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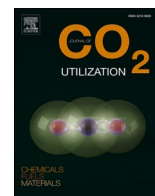
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New insights into the cocatalyst-free carbonation of vegetable oil derivatives using heterogeneous catalysts

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ABSTRACT

Cyclic carbonates are important platform molecules with relevant industrial applications such as polymers precursors, fuel additives and solvents. They can be obtained from epoxidized vegetable oils via a carbonation reaction with carbon dioxide. This process is typically performed using homogenous catalyst or co-catalyzed systems, requiring of a homogenous specie. At the present moment very little have been reported regarding fully heterogeneous catalysts applied to the carbonation of epoxidized vegetable oils. In this study, the carbonation of epoxidized methyl oleate was investigated with various heterogeneous catalysts. Diverse nucleophilic organic salts were supported on silica gel and SBA-15 and screened as single component heterogeneous catalysts for the carbonation of epoxidized methyl oleate as a model compound of vegetable oils. The effect of some textural features of the catalytic materials such as the average pore size and surface area were investigated. An improved catalytic performance was observed as the catalytic species were supported on a mesoporous material. The addition of weak Lewis acidity to the support was found to play an important role in the opening of the oxirane ring and its further conversion to a cyclic carbonate, by providing a source of hydrogen bond donor (HBD) to activate the oxirane ring. The methyl esters of oleic acid, tall oil and cottonseed oil were investigated as substrates. A plausible reaction mechanism was proposed.

1. Introduction

Cyclic carbonates are nowadays a very attractive alternative for the production of polyurethanes which are currently made in industrial scale by the reaction of polyols and di-isocyanates, which is a petroleum-derived reactant obtained from toxic compounds such as phosgene [1]. Therefore, it is of interest to develop new technologies with a more environmentally friendly focus for the production of polyurethanes. In this sense the reaction of poly(cyclic carbonates) and polyamines to produce non-isocyanate polyurethane (NIPUs) is a potential and very attractive route [2,3]. Cyclic carbonates can be directly produced from renewable materials and carbon dioxide which is a highly abundant, inexpensive and a safe C1 feedstock [4]. Moreover, cyclic carbonates also find applications as solvents and intermediates in the production of fine chemicals [5,6].

In recent years a considerable amount of research has been conducted to improve the production of cyclic carbonates [1,5–9], a broad variety of technologies has been implemented to this reaction system in

order to accomplish high conversion and selectivity [10,11]. Although homogenous catalysts are somewhat more efficient than the heterogeneous counterparts, their separation from the final product remains troublesome and catalyst reutilization is difficult. Thus a number of solid catalysts have been developed to address this issue [7,9,12–15,15–18, 18–20]. Various methodologies have been proposed for the preparation of cyclic carbonates, such as oxidative carboxylation of olefins, cycloaddition of CO₂ to epoxides, carboxylation of diols with CO₂ and with urea as well as transesterification of diols with dialkyl carbonates [21–23]. Among these approaches, cycloaddition of CO₂ to epoxides remains the dominating method for the production of cyclic carbonates. This reaction requires a hydrogen bond donor (HBD) which can be present in the catalyst itself in the form of Lewis acidity [9,20,24]. The Lewis acid sites of the catalyst activates the oxirane group of the epoxides for the subsequent CO₂ insertion.

Several authors [7,13,18,25,26] have reported alkene oxides (mainly epichlorohydrin, propene oxide and styrene oxide) as suitable model compounds for the production of cyclic carbonates. A wide set of well-developed catalysts such as metal-organic framework (MOFs) [7,

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Nomenclature

Abbreviations

VO	Vegetable oil
EVO	Epoxidized vegetable oil
MO	Methyl oleate
EMO	Epoxidized methyl oleate
ECSO_FAME	Epoxidized cottonseed oil fatty acid methyl ester
ETO_FAME	Epoxidized tall oil fatty acid methyl ester
CMO	Carbonated methyl oleate
HBD	Hydrogen bond donor
TEA	Triethylamine
TBA	Tributylamine
4-PP	4-Pyrrolidinopyridine
Imid	Imidazole

[14,17], bifunctional catalysts [9,18,19], carbon nitrides [12,27], co-catalyzed system [6,28–31], among others, have successfully and efficiently applied to the carbon dioxide cycloaddition reaction of this family of molecules. Another system that has been explored for the production of cyclic carbonates is carboxylation of diols, such as propylene glycol to obtain propylene carbonate. Various metal-containing catalysts such as metal halides, metal oxides and salen complexes have been tested in this system [21,32,33]. However, the utilization of these well-developed catalytic materials remains restricted to systems where the substrate is a small molecule. The activity of these kind of catalytic materials decreases considerably, if large molecules are used to produce cyclic carbonates. Larger epoxide molecules such as epoxidized vegetable oils (EVOs) and their derivatives differ quite much from alkenes oxides and diols, primarily in their activity, because of steric hindrance due to the location of the epoxide group and their limited diffusion capability. Moreover, there are important differences in the physical properties of molecules of different size (e.g. viscosity). In the case of carbon dioxide cycloaddition to epoxidized vegetable oils, also known as carbonylation reaction, very few studies on the utilization of heterogeneous catalysts have been reported [8,34]. The efficient application of the available heterogeneous catalysts to this system remains a challenging task. At the present moment the carbonylation of epoxidized vegetable oils is predominantly carried out using quaternary ammonium halide salts [35–39] and alkali metal halide salts [36,40,41] as one-component homogenous catalysts, or as co-catalysts in two-component systems [25,36,42].

In this study, we investigated the utilization of silica-anchored nucleophilic species as heterogeneous catalysts for the carbonylation of epoxidized methyl oleate, which is a derivative of oleic acid, a very abundant fatty acid in vegetable oils. Four different catalysts were immobilized by means of a propyl linkage into silica-based materials. The influence of the catalyst pore size was explored by using silica gel and highly ordered mesoporous silica SBA-15. The effect of a source of hydrogen bond donor was also evaluated by doping the support with zinc.

2. Experimental Section

2.1. Materials and chemicals

The following chemicals were used: silica gel 60, tetraethyl orthosilicate ($\geq 98\%$), PEG-PPG-PEG (pluronic123), (3-iodopropyl)trimethoxysilane ($\geq 95\%$), 2-bromoethanol ($\geq 95\%$), 4-pyrrolidinopyridine ($\geq 98\%$), tributylamine ($\geq 99\%$), toluene ($\geq 99.8\%$), methanol ($\geq 99.9\%$), ethyl acetate ($\geq 99.9\%$), oleic acid ($\geq 90\%$), sulfuric acid (95–97%), formic acid ($\geq 98\%$) were all purchased from Sigma Aldrich. Imidazole ($\geq 99\%$), triethylamine (99%) and hydrogen peroxide solution ($\geq 30\%$)

were provided by Fisher Scientific, zinc nitrate ($\geq 99\%$) by Fluka and dichloromethane (DCM) ($\geq 99.9\%$) by Honeywell. The materials and chemicals were used as received unless otherwise stated.

2.2. Catalyst preparation

All the catalytic materials were prepared via very well-known propyl linkage procedures available in literature [9,18–20,43] with few modifications. A brief overview of the synthesis procedures is shown in Fig. 1.

2.2.1. Preparation of the silica and Zn-SBA-15 support

The silica gel support was calcined at 500 °C with a heating rate of 3 °C min⁻¹ for 12 h before use. Zn-SBA-15(x), (where x is the Zn/Si molar ratio) was prepared according to a protocol from literature [20] as it follows: 2.0 g of pluronic123 and a determined amount of zinc nitrate hexahydrated were dissolved in 75 mL HCl 1.6 M for 4 h at 40 °C. After complete dissolution, 4.0 g of TEOS was added slowly. The solution was stirred and kept at 40 °C for 24 h. The resulting mixture was transferred to a Teflon liner and heated to 100 °C in an autoclave for another 24 h under static conditions. Thereafter, the mixture was filtered and the white solid was calcined at 550 °C with a heating rate of 1 °C min⁻¹ for 6 h. The obtained material was stored in a desiccator for future functionalization.

