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Relating extrusion as a method of bifunctional catalysts synthesis and their catalytic performance

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ABSTRACT

Although catalyst shaping by extrusion has been industrially applied for decades to suppress the pressure drop, much less emphasis was put on fundamental understanding of extrusion for catalytic pastes and its effect on the properties of the final catalyst bodies. During recent years intensive research efforts have been put on synthesis of extrudates by systematically varying different synthesis parameters, methods of metal modifications, different types of binders and correlating extrudate properties with their performance in several catalytic reactions. The synthesis method of extrudates can have a large impact on properties, relevant for catalysis, including acidity/basicity, the metal location and the particle size as well as textural properties, which can differ from the properties of the corresponding powder catalysts. Furthermore, a binder can interact with the support changing physico-chemical and catalytic properties. The current review summarizes recent developments related to shaping of catalysts by extrusion addressing also such advanced methods to investigate diffusion of liquid reactants inside the extrudates and interconnectivity of pores, as pulse gradient field NMR spectroscopy and fluorescent probe analysis respectively.

1. Introduction

For industrial applications shaped catalysts are typically required to diminish a large pressure drop inside a reactor. Several shaping methods are commonly used, including pelletizing, extrusion, spray-drying and granulation [1]. Compared to other preparation methods, extrusion allows high throughput at relatively low costs and results in a variety of possible extrudate shapes. Such shapes have a profound influence on the interplay between mass transfer and reaction kinetics. For example, carriers with holes (i.e. rings) in the extrudate decrease the internal mass transfer resistance via shorter diffusion paths. At the same time, an increase in the number of holes in an extruded body will negatively influence the mechanical strength. Irregular surface shapes by decreasing the stagnant layer thickness enhance the external mass transfer at the expense of an increased pressure drop.

On a more negative side, contrary for example to tablets, the extrudates exhibit a non-uniform shape and lower abrasion resistance.

The practical knowledge behind extrusion and understanding on the effects of different additives and preparation methods have been accumulated mainly in industry and is poorly documented in the open scientific literature [2,3]. The technical catalysts, however, besides the active phase, promoters and the support, comprise other components, which are added to improve the flow and rheological properties as well as mechanical stability. The other components are clays and starch for better rheological behaviour, various binders, such as for example bentonite, bleaching earth, attapulgite and sepiolite, for mechanical stability of extrudates, peptizing agents (e.g. nitric acid) for de-agglomeration of solid particles in the extruder, combustible porogens for porosity increase, plasticizers, lubricants and water.

In the recent years several studies have appeared in the open literature to systematic investigations of the effect of the preparation methods [4–6], the amounts and types of various additives, etc. [7–10] on the properties of extrudates relevant for heterogeneous catalysis.

A specific feature of pastes for extrusion is that they have per se poor mouldability and plasticity even after water addition. A compromise has to be found for the composition of the pastes as too low viscosity gives mechanically unstable extrudates, while the opposite simply blocks an extruder. Various organic polymers with a large molecular weight such

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as methylcellulose [11–14], hydroxyethylcellulose [15,16], polyvinyl alcohol, etc. are typically added to improve plasticity.

The addition of inorganic binders can change the properties of the extrudate, for example alumina can act as a Lewis acid. Moreover, because of the mechanical impact during extrusion there could be changes in acidity of the catalytically active phase altering for example the acid strength distribution.

A specific emphasis has recently been put on interactions between a catalytically active phase (a zeolite) and additives [17–19], which might affect catalyst properties. The use of a peptizing agent, its amount and nature have also an impact on the extrusion process and properties of the extrudates [20]. Due to practical significance of extruded catalysts, exact knowledge of how different parameters affect the final extrudate properties is of paramount importance.

