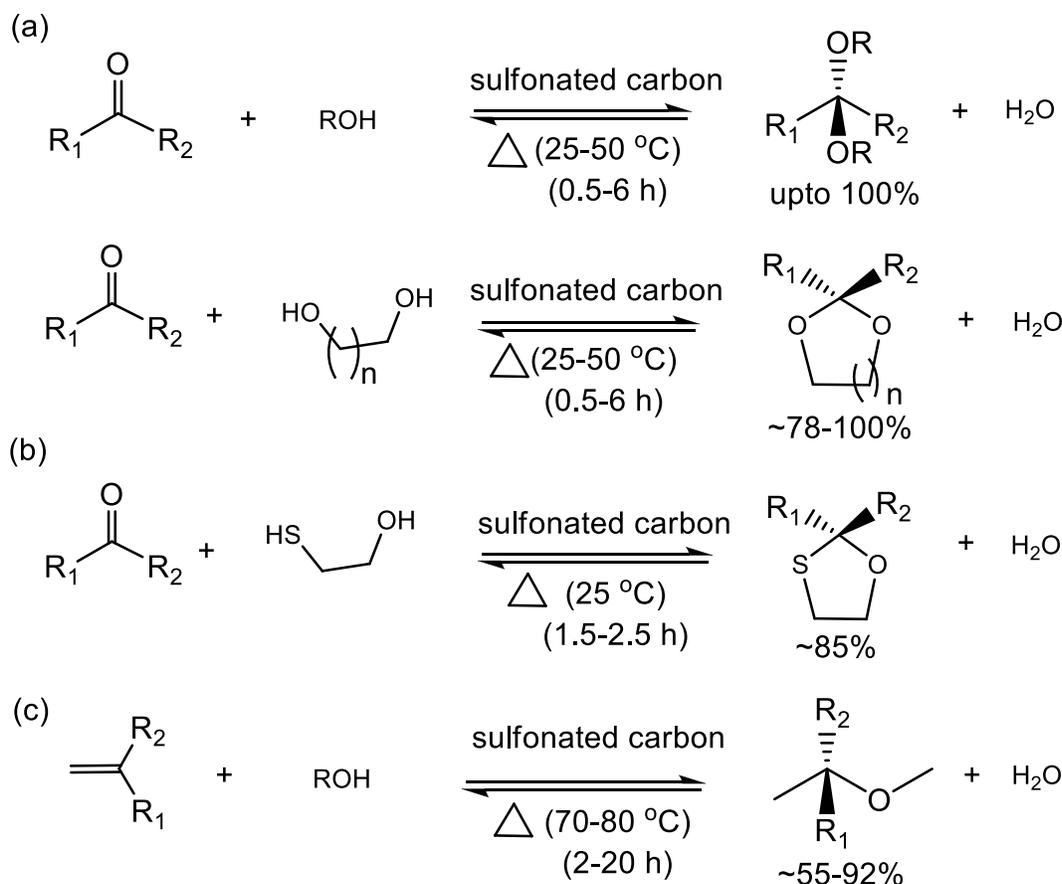
To summarize, sulfonated carbons show excellent potential as alternative acid catalysts in esterification reactions for a wide range of substrates outperforming conventional solid acids and even H₂SO₄ (selected examples, depends on the reactant and catalyst properties). Most importantly, due to the combination of unique SO₃H acidity and surface oxophilicity, sulfonated

carbons are particularly suitable in converting industrially relevant organic acids like levulinic acid and C16-C8 fatty acids into the corresponding esters. Among different acidic carbons, the materials with a flexible hydrophilic structure and a high density of oxygen functional groups present the best initial activity. However, they are more susceptible to deactivation in comparison to the rigid carbons with a moderate density of acid sites. An elaborated discussion on the effects of carbon structure on activation and deactivation is given below in section 6.

5.2. ACETALIZATION AND ETHERIFICATION REACTIONS

Acetalization, oxathioketalization and etherification are related C-O bond forming condensation reactions in which the acidic carbons have shown promising catalytic ability (Scheme 7).^{66,69,123, 125,175,181,119,199,211}

Scheme 7. Reaction scheme for (a) acetalization, (b) oxathioketalization and (c) etherification.



Acidic carbons catalyze the transformation of a wide range of aldehydes and ketones such as acetone, cyclohexanone, benzaldehyde, furfural and methyl levulinate giving rise to high yields (up to 100%) of desired ketals and acetals. In particular, the production of five membered cyclic ketals and acetals obtained from the condensation of glycerol with acetone, furfural or methyl levulinate, hold significant industrial importance as multi-component fuel additives.⁶⁶ It was further demonstrated that the meso/macroporous lignosulfonate derived acidic carbons outperformed the commercial acid catalysts Amberlite-IR120 and Amberlyst-70 upon acetalization of glycerol. Herein the acidic carbocatalysts demonstrated exceptional operational stability and could be operated in a fixed-bed reactor for continuous solketal production without any signs of deactivation during 90 h of operation (conversion >91%).⁶⁶ In another study by Wang *et al.*¹⁹⁹, solketal yields up to ~78% were obtained from stoichiometric mixtures of glycerol and acetone over a sulfonated hollow sphere carbon catalyst. The catalyst activity was comparable to liquid H₂SO₄ and ~1.2 times higher than what was achieved with the most active commercial solid acid catalyst Amberlyst-15 (limited by diffusion). The carbocatalyst also presented exceptional operational stability (constant solketal yield during 4 successive operations). Meanwhile, Wang *et al.*¹¹⁹ demonstrated the high catalytic activity of *p*-toluenesulfonic acid derived hydrothermal carbons in the acetalization of benzaldehyde with methanol.¹¹⁹ Ordered sulfonated silica carbon nanocomposites were also found as catalytically active in the acetalization of large molecules such as benzaldehyde, iso-valeraldehyde, iso-butyraldehyde, benzaldehyde and cyclohexanone, with either ethylene glycol or hexaethylene glycol. When ethylene glycol was applied as the reactant, acetal/ketal yields were >90% for all carbonyl compounds. Meanwhile, for 1,4-butanediol, the yields were reduced by ca. 5%.^{175,181} Similarly, upon oxathioketalization of cyclohexanone with mercaptoethanol sulfonated hydrochar catalysts (derived from furfuraldehyde-hydroxyethylsulfonic or glucose-citric acid-hydroxyethylsulfonic acid mixtures), ketal yields up to 85% were obtained, identical to the yields observed when liquid H₂SO₄ catalyst was applied.^{69,123}

Sulfonated carbons were also demonstrated to be efficient etherification catalysts suitable in the production of high value gasoline additives like tert-amyl methyl ether and glycerol tert-butyl ether. Upon etherification of isopentene with methanol and in the presence of an acidic carbocatalyst with a large amount of SO₃H sites (ca. 3.1 mmol/g), a high isopentene conversion of 55.2% could be reached in 20 h at 80 °C. Furthermore, with respect to TOF, the carbocatalyst outperformed both sulfonic resins (254 vs 150 h⁻¹) and H₂SO₄ (254 vs 44 h⁻¹).¹²⁵ In another study,

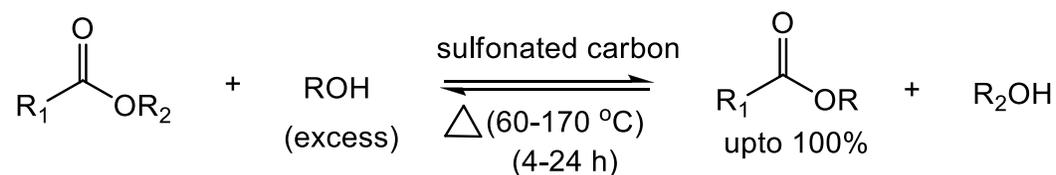
a peanut shell derived sulfonated carbon was performing well in the etherification of isobutylene with glycerol. The reaction was producing a mixture of di-tert-butylglycerols and tri-tert-butylglycerol in 92.1% selectivity, at complete glycerol conversion, under optimized reaction conditions (isobutylene to glycerol mole ratio of 4:1, 2 h and 70 °C) over multiple reaction cycles.²¹¹

Overall, the acidic carbons show excellent potential as alternative acetalization and etherification catalysts demonstrating high TOFs and operational stability in comparison to the conventional solid acids. The unusual and improved activity of sulfonated carbons upon acetalization of aldehydes and ketones with alcohols is also related to their unique oxyphilic properties that promote improved adsorption the oxygenated reactants and presence of stable covalently stable strong SO₃H sites .^{66,69,123}

5.3. TRANSESTERIFICATION REACTIONS

The usefulness of sulfated carbons were also evaluated in ester production by transesterification or ester-exchange reactions. This is an industrially important reaction used in the manufacturing of plasticizers, biofuels and plastic recycling.^{14,41,47,59,61,75,129,130-134,145,147,156,172,184,188,190,215,216} As expected, the transesterification activity of acidic carbons was significantly lower in comparison to the esterification activities, as observed in case of liquid acid catalysts and in agreement with the slower acid catalyzed alcoholysis mechanism (Scheme 8).¹⁶⁵

Scheme 8. Reaction scheme for transesterification of alcohols.



For transesterification of small-alcohol soluble esters like ethyl acetate and triacetin, the reaction rate was independent on the specific surface area and surface chemistry. Product yields and reaction kinetics were only influenced by the density of active SO₃H sites, analogous to the esterification of C2-C3 organic acids.^{75,172,215} However, in case of transesterification of bulkier esters like tricaprins and those present in natural triglycerides (soybean, rapeseed and alike), the catalytic activity was typically reduced by ~8-9 fold. The reduced catalyst activity was mainly

attributed to reduced mass-transfer arising from the immiscibility of larger, hydrophobic triglycerides with alcohol (methanol) and also intraparticle diffusion resistances of large triolein and soybean oil molecules.⁷⁵ Nevertheless, it is possible to improve the trans-esterification activities of sulfonated carbons for large triglycerides by improving the mass-transfer: this can be accomplished through use of higher reaction temperatures (≥ 130 °C), pressure and stoichiometric excess of methanol (~10-55:1 methanol to triglyceride mole ratio).^{14,46,59,61,156} For example, upon triolein trans-esterification, Hara demonstrated the superior catalytic activity of an inexpensive sulfonated carbon (obtained by in-situ carbonization of sulfopolycyclic aromatic compounds in concentrated H₂SO₄, Section 4.1.1), in comparison to conventional solid acids like Amberlyst-15, sulfated zirconia and Nafion. Interestingly, the catalytic material produced methyl oleate (biodiesel) in high yields (~94-99%) over 5 recycles when operating at 130 °C for 5 h. Even though the catalyst gave rise to a high activity (even in the presence of 0.02-2.5 g of water) during multiple recycles, leaching of SO₃H groups was reported (5-10%) at the early stage of the reaction which can have a detrimental effect on the fuel quality.^{14,22} A similar catalyst obtained by sulfonating carbonized glucose in fuming H₂SO₄ (Section 4.2.1), also showed high transesterification activity (ca. 24% ethyl and methyl oleate from triolein at 80 °C).^{132,216} Nevertheless, in the case of glucose derived, amorphous, acidic carbon, significant leaching of acid sites were observed at high temperature and pressure conditions (150 °C, 17 bar). Regardless, a high activity in soybean oil transesterification was reported upon the first cycle (methyl ester yields up to 90%).¹³⁰ In another work, Bitter *et al.*⁶¹ used PhSO₃H grafted carbon nanofibres (Section 4.2.3) as catalysts in the transesterification of triolein (120 °C, 10 mole excess methanol). The highest methanol yield obtained was 73% in 4 h over the most active nanofibre catalyst. This was comparable to the 72% yield recorded over sulfonated, carbonized cellulose catalyst (Section 4.2.1). In terms of the specific activity, the TOF for the nanofibre catalyst was ~24% of H₂SO₄ (0.32 vs 1.36 min⁻¹), but almost 1.7 times higher than a non-porous cellulose based sulfonated catalyst (0.32 vs 0.19 min⁻¹) obtained according to the procedures described in Section 4.2.1. Most importantly, the nanofibre catalyst obtained by radical grafting demonstrated superior reusability due to the presence of highly stable PhSO₃H which did not leach during four successive reaction cycles (0.62 to 0.61 mmol/g). Meanwhile, the amorphous carbon catalyst obtained via H₂SO₄ treatment showed significant leaching of SO₃H sites (1.92 to 1.25 mmol/g) that was accompanied by a parallel loss of activity.⁶¹ Furthermore, also biochars (KOH activated) sulfonated with fuming H₂SO₄ were

introduced as efficient catalysts upon canola oil trans-esterification with methanol, producing methyl ester yields up to 44.2 %. However, the catalysts deactivated rapidly due to the leaching of SO_3H sites.⁴⁶ In another work, carbon nanotubes sulfonated with H_2SO_4 were demonstrated as good catalysts in the trans-esterification of trilaurin with ethanol, producing up to 70% ethyl esters in 1 h at 130 °C. The reaction activation energy was estimated to be 72 ± 4 kJ/mol assuming pseudo-first-order kinetics, while no data was presented in terms of material stability or reusability.⁵⁹

Triolein transesterification proceeded more smoothly over a hydrophobic, microporous sulfonated carbon (obtained by treating zeolite templated carbons with ClSO_3H , section 4.2.1). More than $\geq 99\%$ methyl oleate yield was achieved in 1 h under milder process conditions (80 °C).¹⁵⁶ In terms of TOF, the microporous catalyst (24 h^{-1}) surpassed commercial Amberlyst-15 (0.19 h^{-1}), Nafion-NR50 (0.33 h^{-1}), hydrophilic-non porous sulfonated carbons (1.1 h^{-1})^{14,22} and even H_2SO_4 (7.7 h^{-1}). The enhanced activity of the catalyst was attributed to its high specific surface area and hydrophobic carbon surface, thus enhancing the adsorption of bulky reactant molecules on active sites (a similar non-porous hydrophobic catalyst presented no activity).¹⁵⁶ This observation is in stark contrast to adsorption-enhanced catalysis observed upon esterification of fatty acids (Section 5.1). Most importantly, the catalyst presented good compatibility with H_2O and exceptional reusability was demonstrated with no detectable SO_3H leaching. Assuming pseudo 1st order kinetics, the reaction activation energy was estimated to 61, 43 and 41 kJ/mol for the microporous acidic carbon, hydrophilic-non porous acidic carbon and H_2SO_4 , respectively.¹⁵⁶ Table 5 gives a summary of the activity of acidic carbons upon trans-esterification of large triglycerides.

Unique acidic, surface properties and water tolerance of acidic carbons facilitated their use as bi-functional catalysts in simultaneous esterification and trans-esterification of low-grade triglyceride feeds or acids oils (e.g. waste cooking oil, crude vegetable oils).^{41,47,130-134,145,147,156,188,190,216,216} Hara and co-workers obtained superior or identical catalytic performance of acidic carbons upon direct conversion of simulated feeds containing triolein-oleic acid and triolein-stearic acid mixtures. Other authors also reported similar results upon transesterification-esterification of triglyceride-fatty acid mixtures.^{47,130,131,184} In fact, the presence of free fatty acids in the mix-triglyceride feeds were found to be beneficial in terms of improving the mass-transfer

by solubilization of the triglyceride component in the methanol/alcohol phase thus giving rise to improved trans-esterification and esterification yields under relatively mild conditions (overall FAME yield up to 71% at 80 °C and 91% at 120 °C).^{145,147} On the basis of kinetic experiments conducted with three mix-triglyceride feedstocks containing varying amounts of free fatty acids (21–41 wt%), a direct correlation was demonstrated between the obtained reaction kinetic parameters and initial free fatty acid levels. Konwar *et al.*¹⁴⁷ observed significant variations in the reaction rates, equilibrium constants and activation energies upon trans-esterification-esterification of mixed triglyceride feedstock's over a mesoporous PhSO₃H functionalized active carbon (Section 4.2.3). A higher initial free fatty acid level favors faster kinetics upon trans-esterification due to improved mass-transfer but gives rise to lower biodiesel yields by shifting the trans-esterification equilibrium in backward direction. For example, when the initial acid content in the feedstock increased from 21 to 41 wt%, the esterification rates were almost unaffected while the trans-esterification rates (triglyceride to diglyceride) were enhanced. Also, the equilibrium constants K_{eq1} (fatty acid to ester) and K_{eq4} (monoglyceride to glycerol) were reduced which is consistent with the shifting of reaction equilibrium towards the reactant side. At the same time, activation energies (E_{a1} , E_{a4} , E_{a3} and E_{a4}) were reduced as the reaction mixture changed from a biphasic to a monophasic system due to the surfactant effect caused by increased free fatty acid and monoglyceride concentration.¹⁴⁷

As a conclusion, it can be stated that sulfonated carbons are excellent catalysts in trans-esterification or ester-exchange reactions. These materials were found to be particularly suitable as bifunctional catalysts upon biofuel (biodiesel) production, using low-grade triglyceride feedstocks. However, this is in contrast to the observations obtained upon adsorption-enhanced catalysis of oxygenated molecules like fatty acids, alcohols and related aldehydes and ketones. The presence of hydrophobicity, large pores and a rigid carbon framework structure with stable SO₃H sites are essential to achieve superior activity and stability in trans-esterification of triglycerides. As such, the rigid acidic carbons with low density of acidic sites obtained by sulfonation with 4-benzenediazoniumsulfonate represent the most ideal carbocatalysts for alcoholysis reactions.

Table 5. Comparison of transesterification activity sulfonated carbons upon of large triglycerides

<i>catalyst</i>	<i>description</i>	<i>acidity (mmol/g)</i>		<i>pore size (nm)</i>	<i>specific surface area (m²/g)</i>	<i>T (°C)</i>	<i>MeOH/triglyceride (mol/mol)</i>	<i>time (h)</i>	<i>yield (%)</i>	<i>stability/ no. of recycle</i>	<i>Ref.</i>										
		<i>SO₃H</i>	<i>total^a</i>																		
sulfonated semicarbonized materials	SO ₃ H functionalized semi-carbonized polyaromatics	1.9	4.3	n.r n.r	2	80	10	24	36	stable with H ₂ O washing and drying/5	14,216										
						130 ^b	55	5	98.1	unstable (5–10% SO ₃ H leaching)/5	14										
	SO ₃ H functionalized semi-carbonized glucose	1.3	n.r	n.r	2-5	80	10 ^d	n.r	~24	stable with H ₂ O washing and drying/5	216										
												2.73	n.r	n.r	0.31	150 ^c	30	2	90	unstable (57% SO ₃ H leaching)/n.r	130
	SO ₃ H functionalized semi-carbonized cellulose	1.9	4.3	n.r	2	80	10	6	24.1	n.r/n.r	132										
												1.9	4.3	n.r	2	130 ^b	55	5	98.1	stable with H ₂ O washing and drying/5	132
												1.08	1.9	n.r	n.r	120 ^b	10	4	73	unstable (35% acid site leaching)/n.r	61
	sulfonated carbon nanofibre	PhSO ₃ H functionalized graphitic carbon fiber	0.62	0.63	n.r	n.r	120 ^b	10	4	72	stable with water-ethanol	61									

										washing and drying/4	
sulfonated biochar	SO ₃ H functionalized activated biochar	n.r	1.2 ±0.1	n.r	640	150 ^c	30	3	44.2±1.9	unstable (87% SO ₃ H leaching)/2	46
sulfonated nanotubes	SO ₃ H functionalized carbon nanotubes	1.62*	n.r	5–35	198.9	150	121 ^d	1	97.8	n.r/n.r	59
sulfonic resin	Amberlyst-15	4.7	4.7	n.r	n.r	120 ^b	10	4	22	n.r/n.r	61

* atomic percentage of sulfur

^aSO₃H, carboxylic acid, lactone, phenol and carbonyl groups

^bautogenous pressure

^c17 bar

^dethanol

n.r = not reported

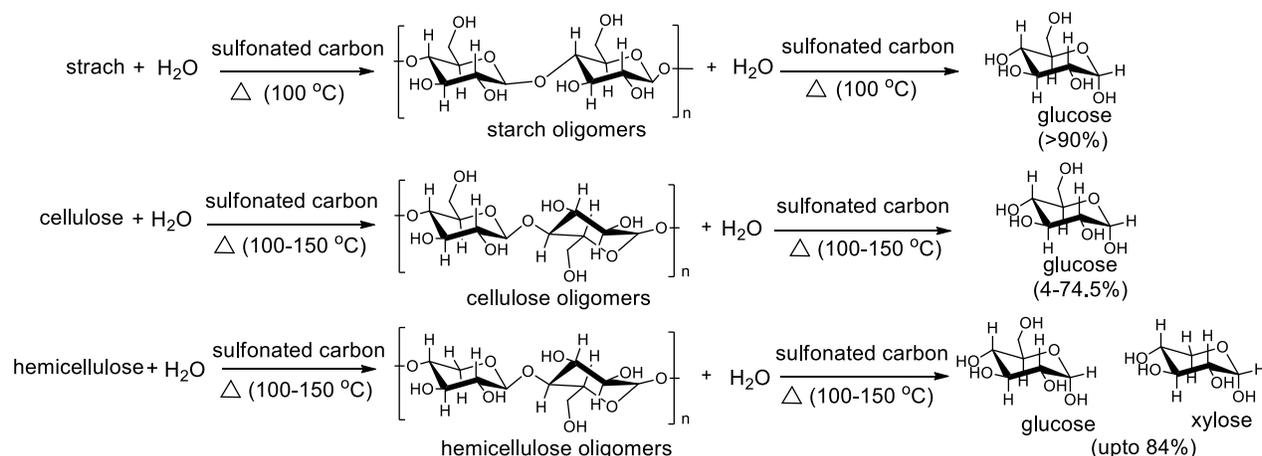
5.4. HYDROLYSIS AND HYDRATION

Sulfonated carbons were also shown to exhibit activity as alternative solid acid catalysts upon hydrolysis and hydration reactions of different refinery and renewable streams. Hydrolysis and hydration are important reactions of industrial significance used in the commercial production of acids, alcohols, aldehydes and ketones from petroleum streams (olefin and acetylene). Hydrolysis is also another important reaction of potential commercial significance for the production of C5 and C6 sugars platforms within the existing and future biorefinery platforms.²²⁰⁻²²⁵

5.4.1. HYDROLYSIS OF POLYSACCHARIDES

Polysaccharide hydrolysis is an industrially important reaction where sulfonated carbons have been extensively studied. Hydrolysis or saccharification involves breaking of α -1,6-glycosidic bond, α -1,4-glycosidic bonds or β -1,4-glycosidic bonds of the large polysaccharide units with H₂O, and produces the building C5 or C6 monosaccharide units (glucose, xylose) (Scheme 9). Within the lignocellulosic biorefinery, glucose and xylose are the key precursors in the production of bio-based platform chemicals (furfural, 5-hydroxymethylfurfural, levulinic acid, lactic acid, formic acid, γ -valerolactone, isosorbide, sorbitol and so-forth) and biofuels (ethanol).^{14,15,220-225}

Scheme 9. Reaction scheme for hydrolysis of starch, cellulose and hemicelluloses (4-72 h).