2.2.2. Iodine pre-functionalization of SiO₂ and Zn-SBA-15

The pre-treated SiO₂/Zn-SBA-15(x) (10.0 g) was dispersed in a 350 mL of 3-iodopropyltrimethoxysilane (50.0 mmol) in toluene solution. The mixture was maintained under reflux conditions and argon atmosphere for 24 h. After cooling, the solid material was filtered and washed with fresh toluene three times, followed by washing with ethanol in a Soxhlet extractor for another 24 h to ensure full removal of free species on the surface. The solid material was dried at 70 °C overnight and stored for further use.

2.2.3. Preparation of SiO₂/SBA-15-supported TEA and TBA (SiO₂-TEAI, SiO₂-TBAl, Zn-SBA-15(x)-TEAI and Zn-SBA-15(x)-TBAl)

These materials were synthesized according to previously published methods [9,43] with some modifications. In a typical synthesis 10.0 g of iodine prefunctionalized SiO₂/Zn-SBA-15(x) and 60.0 mmol of TEA/TBA were mixed in 500 mL of toluene and reflux for 72 h under argon atmosphere. Then after the solid was filtered and washed three times with toluene, dichloromethane, and finally with ethanol in a Soxhlet extractor for 24 h. The catalyst was dried overnight at 70 °C and stored.

2.2.4. Preparation of SiO₂/SBA-15-supported 4-pyrrolidinopyridinium (SiO₂-4PPI and Zn-SBA-15(x)-4PPI)

This catalyst was prepared according to a reported method [43]. In brief, Iodine pre-functionalized SiO₂/Zn-SBA-15 (10.0 g) and 4-pyrrolidinopyridinium (60.0 mmol) were mixed together in 500 mL of toluene and reflux under argon atmosphere. After 24 h the mixture was cooled down and the solid was collected and washed three times with toluene, water and DCM followed by washing with ethanol in the Soxhlet extractor for another 24 h. The catalytic material was dried overnight at 70 °C and stored.

2.2.5. Preparation of SiO₂/SBA-15-supported imidazole (SiO₂-Imid and Zn-SBA-15(x)-Imid)

The supported imidazole was prepared according to a previously reported method [18,19] with few modifications. In a typical procedure, 10.0 g of iodine prefunctionalized SiO₂/Zn-SBA-15(x) and 60.0 mmol of imidazole were dispersed in 500 mL of toluene and reflux under argon atmosphere for 24 h. The mixture was cooled down and the solid material was filtered and washed three times with fresh toluene followed by washing with ethanol in the Soxhlet extractor for 24 h. The resulting

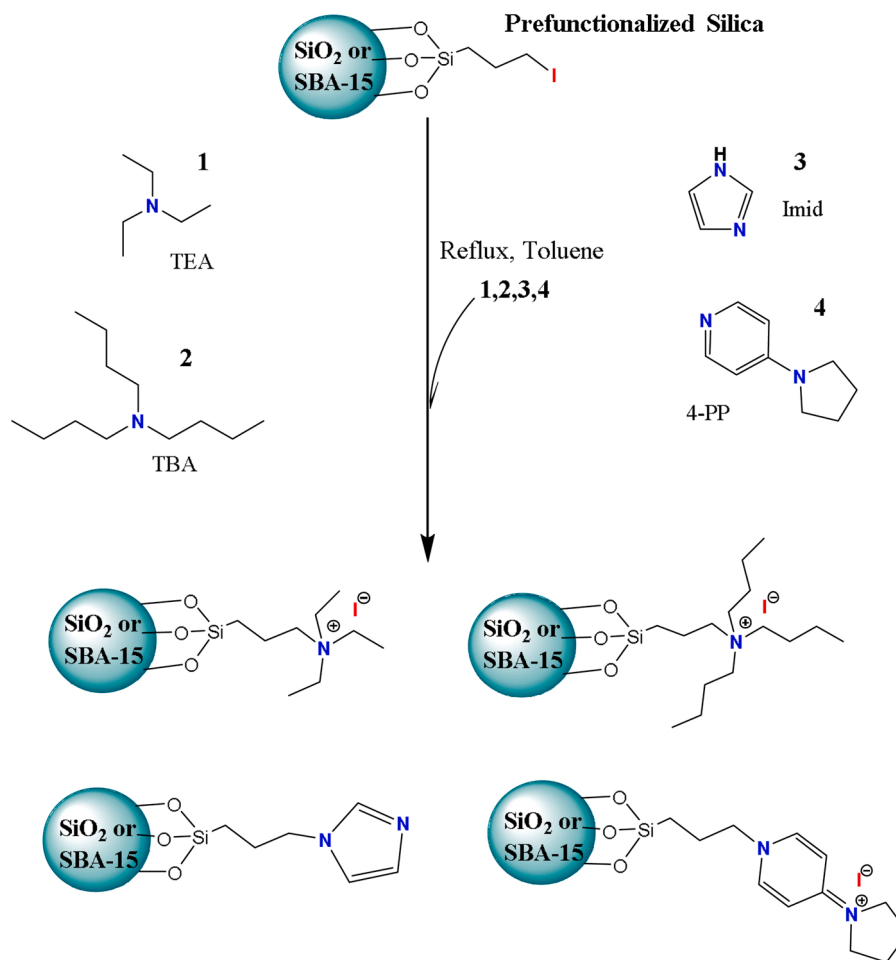


Fig. 1. Overview of catalyst preparation procedures.

solid was dried overnight at 70 °C and stored for catalytic test.

2.3. Catalyst characterization

The surface structures of the supports and functionalized support were observed using high resolution transmission electron microscopy (HR-TEM). The electron microphotographs were recorded in a JEM 1400 plus transmission electron microscope. Thermogravimetric analysis was performed for all catalytic materials using a Mettler Toledo TGA/SDTA 851e instrument to evaluate their thermal stability and to have a raw estimation of the amount of catalyst immobilized onto the silica supports. Nitrogen-physisorption was performed in a Micrometrics 3Flex-3500 device to determine the textural properties of the supports and catalytic materials. Prior to the measurements, all the samples were outgassed at 150 °C for 4 h. The measurement temperature was -196 °C. The specific surface areas of the catalysts were calculated using the BET method, while the pore size distributions and the total pore volumes (V_p) were determined using the DFT method. The concentrations of Lewis and Brønsted acid sites of the different supports were determined by Fourier transform infrared spectroscopy (FTIR) with pyridine ($\geq 99.9\%$) as a probe molecule in an ATI Mattson FTIR Infinity Series spectrometer.

2.4. Carbonation experiments

In a typical experiment 50.0 g of epoxidized methyl oleate prepared according to our previous publication [3] and 4.0 g of catalysts were mixed in a 300 mL autoclave reactor equipped with mechanical stirring. The reactor was sealed and air was purged out by flowing CO₂ three

times. Thereafter the reactor was heated to a target temperature of 140 °C. Once the reaction temperature was reached, CO₂ was continuously introduced at a constant 30 bar pressure during the total reaction time. Excellent mixing was ensured with a gas-entrainment impeller at 1000 rpm during the experiments. After the reaction was completed, the liquid mixture was separated from the solid catalyst by filtration. The products were analyzed using FTIR and the Jay's oxirane titration method [44]. The reaction carbonation reaction of epoxidized methyl oleate and carbon dioxide is displayed in Fig. 2.

The conversion of epoxidized methyl oleate during the carbonation process was calculated using Eq. (1),

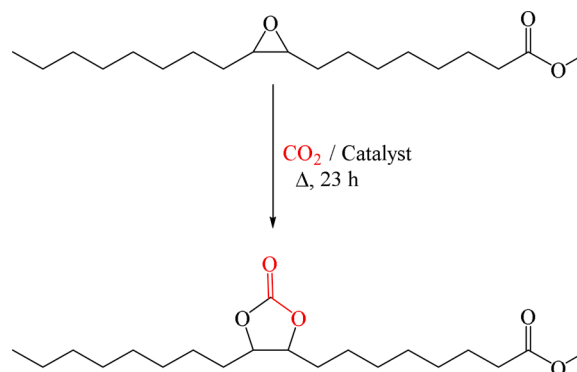


Fig. 2. Overview of the carbonation process of epoxidized methyl oleate and carbon dioxide using synthesized heterogeneous catalysts.

$$\text{Conversion (\%)} = \frac{C_{\text{Oxirane}} - C_{\text{Oxirane}}}{C_{\text{Oxirane}}} * 100 \quad (1)$$

Where C_{Oxirane} is the initial oxirane concentration of the epoxidized methyl oleate and C_{Oxirane} is the oxirane concentration after the carbonation reaction is completed. Both concentration were determined using Jay's titration method for epoxide content [44]. Details on the oxirane analytical method can be found in our previous work [2,3].