In this work some recent developments of mainly our group in the extrudates preparation, characterization of their properties and elucidating catalytic results will be summarized. The main aim is to emphasize how extrudates are prepared and what is the effect of different additives on extrudate properties, for example on the mechanical strength or textural properties or acidity/basicity. In addition to conventional catalyst characterization methods, also advanced methods were used to visualize the structure of extrudate [17], to determine diffusivity of molecules inside extrudates by pulse field NMR spectroscopy [21,22], by uptake staining studies with fluorescent polar microsphere probes [17] and by adsorption [23–25]. Combination of catalytic data with various characterization results for shaped catalysts at various steps of catalyst preparation including extrusion per se can bring valuable information required for catalyst scale up.

It is argued here that fundamental research in development of catalytic materials in the future should not be limited to the so-called research catalysts only, but should consider the impact of various additives in technical catalysts as they can dramatically influence behaviour of catalysts in an industrial environment.

2. Synthesis of extrudates

Selection of a binder and a peptizing agent, namely their types and amounts, is important for extrusion in terms of the suspension rheology and stability of the green bodies. Moreover, the amount of water required for extrusion when using different binders is different, influencing the rheological properties of the slurry [7,11]. In addition, a higher solid content in the suspension can lead to more prominent shrinkage. Just a minor difference in water content (5 wt%) in the suspension for extrusion can significantly change the extrudate structure [7].

Preparation of extrudates from different clays using methylcellulose as an organic binder was studied in [7]. These clays acting as inorganic binders exhibit different acidity, i.e. bindzil, attapulgite and sepiolite have pH of the suspension slurry in water exceeding 8, while the corresponding values for bentonite and bleaching earth are 4.2–4.4. It was also observed, that these clay materials require different amounts of water during shaping. To elucidate this result, contact angles of different clay-methylcellulose mixtures were measured [11]. The contact angles varied for different clay-methylcellulose mixtures in a narrow range of 17 – 26° and thus hydrophobicity per se cannot explain different behaviour occurring during extrusion [11].

Rheological properties of the slurry for synthesizing Beta and Y zeolite extrudates with bentonite and methylcellulose as inorganic and organic binders were studied in depth in [7]. The results showed that e.g. traditional rotational viscometry typically applied for diluted suspensions is not reliable for these highly elastic fluids at high concentration of a solid. For example, viscosity was levelling off when the particle volume concentration was increasing. Dependency of viscosity vs the solid fraction was successfully modelled in [7] with the Brodnyan-Mooney equation.

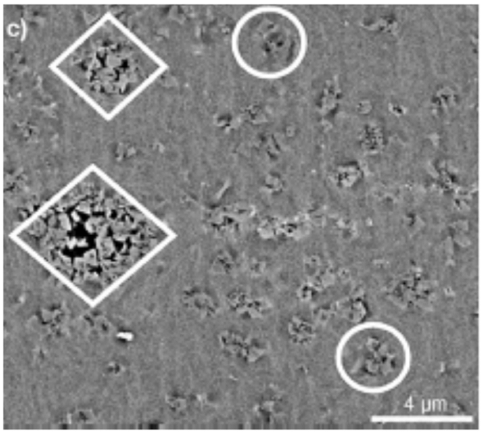

Fig. 1. SEM image of H-USY extrudates using boehmite as a binder. Circles denote small zeolite aggregates while diamonds are porous H-USY clusters [5].

The role of the peptizing agent is to form a double layer between the alumina particles at the same time increasing stability of the particles by “hydrophilic repulsion” according to the Derjaguin-Landau-Verwey-Overbeek theory [26]. As already mentioned a peptizing agent (e.g. nitric acid or HCl) decreases the pH of the extrudate paste in relation to its point of zero charge breaking the agglomerates and improving the flow properties during extrusion. It is also necessary that the peptizing agent can be fully removed during thermal treatment of the catalyst as otherwise presence of a strong acid can influence catalytic behaviour. The amount of nitric acid as a peptizing agent was found crucial for synthesis of boehmite extrudates [20] leading to dissolution of boehmite if an excess of nitric acid was used.

3. Characterization of extrudates

3.1. Properties of acid/base extrudates

Properties of different types of extrudates, such as mechanical strength, textural properties and interconnectivity of pores as well as acidity and basicity will be discussed here.