Sulfonated carbons are good catalysts upon saccharification of cellulose,^{14,15,42,50,53,76,80,91,93,107,111,114,121,124, 127,128,135,179,189,190,206,209,216,218,220,221,222} hemicellulose^{136,219,223} and starch^{71,207,218} and operate under mild hydrothermal conditions. In fact,

these acidic carbons are the most active, selective and stable non-enzymatic catalyst known to hydrolyze the β -glycosidic bonds.^{14,15,53,91,92,206,216,218,222} This is evident from the excellent activity and stability of sulfonated semi-carbonized cellulose (Section 4.2.1) observed upon continuous hydrolysis of cellobiose in a fixed-bed reactor during operations up to ~200 h (Figure 14).^{15,80,221}

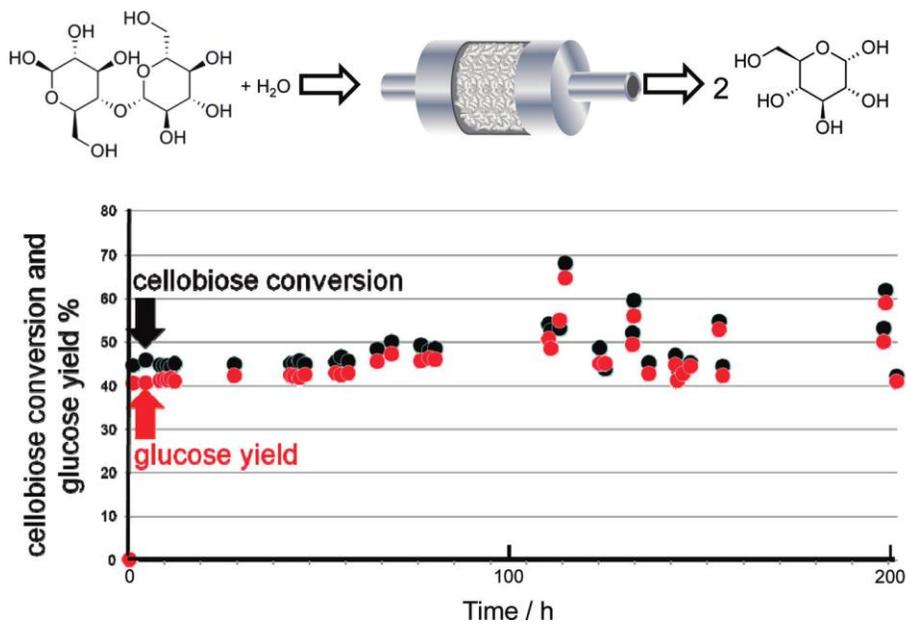


Figure 14. Hydrolysis of cellobiose by cellulose-derived sulfonated carbon catalyst in a fixed-bed reactor (Reaction conditions: temperature: 100 °C, reactor volume: 11 ml, catalyst: 5.3 g, feed: 0.1 ml/min 0.5 wt % cellobiose aqueous solution). Reprinted with permission from Ref. 15. Copyright 2012 American Chemical Society.

In the case of such acidic carbocatalysts, hydrolysis has been proposed to take place via an adsorption promoted mechanism similar to the reactions discussed in section 5.1 and section 5.3. The reaction steps involve the initial binding (or adsorption) of amorphous cellulose or soluble oligomeric fragments (glucans) onto the catalyst surface through hydrogen bonding with oxygenated functional groups and subsequent hydrolysis of the glycosidic bonds by the catalytic action of strongly acidic SO₃H sites (Figure 15).^{14,15,53,91,218}

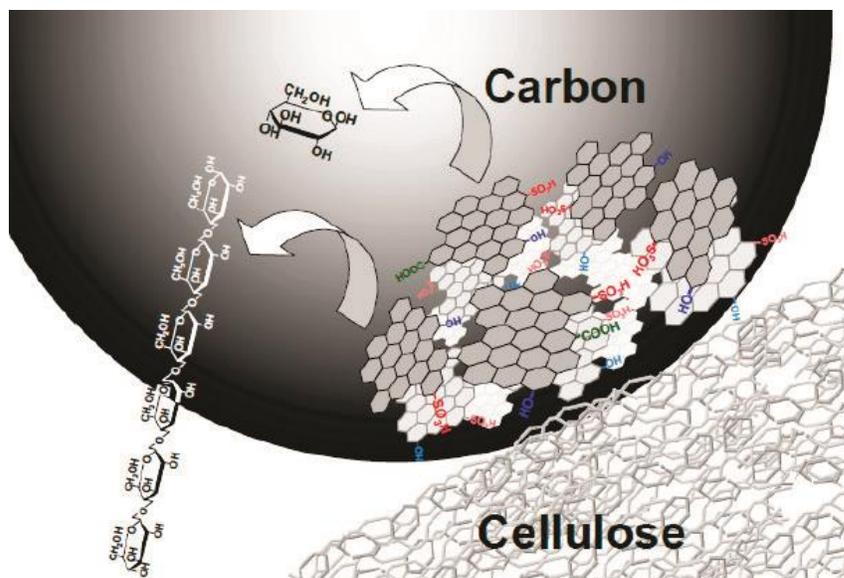


Figure 15. Schematic representation of reaction mechanism for the hydrolysis of β -1,4-glucan by amorphous carbon bearing SO_3H , COOH and phenolic OH groups. Reprinted with permission from Ref. 91. Copyright 2008 American Chemical Society.

As a matter of fact, for solid acid catalysts, a positive correlation has been observed between the amount of surface oxygen functional groups with the adsorption and hydrolysis of water soluble β -1,4 glucans (e.g. cellobiose, cellohexaose).^{14,15,50,53,91,92,107,206,216,218,220-222} Incorporation of Cl sites onto carbon surface was also demonstrated to yield a positive effect on the adsorption of glucans.^{161,220,226} In contrast, over commercial acid resins bearing only SO_3H sites (e.g. Amberlyst-15, Nafion) such adsorption could not be observed. This is in agreement with the inability of SO_3H groups to function as binding sites for glucans and hence, the poor activity and selectivity.^{14,15,107} Among the different oxygen groups, the phenolic OH groups were identified as the dominant sites responsible for hydrogen bonding with β -1,4-glucans, as is evident from the poor absorptive capacity of Amberlite-IRC 76 containing COOH sites.^{14,15} The adsorption of cellulose on carbon surfaces have also been explained in terms of $\text{CH}-\pi$ interaction between the CH groups of cellulose with the π electrons on the polyaromatic surface of carbon materials.²²⁰ The high glucose (monosaccharide) selectivity observed upon hydrolysis of β -glucans have been attributed to the ability of carbons to selectively adsorb larger polysaccharides and reduced tendency to bind with monosaccharides, resulting from weaker $\text{CH}-\pi$ and hydrophobic interactions.^{15,107,220} Table 6 gives a summary of the catalytic activity of different acidic carbons upon saccharification of different cellulosic feedstock's.

Table 6. Saccharification activity of sulfonated carbons upon conversion of cellulosic feedstock's

<i>catalyst</i>	<i>description</i>	<i>pore size (nm)</i>	<i>specific surface area (m²/g)</i>	<i>acidity (mmol/g)</i>		<i>T (°C)</i>	<i>time (h)</i>	<i>conv. (%)</i>	<i>sugar yield (%)</i>	<i>stability/ no. of recycle</i>	<i>Ref.</i>
				<i>SO₃H</i>	<i>total^a</i>						
sulfonated semi-carbonized materials	SO ₃ H functionalized semi-carbonized materials	n.r	2	1.9	4.3	100	3	~65 ^b	4	stable/25 (200 h in fixed bed ^d)	15,91
		n.r	6	2.01	3.96	150	24	~45	~35	n.r/n.r	53
	SO ₃ H functionalized hydrochar	n.r	n.r	0.12	4.22	130	~1.5	n.r	~60 ^c	n.r/n.r	124
		n.r	<1	1.3	4.2	150	24	43	27	n.r/n.r	42
sulfonated active carbons	SO ₃ H functionalized activated carbons	n.r	806	0.44	1.63	150	24	~40	~45	n.r/n.r	218
		n.r	728	0.24	1.03	150	24	43.4	17.9	n.r/n.r	53
		n.r	462	0.23	2.03	150	24	66.6	56	n.r/n.r	53
		n.r	762	0.44	2.23	150	24	74.3	62.6	n.r/n.r	53
	SO ₃ H functionalized microporous carbons	n.r	981	0.33	1.10	150	24	~60	~45	n.r/n.r	53
		n.r	834	0.28	2.08	150	24	~65	~55	n.r/n.r	53
sulfonated mesoporous carbons	SO ₃ H functionalized CMK-3	n.r	412	0.63	2.39	150	24	94.4	74.5	n.r/n.r	53
	PhSO ₃ H functionalized mesoporous carbon	3.9	93	0.7	3.96	150	24	61	53	n.r/n.r	42
		4.8	483	0.84	3.62	150	24	60	46	n.r/n.r	42
sulfonated carbon nanomaterials	SO ₃ H functionalized nanotubes	n.r	96	0.02	0.26	150	24	45	28	n.r/n.r	53
sulfonated carbon composites	SO ₃ H functionalized Silica-Carbon nanocomposites	6.7	332	n.r	0.37	150	24	60.7	50.4	unstable (SO ₃ H leaching)/4	179

sulfonic resins	Amberlyst 15	n.r	n.r	1.7	1.7	150	24	33.7	25.5	n.r/n.r	218
-----------------	--------------	-----	-----	-----	-----	-----	----	------	------	---------	-----

^a*SO₃H, carboxylic acid, lactone, phenol and carbonyl groups*

Reaction conditions: cellulose: catalyst (w/w ratio) = ~1, ca. 1 wt % amorphous cellulose (ball milled or ionic liquid treated) in H₂O

^b*crystalline cellulose*

^c*in ionic liquids*

^d*cellobiose*

n.r = not reported

Comparison of the activity trends presented in Table 6 reveal that saccharification activity of sulfated carbons are influenced by several factors including, (a) textural properties (specific surface area, pore size, pore volume) of catalyst, (b) density of SO₃H sites, (c) density of surface oxygenates (COOH and phenolic OH groups) and (d) crystallinity and the nature of glycosidic linkages in the feedstock. In the case of cellulosic feedstock, typically a pre-treatment step such as ball-milling or an ionic-liquid treatment is beneficial to accelerate the hydrolysis and achieve practical glucose yields.^{42,53,76,107,218} Upon hydrolysis of microcrystalline cellulose, a very low glucose yield of ~4% was reached over sulfonated semi-carbonized cellulose (section 4.2.1), at 100 °C in 3 h.⁹¹ However, the glucose yields increased up to ~40% when ball-milled cellulose was used as the substrate and a high surface area sulfonated active carbon as a catalyst (section 4.2.1).²¹⁸ Furthermore, the advantage of a mesoporous catalyst structure upon saccharification of large polysaccharides is also evident from the 74.5% glucose yield from ball-milled cellulose observed in case of sulfonated CMK-3 catalyst, in-contrast glucose yields were only ~35% and ~53% when a non-porous sulfonated carbon and a microporous sulfonated active carbon were applied as catalyst under identical reaction conditions (24 h, 150 °C).⁵³ The synergistic effect of incorporating a high number of surface oxygenates along with a large amount of SO₃H sites was also evident. Hereupon the glucose yield could be increased from ~18% to ~62% by simultaneously increasing the density of SO₃H groups and surface oxygenates (total acidity) from 0.24 to 0.44 mmol/g and 1.03 to 2.23 mmol/g, respectively.⁵³ Identical trends were also observed upon saccharification of 1-butyl-3-methylimidazolium chloride treated cellulose, with highest glucose yield of ~53% observed over a sulfonated mesoporous active carbon with the highest density of surface oxygenates (total acidity).⁴² The saccharification efficiency and glucose yield depends also on the amount of catalyst, the amount of water and the reaction temperature. For acidic carbons, the saccharification rate and glucose selectivity/yield increased up to 150-160 °C. Thereafter it decreased as subsequent degradation of glucose to 5-hydroxymethylfurfural and levulinic acid became prominent at higher reaction temperatures.^{42,218}

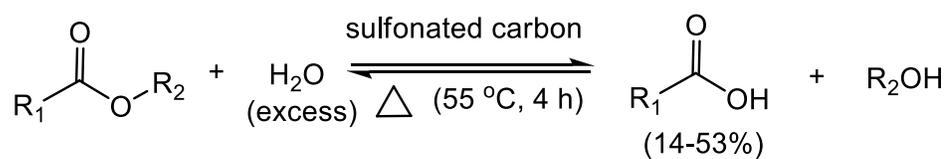
Alternatively, hydrolysis of crystalline cellulose can be directly performed over sulfonated carbocatalysts using ionic liquids (1-butyl-3-methylimidazolium chloride) or aqueous ionic liquids as the reaction media.^{111,114,116,222} Such bi-functional systems have been demonstrated to be more efficient (reaction temperature <150 °C) than pure aqueous systems in terms of hydrolysis rates and monosaccharide yields (glucose yields >50%). The enhanced performance of acidic carbons

in ionic liquids has been attributed to the efficient non-derivatizing dissolution of cellulose in ionic liquid media under reaction conditions which enhances the cellulose adsorption rates onto the catalyst surface.^{111,114,116,222} Similarly, an ionic liquid functionalized sulfonated carbon (biochar) was also demonstrated as a good bi-functional catalysts in direct hydrolysis of cellulose, under microwave irradiation at 90 °C, producing up to 33% glucose in 120 min.²⁰⁶

Hemicelluloses, on the other hand, are much easier to be hydrolyzed with acidic carbons owing to their random, amorphous non-crystalline structure.^{136,219,223,224} Typically, xylan conversions $\geq 85\%$ were observed over sulfonated carbons under relatively mild conditions (<150 °C). These materials have been demonstrated to outperform the commercial sulfonic resins (Amberlyst-15), due to their unique surface structure promoting adsorption of soluble xylan oligomers. Using such catalysts, xylose yields of up to 84.2% have been obtained from corncob.²¹⁹ Similarly, these catalysts also demonstrated high activity, selectivity and reusability upon starch hydrolysis, resulting from the presence of easily hydrolyzable α -glycosidic bonds and enhanced solubility.^{71,207,218} Inulin hydrolysis with acidic carbons also produced identical results, whereupon a mesoporous sulfonated carbon produced by spray pyrolysis outperformed commercial Amberlyst-70.¹⁹⁷

5.4.2. HYDROLYSIS OF CARBOXYLIC ACID ESTERS

Scheme 10. Reaction scheme for hydrolysis of carboxylic acid esters.

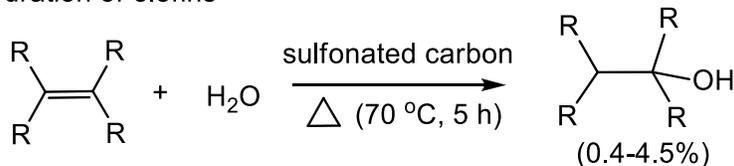


Besides of promoting hydrolysis of glycosidic bonds, these acidic carbons have been shown as active in hydrolyzing carboxylic acid esters (Scheme 10), outperforming sulfonic resins (Nafion, Amberlyst-15) and even H₂SO₄.^{22,56,227} Similar to the esterification reactions, for small C2-C3 carboxylic esters, the hydrolysis rates were independent of the textural properties of the catalyst and only dependent on the acid site concentration. Also, hydrolysis rates decreased with increasing carbon chain length of carboxylic acid esters resulting from the increased hydrophobicity of the reactants.²²⁷

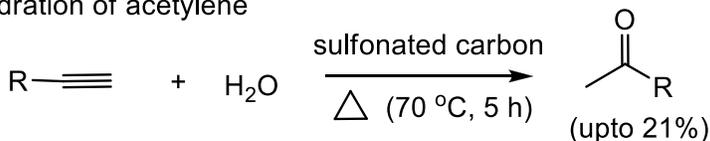
5.4.3. HYDRATION

Scheme 11. Reaction scheme for hydration olefins, acetylene and epoxides.

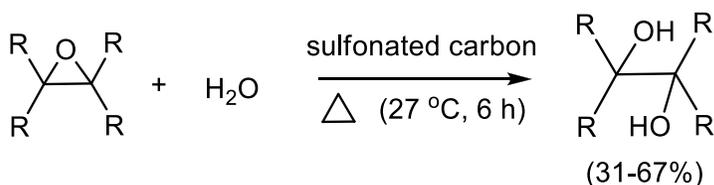
Hydration of olefins



Hydration of acetylene



Hydration epoxides



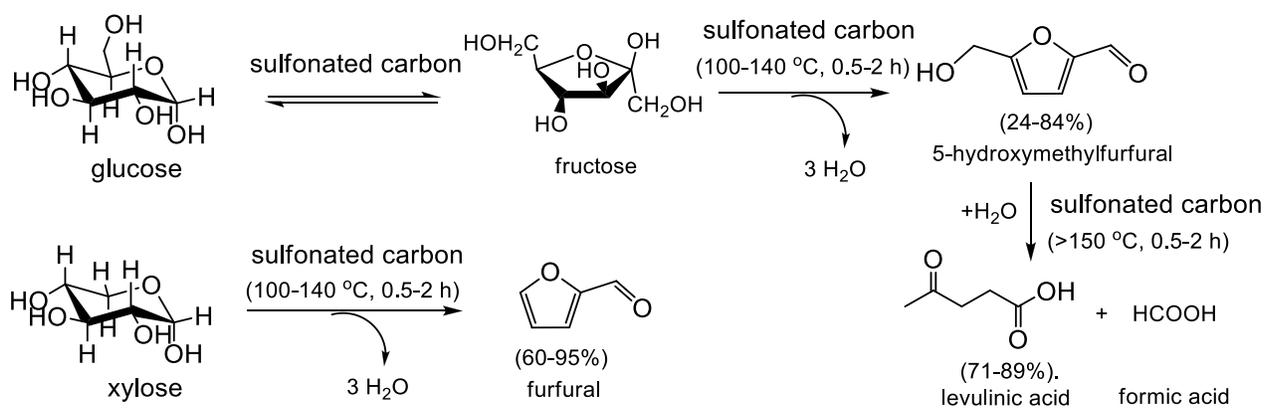
Hydration is a versatile reaction industrially employed for the production of alcohols, aldehydes and ketones from olefin and acetylene streams. Acidic carbons have been demonstrated to be effective catalysts hydration olefins, acetylene and epoxides (Scheme 11).^{16,22,171,228}

For liquid phase hydration of small olefins like 2,3-dimethyl-2-butene presenting negligible mass transfer limitations activity was dependent only on the concentration SO_3H sites, i.e. the carbocatalyst presenting the highest amount of acid sites afforded highest yields of desired product, 2,3-dimethyl-2-butanol.^{16,22} Upon hydration of phenylacetylene to acetophenone a similar trend was also observed, the positive dependence of S and O contents on conversion was consistent with increased rate of hydration for more acidic catalysts (higher SO_3H density) in agreement with a reaction free from diffusional limitations. Acetophenone selectivity >99% for all carbocatalysts and the highest acetophenone yield of ca. 21% was observed for the most acidic carbocatalyst (sulfonated carbonized glucose).²²⁸ In contrast for hydration propylene oxide a combined effect of acidity and surface properties could be observed whereupon the superior activity of sulfonated graphene over a sulfonated ordered mesoporous carbon (SOMC), sulfonated SBA-15 and Amberlyst-15 was attributed to its superior mass transfer and ability to adsorb propylene oxide.¹⁷¹

As a conclusion, sulfonated carbons are versatile reusable acid catalysts for hydrolysis and hydration of different petroleum and renewable streams. In particular, they have been identified as the most active non-enzymatic saccharification catalysts for the production of reducing sugars from cellulosic feedstock. The high activity and selectivity of such carbocatalysts are attributed to their unique surface properties promoting adsorption and catalysis of glucans oligomers (in particular β - glucans) and desorption of monosaccharides. The marginal loss (ca. 5-10%) in catalyst performance reported upon reuse at temperature ≥ 130 °C has been mainly attributed to the blockage of active acid sites by deposition of humins.^{111,114,116,222} Most importantly, these materials have outperformed commercial acid resins and show high stability under hydrothermal environments in fixed-bed reactors which render them potential candidates in large scale applications. Nevertheless, further studies and improvements are needed to understand the stability of such catalysts in large scale batch as well as continuous operations with actual biomass feedstocks (lignocellulose or starch-based feedstocks). Further studies should also be undertaken to evaluate the techno-economic feasibility of such catalysts to replace the existing industrial catalysts.

5.5. DEHYDRATION AND RING OPENING OF MONOSACCHARIDES

Scheme 12. Reaction scheme for dehydration of monosaccharides.



Dehydration of C5 (xylose) and C6 (fructose and glucose) monosaccharides in the presence of a Brønsted acid catalyst produces furfural and 5-hydroxymethylfurfural (Scheme 12). Furfural and 5-hydroxymethylfurfural are the most important chemical intermediates that can be produced within a modern lignocellulosic chemical biorefinery. These chemical building blocks can be converted into a range of high value chemical products including levulinic acid, α -angelica lactone,

levulinate esters, γ -valerolactone, 2-methyltetrahydrofuran, 2-methylfuran, 1,4-pentanediol, 2,5-furandicarboxylic acid, succinic acid, bisphenols and others. To achieve high furfural and 5-hydroxymethylfurfural yields, the dehydration step is usually performed in an organic solvent (dimethyl sulfoxide, γ -valerolactone, chloroform, methyl isobutyl ketone, etc) or in biphasic organic-water mixtures to prevent subsequent decomposition of the desired products into humins and polymeric byproducts.^{155,225-233} Moreover, many of the sugar-derived intermediates such as 2-methylfuran, levulinic acid, angelica lactone and γ -valerolactone can be converted into hydrocarbon building blocks.^{224,225}

Acidic carbons have also been identified as alternative solid catalysts upon dehydration of C5-C6 sugars (fructose, glucose, xylose),^{96,103,109,113,115,137,143,168,186,194,197,230} and sugar alcohols¹⁰⁸. For example, fructose was selectively converted to 5-hydroxymethylfurfural in high yields (~83-94%) over sulfonated hydrochars,^{113,115,194} sulfonated graphene,^{109,168} sulfonated nanotubes,¹⁴³ sulfonated mesoporous carbons,^{96,143,197,230} and sulfonated carbon nitrides¹⁰³ under mild conditions (100-140 °C, 0.5-2 h) (Scheme 12). Table 7 summarizes the important results obtained upon dehydration of monosaccharides using the acidic carbons. It has been observed that with respect to 5-hydroxymethylfurfural selectivity (or yield), dehydration proceeds best in non-aqueous organic solvents like dimethyl sulfoxide or biphasic solvents comprising dimethyl sulfoxide. In contrast, fructose dehydration in water or aqueous (monophasic) systems produces large quantities of levulinic acid and humins as byproducts. Humins are formed by acid catalyzed resinification of furanic aldehydes while levulinic acid is formed upon rehydration of 5-hydroxymethylfurfural at elevated temperatures.^{96,106,109,168,194} Fructose dehydration was also demonstrated in ethanol solvent producing ca. 57% and 68% 5-ethoxymethylfurfural over a sulfonated hydrochar and magnetic sulfonated carbon catalyst at 110 and 140 °C, respectively.^{185,194} Isopropanol was also recently identified as a very good low boiling solvent upon selective dehydration of fructose to 5-hydroxymethylfurfural (yields up to ~91%). In the presence of mesoporous acidic carbons as catalysts, the commonly used bi-phasic systems based on dimethyl sulfoxide or methyl isobutyl ketone (5-hydroxymethylfurfural yields up to ~24-84%) were outperformed by isopropanol under identical conditions (140 °C, 0.5 h).⁹⁶ High 5-hydroxymethylfurfural yields (up to ~83 %) have also been obtained using an ionic liquid 1-butyl-3-methylimidazoliumchloride as a solvent and sulfonated hydrochars as the catalysts.^{113,115}

Table 7. Catalytic activity of sulfonated carbons upon dehydration of monosaccharides/polysaccharides to 5-hydroxymethylfurfural/furfural