The selectivity of carbonated methyl oleate was calculated using Eq. (2), which is based exclusively on the quantification of carbonated product,

$$\text{Selectivity (\%)} = \frac{C_{\text{carbonate}}}{C_{\text{Oxirane}} - C_{\text{Oxirane}}} * 100 \quad (2)$$

Where $C_{\text{carbonate}}$ is the carbonated group concentration of the final product measured after the carbonation reaction is completed. This concentration is obtained through FTIR measurement with the calibration curve displayed in Fig. S2.

3. Results and discussion

3.1. Catalyst characterizations

The TEM images revealed surface morphologies of the supports and catalysts as shown in Fig. 3. The commercial silica gel (Fig. 3a) had an irregular porosity which is typical for amorphous materials, while the synthesized SBA-15 support exhibited very structured features of mesoporous materials with a uniform porosity and periodicity of the pores.

The mesostructure was observed to stay intact when a metal dopant is introduced (Fig. 3c and d). Furthermore, Zn/SBA-15(0.12) shows absence of metal particles on the surface, which evidences the good incorporation of Zn into the structure rather than on the surface. Otherwise, metal nanoparticles were evidenced on the surface of Zn/SBA-15(0.24) (Fig. 3e), probably because of the high metal concentration used during the synthesis, the excess was deposited on the surface. It was also observed that the mesostructures of Zn/SBA-15(0.12) were well preserved after the immobilization of the catalytic species (Fig. 3f).

Large differences between the surface areas of the commercial silica gel ($460 \text{ m}^2 \text{ g}^{-1}$) and the synthesized SBA-15 ($948 \text{ m}^2 \text{ g}^{-1}$) can be noticed in Table 1. This result is in line with the calculated total pore volume of SBA-15 which is almost two times larger than that of the commercial silica gel. The difference can be attributed to the large mesoporous volume of SBA-15. The average pore sizes of both supports were found to be around 7.8 nm and 11.6 nm for silica gel and SBA-15 respectively. The Zn/SBA-15(0.12) support shows almost an identical surface area compared to SBA-15. However, an important reduction of the surface area is observed when a 0.24 Zn/Si molar ratio is used instead, probably because of the deposition of metal nanoparticles on the surface as evidenced in the TEM images. The textural properties of silica and SBA-15 supports were significantly reduced with the introduction of the catalytic species onto the surface. Lower surface areas, pore volumes and pore diameters were obtained for all the supported catalysts (Table 1), which can be attributed to the good anchoring of the catalytic species into the internal pores of the supports and partial blocking of the pore structure [45].

Nitrogen adsorption-desorption isotherms of the silica gel and SBA-

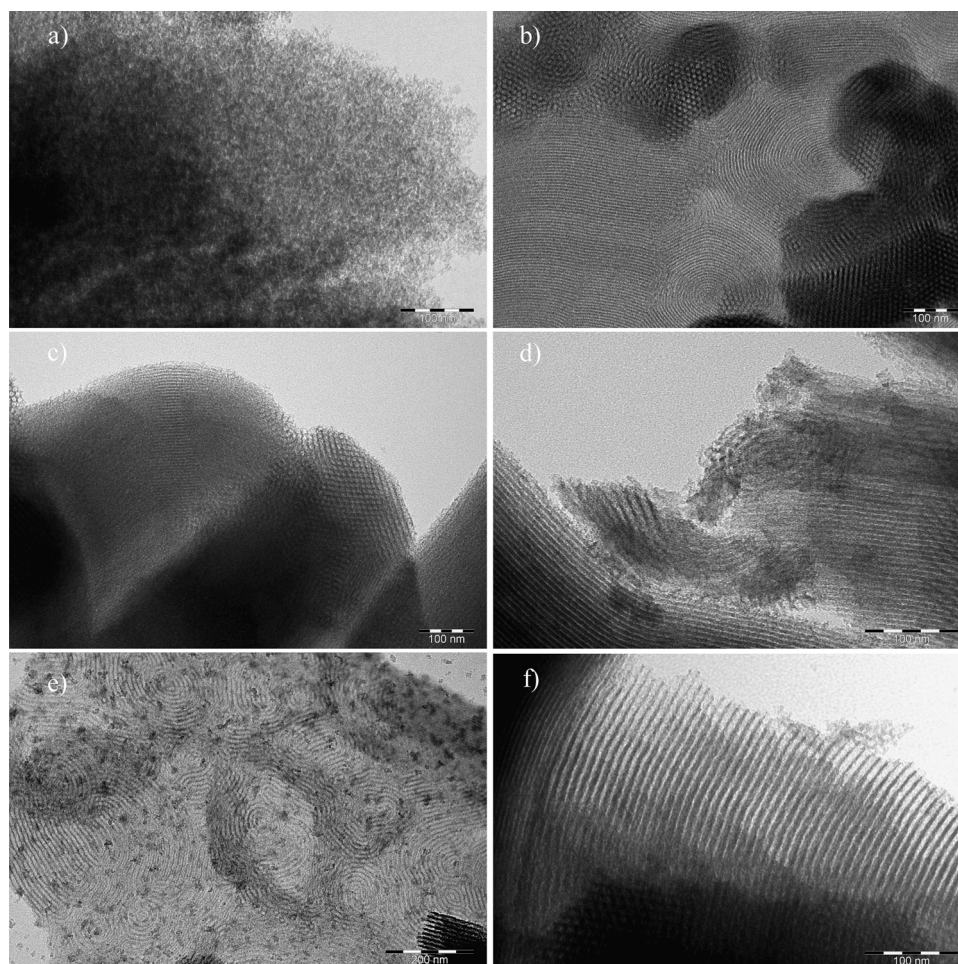


Fig. 3. TEM images of the supports; a) Silica gel, b) SBA-15, c) Zn/SBA-15(0.12), d) Zn/SBA-15(0.24), e) Zn/SBA-15(0.24) (200 nm) and Zn/SBA-15(0.12)-4PPI.

Table 1
Textural properties of the catalysts.

Catalyst	BET surface Area (m ² ·g ⁻¹)	Average Pore size d _p (nm)	Total pore volume V _p (cm ³ ·g ⁻¹)	Micropore volume (cm ³ ·g ⁻¹)	Mesopore volume (cm ³ ·g ⁻¹)
SiO ₂	460	7.8	0.76	0.11	0.65
SBA-15	948	11.6	1.41	0.29	1.12
Zn-SBA-15 (0.12)	999	11.9	1.53	0.29	1.24
Zn-SBA-15 (0.24)	675	11.3	0.97	0.12	0.85
SiO ₂ -Imid	348	6.1	0.45	0.06	0.39
SiO ₂ -TEAI	312	6.3	0.42	0.05	0.37
SiO ₂ -TBAI	290	5.7	0.36	0.04	0.32
SiO ₂ -4PPI	241	7.7	0.33	0.04	0.29
SBA-15-4PPI	479	11.4	0.76	0.12	0.64
Zn-SBA-15 (0.12)-4PPI	296	11.4	0.50	0.07	0.43
Zn-SBA-15 (0.24)-4PPI	276	10.9	0.43	0.06	0.37
Zn-SBA-15 (0.12)-Imid	508	11.3	0.81	0.12	0.69
Zn-SBA-15 (0.12)-TEAI	395	11.5	0.66	0.08	0.58
Zn-SBA-15 (0.12)-TBAI	409	11.2	0.63	0.09	0.54

15 supports are displayed in Fig. S1. Both materials show type IV isotherms, which is characteristic of mesoporous materials with H1 and H2 hysteresis loops for SBA-15 and silica gel respectively. The pore size distributions calculated by the DFT method are displayed in Fig. S1b. Bimodal distributions were obtained, with a maximum at around 11 nm in the case of SBA-15 confirming large mesoporosity, smaller pore sizes were evidenced below 2 nm. A similar distribution of the silica gel pores was obtained. However, a lower and more dispersed mesoporosity was observed between 5 and 11 nm.