The main role of the binder is to facilitate extrusion as well as to increase the mechanical strength of the extrudate. When comparing the mechanical strength of different zeolite-binder extrudates made from a range of binders [27], it was found that the highest mechanical strength among H-Beta-25 extrudates (where 25 denotes Si/Al molar ratio) was observed for Ludox-30 as a binder, while the lowest strength was determined for colloidal silica Bindzil. These results correlated well with the smallest particle size of Ludox-30 and the largest particle size of Bindzil [25]. In [10] the highest mechanical strength of attapulgite-methylcellulose extrudates, being 16 MPa and 8 MPa in vertical and horizontal position, correspondingly, was close to the values for commercial alumina [6], while much lower mechanical strength has been reported for Beta, Y, TS-1, ZSM-5 zeolites and MCM-41 [7,12,14,27–29].

Defects can be formed during extrusion, for example, in preparation of HUSY+Al_2O_3 extrudates due to the presence of aggregates and zeolite clusters in HUSY (Fig. 1) [5]. It is known, that during synthesis of HUSY zeolites mesopores are formed via dealumination decreasing the mechanical strength of the extrudates [28].

A high mechanical strength of hydrotalcite extrudates was found for bentonite and kaolin as binders, while hydrotalcite mixed with montmorillonite, silica and alumina exhibited a low crush strength [19]. The bentonite-hydrotalcite extrudates were tested in synthesis of glycerol carbonate as discussed below.

Textural properties of several types of acidic/basic extrudates have been intensively studied, including Beta and Y zeolite with different binders [29–32], hierarchical ZSM-5 extrudate with silica binder [10],

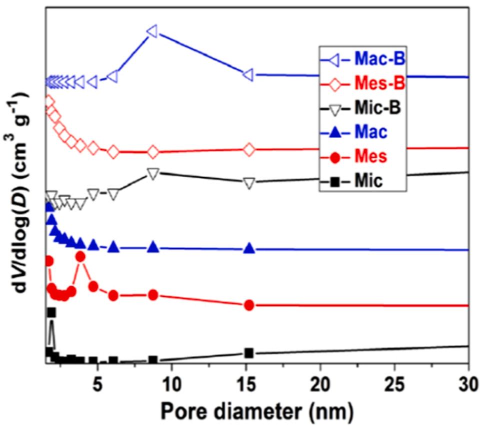

Fig. 2. Pore size distribution of ZSM-5 zeolites and their extruded counterparts [10]. Notation: mic: microporous, mes: mesoporous, mac: microporous, B denotes extrudates.

clay extrudates [11]. Textural properties of powder and extrudate clay-methylcellulose (MC) materials were compared in [11]. The results showed that especially the micropore to mesopore volume ratio increased for sepiolite-MC and attapulgite-MC extrudates in comparison to their powder form. A slight decrease of the specific surface area has been observed for extrudates in comparison to the powder catalysts, which was caused by mechanical forces applied during extrusion [11]. Textural properties were also investigated for several meso/-microporous, macro/microporous and mesoporous ZSM-5 derived catalysts, which were prepared using as templates tetrapropylammonium hydroxide for ZSM-5, cetyltrimethylammonium chloride as a surfactant for meso/microporous ZSM-5, and mesoporous silica beads with ZSM-5 to create macropores. These catalytic materials were extruded using 20:80% ratio of the catalyst to the silica binder [10]. A comparison between the surface areas of micro- meso- and macroporous zeolites and their extruded counterparts was performed showing that even microporous ZSM-5 after extrusion exhibited large pores, which were formed upon addition of the binder (Fig. 2).

For ZSM-5 the pore size was verified optically from SEM images. These catalysts were tested in cracking of 1,3,5-triisopropylbenzene (see below) illustrating that deactivation behaviour was depending on the type of a binder.