<i>catalyst</i>	<i>description</i>	<i>pore size (nm)</i>	<i>surface area (m²/g)</i>	<i>acidity (mmol/g)</i>		<i>T (°C)</i>	<i>time (h)</i>	<i>conv. (%)</i>	<i>yield (%)</i>	<i>feedstock, reaction system, stability/ no. of recycle</i>	<i>Ref.</i>
				<i>SO₃H</i>	<i>total^c</i>						
sulfonated semi-carbonized materials	SO ₃ H functionalized semi-carbonized materials	n.r	317	0.92 ^a	n.r	190 ^d	1	~95	~60	xylose, biphasic water-cyclopentylmethyl ether (3:1) (w/w) system, stable (only 1.2% sulfur leaching), no washing /10	137
	SO ₃ H functionalized hydrochar	n.r	<2	0.62	1.25	120	2	n.r	61	inulin, 1-Allyl-3-methylimidazolium chloride (IL)-water system, stable/5	113
		n.r	<0.5	0.953	n.r	80	0.33	n.r	74	fructose, 1-butyl-3-methylimidazolium chloride system, stable/5	115
		n.r	2	1.33	5.51	110	15	99.4	53.4	fructose, ethanol media, unstable 38% SO ₃ H leaching/4	194
sulfonated active carbons	SO ₃ H functionalized activated carbons	n.r	514	0.172	n.r	80	0.33	n.r	~60	fructose, 1-butyl-3-methylimidazolium chloride, n.r/n.r	115
		n.r	753	2.5	3.8	200	2	47	4.2 ^e	glucose, H ₂ O system, n.r/n.r	109
	PhSO ₃ H functionalized	n.r	n.r	2.89 ^b	1.84	120	0.5	>99	76	fructose, DMSO solvent system, n.r/n.r	143

sulfonated mesoporous carbons	mesoporous carbon					120	24	>99	60 ^e	fructose, ethanol solvent system, n.r/n.r	143
		2.2	636	1.1	0.9	140	0.5	99	87	fructose, 2-propanol solvent system, unstable (humin uptake and ca. 30% SO ₃ H leaching), washing with H ₂ O-2-propanol and drying/4	96
								65	24	H ₂ O/DMSO:2-butanol/MIBK system, n.r/n.r	96
		4.7	665	0.7	0.4	140	0.5	99	91	fructose, 2-propanol solvent system, unstable (H ₂ O, humin uptake and 30% SO ₃ H loss), washing with H ₂ O-2-propanol and drying/4	96
								73	42	H ₂ O/DMSO:2-butanol/MIBK system, n.r/n.r	96
		4.2	530	0.86	n.r	170	0.25	100	80	xylose, γ -Valerolactone solvent system, unstable (~45% SO ₃ H laching), no washing /5	230
	SO ₃ H functionalized	n.r	400	0.59	0.49	120	1.25	>95	n.r	fructose, H ₂ O system, n.r/n.r	197

	mesoporous carbon										
sulfonated carbon nanomaterials	SO ₃ H functionalized graphene oxide	n.r	217	1.2	2.7	200	2	89	78 ^e	glucose, H ₂ O system, unstable (humins deposition and ca. 10% SO ₃ H loss per cycle)/5	109
								91	74 ^e	fructose, H ₂ O system, n.r/n.r	109
	poly(p-styrenesulfonic acid)-grafted functionalized carbon nanotubes	n.r	n.r	5.67 ^b	2.92	120	0.5	>99	89	fructose, DMSO solvent system, n.r/n.r	143
								>99	87	inulin, DMSO solvent system, n.r/n.r	143
								>99	75	sucrose, DMSO solvent system, n.r/n.r	143
								>99	57	glucose, DMSO solvent system, n.r/n.r	143
	PhSO ₃ H functionalized carbon nanotubes	n.r	n.r	1.75 ^b	1.21	120	0.5	>99	69	fructose, DMSO solvent system, n.r/n.r	143
							24	>99	45 ^e	fructose, ethanol solvent system, n.r/n.r	143
	poly(p-styrenesulfonic acid)-	n.r	n.r	4.62 ^b	2.31	120	0.5	>99	80	fructose, DMSO solvent system, n.r/n.r	143
								>99	74	inulin, DMSO solvent system, n.r/n.r	143

	grafted carbon nanofibers							>99	68	sucrose, DMSO solvent system, n.r/n.r	143
								>99	46	glucose, DMSO solvent system, n.r/n.r	143
								24	>99	69	fructose, ethanol solvent system, n.r/n.r
sulfonated carbon nitrides	SO ₃ H functionalized carbon nitride	n.r	10.04	5.47	n.r	100	0.5	n.r	95	xylose, DMSO solvent system, n.r/n.r	103
								n.r	95	xylose, H ₂ O, n.r/n.r	103
								n.r	96	fructose, H ₂ O, n.r/n.r	103
						150	8	n.r	41	glucose, H ₂ O, n.r/n.r	103
commercial sulfonic resin	Amberlyst-36	n.r	33	4.5	4.5	200	2	7	0	glucose, H ₂ O system, n.r/n.r	109
	Amberlyst-70	n.r	n.r	n.r	n.r	120	1.25	>95	n.r	fructose, H ₂ O system, n.r/n.r	197
	Amberlyst-15	n.r	n.r	n.r	n.r	120	0.5	89	70	fructose, DMSO solvent system, n.r/n.r	143
						120	24	>99	73	fructose, ethanol solvent system, n.r/n.r	143

^abased on sulfur elemental analysis

^ddetermined by ion chromatography

^cSO₃H, carboxylic acid, lactone, phenol and carbonyl groups

^dmicro-wave heating

^ealkyl levulinate/ levulinic acid

n.r = not reported

The rehydration products of 5-hydroxymethylfurfural, levulinic acid and formic acid obtained by ring opening are also versatile platform molecules, especially upon the production of synthetic fuels and hydrocarbon precursors.^{224,225} In fact, acidic carbons were also demonstrated to be equally effective upon direct production of levulinic acid and/or alkyl levulinates from fructose in high yields (71-89%, >150 °C).^{103,109,143} Glucose was also similarly converted to levulinic acid and alkyl levulinates over acidic carbons but due to the lack of glucose-to-fructose isomerization ability and resinification of 5-hydroxymethylfurfural the yields of desired products were much lower.^{180,194} Nevertheless by incorporating cation polarization effects or by incorporating Cl sites onto the sulfonated carbons the levulinate yields could be increased up to 51 to 66%.^{161,228}

Liu and co-workers¹⁴³ studied the effect of catalyst SO₃H density in fructose dehydration and observed a linear correlation between the catalyst TOF and SO₃H density.¹⁴³ Hou *et al.*¹⁶⁸ also observed a positive effect upon increasing the number of SO₃H sites on graphene with 5-hydroxymethylfurfural yields.¹⁶⁸ Identical to the acid catalyzed reactions discussed in Sections 5.1-5.4 the activity (yield of 5-hydroxymethylfurfural) was also influenced by the hydrophobicity/hydrophilicity of carbocatalyst. The positive effect of hydrophilicity (expressed as H index=amount of adsorbed water/amount of N₂ adsorbed at P/P₀≈0.92) in terms of fructose conversion and 5-hydroxymethylfurfural yields were observed in both bi-phasic and isopropanol solvent systems. The phenomenon was most likely linked to the enhanced adsorption of fructose on the surface of hydrophilic catalyst.⁹⁶ These carbocatalysts typically demonstrated very good stability, particularly in non-aqueous solvents like dimethyl sulfoxide.^{96,103,143,168} Fructose dehydration was also studied over PhSO₃H and naphthalene-SO₃H functionalized sulfonated ordered mesoporous carbon catalysts in a fixed-bed bi-phasic (4:1= tetrahydrofuran:water) continuous flow reactor. The 5-hydroxymethylfurfural selectivities of 71-74 % at ca. 60% conversion were comparable to the SO₃H functionalized SBA-15 catalyst, however in terms of stability the acidic carbons demonstrated 60 times slower deactivation rates than the SBA-15 catalyst, confirming the superior stability of sulfonated carbons during hydrothermal operations.²³¹

Xylose (C5 monosaccharide) dehydration of with acidic carbons produces furfural,^{103,137,223,186,232} a well-known intermediate for the production of a wide variety of products including bulk chemicals (dimethyl furan, tetrahydrofuran, furfuryl alcohol, 2-methyl furan,

etc.).²²⁴ As in the case of fructose, xylose conversion also proceeded best in non-aqueous solvents like dimethyl sulfoxide reaching with furfural yields reaching up to 95%.^{103,186} On the other hand, furfural yields were reduced to ca. 60% in a bi-phasic mixture of cyclopentylmethyl ether and water (3:1) over a sulfonated biochar catalyst.¹³⁷ However, it is interesting to note that a sulfonated carbon nitride catalyst obtained by treating graphitic carbon nitride with ClSO₃H, demonstrated unique activity and selectivity behavior, converting xylose to furfural under much milder conditions (50-100 °C), in both dimethyl sulfoxide as well as neat water.¹⁰³ As in the case of fructose, a positive correlation was observed between the SO₃H site density and furfural yield upon dehydration of xylose.²²³

In addition to the dehydration of fructose, glucose and xylose, direct dehydration of inulin, sucrose, cellulose and hemicelluloses have also been demonstrated over the acidic carbocatalysts.^{161,185,194,229,230,232} For example, direct conversion of amorphous cellulose with a cellulase-mimetic, mesoporous sulfonated carbon bearing Cl and SO₃H sites, gave rise to up to ~51% of levulinic acid.¹⁶¹ The lower yields (<60%) of levulinic acids and 5-hydroxymethylfurfural observed in case of glucose based carbohydrate feedstock are due to the poor activity of sulfonated carbons in the glucose-to-fructose isomerization step.^{161,180,185,194} In contrast to xylose and fructose rich feedstock's (inulin and hemicelluloses), the yields/selectivities towards the desired dehydration products (furfural, levulinic acids and 5-hydroxymethylfurfural or their alkylated counterparts) were comparatively high (>60%).^{180,185,194,229,230,232} Nevertheless, it was possible to enhance the levulinic acid yields from microcrystalline cellulose up to 66% over a sulfonated humin-derived catalyst by incorporating cation polarization effects in sulfolane-water solutions.²²⁹

Acidic carbons have also demonstrated catalytic activity for dehydration of sugar alcohols, as indicated by the high yields of isosorbide obtained from sorbitol over various SO₃H and PhSO₃H functionalized carbons. Among the tested carbocatalyst a mesoporous acidic carbon with 1.97 mmol/g PhSO₃H groups afforded the highest yield (~83%) of dehydration product isosorbide under solvent-free conditions at 160 °C in 1.5 h, outperforming H₂SO₄ and sulfated zirconia. Also, a positive correlation was observed between catalyst SO₃H density and isosorbide yield in agreement with catalytic effect of strong SO₃H sites.¹⁰⁸

As a summary, sulfonated carbons are efficient, reusable solid acid catalysts upon dehydration of carbohydrate feedstock's (fructose, glucose, xylose, inulin, sucrose, cellulose,

hemicelluloses and alike). These are key steps in the production of versatile chemical building blocks like furfural, 5-hydroxymethylfurfural, levulinic acid or alkyl levulinates within sugar-platform of biorefineries. The high activity, selectivity and stability of such carbocatalysts are attributed to their unique surface properties, hydrothermal stability and stability of covalently bonded SO₃H or PhSO₃H sites. Due to their low-cost, unique water tolerance and compatibility with continuous flow operations, the acidic carbon materials demonstrate potential for large scale applications within the sugar-platform of biorefineries upon production of bio-based products. Nevertheless, further studies and improvements are needed to understand the stability of such carbocatalysts with actual biomass feedstocks (lignocellulose or starch-based feedstocks) in large scale batch as well as continuous operations. Studies should also be undertaken to evaluate the techno-economic feasibility of such catalysts to replace the existing industrial catalysts like H₂SO₄.

5.6. C-C BOND FORMING REACTIONS

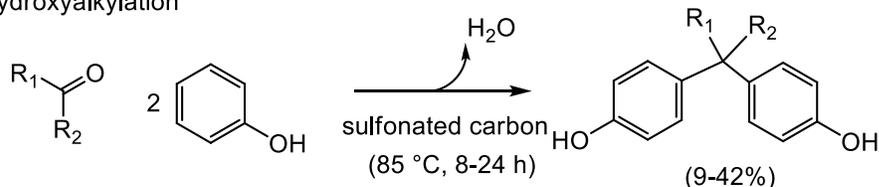
Acidic carbons have also demonstrated high activity as an alternative solid catalysts for C-C bond forming reactions, including alkylation/benzylation,^{52,55,198} olefin dimerization,⁹² alkylation/hydroxylalkylation of sylvan,^{67,212,233,234} aldol condensation,¹⁹² cross-aldol condensation,¹⁵⁷ Knoevenagel condensation²⁰⁷ and Michael addition²⁰⁷ (Scheme 13).

The activity and selectivity of acidic carbons in such reactions are determined by both the textural and surface properties of carbocatalysts as well as the steric and electrophilic effects of reacting molecules.^{50,52,55,67,92,157,198,212,233,234} For conversion of large hydrophobic molecules such as cyclohexanone, α -mesitylene, toluene, benzylchloride and benzaldehyde a catalyst with large pores, large specific surface area and a high density of SO₃H sites is found to be beneficial.^{52,55,92,157,198} For example, upon liquid phase benzylation of toluene with benzyl chloride over sulfonated activated carbons, Hara and co-workers⁵⁵ observed a positive correlation between the specific surface area and the rate of benzyl toluene formation over acidic carbons bearing identical amount of SO₃H sites, Figure 16(a).⁵⁵ Similarly, it was observed that upon oligomerization of α -methylstyrene a SO₃H functionalized mesoporous silica carbon composite (SMSiC) catalyst demonstrated almost two-fold higher activity and selectivity towards the dimerization product when compared to the nonporous sulfonic resins (Amberlyst-15, Nafion NR50 and Nafion SAC13).⁹² Identical trends were also observed upon liquid phase hydroxyalkylation of phenol with acetone (70-85 °C) whereupon acidic carbons obtained from soft

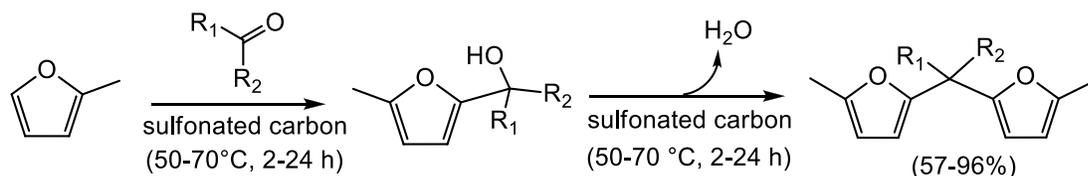
and hard templated ordered mesoporous carbons outperformed the commercial sulfonic resins and a sulfonated semi-carbonized material exhibiting nonporous structure with respect to bisphenol productivity.^{52,198}

Scheme 13. Reaction scheme for selected C-C bond forming reactions catalyzed by sulfonated carbons.

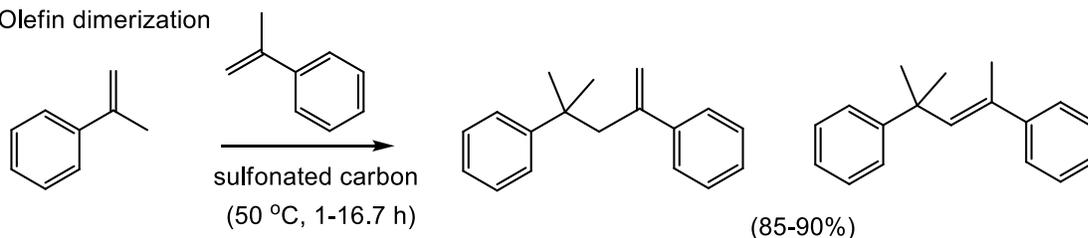
Hydroxyalkylation



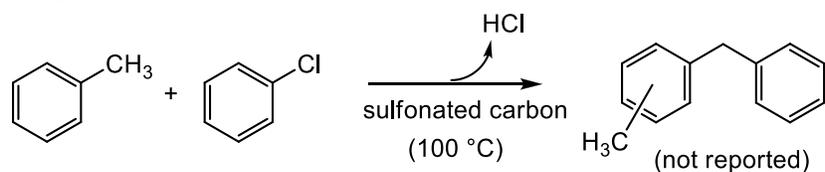
Hydroxyalkylation/alkylation



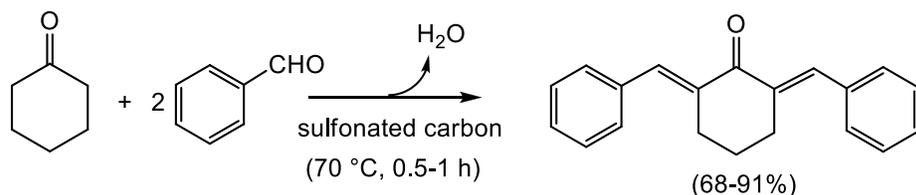
Olefin dimerization



Benylation



Cross aldol condensation



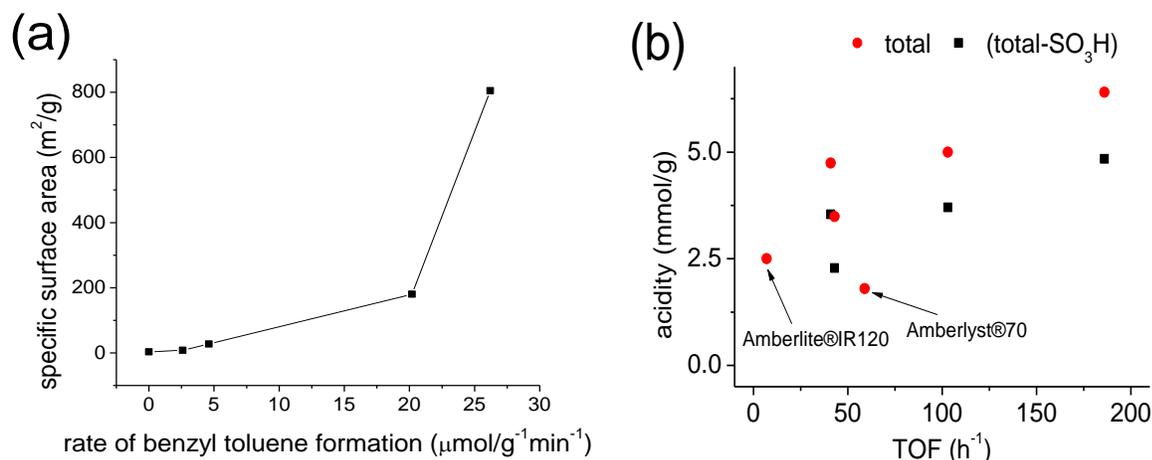


Figure 16. (a) Influence of specific surface area on benzylation of toluene (rate of benzyl toluene formation) over sulfonated active carbon catalysts (compiled from Ref. 55, SO₃H density was fixed at ca. 1.3 mmol/g) and (b) influence of surface acidity on TOF for sylvan condensation with furfural. Reprinted with permission from Ref. 67. Copyright 2018 The Royal Society of Chemistry.

However, condensation of hydrophilic oxygenated molecules however shows very different trends in terms of activity and selectivity, whereupon a strong correlation could be observed between the hydrophobicity/hydrophilicity of the reacting molecules with the surface chemistry of the carbocatalyst.^{67,212,232,234,235} For example, upon liquid phase condensation of sylvan with oxygenated molecules (50-70 °C) such as furfural, 5-hydroxymethylfurfural, acetone, butanal, cyclohexanone, levulinic acid and α -angelica lactone, even the non-porous sulfonic resins and amorphous sulfonated carbons performed well giving a high activity and selectivity towards the production of bisfurylalkanes.^{67,72,212,233} The C-C coupling products (bisfurylalkanes) of low-carbon furanics have been identified as promising hydrocarbon building blocks for the production of synthetic paraffins and isoparaffins via hydrodeoxygenation reaction.^{67,212,224,225} In fact, Konwar *et al.*⁶⁷ observed a positive correlation between the amount of SO₃H groups and total surface acidity with TOF upon sylvan condensation of furfural over meso/macroporous acidic carbons (Figure 16(b)), similar to the trends of carboxylic acid esterification (Figure 12).⁶⁷ However, in another study for a series of sulfonated mesoporous carbocatalysts, bisfurylalkanes yield/selectivity were higher in case of catalysts presenting higher hydrophobicity and larger mesopore volumes; interestingly, these mesoporous carbocatalysts also showed high activity, selectivity and stability upon continuous flow operations producing bisfurylalkanes in yields up to ~23% during 24 h operation at 45 °C.²¹² The high activity which was observed upon sylvan

condensation of oxygenates over acidic carbons was attributed to the stabilization of furanic oxygenates on hydrophilic oxygen functionalities of carbon surfaces through non-covalent (dipolar) interactions. Such stabilizations promoted an adsorption enhanced surface catalysis mechanism similar to C-O bond-forming and C-O bond-breaking reactions of hydrophilic molecules (Section 5.1-Section 5.5).^{67,235}

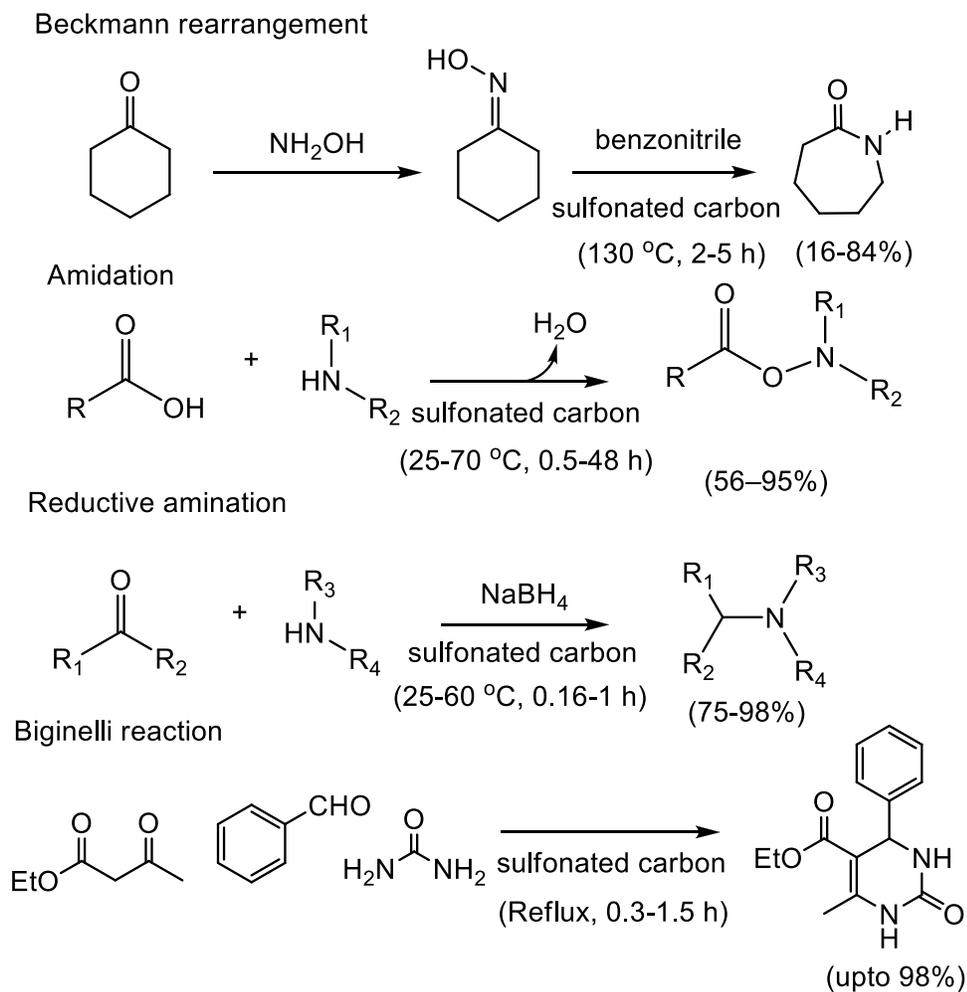
Overall, acidic carbons have demonstrated high activities, selectivities and stability as alternative catalysts upon C-C and C-O coupling reactions in liquid-phase. These materials were found to be particularly suitable in upgrading low-carbon bio-based furanics (2-methylfuran, furfural, 5-hydroxymethylfurfural) and carbonyls (acetone, butanal, cyclohexanone, levulinic acid and α -angelica lactone) into synthetic hydrocarbon precursors. The presence of large pores, hydrophobicity and stable SO₃H sites are essential to achieve superior activity, selectivity and stability in such reactions.

5.7. OTHER INDUSTRIALLY RELEVANT REACTIONS

In addition to the conventional C-O, C-C bond-forming and C-O bond-breaking reactions discussed above (Section 5.1-Section 5.6), the SO₃H functionalized acidic carbons have also shown promise as versatile acid catalysts in Beckmann rearrangement,^{50,98} reductive amination of aldehydes and ketones,^{64,207} amidation¹⁶⁹, Peckmann condensation,¹⁷¹ oxidation^{103,122} and various multi-component organic reactions (e.g. Biginelli reaction)^{101,207,236,237,238} (Scheme 14).