The acidities of the supports determined by FTIR-pyridine are reported in Table 2. The silica gel and SBA-15 supports had negligible Brønsted and Lewis acidities. Otherwise the successful introduction of zinc into the structure of SBA-15 was confirmed by the increase of the Lewis acidity in Zn-SBA-15 (0.12) and Zn-SBA-15 (0.24). As expected, the added acidity due to the incorporation of zinc to the structure of the SBA-15 resulted mainly in weak Lewis acid sites. No Brønsted acidity

Table 2
Supports acidities determined by pyridine-FTIR.

Support	BAS (μmol/g)	LAS (μmol/g)	TAS (μmol/g)
SiO ₂	–	2.5/0/0	2.5
SBA-15	–	1.6/0/0	1.6
Zn-SBA-15 (0.12)	–	14.6/3.7/0	18.6
Zn-SBA-15 (0.24)	–	45.2/8.3/0	53.6

Notes: BAS, Brønsted acid sites (weak/medium/strong); LAS, Lewis acid sites (weak/medium/strong); TAS, total acid sites.

was identified in any of the supports.

Thermogravimetric analysis (TGA) of the samples (Fig. 4) was used to determine their thermal stabilities as well as to estimate the amount of catalytic species attached to the supports. Fig. 4a shows that the SiO₂-Imid and SiO₂-4PPI samples have a common decomposition temperature at around 300 °C with weight losses of 8% and 14 % respectively. SiO₂-TBAI and SiO₂-TEA on the other hand, presented lower thermal stabilities, with weight losses of 14 % and 16 % respectively starting at temperatures around 225 °C. The same decomposition temperatures were observed for all the catalytic species supported on Zn/SBA-15 (Fig. 4b), otherwise, it is evident when comparing Fig. 4a and b that larger amounts of catalytic species are attached on the surface of Zn/SBA-15. Larger weight losses were observed in all cases, presumably because Zn/SBA-15 possesses more available surface area for functionalization.

3.2. Catalyst activity

The carbonation reaction of epoxidized methyl oleate was evaluated with various SiO₂ and SBA-15 supported catalysts, no solvent or co-catalyst were used during the activity tests as shown in Table 3. The conversion of oxirane was quantified by titration using the Jay's method [46] and the selectivity of carbonate product was evaluated with FTIR. A calibration curve (Fig. S2) was obtained using CMO and EMO mixtures of known concentrations. The FTIR spectra of CMO (Fig. 5) shows a strong band at 1804 cm⁻¹ ascribed to the carbonated group, the absorbance of this peak was correlated to its concentration using the –CH group vibration at 2920 cm⁻¹ as a reference band.

The catalytic activities of all the supported catalytic species for the carbonation of epoxidized methyl oleate are reported in Table 3. Supported imidazole on both silica and mesoporous SBA-15 was tested (entries 1 and 15). This catalyst has been previously used by Sankar et al. [19] for the carbon dioxide cycloaddition of various alkene oxides with a profound catalytic activity. However, when this catalyst was applied to vegetable oils derivatives such as EMO, a poor performance was observed with nearly no catalytic activity. Although the hydroxyl functionalization of the imidazole on the catalyst surface (entry 2) slightly improved its performance by providing an extra source of HBDs [18], the conversion remained still very low. TEA, TBA and 4-PP supported on silica (entries 3, 4 and 5) showed low catalytic activities as well. However, the conversion and selectivity were significantly improved when the reaction time was extended to 23 h (entries 6, 7, 8). The TEA and TBA catalysts showed almost identical catalytic performances, the oxirane conversions were 45 % and 42 % respectively, while the selectivity of the carbonated product were 95 % and 94 %, respectively. The conversions and selectivities obtained using SiO₂-4PPI (entry 8) were similar to those obtained for TEA and TBA.

The influence of large mesoporosity in the support is reported in Table 3. The molecular size of vegetables oils and their derivatives is presumed to limit their valorization. Bulky substrates such as fatty acids and their methyl ester do not diffuse easily into microporous materials, which is the case for the vast majority of the high-performance catalysts in the market. Entries 8 and 9 compare the catalytic activities of 4-PP catalyst supported on commercial silica with low mesoporosity and on SBA-15 with larger pores. A moderate increase was observed in the conversion of epoxides as a mesoporous support such as SBA-15 was used, the selectivity of carbonate product remained invariable at 99 %. While the reason for this increase might be the presence of large pores in which the epoxidized methyl ester is more able to diffuse and react, it is also arguable that because of the larger surface area in the SBA-15-4PPI, more catalytic species are incorporated as evidenced in the TGA analysis (Fig. 4), which contributes to a slightly better conversion by providing more active sites for the reaction. Thereafter, the influence of the support acidity was explored. It was found that doping the support with a metal improved the catalyst performance. The addition of Zn to the SBA support was found to increase the catalytic activity as reported in entry

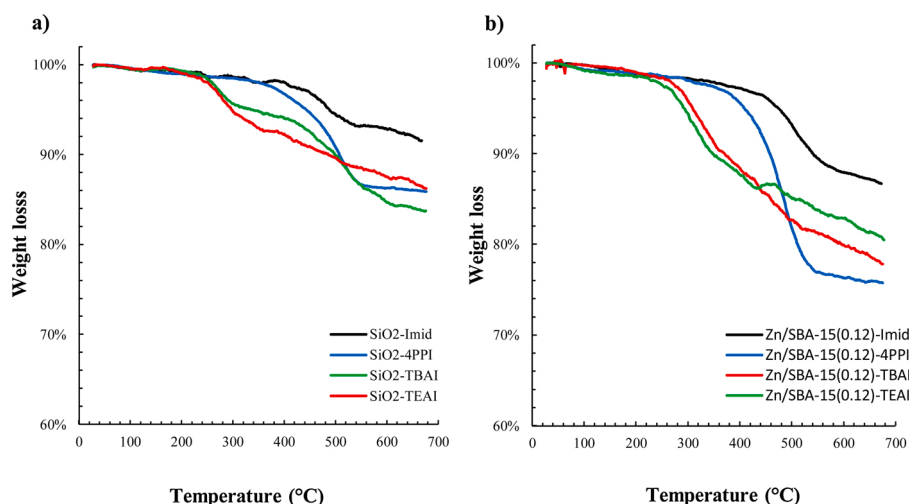


Fig. 4. TGA curves of the catalytic materials; a) Silica gel-supported catalysts, b) SBA-15-supported catalysts.

Table 3

Activities of the synthesized catalysts in the synthesis of carbonated methyl oleate ^a.

Entry	Catalyst	Substrate	Reaction time (h)	Conversion (%)	Selectivity (%)
1	SiO ₂ -Imid	EMO	8	18	19
2	SiO ₂ -ImidBr-OH	EMO	8	17	69
3	SiO ₂ -TEAI	EMO	8	23	93
4	SiO ₂ -TBAI	EMO	8	31	60
5	SiO ₂ -4PPI	EMO	8	24	99
6	SiO ₂ -TEAI	EMO	23	45	95
7	SiO ₂ -TBAI	EMO	23	42	94
8	SiO ₂ -4PPI	EMO	23	42	99
9	SBA-15-4PPI	EMO	23	57	99
10	Zn/SBA-15(0.12)-4PPI	EMO	23	66	90
11	Zn/SBA-15(0.24)-4PPI	EMO	23	63	96
12	Zn/SBA-15(0.12)-4PPI	EMO	32	75	91
13	Zn/SBA-15(0.12)-TEAI	EMO	23	54	90
14	Zn/SBA-15(0.12)-TBAI	EMO	23	55	97
15	Zn/SBA-15(0.12)-Imid	EMO	8	12	24
16	Zn/SBA-15(0.12)-4PPI ^b	EMO	23	47	99
16	Zn/SBA-15(0.12)-4PPI ^c	EMO	23	76	75
17	Zn/SBA-15(0.12)-4PPI ^d	EMO	23	63	65
18	Zn/SBA-15(0.12)-4PPI	ECSO_FAME	23	47	85
19	Zn/SBA-15(0.12)-4PPI	ETO_FAME	23	57	60
20	Zn/SBA-15(0.12)-4PPI-(reuse1)	EMO	23	52	96

(a) Reaction conditions: epoxidized oil (50 g), catalyst (4 g), 30 bar CO₂, 140 °C, 1000 rpm. (b) 120 °C. (c) 160 °C. (d) H₂O = .2 gr.