Interconnectivity of pores and the pore blockage have been investigated by several methods including diffusion of a fluorescent probe into extrudates using fluorescent confocal microscopy [17,32] as well as self-diffusivity of hydrocarbons into extrudates with pulse field NMR spectroscopy [21,22] and with adsorption method [24]. The fluorescent probe molecule diluted in a solvent was introduced into a catalyst body for a specified time period, after which it was dried and imaged with a certain wavelength using confocal fluorescence microscopy [17]. Interestingly, it was observed that argon physisorption method did not reveal differences in potassium modified USY-Attapulgite (K/USY/Att) and USY-Bentonite (K/USY/Bent), while the pore blockage was clearly demonstrated with the probe for K/USY/Bent [33]. In [21] self-diffusivity of heptane and pentadecane into powder and extrudate catalysts was studied at room temperature using PFG NMR spectroscopy. The results revealed lower self-diffusion constants for heptane and pentadecane in extrudates than for the powder catalysts. In addition, the porosity/tortuosity ratio for pentadecane and heptane was also estimated showing that it is 7% higher for powder than for extrudates. Analogously hexadecane diffusion was measured to be lower in H-MCM-41-Bindzil extrudates than in the corresponding powder material [22].

Acidity and basicity are often affected by addition of the binders and other additives [11,34]. A comparative work was performed in [11] to investigate acidity of different clays used as binders. The results showed that bentonite and bleaching earth exhibit more Brønsted acid sites in comparison to attapulgite and sepiolite. This was also in accordance with the pH data of the clay aqueous slurries. The extrudates prepared from different clays using methylcellulose as an organic binder and tested in cyclization of citronellal exhibited different acidic/basic properties, for example sepiolite containing significant amounts of Mg was basic. The highest acidity was observed with sepiolite, while attapulgite displayed a very low Brønsted to Lewis acid ratio. Furthermore, these clay materials do not contain strong acid sites which is in line with the presence of tetrahedral Al atoms determined by MAS ^{27}NMR.

Typically, extrudates prepared from H-Beta-25 with bentonite and methylcellulose exhibited lower acidity than the corresponding powder catalysts [7]. MAS NMR spectra of ^{27}Al can differentiate Al species in the tetrahedral position and in the framework substitution in Si tetrahedral layers corresponding to signal near 0 ppm and 65 ppm, respectively [11]. During calcination, extra-framework aluminium can be formed and at the same time, the concentration of framework Al^{3+} in the tetrahedral position decreased [7]. It was, however, observed in [34] that acidity of Y- and USY zeolite extrudates prepared with pseudo-boehmite as a binder (70 wt%) increased, although ^{27}Al-NMR spectra showed only minor changes. The increased acidity found in Y- and USY-pseudo-boehmite extrudates could be related to the transformations of pseudo-boehmite to γ-Al_2O_3 during calcination as well as formation of new phases originated from the interactions of the zeolite and alumina binder. When pseudo-boehmite is transformed to γ-Al_2O_3, water is also formed, which promotes Al mobility on the zeolite surface and increases accessibility to the active sites [35]. It was furthermore stated that more advanced catalyst characterization methods are required to reveal the nature and location of chemical interactions between the zeolite and the binder, such as for example 2D MQ-MAS. The extrudates mentioned above exhibited also high activity in dealkylation of branched benzene (see below).

Possible interactions between hydrotalcite-bentonite binder were also suggested in [19] based on rather complex spectra ^{27}Al MAS NMR. Furthermore, according to microtome-cut cross-section analysis the presence of an intimate mixture of the binder particles with the mixed oxide was confirmed.

Phosphoric acid was used as an additive for Beta zeolite extrudates with alumina as a binder [34]. In that case, a higher amount of Brønsted acidic sites was detected in Beta zeolite extrudates, which was explained by the reaction between phosphoric acid and hexa-coordinated Al, causing realumination of the zeolite and higher acidity of extrudates [36].

3.2. Properties of bifunctional metal modified extrudates

Properties of bifunctional metal modified extrudates have also been intensively studied in the recent years [4,5,31,32,37,38] with the focus on mechanical strength, the textural properties (e.g. specific surface area and the pore size), location of the metal along with acidity/basicity.