Beckmann rearrangement is an industrially important acid-catalyzed reaction for the production of caprolactam from cyclohexanone oxime, which is a starting material for nylon 6,6. Liquid-phase Beckmann rearrangement of cyclohexanone oxime involves catalysis of a large hydrophobic molecule in hydrophobic solvents like benzonitrile.⁵⁰ As such only hydrophobic acidic carbons with a meso or microporous structure are able to catalyze this reaction as the hydrophobic reactant and solvents cannot be incorporated into the carbon bulk of non-porous hydrophilic amorphous carbons (semi-carbonized sulfonated carbons).^{50,98} The meso or microporous sulfonated carbons characterized by their high hydrophobicity and stability also outperformed sulfonic resins (Dowex 50) and Y-zeolite catalysts upon Liquid-phase Beckmann rearrangement of cyclohexanone oxime.^{50,98}

Scheme 14. Reaction schemes for some of the other industrially important reactions catalyzed by sulfonated carbons.



A PhSO_3H grafted sulfonated graphene was also shown to be active in the amidation of carboxylic acids under ultrasonic irradiation.¹⁶⁹ The carbocatalysts presented high activity and amide selectivity upon conversion of a range of aromatic and aliphatic acids and amines; starting from stoichiometric amounts of reagents, high amide yields (56–95%) could be obtained at room temperature upon multiple reaction cycles.¹⁶⁹ In another work, a sulfonated carbon nitrile catalyst was demonstrated as an efficient catalyst producing benzimidazole from the reaction of furfural with 1,2-phenylenediamine.¹⁰³ Similarly, sulfonated nanotubes⁶⁴ and ionic liquid coated sulfonated carbons²⁰⁷ were shown to be efficient, reusable carbocatalysts upon production of amines by reductive amination of aldehydes and ketones.^{64,207}

Interestingly, sulfonated carbons were also shown to exhibit high activity as an oxidation catalyst upon oxidative transformation of furanic aldehydes (furfural and 5-hydroxymethylfurfural) into important oxidation products like succinic acid, 2,5-diformylfuran

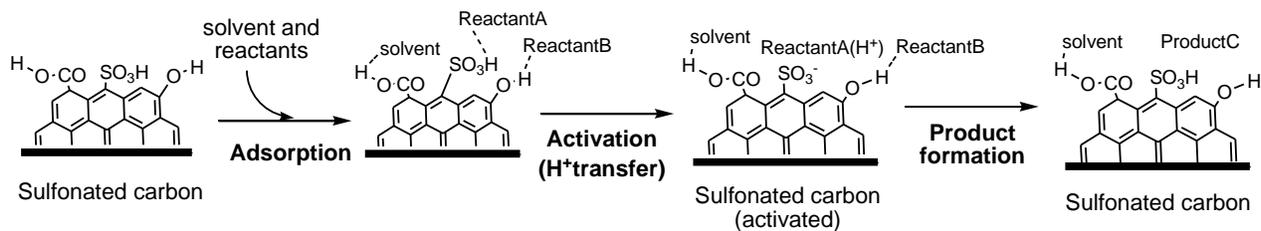
and 5-methylsulfanylmethyl-furan-2-carbaldehyde.^{103,122} The oxidation of furfural into succinic acid was afforded with a sulfonated hydrochar in the presence of H₂O₂ as an oxidant.¹²² In contrast, the use of KBr as an oxidant upon conversion of 5-hydroxymethylfurfural (as well as fructose) over a sulfonated carbon nitride catalyst yielded 94% 2,5-diformylfuran and 97% 5-methylsulfanylmethyl-furan-2-carbaldehyde in H₂O and DMSO, respectively.¹⁰³

The Biginelli reaction is perhaps the most important multiple-component organic reaction shown to be catalyzed by the acidic carbons. The products from Biginelli reaction (dihydropyrimidinones) are in extensive use in the pharmaceutical industry due to their promising pharmacological and biological activities as antiviral, antitumor, antibacterial, anti-HIV agents and anti-inflammatory as well as calcium channel modulators.^{101,237,238} For example, the use of a mesoporous sulfonated graphitic carbon nitride catalyst facilitated the formation of dihydropyrimidinones in yields up to 98% yield in ethanol under reflux conditions.¹⁰¹ In another work, dihydropyrimidinone yields between 82-92% were obtained over a sulfonated naphthalene catalyst under solvent-free conditions, at 140 °C, while a sulfonated graphene catalyst afforded up to 94% in ethanol under reflux.^{237,238} Most importantly, the sulfonated carbocatalysts demonstrated good operational stability and reusability.^{101,237,238}

6. ACTIVATION AND DEACTIVATION

An extensive amount of research effort has been made in the last decade towards exploring new catalytic applications of these acidic carbons functionalized with SO₃H or PhSO₃H groups (Sections 5). It is also evident from the numerous examples discussed in section 5, that during acid catalyzed transformations, such carbocatalysts are activated by an adsorption promoted mechanism irrespective of the carbon structure and nature of reacting molecules. As illustrated in scheme 15, all reactions begin with absorption of organic reactants and solvent molecules onto the catalyst bulk, in the next step the adsorbed reactants are protonated by the Brønsted acidic SO₃H groups to form the activated catalyst (or activated catalyst-substrate complex) that undergoes subsequent transformations to yield the product molecule and protonated catalyst. In case of non-porous acidic carbons (sulfonated hydrochars and sulfonated semi-carbonized materials) catalyst swelling is also critical for high catalytic activity (Figure 13(a), section 5.1), similar to sulfonic resins.

Scheme 15. Schematic illustration of the generalized activation mechanism of sulfonated carbons for acid catalyzed reactions.



On the other hand, only a handful number of studies have been conducted towards understanding the deactivation and stability of sulfonated carbons particularly in hydrothermal and alcoholic reaction environments^{75-80,147,239,240} Even though such acidic carbons present a high thermal stability close to ~ 250 °C, the actual stability of material and particularly the stability of the active (SO_3H) sites in these materials are affected by the operational or process conditions. Reaction parameters such as temperature, pressure, nature of reactants, pH, presence of solvents and H_2O have a direct impact on the stability of such catalysts.^{14,75-80,147,239,240} The operational stability of SO_3H sites/groups is also influenced by the method of sulfonation and carbon framework structure of the support.^{14,22,46,61,223} To ascertain stability of such carbocatalysts the spent catalytic materials or the carbon materials treated under simulated reaction conditions (e.g. hydrothermal or solvothermal treatment) are comprehensively characterized by various analytical and spectroscopic tools discussed in section 2. Subsequent, comparison of the acidic-textural features, compositional and structural properties of these treated materials with the parent acidic carbons gives vital insights into the material stability under process conditions. In particular, solid-state ^{13}C NMR XPS and FT-IR can give key insights into catalyst deactivation by SO_3H leaching, active site derivatization as well as catalyst poisoning by adsorption of H_2O and oxygenated impurities. The leaching of SO_3H sites can also be confirmed from analysis of reaction products by ^1H NMR on the basis aromatic leaching and/or from S analysis by inductively coupled plasma optical emission spectroscopy.^{14,75-80} Table 8 gives a summary of the operational/process stability (deactivation modes) of different types of acidic carbons upon selected industrially important reactions.

Table 8. Summary of stability of different types of acidic carbons upon select industrially important reactions.

<i>carbocatalyst</i>	<i>reaction</i>	<i>cause of deactivation</i>				<i>regeneration</i>
		<i>leaching</i>	<i>derivatization^b</i>	<i>H⁺ exchange</i>	<i>adsorption</i>	
SO ₃ H, OH and COOH functionalized semi-carbonized materials	esterification	yes	yes	no	yes	yes
	transesterification	yes ^a	yes	no	yes	yes
	hydrolysis	yes	no	yes ^c	yes	yes (partial) ^d
	dehydration	yes	no	no	yes	yes (partial) ^d
	C-C and C-O coupling reactions	no	no	no	yes	yes
SO ₃ H, OH and COOH functionalized rigid-carbon materials	esterification	yes	no	no	yes	yes
	transesterification	yes ^a	no	no	yes	yes (partial) ^d
	hydrolysis	yes	no	yes ^c	yes	yes (partial) ^d
	dehydration	yes	no	no	yes	yes (partial) ^d
	C-C and C-O coupling reactions	no	no	no	yes	yes
PhSO ₃ H, OH and COOH functionalized rigid-carbon materials	esterification	no	no	no	yes	yes
	transesterification	no	no	no	yes	yes
	hydrolysis	yes	no	yes ^c	yes	yes (partial) ^d
	dehydration	yes	no	no	yes	yes (partial) ^d
	C-C and C-O coupling reactions	no	no	no	yes	yes

^a at elevated temperature (>100 °C) and pressure (>5 bar)

^b chemical derivatization of acid/active sites (formation of sulfonyl esters or thiols)

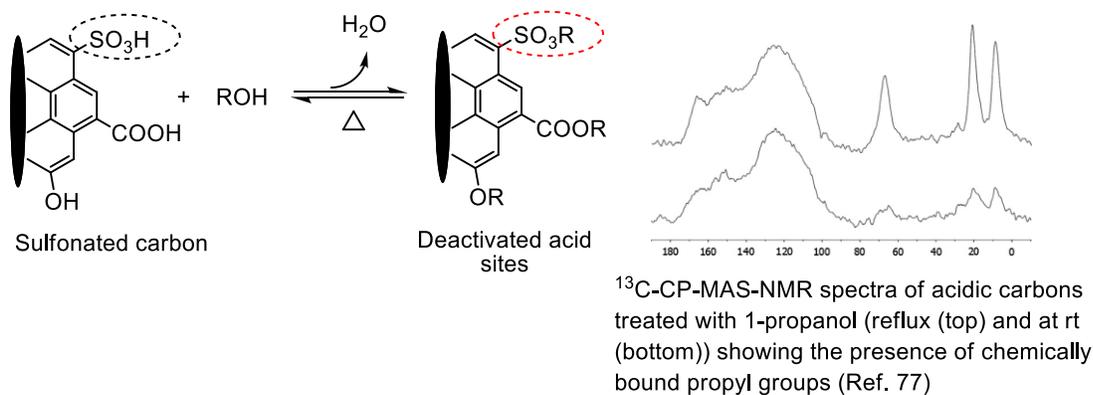
^c H⁺ sites in COOH and SO₃H are exchanged in the presence of Na⁺, K⁺ or Ca²⁺ ions in the aqueous feed solution

^d partial regeneration of SO₃H sites by re-sulfonation (treatment with H₂SO₄, SO₃, ClSO₃H or 4-benzenediazonium sulfonate) and/or H₂O₂ oxidation of humins

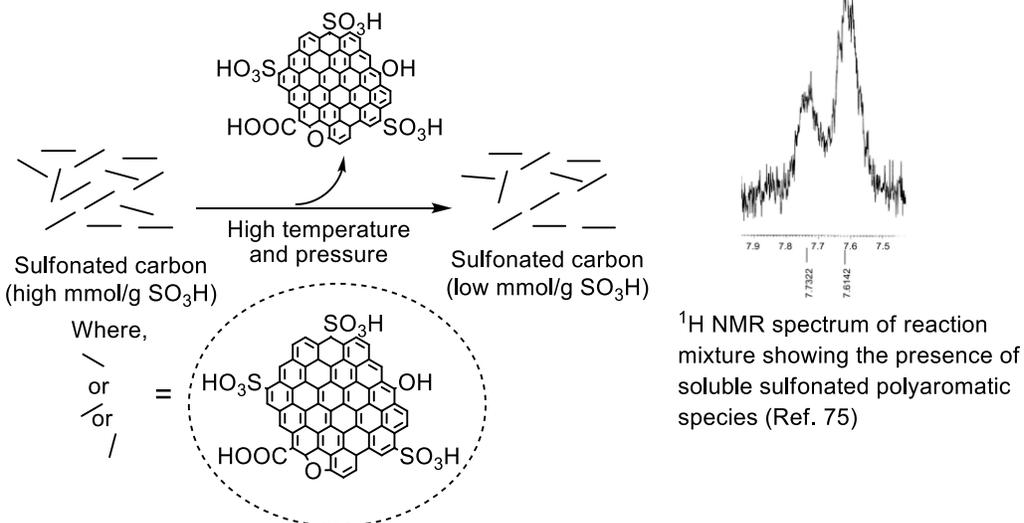
6.1. DEACTIVATION AND REGENERATION IN ALCOHOLIC MEDIA

Scheme 16. Plausible mechanisms for the deactivation of SO₃H functionalized acidic carbons upon reactions in alcoholic media. The inserts in the scheme are reprinted with permission from Ref 77. and Ref. 75 Copyright 2014 Elsevier and 2008 Elsevier.

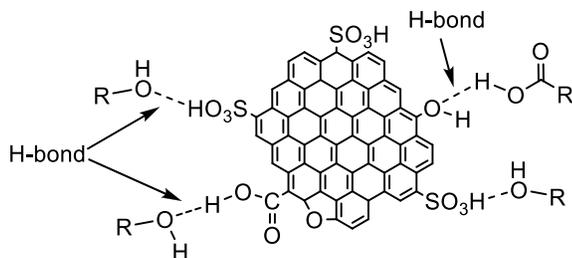
Formation of sulfonate and carboxylic esters on surface of acidic carbons (reversible process)



Leaching of SO₃H containing polyaromatic species



Adsorption of alcohol and related oxygenated molecules on acidic carbons



Upon reactions in alcoholic media such as esterification (Section 5.1), transesterification (Section 5.3) and solvolysis (Section 5.5), the deactivation of SO₃H containing acidic carbons has been attributed mainly to (a) the formation of sulfonate esters (chemical derivatization), (b) the leaching of soluble polyaromatic moieties or species containing SO₃H groups to the reaction media/solvent and (c) pore blockage by adsorption of an alcohol and related oxygenated molecules in reaction media by hydrogen bonds (Scheme 16).^{14,22,75,77-79} An analogous deactivation behavior is also observed for related sulfonic solids such as sulfonic acid functionalized silica materials (propylsulfonic silica and Nafion–silica composite) and commercial sulfonic acid resin (e.g. Dowex 50, Amberlyst 15).⁷⁹ For example, upon esterification of long chain fatty acids (palmitic acid) with methanol over a sulfonated hydrochar (glucose derived) catalyst Fraile and co-workers identified the formation of sulfonate esters to be the dominant deactivation pathway on the basis of solid-state NMR studies (Scheme 16).^{77-79,240} Similarly, Hara and co-workers also reported the formation of sulfonate esters upon alcoholysis/esterification reactions as one of the main causes for active site deactivation of sulfonated carbocatalysts obtained by in-situ carbonization of sulfopolycyclic aromatic compounds in concentrated H₂SO₄ (Section 4.1.1) and by the H₂SO₄ treatment of semi-carbonized sugars (Section 4.2.1).^{14,132,216}

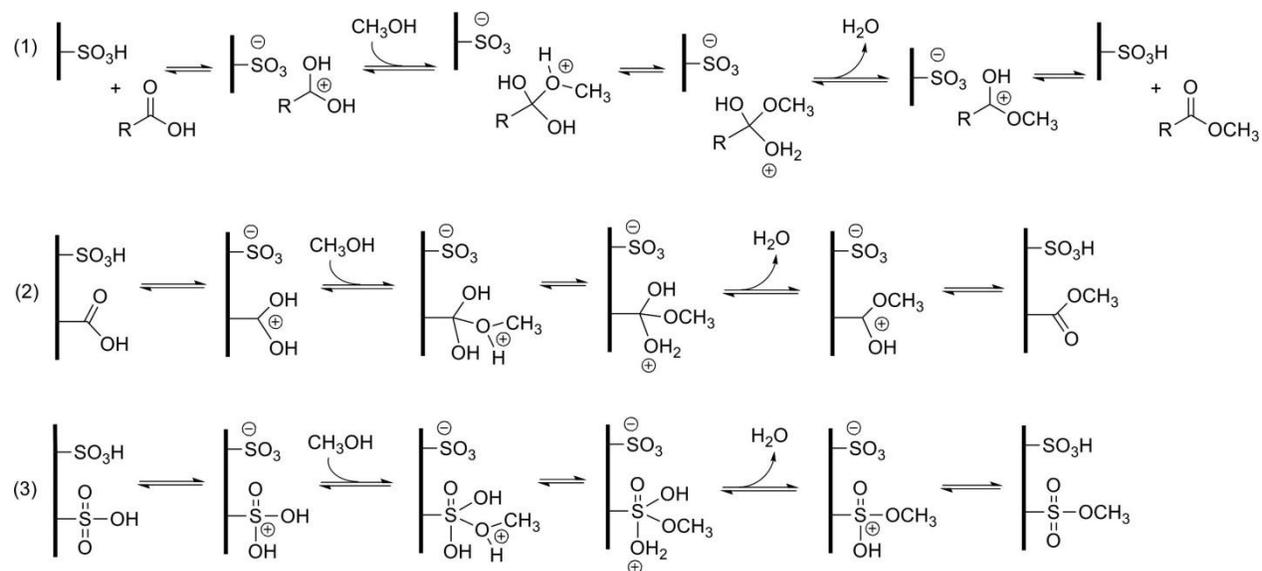
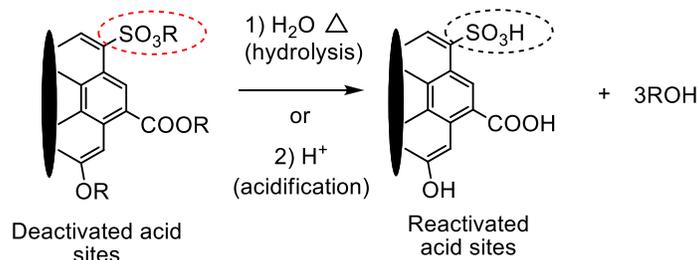


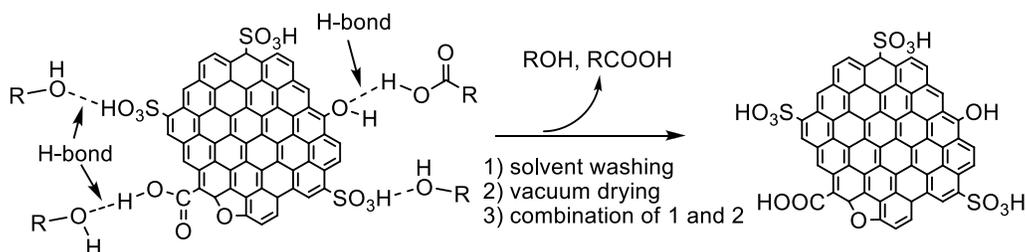
Figure 17. (1) classical esterification mechanism and (2 and 3) proposed analogous mechanisms for the esterification of surface acid groups on solid acids. Reprinted with permission from Ref. 79. Copyright 2015 Elsevier.

Scheme 17. Reaction scheme for the regeneration of surface acid sites of sulfonated carbons deactivated in alcoholic media.

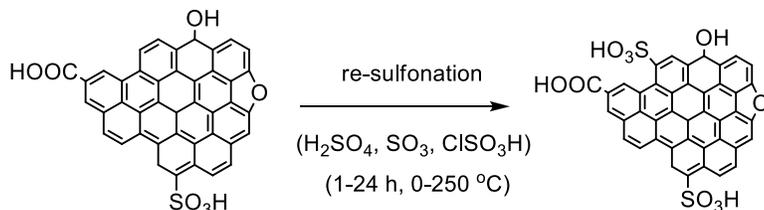
Regeneration by hydrolysis of esters



Regeneration by washing and drying



Partial regeneration of SO₃H sites by re-sulfonation



Interestingly, the deactivation behavior of solid sulfonic acids by chemical derivatization of surface acid sites is also strongly dependent on the framework structures and surface acid site density. García-Bordejé and co-workers observed that during esterification reactions with monohydric alcohols, catalyst deactivation occurs by esterification of surface SO₃H and COOH sites for the highly acidic flexible acidic carbons obtained at carbonization temperatures below 500 °C and by pore blocking (adsorption) for rigid low acidic carbon materials obtained above 500 °C.^{79,240} A similar trend was also observed for sulfonated polystyrenes whereupon formation of surface sulfonate esters were observed for the low cross-linked Dowex 50 but not for the highly cross-linked and rigid Amberlyst 15.⁷⁹ The authors explained these findings on the basis of a proton transfer mechanism similar to the classical esterification requiring two adjacent surface Brønsted

acid (SO_3H and/or COOH) groups, whereupon one of the Brønsted acid groups catalyze the formation of surface esters on the acid site adjacent to it (one site act as catalyst and the other site as reactant) (Figure 17).⁷⁹ Consequently, solid acids with a rigid carbon framework structure and low Brønsted acid (SO_3H density and/or COOH) density (<1 mmol/g) do not undergo deactivation by surface esterification of acid sites (lack of adjacent acid sites). Nevertheless, the sulfonate ester (as well as carboxyl ester/ether) formation is a fully reversible deactivation process, whereupon the acid sites are easily regenerated by the hydrolysis of ester bonds with H_2O or by treatment with dilute acids (Scheme 17).^{77-79,240} In fact, it is possible to suppress formation of surface sulfonyl and carboxyl by addition of small amounts of water (water/fatty acid molar ratio ~ 0.6) to the esterification reaction mixture.⁷⁹ A similar trend was also observed by Hara and co-workers upon alcoholysis (or transesterification) of triglycerides, where pre-addition of small quantities of water (~ 0.02 g) completely eliminated deactivation of sulfonated semi-carbonized materials caused by surface ester formation as the presence of abundant H_2O molecules and high reaction temperature $100\text{-}120$ °C facilitated rapid *in-situ* hydrolysis surface esters.^{14,216}

Leaching of SO_3H sites and/or SO_3H containing polyaromatic moieties, on the other hand, is an irreversible deactivation process that can potentially pollute the high-value product streams with sulfur impurities. Leaching of such sulfur species has been experimentally confirmed on the basis of ^1H NMR spectrum of reaction mixtures recovered after the first reaction cycle of esterification and alcoholysis conducted over sulfonated carbocatalysts (Scheme 16).^{14,75} Deactivation by SO_3H leaching is dependent mainly on the carbon framework structure and the method of sulfonation, and such deactivation is typically observed for the partially-carbonized materials (e.g. hydrochars, biochar or incompletely pyrolyzed organic matter) sulfonated with conc. H_2SO_4 (Section 4.1.1 and Section 4.2.1) presenting a low degree of polycondensation.^{14,22,40,41,75,240} Such leaching is further enhanced at elevated reaction temperatures and pressures which favor irreversible fragmentation of the aromatic carbon structures.^{14,130,240} As such, utmost care must be taken for optimization of reaction parameters at a particular temperature and pressure to prevent permanent catalyst deactivation. Nevertheless, the SO_3H acidity loss upon leaching can be partially recovered by re-sulfonation (Scheme 17). In contrast, the rigid carbon materials functionalized by strong sulfonating reagents like ClSO_3H and by the chemical reduction of 4-benzenediazoniumsulfonate, demonstrated no detectable leaching of SO_3H containing polyaromatic moieties under identical reaction conditions, owing to the

presence of a chemically stable, aromatic graphite like framework structures covalently bonded to the SO₃H or PhSO₃H sites.^{42,61,156} The nominal deactivation observed for such types of rigid carbon materials are typically attributed to the reversible formation of sulfonate esters and pore blocking caused by strong chemisorption of organic species (Scheme 16).^{42,147} Deactivation by adsorption of an alcohol and oxygenated molecules is also easily reversed upon solvent washing, drying (or vacuum drying) and/or combination of both processes (Scheme 17).^{77-79,240} Typically, the porous, high surface area, rigid acidic carbons with a low density of surface SO₃H and oxygen groups are deactivated by such adsorptions processes.⁷⁹ Such adsorptions are also the main cause of deactivation in majority of the C-C and C-O bond forming reactions (alkylation, benzylation, acetalization, etc) catalyzed by such acidic carbocatalysts. Even so, further activation-deactivation studies are needed with sulfonated active carbons, sulfonated ordered carbons, sulfonated N-doped carbons and sulfonated carbon composites to gain more insights into the effect of carbon structure, doping and functional groups on their stability. Particularly studies in fixed-bed operation and in-situ spectroscopic techniques (such as NMR, FT-IR or mass spectroscopy) may provide vital insights into the mechanism of deactivation/leaching of such materials.