10. 4-PP supported on Zn/SBA-15(0.12) presents 24 % higher conversion of epoxides than 4-PP supported on commercial silica. This increase in the efficiency results from the ability of the Zn atoms to assist and activate the oxirane group in the epoxidized methyl oleate for its opening. An increase in performance was also evidenced when Zn/SBA-15(0.12) was used as the support for TEA and TBA (entries 13 and 14). Otherwise, it seems that a further increase on the Zn/Si molar ratio in the structure of SBA-15 did not improve the efficiency as reported in entry 11. This behavior might be caused by the deposition of metal nanoparticles on the surface when higher metal concentrations are used as evidenced by the TEM analysis (Fig. 3). As reported in Table 1, the Zn/SBA-15(0.24) support shows a smaller available surface area than Zn/SBA-15(0.12).

Among the four different catalytic species supported on amorphous silica, metal-free SBA-15 and Zn-doped SBA-15, 4-pyrrolidone pyridine

supported in SBA-15 with a 0.12 Zn/Si molar ratio was found to be the most active one. Epoxide conversion of up to 75 % and carbonate selectivity of 91 % were obtained after 32 h of reaction at 140 °C and constant 30 bar CO₂ pressure. Fig. 6a show the evolution of epoxides conversion and carbonate product selectivity as a function of the reaction time using Zn/SBA-15(0.12)-4PPI as the heterogeneous catalyst. An analysis of the kinetic data is displayed in Fig. 6b. By plotting the $-\ln(1-\text{conversion})$ versus $t^* \rho_b$, where t is reaction time and ρ_b is the catalyst bulk density: $\rho_b = m_{\text{cat}}/V$, it is revealed that carbonation process follows first-order kinetics with respect to the epoxide concentration.

Besides EMO, the fatty acid methyl esters (FAMES) of cottonseed oil and tall oil were investigated using Zn/SBA-15(0.12)-4PPI under similar operation conditions (entries 18 and 19). A decrease in the catalytic performance was observed. The oxirane conversion and the carbonate selectivity were lower than those for EMO (entry 10). The reason is

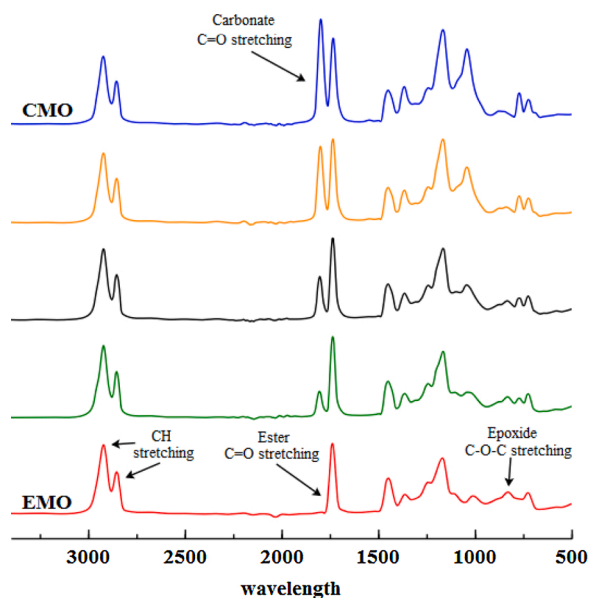


Fig. 5. FTIR-spectra of (—) EMO, (—) CMO and (—, —, —) EMO/CMO mixtures.

presumed to be the different composition of the FAMES of cottonseed oil and tall oil. Both oils contain a high percentage of linoleic acid, which bears two double bonds in the same carbon chain rather than one as in oleic acid and hence their epoxidized derivatives are expected to have higher concentration of oxirane. Moreover, some impurities such as rosin acids and unsaponifiable are also present in those oils, which could contribute to catalyst deactivation and blockage of active sites.

The influence of the reaction temperature on the carbonation process using Zn/SBA-15(0.12)-4PPI was verified (Fig. 7). A higher conversion of epoxidized methyl oleate was obtained with increasing temperature, but the selectivity of the carbonated product decreased as the temperature was increased. Analogously, a lower reaction temperature resulted in a lower conversion and a higher selectivity. The carbon dioxide solubility is probably the main reason behind this result, because carbon dioxide is less soluble in the liquid phase at elevated temperatures [11, 38], less carbon dioxide is available in the reaction medium, and in consequence, the insertion step of carbon dioxide into the epoxide is slower.

The addition of water as an extra hydrogen bond donor source have been previously studied in the carbonation short-chain epoxides [47–53] and epoxidized vegetable oils [54] in the presence of homogeneous catalysts, indicating that the conversion of epoxides is improved if a small amount of water is present. Otherwise, it is clear from Table 3

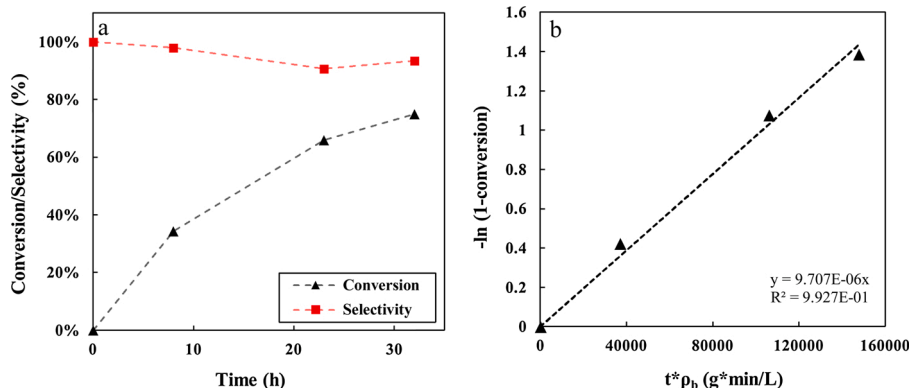


Fig. 6. Carbonation of epoxidized methyl oleate with CO₂ using Zn/SBA-15(0.12)-4PPI as an heterogeneous catalyst at 140 °C, 30 bar, 7.4 wt% catalyst and 1000 rpm; a) Conversion and selectivity, b) First-order kinetics test with respect to the epoxide concentration.

that addition of water to the system does not provide any increase in the conversion when compared to the water-free system (entries 10 and entry 17), possibly because of the deactivation of zinc-based catalysts reported in literature [47,54]. Conversely, the selectivity decreased to 65 %, which is probably caused by secondary hydrolysis reactions of the epoxide [47,48,52,53], this was confirmed in the IR-spectra of the samples (Fig. S3) by the presence of broad peak in the range of 3550–3200 cm⁻¹ corresponding to OH functionalities.

Finally, the stability of Zn/SBA-15(0.12)-4PPI catalyst was investigated by reusing the spent catalyst. After the carbonation reaction was completed, the spent catalyst was filtered, washed by ethyl acetate to remove the adsorbed reaction mixture, and dried at 70 °C overnight. As evidenced in Fig. 8, the catalyst presented some deactivation. The catalytic activity decreased considerably after the first cycle. The reason for the deactivation was investigated using ICP-EOS (Fig. S4), and it was found that a small amount of iodine had leached from the catalytic species at every cycle.