It has been generally reported and discussed above, that addition of the binder increased the mechanical strength of the extrudates. It was also found that location of a catalytically active metal in a composite can affect the mechanical strength of extrudates. Thus, the mechanical strength of Ru-H-Beta-bentonite in the vertical direction was shown to decrease when the metal was located on the binder [4], while a higher vertical mechanical strength was measured for the extrudate in which Ru was located both on the zeolite and the binder. In case of Pt the highest mechanical strength was found for the metal loaded primarily on the zeolite followed by mixing with bentonite and subsequent extrusion [4]. These results show that selection of the preparation method for bifunctional extrudates containing both metal and acid sites is crucial for their properties.

The textural properties of Pt/H-USY extrudates with the zeolite to binder weight ratio of 1: 4.9 were, however, not largely changed in comparison to Pt/H-USY zeolite [5]. The same was valid for

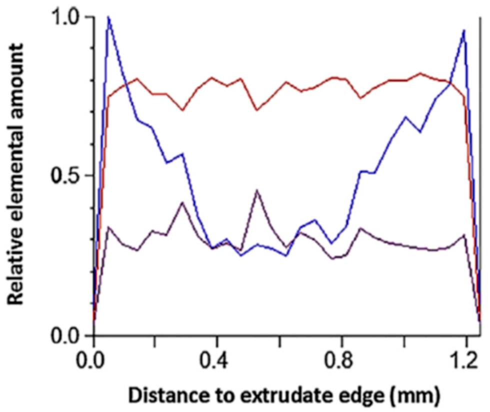

Fig. 3. Results from Pt, Al and Si distribution across the extrudate for 0.07 wt% Pt/(H-USY+Al_2O_3) determined by electron probe microanalysis [5]. Notation: blue - Pt, red - Al and black - Si.

Pt-Beta-bentonite extrudates, which were prepared by different methods (see below). A slight decrease of the specific surface area has also been found for zeolite-binder extrudates [6,7,21,22,39–43].

Metal location and metal loading in extrudates can be varied by selection of a preparation method [4,38]. For loading of Pt by ion-exchange extrudates it was demonstrated that the metal location varied as a function of Pt loading [5]. In that work HUSY extrudates were made using boehmite as a binder and methocel (a polymer containing methylcellulose or hydroxypropyl methylcellulose) with the weight ratio of 17:83:1 on dry basis and applying nitric acid as a peptizing agent. After kneading also an ammonium salt (not defined) was added followed by extrusion of the paste, drying and calcination.

The amount of Pt to be loaded on extrudates by ion-exchange method affected its distribution in the extrudates [5]. When Pt was deposited on extrudates using an excess of $[Pt(NH_3)_4Cl_2]{*}H_2O$ together with ammonium nitrate, the metal was preferentially deposited on the zeolite due to the exchange occurring on the Brønsted sites of the proton with Pt$(NH_3)_4^{2+}$ when the pH of the solution is above the point of zero charge of the zeolite and below that of alumina [42]. A small pore size of H-USY limited accessibility of the Pt precursor. The concentration profiles of Pt and Si were determined along the extrudate cross cut section by electron probe microanalysis. The results revealed also that when Pt loading was very small, the concentration of Pt particles was lower in the middle of the extrudate, which was also depicted as a distribution coefficient of Pt as a function of its loading (Fig. 3). This egg-shell location of Pt was explained by the preferential adsorption of Pt on the edges when the solution starts penetrating in the extrudate. Ion exchange is a faster process than solution diffusion and Pt present in low amounts is accumulated on the outer shell of the extrudate.

Selective metal deposition on the alumina binder could be achieved by ionic exchange with competition [38]. In this method, the humidified extrudates were exchanged with HCl followed by ion exchange with H_2PtCl_6. The catalytic results of these extrudates in hydroisomerization of hexadecane are discussed in Section 4.2.