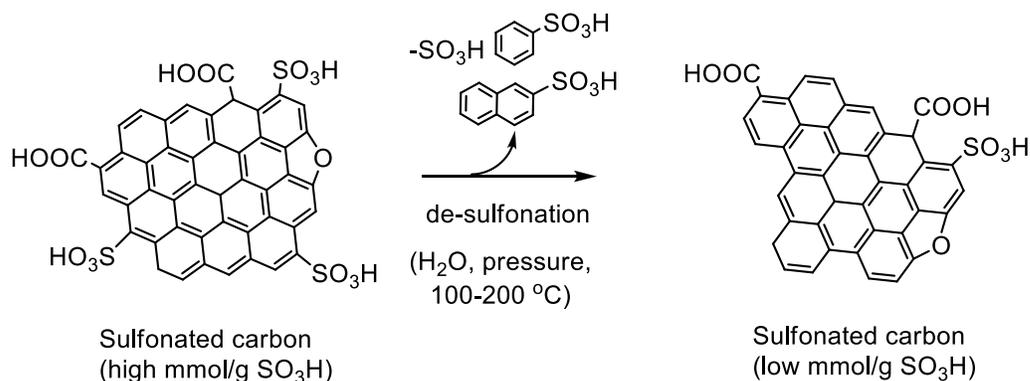
6.2. DEACTIVATION AND REGENERATION IN HYDROTHERMAL AND SOLVOTHERMAL ENVIRONMENTS

Upon reactions involving hydrothermal environments such as hydrolysis, saccharification (Section 5.4) and dehydration (Section 5.5), acidic carbons are deactivated mainly through (a) leaching of SO₃H groups (b) ion-exchange protons of SO₃H sites with the cations contained in the aqueous feeds and (c) active site blocking by pore blockage (adsorption of oxygenated molecules) (Scheme 18).^{76,80,239,240} Anderson and co-workers observed that the sulfur-containing functional groups of acidic carbons sulfonated by fuming H₂SO₄ could not withstand extended exposure (24 h) to condensed-phase water at 160 °C, irrespective of the carbonization conditions (hydrothermal or dry-pyrolysis at moderate temperatures 300-600 °C).²⁴⁰ Generally, the carbon catalysts treated at lower temperatures were observed to present the best stability in terms of SO₃H leaching (lowest leaching). Structural models generated from solid-state NMR showed that such catalysts contained a significant fraction of furan rings and only a small amounts of polycondensed aromatic rings.²⁴⁰ Similarly, also Vogel *et al.*⁸⁰ observed analogous trends of SO₃H leaching (40-68%), at 180 °C, during continuous hydrothermal treatment of sulfonated carbonized cellulose obtained by fuming

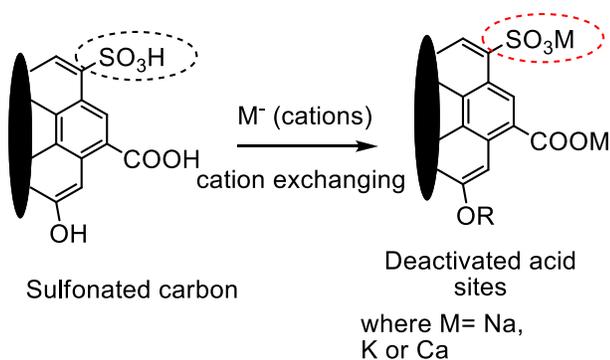
H₂SO₄ treatment (Section 4.1.2). For example, in the case of the most active sulfonated carbon derived from cellulose carbonization at 350 °C, 42% of its initial sulfur content leached within 4 h TOS, followed by a more gradual loss (up to 49%) within the next 20 h. On the contrary, materials carbonized at <450 °C contained sulfur/SO₃H sites that were stable during the continuous hydrothermal treatment. The observed trends were explained by the presence of adjacent electron-donating or withdrawing substituents increasing or decreasing the electron density and stability of C-S bonds.⁸⁰ The same authors also observed that the presence of cations i.e. Na⁺, K⁺ or Ca²⁺ in the aqueous feed solutions can also induce accelerated deactivation of acidic carbons by exchanging with the acidic protons of SO₃H and COOH sites. Although reversible by treatment with aqueous acids (e.g. 0.2 M CF₃SO₃H) (Scheme 19), such deactivation may be unavoidable when dealing with real bio-based aqueous feeds. Vogel *et al.* also demonstrated that by adding complexation agents like crown ethers and ethylenediaminetetraacetic acid in the feed mixtures, the ability of cations to exchange with protons of SO₃H groups could be suppressed without compromising the catalyst activity and stability.⁸⁰ In another work, a sulfonated glucose catalyst G-TsOH (obtained by hydrothermal treatment of glucose with *p*-toluenesulfonic acid, Section 4.1.2) was reported to show SO₃H leaching and deactivation problems similar to the acidic carbons reported by Anderson *et al.*²⁴⁰ and Vogel *et al.*⁸⁰ under hydrothermal environments. In fact, it was concluded that such deactivation is independent of carbon precursor, synthesis methods and textural properties.⁷⁶ Further, a careful analysis of filtrates from hydrothermally treated catalysts by NMR and laser scanning revealed the presence of the characteristic peaks of *p*-toluene sulfonic acid, the intensity of which increased with increasing treatment temperature. The authors proposed that such groups are most likely forming upon exfoliation of SO₃H bearing colloidal carbon particles followed by subsequent decomposition into carbon moieties and soluble *p*-toluenesulfonic acid like moieties (Scheme 18).⁷⁶ Active site blockage by the deposition of oligomeric humins is another well documented mechanism of deactivation for acidic carbons. Humins are formed via oligomerization and polymerization of reactive furanic intermediates in a similar way to the reactions in a hydrothermal carbonization process.^{76,80,239,240}

Scheme 18. Plausible mechanisms for the deactivation of SO₃H functionalized acidic carbons upon reactions under hydrothermal environments.

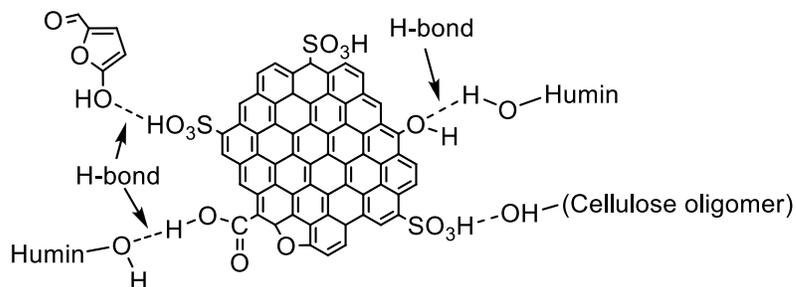
Leaching of SO₃H groups under hydrothermal environments



Cation exchanging of SO₃H groups under hydrothermal environments

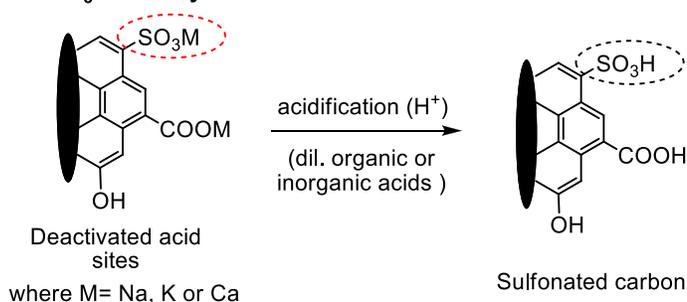


Adsorption of oxygenated molecules on acidic carbon

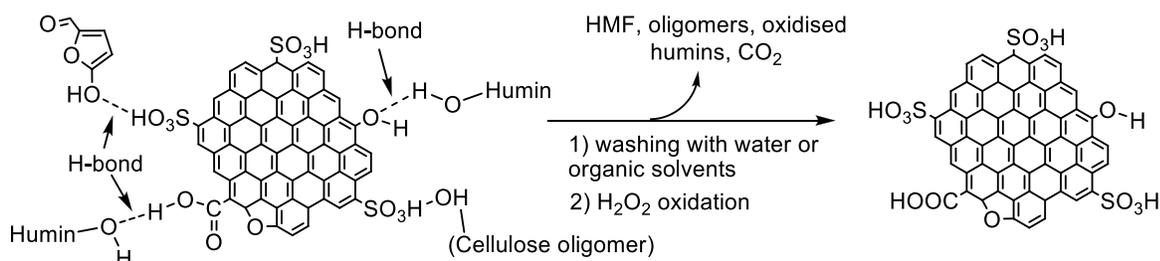


Scheme 19. Reaction scheme for the regeneration of surface acid sites of sulfonated carbons deactivated in hydrothermal environments.

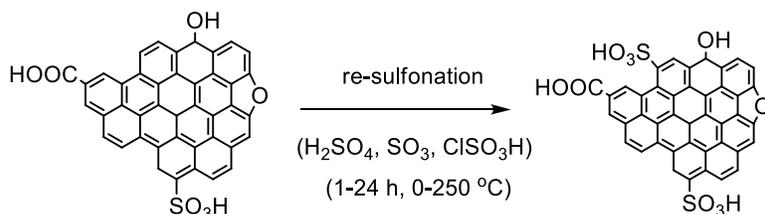
Regeneration of SO₃H sites by dil. acid treatment



Regeneration of SO₃H sites by washing and H₂O₂ oxidation



Partial regeneration of SO₃H sites by re-sulfonation



The deactivation of acidic carbons is also influenced by the nature of reactants and solvents used in the reaction, as observed upon solvolysis and dehydration of carbohydrates at elevated temperatures (100-200 °C) (Section 5.5) and the different C-O and C-C bond forming condensation reactions (Section 5.2 and Section 5.6). When such reactions are performed in a non-aqueous organic solvents such as dimethyl sulfoxide and methyl isobutyl ketone, no or almost negligible deactivation is observed for acidic carbons, while a rapid deactivation and immediate loss of catalytic activity is observed upon water or aqueous solvent systems. The rapid deactivation in aqueous solvents is mainly attributed to the resinification or polymerization of dehydration products (5-hydroxymethylfurfural and furfural) on catalyst surface, leading to the deposition of humins on the catalyst pores that block the active sites.^{96,106,109,168,194} In contrast, in biphasic or organic solvent systems the dehydration products 5-hydroxymethylfurfural and furfural are stabilized and readily desorbed from the catalyst surface acid sites. As a matter of fact, minimizing the formation of polymeric humins is identified as one of the key challenges upon optimizing the yield of the

targeted dehydration products (5-hydroxymethylfurfural, furfural and levulinic acid) from carbohydrates with acid catalysts. The addition of salt (e.g. NaCl or KCl) is a possible way to improve 5-hydroxymethylfurfural yield and inhibit humin formation; however, use of salts may promote catalyst poisoning by ion-exchange. Sulfur leaching may also contribute to the activity loss; especially in case of hydrophilic acidic carbons with a defective/flexible framework obtained by H₂SO₄ treatment (e.g. sulfated hydrochars and semi-carbonized materials). Due to their surface properties, such hydrophilic carbons with low degree of crosslinking are also more likely to promote poisoning by humin deposition as compared to the acidic carbons based on hydrophobic supports (ordered mesoporous carbon, carbon nanotubes, etc.). Nevertheless, PhSO₃H and naphthalene-SO₃H functionalized sulfonated ordered mesoporous carbon catalysts presented ca. 60 times slower deactivation rates than that of a SO₃H functionalized SBA-15 catalyst upon dehydration of fructose to 5-hydroxymethylfurfural in a fixed-bed, bi-phasic, continuous flow operations confirming the superiority of acidic carbons for carbohydrate dehydration. This behavior was attributed to the superior hydrothermal stability of the covalently bonded PhSO₃H (or naphthalene-SO₃H) sites and rigid hydrophobic carbon framework of ordered mesoporous carbons.²²⁷

In contrast, upon C-O and C-C bond forming condensation reactions performed in less aggressive solvents and less detrimental reactants (non-reactive to carbon surface sites) such as acetalization of carbonyls and hydroxyalkylation/alkylation of 2-methylfuran, acidic carbons deactivate neither via leaching nor via derivatizations (esterification). The nominal loss of catalyst activity observed upon performing such reactions is attributed only to the blockage of active sites caused by chemisorption of reactants or product molecules on surface oxygenates by hydrogen bonding like interactions (section 5.2 and section 5.6). Such deactivations are also most common in case of hydrophilic carbocatalysts with a high density surface oxygenates and SO₃H sites. Nevertheless, this type of deactivation (due to pore blockage or active site blocking) is a reversible deactivation process whereupon the adsorbed impurities or poisons are easily removed upon washing with water or organic solvents (e.g. methanol, acetone, 2-propanol) (Scheme 19) followed by drying.^{66,67} In fact, it has been suggested that it is even possible to remove polymeric humins impurities deposited on solid catalyst surfaces using oxidizing H₂O₂ solutions that also regenerate the active sites (Scheme 19).^{161,241,242} The SO₃H acidity loss upon leaching in hydrothermal environments can also be partially recovered by re-sulfonation similar to the materials described in section 6.3 (Scheme 19). Nevertheless, further experiments with additional carbocatalysts (e.g.

sulfonated ordered carbons, sulfonated N-doped carbons and sulfonated carbon composites), fixed-bed studies and in-situ spectroscopic monitoring (e.g. NMR, FT-IR and mass spectrometry) are needed to gain mechanistic insights into the exact mechanism of active site leaching and humin deposition on the surface of such acidic carbocatalysts.

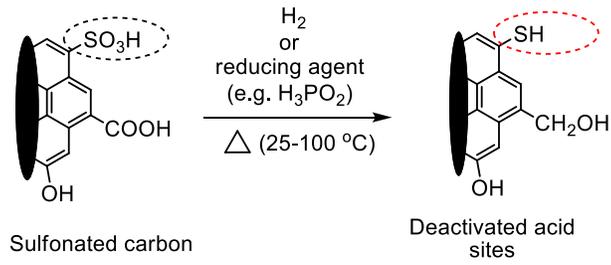
6.3. OTHER MODES OF DEACTIVATION AND REGENERATION

In addition to the standard modes of acidic carbon deactivation via active site (SO_3H group) leaching, derivatizations (esterification) and pore blocking caused by strong chemisorption of organic species; the SO_3H sites of functionalized carbons are also susceptible to deactivation by reduction into low oxidation state S species. This is evident from the reduction of active sites as evident from the reduction of PhSO_3H to SH upon extended exposure to strong reducing agents like H_3PO_2 as well as the carbothermal reduction of SO_3H sites bonded to polycondensed aromatics to low-valent S species (Scheme 20).^{42,66,67} The surface reduction of SO_3H to SH sites was also observed under hydrogenation conditions, as observed in the case of bi-functional mesoporous carbocatalysts containing Ru as an active metal sites and SO_3H as acid sites. In case of 1 wt % Ru containing sulfonated carbocatalysts, XPS analysis of the catalytic materials after pretreatment (reduction) and catalytic hydrogenation of levulinic acid showed a clear increase in the concentration of reduced sulfide (deactivated) species (Figure 18).²⁴³ Such deactivation of SO_3H sites under hydrogenation or reducing conditions significantly limits the potential applications of sulfonated carbons. For the same reason the use of acidic sulfonated carbons (as a support) for fabrication of bifunctional hydrogenation, hydrodeoxygenation catalysts is very limited as the reduction of SO_3H sites to sulfide species (SH or related low-valent S sites) are likely to contribute to deactivation of metal sites by sulfur-poisoning. This limits the application of such materials to acid catalyzed reactions; even so, such metal loaded (e.g. Pd) bifunctional sulfonated carbons may be useful in e.g. direct synthesis of hydrogen peroxide, or selective hydrogenation.

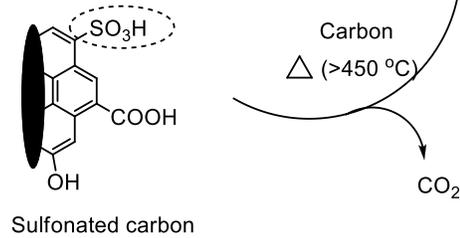
Scheme 20. Plausible mechanisms for the (a) deactivation of SO_3H functionalized acidic carbons upon reactions under reducing environments and (b) reaction scheme for the regeneration of surface SO_3H sites.

(a) Deactivation of functionalized acidic carbons

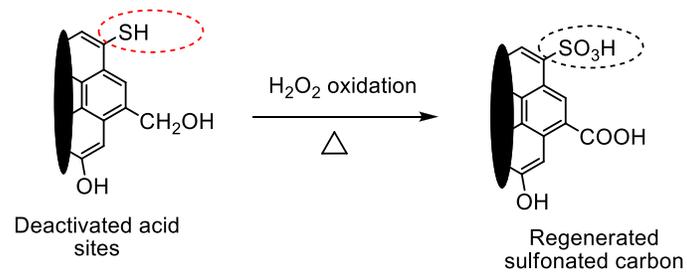
Chemical reduction of SO₃H sites



Carbothermal reduction of SO₃H sites



(b) Regeneration of SO₃H sites of functionalized acidic carbons



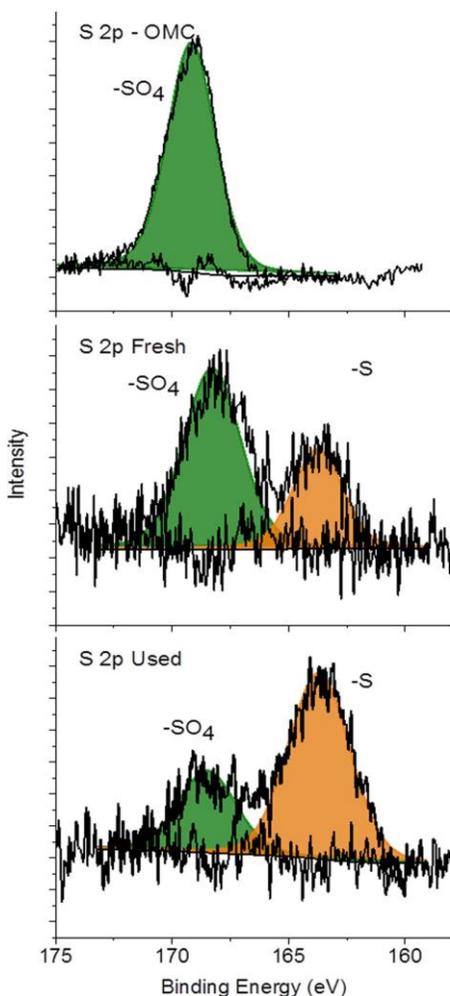


Figure 18. XPS data collected for a sulfonated ordered mesoporous carbon (SOMC), fresh 1 wt% Ru/ SOMC and 1% Ru/ SOMC recovered after levulinic acid hydrogenation. Reprinted with permission from Ref. 243. Copyright 2015 John Wiley and Sons.

7. CONCLUSIONS AND FUTURE OUTLOOK

Carbon materials covalently functionalized with SO_3H groups via C- PhSO_3H or C- SO_3H linkages can act as versatile water-tolerant solid Brønsted acids. The SO_3H functionalized acidic carbon materials or ‘sulfonated carbons’ characterized by their unique carbon structure and Brønsted acidity ($H_0 \leq -11$) *on par* to conc. H_2SO_4 are a new addition to the family of solid protonic acids and metal-free carbocatalysts. Due to their unique surface chemistry, tailorable pore structures and chemical, mechanical and thermal stability, they are regarded as potential substitutes to liquid H_2SO_4 in applications including catalysis, electrocatalysis, water treatment and alike.

Catalysis is one of the important areas in which sulfonated carbons have shown exceptional promise. These carbons demonstrate high activity as a reusable Brønsted acid catalyst upon industrially relevant organic transformations of different bio-renewable and refinery streams where they are often outperforming the alternative solid acids presenting similar acidic strengths (commercial sulfonic resins, Nafion, sulfated metal oxide and acidic zeolites). Liquid phase esterification, ester-exchange (trans-esterification), acetalization, etherification, hydrolysis, dehydration and C-C bond forming alkylation, alkylation/hydroxylalkylation, cross-aldol condensation, Beckmann rearrangement, Knoevenagel condensation, reductive amination, amidation, oxidation and multicomponent organic reactions like the Biginelli reaction are some of the important organic reactions catalyzed by the acidic carbons. The superior activity of sulfonated carbons has mainly been attributed to their unique surface properties that create synergistic effects of active sites (SO_3H or PhSO_3H groups) and surface oxygenates bonded to the network of carbon sheets, thus promoting selective adsorption and catalysis of various reactant molecules. Although, the mechanism of adsorption may differ for different reactants and carbon supports, in most cases such adsorption phenomena take place through non-covalent hydrogen bonding or $\text{CH}-\pi$ and hydrophobic interactions. For non-porous hydrophilic sulfonated carbons (e.g. sulfonated hydrochars and sulfonated semi-carbonized materials), catalyst swelling also plays an important role in case of reactions in polar-media and catalysis of large hydrophilic molecules whereupon unfolding of ultramicropores facilitates adsorption of reactants onto the carbon bulk of catalyst. Both carbon support (or/and carbonization condition) and sulfonation step affect the structure and acidity of the carbon material which in turn influences the summarized catalytic activity, selectivity and stability.

Such metal-free carbocatalysts have been obtained from a wide range of carbon precursors/carbon supports including commercial carbons, activated carbons, N-doped carbons, carbon nitrides, templated carbons, nanostructured carbons as well as inexpensive semi-carbonized materials (biochars and hydrochars) derived from natural organic matter. Nevertheless, the feasibility of using carbon nanomaterials and templated carbons in large-scale fabrication of acidic carbons is limited due to their heavy environmental impact (multistep synthesis, use of hazardous reagents like hydrofluoric acid) and limited availability. A number of approaches has also been developed for the functionalization or grafting SO_3H groups. Simultaneous sulfonation and carbonization with H_2SO_4 is an efficient and simple route to obtain acidic carbocatalysts with a

high degree of SO₃H functionalization, albeit these materials pose negligible porosity, high density of oxygen functional sites and a poor thermal stability (<200 °C). Further, simultaneous sulfonation and carbonization of organic matter in the presence of organosulfates offers several advantages in terms of environmental safety and energy input but results in almost similar carbon materials with high hydrophilicity and poor thermal stability. On the other hand, in the post-grafting functionalization approaches based on the treatment of carbonized materials with various sulfonating reagents to create covalently bonded SO₃H sites, the biggest advantage is the preservation of the original mesostructure/nanostructure of carbon. Thus, a wide range of materials with different surface chemistry (hydrophobicity/hydrophilicity), textural properties and degree of SO₃H functionalization can be obtained using concentrated and fuming H₂SO₄ as the most versatile and inexpensive sulfonating reagents to be used upon efficient grafting of carbon surfaces with SO₃H sites. Nevertheless, the use of such aggressive, oxidizing reagents for sulfonation poses significant challenges in terms of environmental hazards, safety and process upscaling. Also, such reagents are less efficient upon sulfonating graphite like carbons (i.e. templated carbons and activated carbons obtained at >700 °C). In other words, such reagents have limited utility in terms of obtaining carbon catalysts simultaneously possessing high porosity (large pore size, pore-volume, specific surface area), rigid poly condensed structure and a high density of stable SO₃H sites, both of which are vital features when considering applications in large molecule catalysis.

The functionalization of carbon surfaces through electrochemical or chemical reduction is regarded as one of the most efficient routes to produce functional carbon materials with moderate to very high density of PhSO₃H sites. This approach preserves the mesoporous channels and surface properties of the parent material and offers excellent control over the material (acidic carbon) properties. This method *addresses all major drawbacks and environmental hazards* related to the use of conventional sulfonating reagents such as H₂SO₄, ClSO₃H and SO₃. Drawbacks are the higher cost of reagents (sulfanilic acid, isoamyl nitrate or NaNO₂) and bulky size of PhSO₃H moieties that significantly decreases the specific surface area and pore volume of the resulting functionalized material. Besides, the covalently attached PhSO₃H groups are expected to provide stronger proton release ability due to electron-withdrawal effect of aryl groups, so the stronger acidity and higher catalytic ability of as-prepared catalysts will be expected when compared with the carbon-based acids presenting SO₃H sites. Also, several other non-conventional approaches have been developed in recent years and among them, the direct pyrolysis of

lignosulfonates and spray pyrolysis with dil. H₂SO₄ show potential in large-scale production of acidic carbons as they address several issues related to the conventional methods (eliminating use of conc. H₂SO₄, acid waste generation and release of acid gases) without compromising the properties of the resulting materials. As a summary, with a judicious combination of carbon precursor and sulfonation method, it is possible to fine-tune the properties of sulfonated carbons and, therefore, also enable the development of “designer” acid catalysts for specific applications.