3.3. Reaction mechanism

As evidenced by our results and in line with previous studies [20,24], the carbon dioxide cycloaddition to epoxide is mainly carried out by bifunctional catalysts and co-catalyzed systems, in which a cooperative acid-base mechanism takes place. The utilization of a Lewis acid metal centre has been demonstrated to enhance the reaction by proving a source of hydrogen bond donor. However, our experimental results revealed that the reaction can also proceed at slower rates in the absence

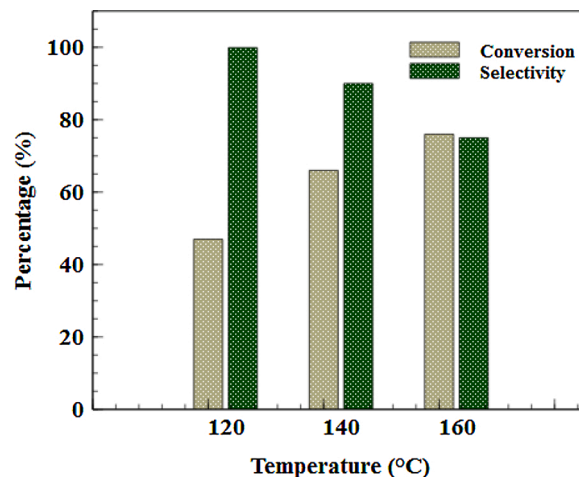


Fig. 7. Effect of temperature on the conversion and selectivity in the carbonation of EMO at 7.4 wt% of Zn/SBA-15(0.12)-4PPI catalyst, 1000 rpm and 23 h.

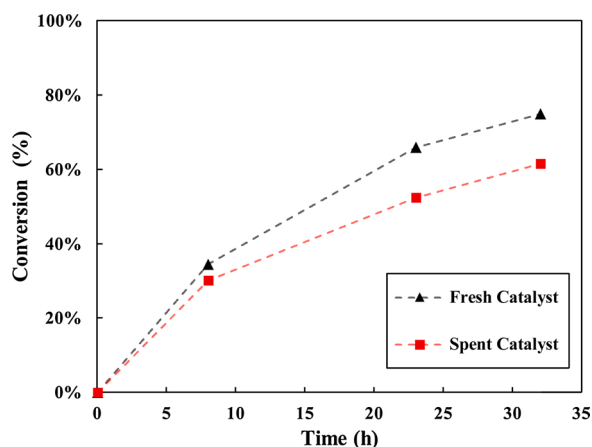


Fig. 8. Stability test for Zn/SBA-15(0.12)-4PPI catalyst at 140 °C, 30 bar, 7.4 wt% catalyst and 1000 rpm.

of Lewis acid metal sites as demonstrated in the carbonation experiments with silica-supported catalyst in the absence of Zn (Table 3; entry 1–9). These results are in accordance with some previous reports [25, 26] where it has been proposed that the OH species on the silica surface can act as Lewis acid to synergistically activate the oxirane ring for its opening. Based on these considerations, a plausible molecular mechanism is proposed in Fig. 9. In the first step, the oxirane ring is adsorbed into the surface either by Lewis acid metal centre or OH groups on the

silica support, which results in the activation of the oxirane ring by polarization. Then the active epoxide is attacked through the less hindered carbon by the halide anion of the catalytic species to produce a ring-opening complex. Thereafter, the CO₂ insertion proceeds and a new carbonate intermediate is formed on the surface. Finally, the ring closure results in the formation of cyclic carbonate, which is desorbed from the surface.

4. Conclusions

The carbonation reaction of vegetable oils was explored under solventless and co-catalyst free conditions with a variety of heterogeneous bifunctional catalysts. It was found that when the catalytic species is attached to molecular sieves such as SBA-15, an improved level of the epoxide conversion was achieved, probably because of larger pores and larger available surface areas. The influence of the Lewis acidity on the catalyst activity and selectivity was investigated by doping the silica support with a metal (Zn). An increase in the epoxide conversion was evidenced when the support was doped with Lewis metal centres. Otherwise, it was observed that increasing the amount of doped metal does not provide any further improvement. A low Zn/Si molar ratio in the support is sufficient to obtain an improved catalyst performance.

The influence of the reaction temperature on the system was evaluated. It was found that higher temperature leads to a higher conversion of epoxides, otherwise it was observed that the selectivity of carbonated product decreased due to a lower carbon dioxide concentration in the liquid phase. A reaction mechanism was proposed based on the

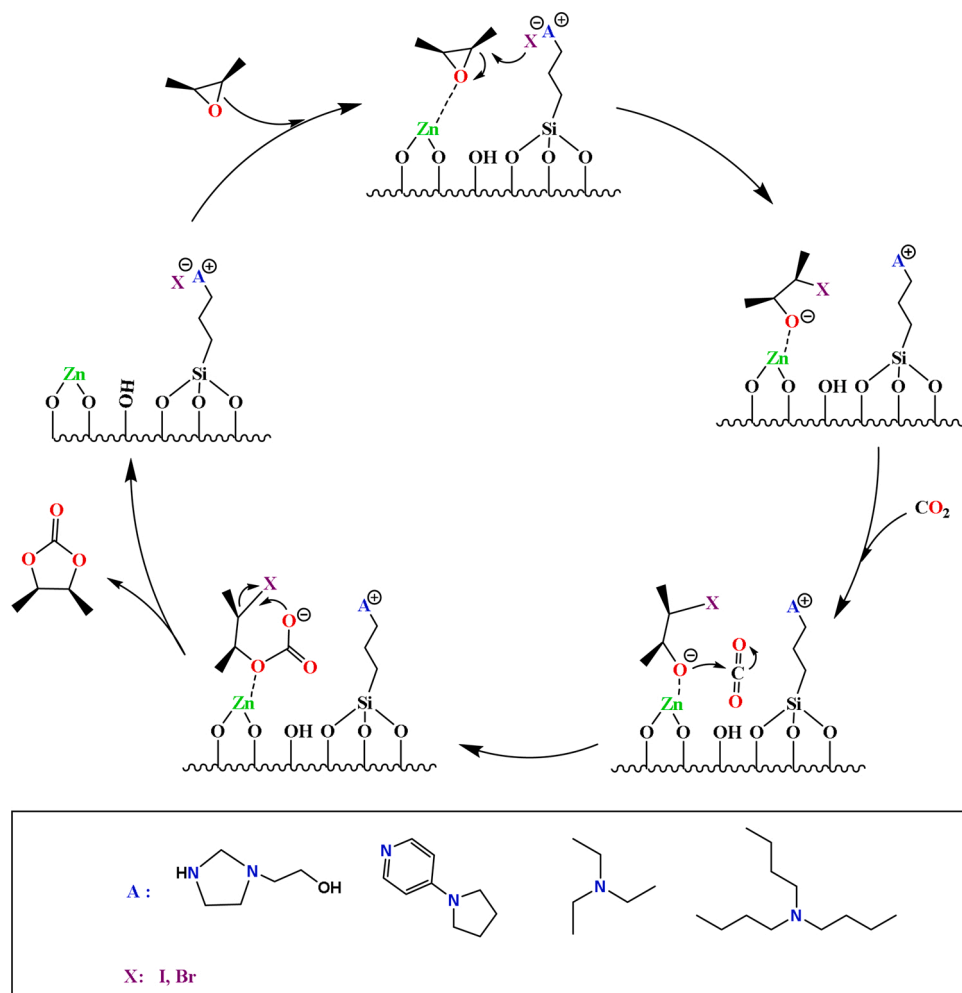


Fig. 9. Proposed mechanism for the carbonation reaction of EMO with various nucleophilic catalysts on a Zn-doped support.

experimental observations. The presented work provides insights for the further development of co-catalyst free heterogeneous catalytic systems for the carbonation process of vegetable oils, which are scarcely reported in literature.

CRedit authorship contribution statement

Wander Y. Perez-Sena: Conceptualization, Data curation, Formal analysis, Software, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. **Kari Eränen:** Project administration, Resources, Software, Supervision. **Narendra Kumar:** Data curation, Formal analysis, Investigation, Methodology. **Lionel Estel:** Conceptualization, Funding acquisition, Resources, Supervision. **Sébastien Leveueur:** Conceptualization, Formal analysis, Investigation, Methodology, Validation, Funding acquisition, Resources, Supervision, Writing - original draft, Writing - review & editing. **Tapio Salmi:** Conceptualization, Formal analysis, Investigation, Methodology, Validation, Funding acquisition, Resources, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jcou.2021.101879>.