Sulfonated carbons retain the structure and textural properties of parent carbon support, irrespective of the sulfonation reaction conditions. Successful sulfonation of carbon materials is usually reflected in terms of decreased thermal stability (hydrochars are an exception) and the positive changes in surface acidity and hydrophilicity. However, the acidity values obtained by different analytical methods differ and, as such, it is recommended to use a combination of measurement techniques to estimate the surface acidity and hydrophilicity of sulfonated carbons. Overall, in terms of catalysis, the activities of non-porous semi-carbonized sulfonated materials are generally comparable to their large pore counterparts, exhibiting comparable activity in large molecule catalysis in polar media. As such, these semi-carbonized acidic carbons show high potential for industrial scale-up due to their low cost, ease of production and other cost benefits. The sulfonated carbons presenting large specific surface areas and low-costs i.e. waste-derived sulfonated activated carbons are promising catalysts within the sugar platform and triglyceride biorefineries, due to their unique ability to adsorb and catalyze the transformation of large hydrophilic as well hydrophobic molecules, water tolerance and compatibility in hydrothermal reaction environments. In fact, these acidic carbons are *the most active, selective and stable non-enzymatic catalysts* known to hydrolyze the β -glycosidic bonds of carbohydrate feedstocks. These carbon-based solid acids bearing SO₃H, COOH and PhOH groups have strong affinity for polysaccharide chains that render them highly effective as saccharification/solvolytic catalysts. Besides, the integration of waste/side streams of existing biorefineries for the production of carbon catalysts would not only resolve a major waste disposal issue but also contribute to higher carbon efficiencies through better utilization of starting biomass.

The catalytic performance and stability of sulfonated carbons are dependent on many parameters including process conditions (temperature, pressure, pH and reaction media), carbon structure (nature of functional group, doping and structural ordering) and the surface-textural

properties of carbon used and, therefore, are strongly influenced by the sulfonation route and carbon precursors. The activation and deactivation studies conducted on such materials have revealed the existence of several mechanism or pathways for active site deactivation of such materials, including (a) reversible deactivation by ion-exchanging, active site derivatization (surface esterification) and pore-blocking/adsorption as well as (b) irreversible deactivation by leaching SO_3H sites and/or solubilization of SO_3H containing polyaromatic species. It has been generally observed that the carbon materials presenting a low degree of polycondensation (hydrochars, biochars and partially carbonized materials) and functionalized by H_2SO_4 treatment are susceptible to rapid irreversible deactivation under strong hydrothermal environments. The same materials are also deactivated in alcoholic media due to formation of sulfonate esters as well as solubilization of SO_3H containing polyaromatic fragments, particularly under high pressures. In contrast, the graphitic carbon materials presenting a high degree of polycondensation (i.e. templated carbons and activated carbons obtained at $>700^\circ\text{C}$) do not undergo similar deactivation by leaching or derivatization; In fact, the activity loss of such catalysts is typically associated with reversible deactivation by ion-exchanging and pore blocking caused by adsorption of impurities. Nevertheless, the exact mechanisms of activation and deactivation of such acidic carbons are still not well understood. Further experimental studies by in-situ spectroscopic techniques (such as NMR, FT-IR and mass spectroscopy), reaction kinetics and molecular modeling techniques may provide useful insights into the active sites activation, deactivation and stability under different process conditions. Mathematical modeling of the reaction kinetics is considered one of the most crucial steps in the chemical process development for industrial applications. Molecular modeling and density functional theory (DFT) studies may also provide fundamental insights into understanding the adsorption-desorption of reactants, products and impurities (such as humins, H_2O) onto active sites of these carbocatalysts. Such studies can give vital insights to the activity, selectivity and activation-deactivation of sulfonated carbons. In particular, additional studies should be undertaken in continuous flow fixed-bed reactors to evaluate the catalyst stability under industrially relevant conditions. Studies are also needed to evaluate the stability of SO_3H sites in the presence of hydrogen/reducing and oxidizing environments, as these materials have also demonstrated potential for fabrication of bifunctional metal catalysts via selective deposition of metal/metal precursors on to the surface oxygenates.

Overall, numerous industrial reactions have been tested in terms of practical applications of these acidic carbons and their fabrication has even been demonstrated in a medium-scale plant from waste materials.¹⁵ Even so, these carbocatalysts are far from being an “ideal replacement catalyst” for homogeneous H₂SO₄. One of the key points to be considered to establish the industrial competence and environmental benignity of such materials is to prove their long term stability and cost-effective regeneration, as fabrication of such materials is also associated with enormous volumes of liquid (H₂SO₄ or dil acid waste) and gaseous acid waste (SO₂, SO₃) generation. If such materials are susceptible to leaching or rapid deactivation in a chemical process the direct use of small (catalytic) quantities of mineral acids would still be more cost-effective and environmentally benign. Nevertheless, with the available data/literature, it is very difficult to comment on the industrial scale feasibility of these acidic carbocatalysts. To reach industrial targets there are several major bottlenecks to be addressed which include: (a) *large/pilot scale techno-economic studies in comparison with existing industrial acid catalysts taking into account stability, activation-deactivation behavior and catalyst regeneration in industrially relevant conditions (batch or continuous flow)*, (b) *experiments with real-world feedstocks e.g. lignocellulose, waste oils, untreated starch feedstocks (majority of existing catalytic studies applies semi-empirical approach, either using pure compounds or impurity-free simulated feeds)* and (c) *reaction kinetics and molecular modeling to understand reaction pathways and develop advanced kinetic models*. Overall, from the viewpoint of catalytic performance, mechanistic understanding, active site stability (under process conditions), mechanical strength and processing, significant improvements are still needed before such materials can replace H₂SO₄.

AUTHOR INFORMATION

CORRESPONDING AUTHORS

*Konwar, L.J. e-mail: lakhya07@gamil.com, lakhya.konwar@umu.se

BIOGRAPHIES

Dr. Lakhya Jyoti Konwar was born in 1987 in Assam, India. He obtained his bachelor's degree in chemistry from Gauhati University (India) in 2008; from the same university, he obtained a master's degree in chemistry in 2010. He started his doctoral studies in the field of heterogeneous catalysis at Tezpur University (India) in 2011 and obtained his Ph.D. degree in 2015. In 2016, he

obtained a Dr.Sc. (Tech.) degree from Åbo Akademi University, Finland (the thesis concerned catalytic applications and kinetic analysis of novel carbocatalysts upon valorization of different bio-based molecules). Since, June 2016 he has been working as a researcher (postdoctoral) at the Department of Chemistry (Technical chemistry, Prof. Jyri-Pekka Mikkola group) Umeå University, Sweden. His research interests include heterogeneous catalysis in particular carbocatalysis, development of hydrothermally stable functional materials, biofuels and catalytic utilization of renewables (biomass, biomolecules and CO₂). To date, Dr. Konwar has authored or co-authored more than 28 peer-reviewed publications, including a review and a book chapter in the field of catalytic utilization of renewables.

Associate professor Dr. Päivi Mäki-Arvela received her Doctor of Technology (chemical engineering) degree in 1994 at Åbo Akademi University, Turku, Finland. Her main research areas are catalytic three-phase reactions, especially transformations of renewable raw materials to valuable products using homogeneous, heterogeneous, and enzyme catalysts as well as applications for ionic liquids, such as wood dissolution and CO₂ capture. Ass. prof. Mäki-Arvela is an author of more than 300 peer-reviewed publications, including 5 review papers in the field of wood dissolution with ionic liquids and transformation of wood biomass to fine and specialty chemicals. Furthermore, she is the author of several conference publications and patents. Her research has been acknowledged by several research and patent prizes. Ass. prof. Mäki-Arvela has served as President of the Nordic Catalysis Society and President of the Finnish Catalysis Society.

Prof. Jyri-Pekka Mikkola, born in Nousiainen, Finland in 1966. He received his M.Sc. in chemical engineering from Åbo Akademi Univ., Åbo-Turku, Finland in 1992. After spending a few years at the industry he returned to the academia to complete his PhD in chemical engineering from Åbo Akademi Univ., Åbo-Turku, Finland, 1999. Since 2008 he is a professor (Sustainable Chemical technology) at both Umeå Univ., Sweden and Åbo Akademi, Finland. He has co-authored more than 300 scientific articles and holds a number of patents. The principal areas of interest are green chemistry; heterogeneous catalysis; ionic liquid technologies; chemical kinetics; and novel materials. He is a member of the editorial board member of *Frontiers in Chemistry*; *Progress in Industrial Ecology, An International Journal*, Inderscience Publishers. He is also member of the scientific advisory board in the 'Biorefinery of the Future'; Finnish Society for Industrial Ecology; Finnish Catalysis Society; steering group member of 'Bio4Energy' research programme

(www.bio4energy.se); member of scientific advisory board, Spinchem AB; member of the scientific advisory board of Biofuel Technology Center (www.btk.slu.se); Management committee member of number of COST actions and co-owner of ECO-OIL AB. In 2004 he was appointed as Academy Research Fellow and received 'The Incentive Award' by the Academy of Finland. In 2009 he received the Umeå University 'Young scientist Award' and 2018 the Umeå University's Baltics prize for entrepreneurship.

NOTES

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is part of the activities of the Technical Chemistry, Department of Chemistry, Chemical-Biological Centre, Umeå University, Sweden as well as the Johan Gadolin Process Chemistry Centre at Åbo Akademi University in Finland. First and foremost, the Kempe Foundations is acknowledged so that this research was possible. The Bio4energy program and Wallenberg Wood Science Center under auspices of Alice and Knut Wallenberg Foundation are also gratefully acknowledged.

REFERENCES

- (1) Ashar, N.G.; Golwalkar, K.R.A. *Practical guide to the manufacture of sulfuric acid, oleums, and sulfonating agents*, Springer international publishing Switzerland, **2013**.
- (2) King, M.J.; Michael, M.; Davenport, W.G. *Sulfuric acid manufacture: analysis, control and optimization*, Elsevier, 2013. eBook ISBN: 9780080982267, Hardcover ISBN: 9780080982205,
- (3) Jones, E. M. Chamber process manufacture of sulfuric acid. *Ind. Eng. Chem.* **1950**, *42(11)*, 2208-2210.
- (4) Zumdahl, S.S. *Chemical Principles 6th Ed.*; Houghton Mifflin Company, 2009. ISBN 0-618-94690-X
- (5) G. de Vries, J.; Jackson, S.D. Homogeneous and heterogeneous catalysis in industry. *Catal. Sci. Technol.* **2012**, *2*, 2009-2009
- (6) Kulprathipanja, S. *Zeolites in Industrial Separation and Catalysis*, Wiley-VCH Verlag GmbH & Co. KgaA, 2010. Print ISBN: 9783527325054, Online ISBN: 9783527629565.
- (7) Kozhevnikov, I. V.; Matveev, K. I. Homogeneous catalysts based on heteropoly acids-A review. *Appl. Catal.* **1983**, *5*, 135-150.

- (8) Wu, Y.; Ye, X.; Yang, X.; Wang, X.; Chu, W.; Hu, Yucai. Heterogenization of heteropolyacids: a general discussion on the preparation of supported acid catalysts. *Ind. Eng. Chem. Res.* **1996**, *35*, 2546–2560.
- (9) Wu, Zhou.; Nikolaos, Soultanidis.; Hui, Xu.; Michael, S.W.; Matthew, N.; Christopher, J. K.; Israel, E. Wachs, Nature of catalytically active sites in the supported WO₃/ZrO₂ solid acid system: a current perspective. *ACS Catal.* **2017**, *7*(3), 2181–2198
- (10) Venkatesh, K. R.; Hu, Jianli.; Dogan, C.; Tierney, J.W.; Wender, I. Sulfated metal oxides and related solid acids: comparison of protonic acid strengths. *Energy Fuels* **1995**, *9*, 888–893.
- (11) Gelbard, G. Organic synthesis by catalysis with ion-exchange resins. *Ind. Eng. Chem. Res.* **2005**, *44*, 8468–8498.
- (12) Kusoglu, A.; Weber, A. Z.; New insights into perfluorinated sulfonic-acid ionomers. *Chem. Rev.* **2017**, *117*, 987–1104.
- (13) Serp, P.; Machado, B. *Nanostructured carbon materials for catalysis, catalysis series (Book 23)*, Royal society of chemistry, **2015**. Print ISBN: 978-1-84973-909-2 PDF eISBN: 978-1-78262-256-7.
- (14) Hara, M. Biomass conversion by a solid acid catalyst. *Energy Environ. Sci.* **2010**, *3*, 601-607.
- (15) Nakajima, K.; Hara, M. Amorphous carbon with SO₃H groups as a solid Brønsted acid catalyst. *ACS Catal.* **2012**, *2*, 1296–1304.
- (16) Okamura, M.; Takagaki, A.; Toda, M.; Kondo, J.N.; Domen, K.; Tatsumi, T.; Hara, M.; Hayashi, S. Acid-catalyzed reactions on flexible polycyclic aromatic carbon in amorphous carbon. *Chem. Mater.* **2006**, *18*, 3039–3045.
- (17) Shen, Y.; Baoliang, C. Sulfonated graphene nanosheets as a superb adsorbent for various environmental pollutants in water. *Environ. Sci. Technol.* **2015**, *49*, 7364–7372.
- (18) Sun, Y.; Zhao, J.; Wang, J.; Tang, Nan.; Zhao, R.; Zhang, D.; Guan, T.; Li, K. Sulfur-doped millimeter-sized microporous activated carbon spheres derived from sulfonated poly(styrene–divinylbenzene) for CO₂ capture. *J. Phys. Chem. C* **2017**, *121*, 10000–10009.
- (19) Choi, Y.; Kwon, Y.; Kyung, K.; Kang, Y.; Lee, J.S. A composite electrolyte membrane containing high-content sulfonated carbon spheres for proton exchange membrane fuel cells. *Carbon* **2011**, *49*, 1367-1373.
- (20) Imaizumi, S.; Matsumoto, H.; Ashizawa, M.; Minagawa, M.; Tanioka, A. Nanosize effects of sulfonated carbon nanofiber fabrics for high capacity ion-exchanger. *RSC Adv.* **2012**, *2*, 3109–3114.
- (21) Liu, J.; Xue, Y.; Dai, L. Sulfated graphene oxide as a hole-extraction layer in high-performance polymer solar cells. *J. Phys. Chem. Lett.* **2012**, *3*, 1928–1933.
- (22) Hara, M.; Yoshida, T.; Takagaki, A.; Takata, T.; Kondo, J. N.; Domen, K.; Hayashi, S. A carbon material as a strong protonic acid. *Angew. Chem. Int. Ed.* **2004**, *43*, 2955–2958.
- (23) Toda, M.; Takagaki, A.; Okamura, M.; Kondo J. N.; Hayashi, S.; Domen, K.; Hara, M. Green chemistry: biodiesel made with sugar catalyst. *Nature* **2005**, *438*,178.

- (24) Corma, A. Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions. *Chem. Rev.* **1995**, *95*, 559–614.
- (25) Kenneth, A. M.; Moore, R.B. State of understanding of Nafion. *Chem. Rev.*, **2004**, *104*, 4535–4586.
- (26) Chakrabarti, A.; Sharma, M.M. Cationic ion exchange resins as catalyst. *Reactive Polymers.* **1993**, *20*, 1-45.
- (27) Primo, A.; Garcia, H. Zeolites as catalysts in oil refining. *Chem. Soc. Rev.* **2014**, *43*, 7548-7561.
- (28) Ennaert, T.; Aelst, J. V.; Dijkmans, J.; Clercq, R. D.; Schutyser, W.; Dusselier, M.; Verboekend, D.; Sels, B.F. Potential and challenges of zeolite chemistry in the catalytic conversion of biomass. *Chem. Soc. Rev.* **2016**, *45*, 584-611.
- (29) Donnet, J-B-A. Noir de carbone modifié, sa préparation et ses applications. FR1215895, **1960**.
- (30) Aboytes, P. Sulfonated carbon black. US3528840A, **1970**.
- (31) Jerome, A.; Leighton, B.R.; Donald, R. Sulfonated carbon blacks. US3442679A, **1966**.
- (32) Bollepalli, S.; Dotson, A. O. Proton conductive carbon material. CA2486698A1, **2003**.
- (33) Bollepalli, S. Sulfonated carbonaceous materials. US7241334B2, **2007**.
- (34) Belmont, J. A.; Acton, M. Process for preparing carbon materials with diazonium salts and resultant carbon products. US005554739A, **1994**.
- (35) Lee, D. Preparation of a sulfonated carbonaceous material from lignosulfonate and its usefulness as an esterification catalyst. *Molecules* **2013**, *18*, 8168-8180.
- (36) Zong, M. Hua.; Duan, Z. Q.; Lou, W. Y.; Smith, T. J.; Wu, H. Preparation of a sugar catalyst and its use for highly efficient production of biodiesel. *Green Chem.* **2007**, *9*, 434–437.
- (37) Hara, M. Environmentally benign production of biodiesel using heterogeneous catalysts. *ChemSusChem* **2009**, *2*, 129-135.
- (38) Morine, G. H.; Spigarelli, S. A. Ion exchange materials produced from hydrolyzed, debituminized, sulfonated peat. US5314638A, **1991**.
- (39) Galhardo, T. S.; Simone, N.; Gonçalves, M.; Figueiredo, F. C. A.; Mandelli, Dalmo.; Carvalho, W. A. Preparation of sulfonated carbons from rice husk and their application in catalytic conversion of glycerol. *ACS Sustainable Chem. Eng.* **2013**, *1*, 1381–1389.
- (40) Rao, B.V.S.K.; Mouli, K.C.; Rambabu, N.; Dalai, A.K.; Prasad, R.B.N. Carbon-based solid acid catalyst from de-oiled canola meal for biodiesel production. *Catal. Commun.* **2011**, *14*, 20–26.
- (41) Arancon, R.A.; Barros Jr., H.R.; Balu, A.M.; Vargas, C.; Luque, R Valorisation of corncob residues to functionalised porous carbonaceous materials for the simultaneous esterification/transesterification of waste oils. *Green Chem.* **2011**, *13*, 3162–3167.
- (42) Konwar, L.J.; Mäki-Arvela, P.; Salminen, E.; Kumar, N.; Thakur, A.J.; Mikkola, J-P.; Deka, D. Towards carbon efficient biorefining: multifunctional mesoporous solid acids

- obtained from biodiesel production wastes for biomass conversion. *Appl. Catal., B* **2015**, *176–177*, 20–35.
- (43) Benyounes, A.; Ouanji, F.; Louisia, S.; Ziyad, M.; Serp, P.; Kacimi, M. Coexistence of sulfonic and pyridinic sites on H₂SO₄ treated N-doped carbon nanotubes. *Catal. Today* **2018**, *301*, 183–190.
- (44) Gonçalves, M.; Souza, V.C.; Galhardo, T. S.; Mantovani, M.; Figueiredo, F. C. A.; Mandelli, D.; Carvalho, W. A. Glycerol conversion catalyzed by carbons prepared from agroindustrial wastes. *Ind. Eng. Chem. Res.* **2013**, *52*, 2832–2839.
- (45) Devi, B.L.A.P.; Gangadhar, K.N.; Prasad, P.S.S.; Jagannadh, B.; Prasad, R.B.N. Glycerol-based carbon catalyst for the preparation of biodiesel. *ChemSusChem* **2009**, *2*, 617–620.
- (46) Yu, J.T.; Dehkhoda, A.M.; Ellis, N. Development of biochar-based catalyst for transesterification of canola oil. *Energy Fuels* **2010**, *25*, 337–344.
- (47) Shu, Q.; Gao, J.; Nawaz, Z.; Liao, Y.; Wang, D.; Wang, J. Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst. *Appl. Energy* **2010**, *87*, 2589–2596.
- (48) Zhang, X.J.; Wang, Y.Y.; Jiang, Z.C.; Wu, P.T.; Jin, Y.M.; Hu, Y.Q. One-pot preparation of sulfonated ordered mesoporous carbon and its catalytic performance. *Carbon* **2014**, *70*, 322.
- (49) Chang, B.; Fu, J.; Tian, Y.; Dong, X. Soft-template synthesis of sulfonated mesoporous carbon with high catalytic activity for biodiesel production. *RSC Adv.* **2013**, *3*, 1987–1994.
- (50) Fukuhara, K.; Nakajima, K.; Kitano, M.; Hayashi, S.; Hara, M. Synthesis and acid catalysis of zeolite-templated microporous carbons with SO₃H groups. *Phys. Chem. Chem. Phys.* **2013**, *15*, 9343–9350.
- (51) Janaun, J.; Ellis, N. Role of silica template in the preparation of sulfonated mesoporous carbon catalysts. *Appl. Catal., A* **2011**, *394*, 25–31.
- (52) Wang, X.; Liu, R.; Waje, M. M.; Chen, Z.; Yan, Y.; Bozhilov, K. N.; Feng, P. Sulfonated ordered mesoporous carbon as a stable and highly active protonic acid catalyst. *Chem. Mater.* **2007**, *19*, 2395–2397.
- (53) Pang, J.; Wang, A.; Zhenga, M.; Zhang, T. Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures. *Chem. Commun.* **2010**, *46*, 6935–6937.
- (54) Aldana-Pérez, A.; Lartundo-Rojas, L.; Gómez, R.; Niño-Gómez, M.E. Sulfonic groups anchored on mesoporous carbon Starbons-300 and its use for the esterification of oleic acid. *Fuel* **2012**, *100*, 128–138.
- (55) Kitano, M.; Arai, K.; Kodama, A.; Kousaka, T.; Nakajima, K.; Hayashi, S.; Hara, M. Preparation of a sulfonated porous carbon catalyst with high specific surface area. *Catal. Lett.* **2009**, *131*, 242–249.
- (56) Ji, J.; Zhang, G.; Chen, H.; Wang, S.; Zhang, G.; Zhang F.; Fan, X. Sulfonated graphene as water-tolerant solid acid catalyst. *Chem. Sci.* **2011**, *2*, 484–487.
- (57) Nguyen, V. C.; Bui, N.Q.; Mascunan, P.; Vu, T. T.H.; Fongarland, P.; Essayem, N. Esterification of aqueous lactic acid solutions with ethanol using carbon solid acid

- catalysts: Amberlyst 15, sulfonated pyrolyzed wood and graphene oxide. *Appl. Catal., A* **2018**, *552*, 184-191.
- (58) Yu, H.; Jin, Y.; Li, Z.; Peng, F.; Wang, H. Synthesis and characterization of sulfonated single-walled carbon nanotubes and their performance as solid acid catalyst. *J. Solid State Chem.* **2008**, *181*, 432-438.
- (59) Guan, Q.; Li, Y.; Chen, Y.; Shi, Y.; Gu, J.; Li, B.; Miao, R.; Chena Q.; Ning, P. Sulfonated multi-walled carbon nanotubes for biodiesel production through triglycerides transesterification. *RSC Adv.* **2017**, *7*, 7250-7258.
- (60) OliveiraVictor, B. L.; da Silva, T. Sulfonated carbon nanotubes as catalysts for the conversion of levulinic acid into ethyl levulinate, *Catal. Today.* **2014**, *234*, 257-263.
- (61) Stellwagen, D. R.; van der Klis, F.; van Es, D. S.; de Jong, K. P.; Bitter, J. H. Functionalized carbon nanofibers as solid-acid catalysts for transesterification. *ChemSusChem* **2013**, *6*, 1668-1672.
- (62) Nakhate, A. V.; Yadav, G. D. Synthesis and characterization of sulfonated carbon-based graphene oxide monolith by solvothermal carbonization for esterification and unsymmetrical ether formation. *ACS Sustainable Chem. Eng.* **2016**, *4*, 1963-1973.
- (63) Oger, N.; Lin, Y. F.; Labrugere, C.; Le Grogneq, E.; Rataboul, F.; Felpin, F. X. Practical and scalable synthesis of sulfonated grapheme. *Carbon* **2016**, *96*, 342-350.
- (64) Doroodmand, M. M.; Sobhani, S.; Ashoori, A. Sulfonated multiwalled carbon nanotubes (MWCNTs) as a new, efficient, and recyclable heterogeneous nanocatalyst for the synthesis of amines. *Can. J. Chem.* **2012**, *90*, 701-707.
- (65) Zhang, B.; Ren, J.; Liu, X.; Guo, Y.; Guo, Y.; Lu, G.; Wang, Y. Novel sulfonated carbonaceous materials from p-toluenesulfonic acid/glucose as a high-performance solid-acid catalyst. *Catal. Commun.* **2010**, *11*, 629-632.
- (66) Konwar, L.J.; Samikannu, A.; Mäki-Arvela, P.; Boström, D.; Mikkola, J-P.; Lignosulfonate-based macro/mesoporous solid protonic acids for acetalization of glycerol to bio-additive. *Appl. Catal., B* **2018**, *220*, 314-323.
- (67) Konwar, L.J.; Samikannu, A.; Mäki-Arvela, P.; Mikkola, J-P. Efficient C-C coupling of bio-based furanics and carbonyl compounds to liquid hydrocarbon precursors over lignosulfonate derived acidic carbocatalysts. *Catal. Sci. Technol.* **2018**, *8*, 2449-2459.
- (68) Hines, D.; Bagreev, A.; Bandosz, T.J. Surface properties of porous carbon obtained from polystyrene sulfonic acid-based organic salts. *Langmuir* **2004**, *20*, 3388-3397.
- (69) Xiao, H.; Guo, Y.; Liang, X.; Qi, C. One-step synthesis of novel biacidic carbon via hydrothermal carbonization. *J. Solid State Chem.* **2010**, *183*, 1721-1725.
- (70) Jia, R.; Ren, J.; Liu, X.; Lu, G.; Wang, Y. Design and synthesis of sulfonated carbons with amphiphilic properties. *J. Mater. Chem. A* **2014**, *2*, 11195-11201.
- (71) Nata, I. F.; Irawan, C.; Mardina, P.; Lee, C. K. Carbon-based strong solid acid for corn starch hydrolysis. *J. Solid State Chem.* **2015**, *230*, 163-168.
- (72) Li, S.; Li, N.; Li, G.; Li, L.; Wang, A.; Cong, Y.; Wang, X.; Zhang, T. Lignosulfonate-based acidic resin for the synthesis of renewable diesel and jet fuel range alkanes with 2-methylfuran and furfural. *Green Chem.* **2015**, *17*, 3644-3652.

- (73) Zhang, X.; Zhang, Z.; Wang, F.; Wang, Y.; Song, Q.; Xu, J. Lignosulfonate-based heterogeneous sulfonic acid catalyst for hydrolyzing glycosidic bonds of polysaccharides. *J Mol Catal A-Chem.* **2013**, *377*, 102–107.
- (74) Liu, F.; Kong, W.; Qi, C.; Zhu, L.; Xiao, F. S. Design and synthesis of mesoporous polymer-based solid acid catalysts with excellent hydrophobicity and extraordinary catalytic activity. *ACS Catal.* **2012**, *2*, 565–572.
- (75) Mo, X.; López, D. E.; Suwannakarn, K.; Liu, Y.; Lotero, E.; Goodwin Jr., J. G.; Lu, C. Activation and deactivation characteristics of sulfonated carbon catalysts. *J Catal.* **2008**, *254*, 332–338.
- (76) Chen, G.; Wang, X.; Jiang, Y.; Mu, X.; Liu, H. Insights into deactivation mechanism of sulfonated carbonaceous solid acids probed by cellulose hydrolysis. *Catal. Today.* **2019**, *319*, 25-30.
- (77) Fraile, J.M.; García-Bordejé, E.; Pires, E.; Roldán, L. New insights into the strength and accessibility of acid sites of sulfonated hydrothermal carbon. *Carbon* **2014**, *77*, 1157–1167.
- (78) Fraile, J.M.; García-Bordejé, E.; Pires, E.; Roldán, L. Deactivation of sulfonated hydrothermal carbons in the presence of alcohols: Evidences for sulfonic esters formation. *J. Catal.* **2012**, *289*, 73–79.
- (79) Fraile, J.M.; García-Bordejé, E.; Pires, E.; Roldán, L. Catalytic performance and deactivation of sulfonated hydrothermal carbon in the esterification of fatty acids: Comparison with sulfonic solids of different nature. *J. Catal.* **2015**, *324*, 107–118.
- (80) Scholz, D. F.; Kröcher, O.; Vogel, F. Deactivation and regeneration of sulfonated carbon catalysts in hydrothermal reaction environments. *ChemSusChem* **2018**, *11*, 2189–2201.
- (81) Boonoun, P.; Laosiripojana, N.; Muangnapoh, C.; Jongsomjit, B.; Panpranot, J.; Mekasuwandumrong, O.; Shotipruk, A. Application of sulfonated carbon-based catalyst for reactive extraction of 1,3-propanediol from model fermentation mixture. *Ind. Eng. Chem. Res.* **2010**, *49*, 12352–12357.
- (82) Brown D. R.; Groszek, A. J. Heats of adsorption of ammonia on a zeolite catalyst and an acid-activated clay catalyst determined by flow adsorption microcalorimetry. *Langmuir* **2000**, *16*, 4207-4212.
- (83) Brown, A.S. C.; Hargreaves, J. S. J. sulfated metal oxide catalysts. superactivity through superacidity. *Green Chem.* **1999**, *1*, 17-20.
- (84) Katada, N.; Nouno, K.; Lee, J.K.; Shin, J.; Hong, S. B.; Niwa, M. Acidic properties of cage-based, small-pore zeolites with different framework topologies and their silicoaluminophosphate analogues. *J. Phys. Chem. C* **2011**, *115*, 22505–22513.
- (85) Newman, A.D.; Brown, D. R.; Siril, P.; Lee A. F.; Wilson, K. Structural studies of high dispersion H₃PW₁₂O₄₀/SiO₂ solid acid catalysts. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2893–2902.
- (86) Venkatesh, K. R.; Hu, J.; Dogan, C.; Tierney, J. W.; Wender, I. Sulfated metal oxides and related solid acids: comparison of protonic acid strengths. *Energy Fuels.* **1995**, *9*, 888–893.

- (87) Drago, R. S.; Kob, N. Acidity and reactivity of sulfated zirconia and metal-doped sulfated zirconia. *J. Phys. Chem., B* **1997**, *101*, 3360–3364;
- (88) Vartuli, J. C.; Santiesteban, J. G.; Traverso, P.; Cardona-Martin, N.; Chang, C. D.; Stevenson, S. A. Characterization of the acid properties of tungsten/zirconia catalysts using adsorption microcalorimetry and n-pentane isomerization activity. *J. Catal.* **1999**, *187*, 131–138.
- (89) *Calorimetry and thermal methods in catalysis*, Auroux, A. (Ed.); Springer-Verlag Berlin Heidelberg, **2013**.
- (90) Siril, P.F.; Shiju, N.R.; Brown, D.R.; Wilson, K. Optimising catalytic properties of supported sulfonic acid catalysts. *Appl. Catal., A* **2009**, *364*, 95–100.
- (91) Suganuma, S.; Nakajima, K.; Kitano, M.; Yamaguchi, D.; Kato, H.; Hayashi, S.; Hara, M. Hydrolysis of cellulose by amorphous carbon bearing SO₃H, COOH, and OH groups, *J. Am. Chem. Soc.* **2008**, *130*, 12787-12793.
- (92) Nakajima, K.; Okamura, M.; Kondo, J. N.; Domen, K.; Tatsumi, T.; Hayashi, S.; Hara, M. Amorphous carbon bearing sulfonic acid groups in mesoporous silica as a selective catalyst. *Chem. Mater.* **2009**, *21*, 186–193.
- (93) Fukuhara, K.; Nakajima, K.; Kitano, M.; Kato, H.; Hayashi, S.; Hara, M. Structure and catalysis of cellulose-derived amorphous carbon bearing SO₃H groups. *ChemSusChem*. **2011**, *4*, 778-784.
- (94) Kastner, J. R.; Millera, J.; Geller, D.P.; Locklin, J.; Keith, L.H.; Johnson, T. Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon. *Catal. Today* **2012**, *190*, 122–132.
- (95) Malins, K.; Kampars, V.; Brinks J.; Neibolte I.; Murnieks, R. Synthesis of activated carbon based heterogenous acid catalyst for biodiesel preparation. *Appl. Catal., B* **2015**, *176–177*, 553-558.
- (96) Karimi, B.; Mirzaei, H. M.; Behzadnia, H.; Vali, H. Novel ordered mesoporous carbon based sulfonic acid as an efficient catalyst in the selective dehydration of fructose into 5-HMF: the role of solvent and surface chemistry. *ACS Appl. Mater. Inter.* **2015**, *7*, 19050–19059.
- (97) Siril, P. F.; Brown, D. R. New polystyrene sulfonic acid resin catalysts with enhanced acidic and catalytic properties. *J. Mol. Catal. A-Chem.* **2006**, *252*, 125–131.
- (98) Xing, R.; Liu, Y.; Wang, Y.; Chen, L.; Wu, H.; Jiang, Y.; He, M.; Wu, P. Active solid acid catalysts prepared by sulfonation of carbonization-controlled mesoporous carbon materials, *Microporous and Mesoporous Mater.* **2007**, *105*, 41–48.
- (99) Liu, R.; Wang, X.; Zhao, X.; Feng, P. Sulfonated ordered mesoporous carbon for catalytic preparation of biodiesel. *Carbon* **2008**, *46*, 1664–1669.
- (100) Chen, P.; Yang, C.; He, Z.; Guo, K. One-pot facile route to fabricate the precursor of sulfonated graphene/N-doped mesoporous carbons composites for supercapacitors. *J. Mater. Sci.* **2019**, *54*, 4180-4191.
- (101) Douzandegi, M. A.; Ghafuri F. H.; Rashidizadeh, A. Sulfonated highly ordered mesoporous graphitic carbon nitride as a super active heterogeneous solid acid catalyst for Biginelli reaction. *Microporous and Mesoporous Mater.* **2019**, *274*, 83-93.

- (102) Baig, R. B. N.; Verma, S.; Nadagouda, M. N.; Varma, R. S. Room temperature synthesis of biodiesel using sulfonated graphitic carbon nitride. *Sci. Rep.* **2016**, *6*, 39387-.
- (103) Verma, S.; Nasir Baig, R. B.; Nadagouda, M. N.; Lenc, C.; Varma, R. S. Sustainable pathway to furanics from biomass via heterogeneous organo-catalysis, *Green Chem.* **2017**, *19*, 164–168.
- (104) Puente-Santiago, A. R.; Rodríguez-Padrón D.; Quan, X.; Muñoz Batista, M. J.; Martins, L. O.; Verma, S.; Varma, R.S.; Zhou, J.; Luque, R. Unprecedented wiring efficiency of sulfonated graphitic carbon nitride materials: toward high-performance amperometric recombinant cota laccase biosensors. *ACS Sustainable Chem. Eng.* **2019**, *7*, 1474–1484.
- (105) Liu, X.Y.; Huang, M.; Ma, H. L.; Zhang, Z. Q.; Gao, J. M.; Zhu, Y. L.; Han, X.J.; Guo, X.Y. Preparation of a carbon-based solid acid catalyst by sulfonating activated carbon in a chemical reduction process. *Molecules* **2010** *15*, 7188–7196.
- (106) Geng, L.; Wang, Y.; Yu, G.; Zhu, Y. Efficient carbon-based solid acid catalysts for the esterification of oleic acid. *Catal. Commun.* **2011**, *13*, 26–30.
- (107) Dornath, P.; Ruzycky, S.; Pang, S.; He, L.; Dauenhauer, P.; Fan, W. Adsorption-enhanced hydrolysis of glucan oligomers into glucose over sulfonated three-dimensionally ordered mesoporous carbon catalysts. *Green Chem.* **2016**, *18*, 6637-6647.
- (108) Zhang, Tong Chen, Y. T.; Zhang, G.; Wang G.; Zhang, H. Efficient production of isosorbide from sorbitol dehydration over mesoporous carbon-based acid catalyst, *Appl.Catal., A* **2019**, *575*, 38-47.
- (109) Upare, P. P.; Yoon, J. W.; Kim, M. Y.; Kang, H.Y.; Hwang, D.W.; Hwang, Y. K.; Kungc, H. H.; Chang, J.S. Chemical conversion of biomass-derived hexose sugars to levulinic acid over sulfonic acid-functionalized graphene oxide catalysts. *Green Chem.* **2013**, *15*, 2935-2943.
- (110) Maci-Agull, J. A.; Sevilla, M.; Diez, M. A.; Fuertes, A. B. Synthesis of carbon-based solid acid microspheres and their application to the production of biodiesel. *ChemSusChem* **2010**, *3*, 1352-1356.
- (111) Guo, H.; Qi, X.; Li, L.; Smith Jr., R. L. Hydrolysis of cellulose over functionalized glucose-derived carbon catalyst in ionic liquid. *Bioresour. Technol.* **2012**, *116*, 355–359.
- (112) ViTran, T. T.; Kaiprommarat, S.; Kongparakul, S.; Reubroycharoen, P.; Guan, G.; Nguyen, M. H.; Samart, C. Green biodiesel production from waste cooking oil using an environmentally benign acid catalyst. *Waste Manage.* **2016**, *52*, 367-37.
- (113) Kang, S.; Ye, J.; Zhang Y.; Chang, J. Preparation of biomass hydrochar derived sulfonated catalysts and their catalytic effects for 5-hydroxymethylfurfural production. *RSC Adv.* **2013**, *3*, 7360-7366.
- (114) Liu, M.; Jia, S.; Gong, Y.; Song, C.; Guo, X. Effective hydrolysis of cellulose into glucose over sulfonated sugar-derived carbon in an ionic liquid. *Ind. Eng. Chem. Res.* **2013**, *52*, 8167–8173.
- (115) Qi, X.; Guo, H.; Li, L.; Smith, Jr., R. L. Acid-catalyzed dehydration of fructose into 5-hydroxymethylfurfural by cellulose-derived amorphous carbon. *ChemSusChem* **2012**, *5*, 2215-2220.
- (116) Gan, L.; Zhu, J.; Lv, L. Cellulose hydrolysis catalyzed by highly acidic lignin-derived carbonaceous catalyst synthesized via hydrothermal carbonization. *Cellulose* **2017**, *24*, 5327-5339.

- (117) Shimin, K.; Jie, C.; Chin, F.J. One step preparation of sulfonated solid catalyst and its effect in esterification reaction. *Chinese J Chem. Eng.* **2014**, *22*, 392-397.
- (118) Toro, M. J. J.; Dou, X.; Ajewole, I.; Wang, J.; Chong, K.; Ai, N.; Zeng, G.; Chen, T. Preparation and optimization of macroalgae-derived solid acid catalysts. *Waste Biomass Valori.* **2019**, *10*, 805-816.
- (119) Zhang, W.; Tao, H.; Zhang, B.; Ren, J.; Lu, G.; Wang, Y. One-pot synthesis of carbonaceous monolith with surface sulfonic groups and its carbonization/activation. *Carbon* **2011**, *49*, 1811–1820.
- (120) Thombal, R.S.; Jadhav, A. R.; Jadhav, V. H. Biomass derived β -cyclodextrin-SO₃H as a solid acid catalyst for esterification of carboxylic acids with alcohols. *RSC Adv.* **2015**, *5*, 12981-12986.
- (121) Shen, F.; Guo, T.; Bai, C.; Qiu, M.; Qi, X.; Hydrolysis of cellulose with one-pot synthesized sulfonated carbonaceous solid acid. *Fuel Process Technol.* **2018**, *169*, 244-247.
- (122) Manechakr, P.; Karnjanakom, S. Catalytic transformation of furfural into bio-based succinic acid via ultrasonic oxidation using β -cyclodextrin-SO₃H carbon catalyst: A liquid biofuel candidate. *Energy Convers. Manag.* **2017**, *154*, 299–310.
- (123) Liang, X.; Zeng, M.; Qi, C. One-step synthesis of carbon functionalized with sulfonic acid groups using hydrothermal carbonization. *Carbon* **2010**, *48*, 1844-1848.
- (124) Qi, X.; Lian, Y.; Yan, L.; Smith Jr. R. L. One-step preparation of carbonaceous solid acid catalysts by hydrothermal carbonization of glucose for cellulose hydrolysis. *Catal. Commun.* **2014**, *57*, 50–54.
- (125) Zhao, Y.; Wang, H.; Zhao, Y.; Shen, J. Preparation of a novel sulfonated carbon catalyst for the etherification of isopentene with methanol to produce *tert*-amyl methyl ether. *Catal Commun.* **2010**, *11*, 824–828.
- (126) Samikannu, A.; Konwar, L.J.; Mäki-Arvela, P.; Mikkola, J-P. Renewable N-doped active carbons as efficient catalysts for direct synthesis of cyclic carbonates from epoxides and CO₂. *Appl. Catal., B* **2019**, *241*, 41-51.
- (127) Suganuma, S.; Nakajima, K.; Kitano, M.; Yamaguchi, D.; Kato, H.; Hayashi, S.; Hara, M. Synthesis and acid catalysis of cellulose-derived carbon-based solid acid. *Solid State Sci.* **2010**, *12*, 1029-1034.
- (128) Suganuma, S.; Nakajima, K.; Kitano, Hayashi, S.; Hara, M. Sp³-linked amorphous carbon with sulfonic acid groups as a heterogeneous acid catalyst. *ChemSusChem* **2012**, *5*, 1841-1847.
- (129) Lou, W.Y.; Guo, Q.; Chen, W.J.; Zong, M. H.; Wu, H.; Smith, T. J. A highly active bagasse-derived solid acid catalyst with properties suitable for production of biodiesel. *ChemSusChem* **2012**, *5*, 1533-1541.
- (130) Lien, Y. S.; Hsieh, L. S.; Wu, J.C. S. Biodiesel synthesis by simultaneous esterification and transesterification using oleophilic acid catalyst. *Ind. Eng. Chem. Res.* **2010**, *49*, 2118–2121.
- (131) Lou, W.Y.; Zong, M. H.; Duan, Z. Q. Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts. *Bioresour. Technol.* **2008**, *99*, 8752–8758.
- (132) Hara, M. Biodiesel production by amorphous carbon bearing SO₃H, COOH and phenolic OH groups, a solid Brønsted acid catalyst. *Top Catal.* **2010**, *53*, 805–810.

- (133) Dehkhoda, A. M.; West, A.H.; Ellis, N. Biochar based solid acid catalyst for biodiesel production. *Appl Catal., A* **2010**, *382*, 197–204.
- (134) Dehkhoda, A. M.; Ellis, N. Biochar-based catalyst for simultaneous reactions of esterification and transesterification. *Catal. Today* **2013**, *207*, 86–92.
- (135) Li, S.; Gu, Z.; Bjornson, B. E.; Muthukumarappan, A. Biochar based solid acid catalyst hydrolyze biomass. *J Environ Chem Eng.* **2013**, *1*, 1174–1181.
- (136) Ormsby, R.; Kastner, J.R.; Miller, J. Hemicellulose hydrolysis using solid acid catalysts generated from biochar. *Catal. Today* **2012**, *190*, 89-97.
- (137) Wang Y.; Delbecq, F.; Kwapinski, W.; Len, C. Application of sulfonated carbon-based catalyst for the furfural production from d-xylose and xylan in a microwave-assisted biphasic reaction. *Mol. Catal.* **2017**, *438*, 167–172.
- (138) S.; Dora, Bhaskar, T.; Singh, R.; Naik, D. V.; Adhikari, D. K. Effective catalytic conversion of cellulose into high yields of methyl glucosides over sulfonated carbon based catalyst. *Bioresour. Technol.* **2012**, *120*, 318–321.
- (139) Hosseinia, S.; Janaunc, J.; Choong, T. S.Y. Feasibility of honeycomb monolith supported sugar catalyst to produce biodiesel from palm fatty acid distillate (PFAD). *Process Saf Environ.* **2015**, *98*, 285–295.
- (140) Guo, F.; Xiu, Z. L.; Liang, Z. X. Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. *Appl. Energ.* **2012**, *98*, 47–52.
- (141) Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Baltork, I. M.; Mahdavi, M. Preparation of an improved sulfonated carbon-based solid acid as a novel, efficient, and reusable catalyst for chemoselective synthesis of 2-oxazolines and bis-oxazolines. *Monatsh Chem.* **2009**, *140*, 1489–1494.
- (142) Wu, Y.; Fu, Z.; Yin, D.; Xu, Q.; Liu, F.; Lu, C.; Mao, L.; Microwave-assisted hydrolysis of crystalline cellulose catalyzed by biomass char sulfonic acids. *Green Chem.* **2010**, *12*, 696–700.
- (143) Liu, R.; Chen, J.; Huang, X.; Chen, L.; Ma, L.; Li, X. Conversion of fructose into 5-hydroxymethylfurfural and alkyl levulinates catalyzed by sulfonic acid-functionalized carbon materials. *Green Chem.* **2013**, *15*, 2895–2903.
- (144) Price, B. K.; Tour, J. M. Functionalization of single-walled carbon nanotubes “on water”. *J. Am. Chem. Soc.* **2006**, *128*, 12899-12904.
- (145) Konwar, L.J.; Das, R.; Thakur, A.J.; Salminen, E.; Mäki-Arvela, P.; Kumar, N.; Mikkola, J.P.; Deka, D. Biodiesel production from acid oils using sulfonated carbon catalyst derived from oil-cake waste. *J Mol Catal A-Chem.* **2014**, *388–389*, 167-176.
- (146) Konwar, L.J.; Mäki-Arvela, P.; Begum, P.; Kumar, N.; Thakur, A.J.; Mikkola, J-P.; Deka, R.C.; Deka, D. Shape selectivity and acidity effects in glycerol acetylation with acetic anhydride: selective synthesis of triacetin over Y-Zeolite and sulfonated mesoporous carbons. *J. Catal.* **2015**, *329*, 237-247.
- (147) Konwar, L.J.; Wärnä, J.; Mäki-Arvela, P.; Kumar, N.; Mikkola, J-P. Reaction kinetics with catalyst deactivation in simultaneous esterification and transesterification of acid oils to biodiesel (FAME) over a mesoporous sulphonated carbon catalyst. *Fuel* **2016**, *166*, 1-11.
- (148) Konwar, L.J.; Mäki-Arvela, P.; Thakur, A.J.; Kumar, N.; Mikkola, J-P. Sulfonated carbon as a new, reusable heterogeneous catalyst for solvent free synthesis of acetone soluble cellulose acetate. *RSC Adv.* **2016**, *6*, 8829-8837.