References

- O. Kreye, H. Mutlu, M.A.R. Meier, Sustainable routes to polyurethane precursors, *Green Chem.* 15 (May (6)) (2013) 1431–1455, <https://doi.org/10.1039/C3GC40440D>.
- W.Y. Pérez-Sena, et al., Aminolysis of cyclic-carbonate vegetable oils as a non-isocyanate route for the synthesis of polyurethane: a kinetic and thermal study, *Chem. Eng. J.* 346 (Aug) (2018) 271–280, <https://doi.org/10.1016/j.cej.2018.04.028>.
- A.F. Guzmán Agudelo, W.Y. Pérez-Sena, N. Kebir, T. Salmi, L.A. Ríos, S. Leveueur, Influence of steric effects on the kinetics of cyclic-carbonate vegetable oils aminolysis, *Chem. Eng. Sci.* 228 (Dec) (2020) 115954, <https://doi.org/10.1016/j.ces.2020.115954>.
- Z.S. Petrović, Polyurethanes from vegetable oils, *Polym. Rev.* 48 (Feb. (1)) (2008) 109–155, <https://doi.org/10.1080/15583720701834224>.
- D.C. Webster, Cyclic carbonate functional polymers and their applications, *Prog. Org. Coat.* 47 (Jul. (1)) (2003) 77–86, [https://doi.org/10.1016/S0300-9440\(03\)00074-2](https://doi.org/10.1016/S0300-9440(03)00074-2).
- V.B. Saptal, B.M. Bhanage, Current advances in heterogeneous catalysts for the synthesis of cyclic carbonates from carbon dioxide, *Curr. Opin. Green Sustain. Chem.* 3 (Feb) (2017) 1–10, <https://doi.org/10.1016/j.cogsc.2016.10.006>.
- J. Kim, S.-N. Kim, H.-G. Jang, G. Seo, W.-S. Ahn, CO₂ cycloaddition of styrene oxide over MOF catalysts, *Appl. Catal. Gen.* 453 (Feb) (2013) 175–180, <https://doi.org/10.1016/j.apcata.2012.12.018>.
- H. Liang, J. Wang, F. Wang, Y. Feng, M. Kang, Z. Wang, An efficient heterogeneous LiBr/γ-Al₂O₃ catalyst for the cycloaddition of CO₂ with diglycidyl ethers: An efficient heterogeneous LiBr/γ-Al₂O₃ catalyst for the cycloaddition of CO₂ with diglycidyl ethers, *J. Chem. Technol. Biotechnol.* 93 (Aug. (8)) (2018) 2271–2280, <https://doi.org/10.1002/jctb.5570>.
- C. Kohrt, T. Werner, Recyclable bifunctional polystyrene and silica gel-supported organocatalyst for the coupling of CO₂ with epoxides, *ChemSusChem* 8 (Jun. (12)) (2015) 2031–2034, <https://doi.org/10.1002/cssc.201500128>.
- X.-B. Lu, D.J. Darensbourg, Cobalt catalysts for the coupling of CO₂ and epoxides to provide polycarbonates and cyclic carbonates, *Chem. Soc. Rev.* 41 (4) (2012) 1462–1484, <https://doi.org/10.1039/C1CS15142H>.
- M. Alves, B. Grignard, S. Gennen, C. Detrembleur, C. Jerome, T. Tassaing, Organocatalytic synthesis of bio-based cyclic carbonates from CO₂ and vegetable oils, *RSC Adv.* 5 (66) (2015) 53629–53636, <https://doi.org/10.1039/C5RA10190E>.
- Q. Su, J. Sun, J. Wang, Z. Yang, W. Cheng, S. Zhang, Urea-derived graphitic carbon nitride as an efficient heterogeneous catalyst for CO₂ conversion into cyclic carbonates, *Catal. Sci. Technol.* 4 (6) (2014) 1556, <https://doi.org/10.1039/c3cy00921a>.
- L. Zhao, N. Liu, H. Huang, X. Wang, X. Huang, Synthesis of propylene carbonate from carbon dioxide through high activity of magnesium oxide, *J. Chem. Eng. Jpn.* 52 (May (5)) (2019) 406–412, <https://doi.org/10.1252/jcej.18we073>.
- A. Ahmed, et al., Macroporous metal-organic framework microparticles with improved liquid phase separation, *J. Mater. Chem. A* 2 (24) (2014) 9085–9090, <https://doi.org/10.1039/C4TA00138A>.
- H. Yan, Soft-Template Synthesis of Mesoporous Carbon Nitride with Enhanced Photocatalytic H₂ Evolution Under Visible Light, 2012, p. 6.
- L. Hu, Z. Yan, X. Mo, X. Peng, L. Chen, Hierarchical Co/ZIF-8 as an efficient catalyst for cycloaddition of CO₂ and epoxide, *Microporous Mesoporous Mater.* 294 (Mar) (2020) 109917, <https://doi.org/10.1016/j.micromeso.2019.109917>.
- L. Hu, et al., Bifunctional metal-doped ZIF-8: a highly efficient catalyst for the synthesis of cyclic carbonates from CO₂ cycloaddition, *Microporous Mesoporous Mater.* 299 (Jun) (2020) 110123, <https://doi.org/10.1016/j.micromeso.2020.110123>.
- W.-H. Zhang, et al., Graphene oxide grafted hydroxyl-functionalized ionic liquid: a highly efficient catalyst for cycloaddition of CO₂ with epoxides, *Appl. Catal. Gen.* 509 (Jan) (2016) 111–117, <https://doi.org/10.1016/j.apcata.2015.10.038>.
- M. Sankar, T.G. Ajithkumar, G. Sankar, P. Manikandan, Supported imidazole as heterogeneous catalyst for the synthesis of cyclic carbonates from epoxides and CO₂, *Catal. Commun.* 59 (Jan) (2015) 201–205, <https://doi.org/10.1016/j.catcom.2014.10.026>.
- M. Liu, B. Liu, L. Liang, F. Wang, L. Shi, J. Sun, Design of bifunctional NH₃Zn/SBA-15 single-component heterogeneous catalyst for chemical fixation of carbon dioxide to cyclic carbonates, *J. Mol. Catal. Chem.* 418–419 (Jul) (2016) 78–85, <https://doi.org/10.1016/j.molcata.2016.03.037>.
- M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa, K. Tomishige, Direct cyclic carbonate synthesis from CO₂ and diol over carboxylation/hydration cascade catalyst of CeO₂ with 2-cyanopyridine, *ACS Catal.* 4 (Jun. (6)) (2014) 1893–1896, <https://doi.org/10.1021/cs500301d>.
- T. Sakakura, J.-C. Choi, H. Yasuda, Transformation of carbon dioxide, *Chem. Rev.* 107 (Jun. (6)) (2007) 2365–2387, <https://doi.org/10.1021/cr068357u>.
- M. Aresta, A. Dibenedetto, Utilisation of CO₂ as a chemical feedstock: opportunities and challenges, *Dalton Trans.* (Jul. (28)) (2007) 2975–2992, <https://doi.org/10.1039/B700658F>.
- R. Luo, X. Zhou, W. Zhang, Z. Liang, J. Jiang, H. Ji, New bi-functional zinc catalysts based on robust and easy-to-handle N-chelating ligands for the synthesis of cyclic carbonates from epoxides and CO₂ under mild conditions, *Green Chem.* 16 (Aug. (9)) (2014) 4179–4189, <https://doi.org/10.1039/C4GC00671B>.
- L. Longwitz, J. Steinbauer, A. Spannenberg, T. Werner, Calcium-based catalytic system for the synthesis of bio-derived cyclic carbonates under mild conditions, *ACS Catal.* 8 (Jan. (1)) (2018) 665–672, <https://doi.org/10.1021/acscatal.7b03367>.
- J.W. Comerford, I.D.V. Ingram, M. North, X. Wu, Sustainable metal-based catalysts for the synthesis of cyclic carbonates containing five-membered rings, *Green Chem.* 17 (4) (2015) 1966–1987, <https://doi.org/10.1039/C4GC01719F>.
- Z. Huang, F. Li, B. Chen, G. Yuan, Cycloaddition of CO₂ and epoxide catalyzed by amino- and hydroxyl-rich graphitic carbon nitride, *Catal. Sci. Technol.* 6 (9) (2016) 2942–2948, <https://doi.org/10.1039/C5CY01805F>.
- C. Calabrese, F. Giacalone, C. Aprile, Hybrid catalysts for CO₂ conversion into cyclic carbonates, *Catalysts* 9 (Apr. (4)) (2019) 325, <https://doi.org/10.3390/catal9040325>.
- M. North, R. Pasquale, C. Young, Synthesis of cyclic carbonates from epoxides and CO₂, *Green Chem.* 12 (9) (2010) 1514, <https://doi.org/10.1039/c0gc00065e>.
- A. Monfared, R. Mohammadi, A. Hoesseinian, S. Sarhandi, P.D. Kheirollahi Nezhad, Cycloaddition of atmospheric CO₂ to epoxides under solvent-free conditions: a straightforward route to carbonates by green chemistry metrics, *RSC Adv.* 9 (7) (2019) 3884–3899, <https://doi.org/10.1039/C8RA10233C>.
- A. Decortes, M.M. Belmonte, J. Benet-Buchholz, A.W. Kleij, Efficient carbonate synthesis under mild conditions through cycloaddition of carbon dioxide to oxiranes using a Zn(salphen) catalyst, *Chem. Commun.* 46 (25) (2010) 4580–4582, <https://doi.org/10.1039/C000493F>.
- Y. Du, et al., Sn-catalyzed synthesis of propylene carbonate from propylene glycol and CO₂ under supercritical conditions, *J. Mol. Catal. Chem.* 241 (Nov. (11)) (2005) 233–237, <https://doi.org/10.1016/j.molcata.2005.07.030>.
- J.A. Castro-Osma, J.W. Comerford, R.H. Heyn, M. North, E. Tangstad, New catalysts for carboxylation of propylene glycol to propylene carbonate via high-throughput screening, *Faraday Discuss.* 183 (Dec. (0)) (2015) 19–30, <https://doi.org/10.1039/C5FD00061K>.
- M. Bähr, R. Müllhaupt, Linseed and soybean oil-based polyurethanes prepared via the non-isocyanate route and catalytic carbon dioxide conversion, *Green Chem.* 14 (2) (2012) 483, <https://doi.org/10.1039/c2gc16230j>.
- L. Ruiz, et al., Upgrading castor oil: from heptanal to non-isocyanate poly(amide-hydroxyurethane)s, *Polymer* 124 (Aug) (2017) 226–234, <https://doi.org/10.1016/j.polymer.2017.07.070>.
- D. Miloslavskiy, E. Gotlib, O. Figovsky, D. Pashin, Cyclic carbonates based on vegetable oils, *Int. Lett. Chem. Phys. Astron.* 27 (Feb) (2014) 20–29, <https://doi.org/10.18052/www.scipress.com/ILCPA.27.20>.