- (149) Ryoo, R.; Joo, S. H.; Kruk, M.; Jaroniec, M. Ordered mesoporous carbons. *Adv. Mater.* **2001**, *13*, 677–681.
- (150) Eftekhari, A.; Fanc, Z. Ordered mesoporous carbon and its applications for electrochemical energy storage and conversion. *Mater. Chem. Front.* **2017**, *1*, 1001-1027.
- (151) Sakintuna, B.; Yurum, Y. Templated porous carbons: a review article. *Ind. Eng. Chem. Res.* **2005**, *44*, 2893-2902.
- (152) Doustkhah, E.; Lin, J.; Rostamnia, S.; Len, C.; Luque, R.; Luo, X.; Bando, Y.; Wu, K.C.-W.; Kim, J.; Yamauchi, Y. *et al.* Development of sulfonic-acid-functionalized mesoporous materials: synthesis and catalytic applications. *Chem. Eur. J.* **2018**, *25*, 1614-1635.
- (153) Peng, L.; Philippaerts, A.; Ke, X.; Noyen, J.V.; Clippel, F.D.; Tendeloo, G.V.; Jacobs, P.A.; Sels, B.F. Preparation of sulfonated ordered mesoporous carbon and its use for the esterification of fatty acids. *Catal. Today.* **2010**, *150*, 140–146.
- (154) Chang, B.; Fu, J.; Tian, Y.; Dong, X. Multifunctionalized ordered mesoporous carbon as an efficient and stable solid acid catalyst for biodiesel preparation. *J. Phys. Chem. C.* **2013**, *117*, 6252-6258.
- (155) Krawiec, P.; Kockrick, E.; Borchardt, L.; Geiger, D.; Corma, A.; Kaskel, S. Ordered mesoporous carbide derived carbons: novel materials for catalysis and adsorption. *J. Phys. Chem. C.* **2009**, *113*, 7755–7761.
- (156) Fukuhara, K.; Nakajima, K.; Kitano, M.; Hayashi, S.; Hara, M. Transesterification of triolein over hydrophobic microporous carbon with SO₃H groups. *ChemCatChem* **2015**, *7*, 3945–3950.
- (157) Lin, P.; Li, B.; Li, J.; Wang, H.; Bian, X.; Wang, X. Synthesis of sulfonated carbon nanocage and its performance as solid acid catalyst. *Catal. Lett.* **2011**, *141*, 459–466.
- (158) Zareyee, D.; Serehneh, M. Recyclable CMK-5 supported sulfonic acid as an environmentally benign catalyst for solvent-free one-pot construction of coumarin through Pechmann condensation. *J Mol Catal A-Chem.* **2014**, *391*, 88-91.
- (159) Geng, L.; Yu, G.; Wang, Y.; Zhu, Y. Ph-SO₃H-modified mesoporous carbon as an efficient catalyst for the esterification of oleic acid. *Appl. Catal., A* **2012**, *427–428*, 137–144.
- (160) Gao, Z.; Tang, S.; Cui, X.; Tian, S.; Zhang, M. Efficient mesoporous carbon-based solid catalyst for the esterification of oleic acid. *Fuel* **2015**, *140*, 669–676.
- (161) Shen, F.; Smith, Jr., R.L.; Li, L.; Yan, L.; Qi, X. Eco-friendly method for efficient conversion of cellulose into levulinic acid in pure water with cellulase-mimetic solid acid catalyst. *ACS Sustainable Chem. Eng.* **2017**, *5*, 2421–2427.
- (162) Suganuma, S.; Nakajima, K.; Kitano, M.; Kato, H.; Tamura, A.; Kondo, H.; Yanagawa, S.; Hayashi, S.; Hara, M. SO₃H-bearing mesoporous carbon with highly selective catalysis. *Microporous Mesoporous Mater.* **2011**, *143*, 443–450.

- (163) Clark, J.H.; Budarin, V.; Dugmore, T.; Luque, R.; Macquarrie, D.J.; Strelko, V. Catalytic performance of carbonaceous materials in the esterification of succinic acid. *Catal. Commun.* **2008**, *9*, 1709–1714.
- (164) Serp, P.; Machado, B.; CHAPTER 5. Nanostructured carbon materials as catalysts. (n.d.). Nanostructured carbon materials for catalysis. **2015**, 223–267. doi:10.1039/9781782622567-00223
- (165) Konwar, L.J.; Boro, J.; Deka, D. Review on latest developments in biodiesel production using carbon-based catalysts, *Renew Sust Energ Rev.* **2014**, *29*, 546–564.
- (166) Kuznetsov, O.; Sun, Y.; Thaner, R.; Bratt, A.; Shenoy, V.; Wong, M.S.; Jones, J.; Billups, W. E. Water-soluble nanodiamond. *Langmuir.* **2012**, *28*, 5243–5248.
- (167) Liu, Y.; Gu, Z.; Margrave, J.L.; Khabashesku, V.N. Functionalization of nanoscale diamond powder:fluoro-, alkyl-, amino-, and amino acid-nanodiamond derivatives. *Chem. Mater.* **2004**, *16*, 3924–3930
- (168) Hou, Q.; Li, W.; Ju, M.; Liu, L.; Chen, Y.; Yang, Q. One-pot synthesis of sulfonated graphene oxide for efficient conversion of fructose into HMF. *RSC Adv.* **2016**, *6*, 104016–104024.
- (169) Mirza-Aghayan, M.; Tavana, M.M.; Boukherroub, R. Sulfonated reduced graphene oxide as a highly efficient catalyst for direct amidation of carboxylic acids with amines using ultrasonic irradiation. *Ultrason Sonochem.* **2016**, *29*, 371–379.
- (170) Garg, B.; Bisht, T.; Ling, Y-C. Sulfonated graphene as highly efficient and reusable acid carbocatalyst for the synthesis of ester plasticizers, *RSC Adv.* **2014**, *4*, 57297–57307.
- (171) Liu, F.; Sun, J.; Zhu, L.; Meng, X.; Qi, C.; Xiao, F-S. Sulfated graphene as an efficient solid catalyst for acid-catalyzed liquid reactions. *J. Mater. Chem.* **2012**, *22*, 5495-5502.
- (172) Wang, L.; Wang, D.; Zhang, S.; Tian, H. Synthesis and characterization of sulfonated graphene as a highly active solid acid catalyst for the ester-exchange reaction. *Catal. Sci. Technol.* **2013**, *3*, 1194-1197
- (173) Gupta, P.; Paul, S. Amorphous carbon-silica composites bearing sulfonic acid as solid acid catalysts for the chemoselective protection of aldehydes as 1,1-diacetates and for N-, O- and S-acylations. *Green Chem.* **2011**, *13*, 2365-2372.
- (174) Valle-Vigón, P.; Sevilla, M.; Fuertes, A.B. Sulfonated mesoporous silica-carbon composites and their use as solid acid catalysts. *Appl Surf Sci.* **2012**, *261*, 574-583.
- (175) Lin, F.; Kun, Z.; Lu, C.; Peng, W. Carbon-coated mesoporous silica functionalized with sulfonic acid groups and its application to acetalization. *Chinese J Catal.* **2013**, *34*, 932–941.
- (176) Russo, P.A.; Antunes, M.M.; Neves, P.; Wiper, P.V.; Fazio, E.; Neri, F.; Barreca, F.; Mafra, L.; Pillinger, M.; Pinna, N.; Valente, A.A. Mesoporous carbon-silica solid acid catalysts for producing useful bio-products within the sugar platform of biorefineries. *Green Chem.* **2014**, *16*, 4292–4305.

- (177) Russo, P.A.; Antunes, M.M.; Neves, P.; Wiper, P.V.; Fazio, E.; Neri, F.; Barreca, F.; Mafra, L.; Pillinger, M.; Pinna, N *et al.* Solid acids with SO₃H groups and tunable surface properties: versatile catalysts for biomass conversion. *J. Mater. Chem. A*. **2014**, *2*, 11813–11824.
- (178) Wang, Y.; Wang, D.; Tan, M.; Jiang, B.; Zheng, J.; Tsubaki, N.; Wu, M. Monodispersed hollow SO₃H-functionalized carbon/silica as efficient solid acid catalyst for esterification of oleic acid. *ACS Appl. Mater. Interfaces*. **2015**, *7*, 26767–26775.
- (179) de Vyver, S.V.; Peng, L.; Geboers, J.; Schepers, H.; de Clippel, F.; Gommès, C.J.; Goderis, B.; Jacobs, P.A.; Sels, B.F. Sulfonated silica/carbon nanocomposites as novel catalysts for hydrolysis of cellulose to glucose. *Green Chem*. **2010**, *12*, 1560–1563.
- (180) Zhong, R.; Yu, F.; Schutyser, W.; Liao, Y.; de Clippel, F.; Peng, L.; Sels, B. F. Acidic mesostructured silica-carbon nanocomposite catalysts for biofuels and chemicals synthesis from sugars in alcoholic solutions. *Appl. Catal., B* **2017**, *206*, 74–88.
- (181) Yue, Q.; Wang, M.; Wei, J.; Deng, Y.; Liu, T.; Che, R.; Tu, B.; Zhao, D. A template carbonization strategy to synthesize ordered mesoporous silica microspheres with trapped sulfonated carbon nanoparticles for efficient catalysis. *Angew Chem Int Ed Engl*. **2012**, *51*, 10368-10372.
- (182) Nandan, D.; Sreenivasulu, P.; Saxena, S.K.; Viswanadham, N. Facile synthesis of a sulfonated carbon silica-meso composite and mesoporous silica. *Chem. Commun*. **2011**, *47*, 11537–11539.
- (183) Kour, M.; Paul, S.; Sulfonated carbon/nano-metal oxide composites: a novel and recyclable solid acid catalyst for organic synthesis in benign reaction media. *New J. Chem*. **2015**, *39*, 6338-6350.
- (184) Zhang, F.; Fang, Z.; Wang, Y-T. Biodiesel production direct from high acid value oil with a novel magnetic carbonaceous acid. *Appl Energ*. **2015**, *155*, 637–647.
- (185) Yuan, Z.; Zhang, Z.; Zheng, J.; Lin, J. Efficient synthesis of promising liquid fuels 5-ethoxymethylfurfural from carbohydrates. *Fuel* **2015**, *150*, 236–242.
- (186) Liu, W-J.; Tian, K.; Jiang, H.; Yu, H-Q. Facile synthesis of highly efficient and recyclable magnetic solid acid from biomass waste. *Sci. Rep*. **2013**, *3*, 2419.
- (187) Deng, Y.; Xie, Y.; Zou, K.; Ji, X. Review on recent advances in nitrogen-doped carbons: preparations and applications in supercapacitors. *J. Mater. Chem. A* **2016**, *4*, 1144–1173.
- (188) Mardhiah, H.H.; Ong, H.C.; Masjuki, H.H.; Lim, S.; Pang, Y.L. Investigation of carbon-based solid acid catalyst from *Jatropha curcas* biomass in biodiesel production. *Energy Convers. Manag*. **2017**, *144*, 10–17.
- (189) Fraga, A. C.; Quitetea, C.P.B.; Ximenes, V.L.; Sousa-Aguiar, E.F.; Fonseca, I.M.; Rego, A.M.B. Biomass derived solid acids as effective hydrolysis catalysts. *J Mol Catal A Chem*. **2016**, *422*, 248-257.

- (190) Noshadi, I.; Kanjilal, B.; Liu, F. Porous carbonaceous solid acids derived from farm animal waste and their use in catalyzing biomass transformation. *Appl. Catal., A* **2016**, *513*, 19–29.
- (191) Devi, B.L.A.P.; Gangadhar, K.N.; Prasad, P.S.S.; Prasad, R.B.N. Glycerol-based solid acid catalysts useful for the esterification of fatty acids, a process and use thereof. US8445400B2, **2007**.
- (192) Xu, Q.; Yang, Z.; Yin, D.; Zhang, F. Synthesis of chalcones catalyzed by a novel solid sulfonic acid from bamboo. *Catal. Commun.* **2008**, *9*, 1579–1582.
- (193) Malins, K.; Brinks, J.; Kampars, V.; Malina, I. Esterification of rapeseed oil fatty acids using a carbon-based heterogeneous acid catalyst derived from cellulose. *Appl. Catal., A* **2016**, *519*, 99–106.
- (194) Yu, X.; Peng, L.; Gao, X.; He, L.; Chen, K. One-step fabrication of carbonaceous solid acid derived from lignosulfonate for the synthesis of biobased furan derivatives. *RSC Adv.* **2018**, *8*, 15762–15772.
- (195) Nata, I.F.; Putra, M.D.; Irawan, C.; Lee, C-K. Catalytic performance of sulfonated carbon-based solid acid catalyst on esterification of waste cooking oil for biodiesel production. *J Environ Chem Eng.* **2017**, *5*, 2171–2175.
- (196) Xiao, H.; Guo, X.; Liang, X.; Qi, C. One-step synthesis of a novel carbon-based strong acid catalyst through hydrothermal carbonization. *Monatsh Chem.* **2010**, *141*, 929–932.
- (197) Duyckaerts, N.; Trotus, I.-T.; Nese, V.; Swertz, A.-C.; Auris, S.; Wiggers, H.; Schüth F. Mesoporous sulfonated carbon materials prepared by spray pyrolysis. *ChemCatChem* **2015**, *7*, 2891–2896.
- (198) Dong, X.; Jiang, Y.; Shanab, W.; Zhang, M.; A novel highly ordered mesoporous carbon-based solid acid for synthesis of bisphenol-A. *RSC Adv.* **2016**, *6*, 17118–17124.
- (199) Wang, L.; Zhang, J.; Yang, S.; Sun, Q.; Zhu, L.; Wu, Q.; Zhang, H.; Meng, X.; Xiao, F-S. Sulfonated hollow sphere carbon as an efficient catalyst for acetalisation of glycerol. *J. Mater. Chem. A.* **2013**, *1*, 9422–9426.
- (200) Mo, X.; Lotero, E.; Lu, C.; Liu, Y.; Goodwin, J.G. A Novel sulfonated carbon composite solid acid catalyst for biodiesel synthesis. *Catal Lett.* **2008**, *123*, 1–6.
- (201) Delamar, M.; Hitmi, R.; Pinson, J.; Saveant, J.M. Covalent modification of carbon surfaces by grafting of functionalized aryl radicals produced from electrochemical reduction of diazonium salts, *J. Am. Chem. Soc.* **1992**, *114*, 5883–5884.
- (202) Bahr, J.L.; Yang, J.; Kosynkin, D.V.; Bronikowski, M.J.; Smalley, R.E.; Tour, J.M. Functionalization of carbon nanotubes by electrochemical reduction of aryl diazonium salts: a bucky paper electrode. *J. Am. Chem. Soc.* **2001**, *123*, 6536–6542.
- (203) Stephenson, J.J.; Sadana, A.K.; Higginbotham, A.L.; Tour, J.M. Highly functionalized and soluble multiwalled carbon nanotubes by reductive alkylation and arylation: The Billups Reaction. *Chem. Mater.* **2006**, *18*, 4658–4661.

- (204) Liang, F.; Sadana, A.K.; Peera, A.; Chattopadhyay, J.; Gu, Z.; Hauge, R.H.; Billups, W. E. A convenient route to functionalized carbon nanotubes. *Nano Lett.* **2004**, *4*, 1257-1260.
- (205) Song, D.; An, S.; Lu, B.; Guo, Y.; Leng, J. Arylsulfonic acid functionalized hollow mesoporous carbon spheres for efficient conversion of levulinic acid or furfuryl alcohol to ethyl levulinate. *Appl. Catal., B* **2015**, *179*, 445-457.
- (206) Zhang, C.; Fu, Z.; Liu, Y.C.; Dai, B.; Zou, Y.; Gong, X.; Wang, Y.; Deng, X.; Wu, H.; Xu, Q. *et al.* Ionic liquid-functionalized biochar sulfonic acid as a biomimetic catalyst for hydrolysis of cellulose and bamboo under microwave irradiation. *Green Chem.* **2012**, *14*, 1928–1934.
- (207) Gupta, P.; Kour, M.; Paul, S.; Clark, J.H. Ionic liquid coated sulfonated carbon/silica composites: novel heterogeneous catalysts for organic syntheses in water. *RSC Adv.* **2014**, *4*, 7461–7470.
- (208) Zhang, L.; Li, Z.; Du, X.; Chang, X. Activated carbon functionalized with 1-amino-2-naphthol-4-sulfonate as a selective solid-phase sorbent for the extraction of gold(III). *Microchim Acta.* **2011**, *174*, 391–398.
- (209) Li, O.L.; Ikurac, R.; Ishizaki, T. Hydrolysis of cellulose to glucose over carbon catalysts sulfonated via a plasma process in dilute acids. *Green Chem.* **2017**, *19*, 4774-4777
- (210) Konwar, L.J.; Mäki-Arvela, P.; Kumar, N.; Sarma A.K.; Mikkola, J-P.; Deka, D. Selective esterification of fatty acids with glycerol to monoglycerides over $-\text{SO}_3\text{H}$ functionalized carbon catalysts. *Reac Kinet Mech Cat.* **2016**, *119*, 121–138.
- (211) Zhao, W.; Yang, B.; Yi, C.; Lei, Z.; Xu, Z. Etherification of glycerol with isobutylene to produce oxygenate additive using sulfonated peanut shell catalyst. *Ind. Eng. Chem. Res.* **2010**, *49*, 12399–12404.
- (212) Ogino, I.; Suzuki Y.; Mukai, S.R. Tuning the pore structure and surface properties of carbon-based acid catalysts for liquid-phase reactions. *ACS Catal.* **2015**, *5*, 4951–4958.
- (213) Ogino, I.; Suzuki Y.; Mukai, S.R. Esterification of levulinic acid with ethanol catalyzed by sulfonated carbon catalysts: promotional effects of additional functional groups. *Catal Today.* **2018**, *314*, 62-69.
- (214) Pileidis, F.D.; Tabassum, M.; Coutts, S.; Titirici, M.-M. Esterification of levulinic acid into ethyl levulinate catalysed by sulfonated hydrothermal carbons. *Chin. J. Catal.* **2014**, *35*, 929–936.
- (215) Iranpoor, N.; Firouzabadi, H.; Farahi, S. Sulfonated charcoal as a mild and efficient catalyst for esterification and trans-esterification reactions. *J. Sulfur Chem.* **2007**, *28*, 581–587
- (216) Nakajima, K.; Hara, M.; Hayashi, S. Environmentally benign production of chemicals and energy using a carbon-based strong solid acid. *J. Am. Ceram. Soc.* **2007**, *90*, 3725–3734.

- (217) Yamaguchi, D.; Hara, M. Starch saccharification by carbon-based solid acid catalyst. *Solid State Sci.* **2010**, *12*, 1018–1023.
- (218) Onda, A.; Ochi, T.; Yanagisawa, K. Selective hydrolysis of cellulose into glucose over solid acid catalysts. *Green Chem.* **2008**, *10*, 1033–1037.
- (219) Li, X.; Shu, F.; He, C.; Liu, S.; Leksawasdi, N.; Wang, Q.; Qi, W.; Alam, Md.A.; Yuanbd, Z.; Gao, Y. Preparation and investigation of highly selective solid acid catalysts with sodium lignosulfonate for hydrolysis of hemicellulose in corncob. *RSC Adv.* **2018**, *8*, 10922-10929.
- (220) Shrotri, A.; Kobayashi, H.; Fukuoka, A. Cellulose depolymerization over heterogeneous catalysts. *Acc. Chem. Res.* **2018**, *51*, 761–768.
- (221) Foo, G.S.; Pelt, A.H.V.; Krötschel, D.; Sauk, B.F.; Rogers, A.K.; Jolly, C.R.; Yung, M.M.; Sievers, C. Hydrolysis of cellobiose over selective and stable sulfonated activated carbon catalysts. *ACS Sustain. Chem. Eng.* **2015**, *3*, 1934–1942.
- (222) Guo, H.; Lian, Y.; Yan, L.; Qi, X.; Smith, Jr., R.L.; Cellulose-derived superparamagnetic carbonaceous solid acid catalyst for cellulose hydrolysis in an ionic liquid or aqueous reaction system. *Green Chem.* **2013**, *15*, 2167-2174.
- (223) Lin, Q.; Zhang, C.; Wang, X.; Cheng, B.; Mai, N.; Ren, J. Impact of activation on properties of carbon-based solid acid catalysts for the hydrothermal conversion of xylose and hemicelluloses. *Catal Today.* **2019**, *319*, 31-40.
- (224) Climent, M.J.; Corma, A.; Iborra, S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. *Green Chem.* **2014**, *16*, 516-547.
- (225) Huber, G.W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106*, 4044–4098.
- (226) Hu, S.; Smith, T.J.; Lou, W.; Zong, M. Efficient hydrolysis of cellulose over a novel sucralose-derived solid acid with cellulose-binding and catalytic sites. *J. Agric. Food Chem.* **2014**, *62*, 1905–1911.
- (227) Fu, Z.; Wan, H.; Cui, Q.; Xie, J.; Tang, Y.; Guan, G.; Hydrolysis of carboxylic acid esters catalyzed by a carbon-based solid acid. *React. Kinet. Mech. Cat.* **2011**, *104*, 313-321.
- (228) Yan, P.; Xie, Z.; Tian, S.; Li, F.; Wang, D.; Su, D.S.; Qi, W. Hydration of phenylacetylene on sulfonated carbon materials: active site and intrinsic catalytic activity. *RSC Adv.* **2018**, *8*, 38150-38156.
- (229) Wang, K.; Jiang, J-C.; Liang, X.; Wu, H.; Xu, J. Direct conversion of cellulose to levulinic acid over multifunctional sulfonated humins in sulfolane-water solution. *ACS Sustain. Chem. Eng.* **2018**, *6*, 15092–15099.
- (230) Zhu, Y.; Li, W.; Lu, Y.; Zhang, T.; Jameel, H.; Chang, H-M.; Ma, L. Production of furfural from xylose and corn stover catalyzed by a novel porous carbon solid acid in γ -valerolactone. *RSC Adv.* **2017**, *7*, 29916-29924.

- (231) Gallo, J.M.R.; Alamillo, R.; Dumesic, J.A. Acid-functionalized mesoporous carbons for the continuous production of 5-hydroxymethylfurfural. *J. Mol. Catal. A: Chem.* **2016**, *422*, 13-17.
- (232) Daengprasert, W.; Boonnoun, P.; Laosiripojana, N.; Goto, M.; Shotipruk, A. Application of sulfonated carbon-based catalyst for solvothermal conversion of cassava waste to hydroxymethylfurfural and furfural. *Ind. Eng. Chem. Res.* **2011**, *50*, 7903–7910.
- (233) Zhong, R.; Liao, Y.; Shu, R.; Ma, L.; Sels, B. F. Vapor-phase assisted hydrothermal carbon from sucrose and its application in acid catalysis. *Green Chem.* **2018**, *20*, 1345-1353.
- (234) Li, G.; Li, N.; Yang, J.; Wang, A.; Wang, X.; Cong, Y.; Zhang, T. Synthesis of renewable diesel with the 2-methylfuran, butanal and acetone derived from lignocellulose. *Bioresour. Technol.* **2013**, *134*, 66–72.
- (235) Dutta, S.; Bohre, A.; Zheng, W.; Jenness, G.R.; Núñez, M.; Saha, B.; Vlachos, D. G. Solventless C-C coupling of low carbon furanics to high carbon fuel precursors using an improved graphene oxide carbocatalyst. *ACS Catal.* **2017**, *7*, 3905–3915.
- (236) Kour, M.; Bhardwaj, M.; Sharma, H.; Paul, S.; Clark, J.H. Ionic liquid coated sulfonated carbon@titania composites for the one-pot synthesis of indeno[1,2-b]indole-9,10-diones and 1H-pyrazolo[1,2-b]phthalazine-5,10-diones in aqueous media. *New J. Chem.* **2017**, *41*, 5521-5532.
- (237) Moghaddas, M.; Davoodnia, A.; Heravi, M.M.; Tavakoli-Hoseini, N. Sulfonated carbon catalyzed biginelli reaction for one-pot synthesis of 3,4-dihydropyrimidin-2(1h)-ones and-thiones. *Chinese J Catal.* **2012**, *33*, 706-710.
- (238) Safari, J.; Gandomi-Ravandi, S.; Ashiri, S.; Organosilane sulfonated graphene oxide in the Biginelli and Biginelli-like reactions. *New J. Chem.* **2016**, *40*, 512-520.
- (239) Anderson, J.M.; Johnson, R.L.; Schmidt-Rohr, K.; Shanks, B.H. Solid state NMR study of chemical structure and hydrothermal deactivation of moderate-temperature carbon materials with acidic SO₃H sites. *Carbon* **2014**, *74*, 333-345.
- (240) Roldán, L.; Pires, E.; Fraile, J.M.; García-Bordejé, E. Impact of sulfonated hydrothermal carbon texture and surface chemistry on its catalytic performance in esterification reaction. *Catal. Today.* **2015**, *249*, 153-160.
- (241) Alonso, D. M.; Gallo, J. M. R.; Mellmer, M. A.; Wettstein, S. G.; Dumesic, J. A. Direct conversion of cellulose to levulinic acid and gamma-valerolactone using solid acid catalysts. *Catal. Sci. Technol.* **2013**, *3*, 927–931.
- (242) Zuo, Y.; Zhang, Y.; Fu, Y. Catalytic conversion of cellulose into levulinic acid by a sulfonated chloromethyl polystyrene solid acid catalyst. *ChemCatChem* **2014**, *6*, 753–757.
- (243) Villa, A.; Schiavoni, M.; Chan-thaw, C.; Fulvio, P.; Mayes, R.T.; Dai, S.; More, K.L.; Veith, G.M.; Prati, L. Acid-functionalized mesoporous carbon: an efficient support for ruthenium-catalyzed γ -valerolactone production. *ChemSusChem* **2015**, *8*, 2520-2528.

TOC graphic (graphical abstract)