- [37] L. Peña Carrodegua, et al., Fatty acid based biocarbonates: Al-mediated stereoselective preparation of mono-, di- and tricarbonates under mild and solventless conditions, *Green Chem.* 19 (15) (2017) 3535–3541, <https://doi.org/10.1039/C7GC01206C>.
- [38] X. Cai, J.L. Zheng, J. Wärnå, T. Salmi, B. Taouk, S. Leveneur, Influence of gas-liquid mass transfer on kinetic modeling: carbonation of epoxidized vegetable oils, *Chem. Eng. J.* 313 (Apr) (2017) 1168–1183, <https://doi.org/10.1016/j.cej.2016.11.012>.
- [39] X. Cai, M. Matos, S. Leveneur, Structure–reactivity: comparison between the carbonation of epoxidized vegetable oils and the corresponding epoxidized fatty acid methyl ester, *Ind. Eng. Chem. Res.* 58 (Jan. (4)) (2019) 1548–1560, <https://doi.org/10.1021/acs.iecr.8b05510>.
- [40] B. Schäffner, et al., Synthesis and application of carbonated fatty acid esters from carbon dioxide including a life cycle analysis, *ChemSusChem* 7 (4) (2014) 1133–1139, <https://doi.org/10.1002/cssc.201301115>.
- [41] P.G. Parzuchowski, M. Jurczyk-Kowalska, J. Ryszkowska, G. Rokicki, Epoxy resin modified with soybean oil containing cyclic carbonate groups, *J. Appl. Polym. Sci.* 102 (3) (2006) 2904–2914, <https://doi.org/10.1002/app.24795>.
- [42] H. Büttner, J. Steinbauer, C. Wulf, M. Dindaroglu, H.-G. Schmalz, T. Werner, Organocatalyzed synthesis of oleochemical carbonates from CO₂ and renewables, *ChemSusChem* 10 (Mar. (6)) (2017) 1076–1079, <https://doi.org/10.1002/cssc.201601163>.
- [43] K. Motokura, S. Itagaki, Y. Iwasawa, A. Miyaji, T. Baba, Silica-supported aminopyridinium halides for catalytic transformations of epoxides to cyclic carbonates under atmospheric pressure of carbon dioxide, *Green Chem.* 11 (11) (2009) 1876, <https://doi.org/10.1039/b916764c>.
- [44] R.R. Jay, Direct titration of epoxy compounds and aziridines, *Anal. Chem.* 36 (Mar. (3)) (1964) 667–668, <https://doi.org/10.1021/ac60209a037>.
- [45] A.S. Maria Chong, X.S. Zhao, Functionalization of SBA-15 with APTES and characterization of functionalized materials, *J. Phys. Chem. B* 107 (Nov. (46)) (2003) 12650–12657, <https://doi.org/10.1021/jp035877+>.
- [46] Daniel Swern, T.W. Findley, G.N. Billen, J.T. Scanlan, Determination of oxirane oxygen, *Anal. Chem.* 19 (Jun. (6)) (1947) 414–415, <https://doi.org/10.1021/ac60006a018>.
- [47] J. Sun, J. Ren, S. Zhang, W. Cheng, Water as an efficient medium for the synthesis of cyclic carbonate, *Tetrahedron Lett.* 50 (Jan. (4)) (2009) 423–426, <https://doi.org/10.1016/j.tetlet.2008.11.034>.
- [48] X. Zhou, Y. Zhang, X. Yang, J. Yao, G. Wang, Hydrated alkali metal halides as efficient catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides, *Chin. J. Catal.* 31 (Jul. (7)) (2010) 765–768, [https://doi.org/10.1016/S1872-2067\(09\)60086-3](https://doi.org/10.1016/S1872-2067(09)60086-3).
- [49] W.-L. Wong, P.-H. Chan, Z.-Y. Zhou, K.-H. Lee, K.-C. Cheung, K.-Y. Wong, A robust ionic liquid as reaction medium and efficient organocatalyst for carbon dioxide fixation, *ChemSusChem* 1 (Feb. (1–2)) (2008) 67–70, <https://doi.org/10.1002/cssc.200700097>.
- [50] J.-Q. Wang, J. Sun, W.-G. Cheng, K. Dong, X.-P. Zhang, S.-J. Zhang, Experimental and theoretical studies on hydrogen bond-promoted fixation of carbon dioxide and epoxides in cyclic carbonates, *Phys. Chem. Chem. Phys.* 14 (31) (2012) 11021, <https://doi.org/10.1039/c2cp41698k>.
- [51] M. Liu, et al., Insights into hydrogen bond donor promoted fixation of carbon dioxide with epoxides catalyzed by ionic liquids, *Phys. Chem. Chem. Phys.* 17 (8) (2015) 5959–5965, <https://doi.org/10.1039/C4CP05464D>.
- [52] J. Tharun, R. Roshan, A.C. Kathalikkattil, K.D. Heon, H. Mo, D.-W. Park, Natural Amino Acids/H₂O as Metal- and Halide-Free Catalyst System for the Synthesis of Propylene Carbonate From Propylene Oxide and CO₂ Under Moderate Conditions, 2012, p. 8.
- [53] M. Ramin, J.-D. Grunwaldt, A. Baiker, Behavior of homogeneous and immobilized zinc-based catalysts in cycloaddition of CO₂ to propylene oxide, *J. Catal.* 234 (Sep. (2)) (2005) 256–267, <https://doi.org/10.1016/j.jcat.2005.06.020>.
- [54] P. Mazo, L. Rios, Carbonation of epoxidized soybean oil improved by the addition of water, *J. Am. Oil Chem. Soc.* 90 (May (5)) (2013) 725–730, <https://doi.org/10.1007/s11746-013-2214-3>.