Different synthesis methods were used to determine the metal location in the extrudates, such as loading of the metal on extrudates, mixing a support and a binder and thereafter impregnating with the metal followed by extrusion, metal impregnation on a binder followed by addition of a zeolite and extrusion, and finally metal deposition on a zeolite followed by addition of a binder and extrusion (Fig. 4) [4]. For these materials with Pt loaded on H-Beta-25-bentonite extrudates, the preparation methods have a major effect on mechanical stability and acidity, although textural properties were not largely affected [4].

Acidity of extrudates prepared by the methods described above [4] was the highest for Pt deposited on extrudates (post synthesis) being the lowest for the extrudates when Pt was first loaded on Beta-zeolite followed by mixing with a bentonite binder and extrusion (in-situ

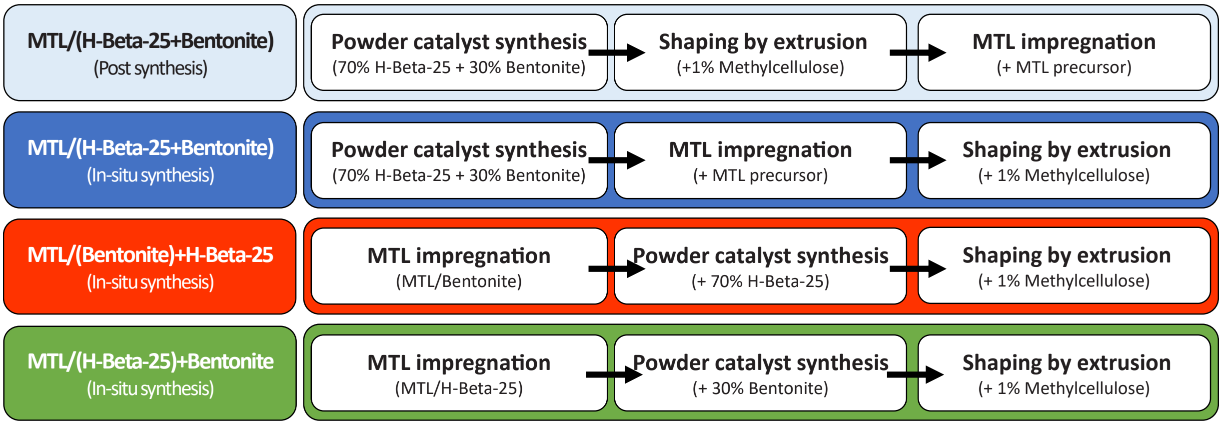

Fig. 4. Different methods to adjust the metal location in extrudates [4].

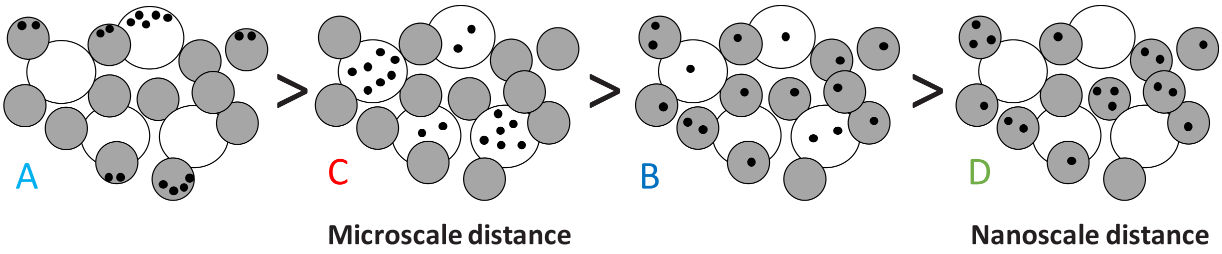

Fig. 5. Schematic picture of the extrudate composition for A) deposition of the metal on both Beta and the Bindzil binder after extrusion, B) Pt loaded on a powder mechanical mixture of Beta and Bindzil binder followed by extrusion, C) deposition of Pt on the powder Bindzil binder followed by extrusion with zeolite Beta, D) deposition of Pt on the powder zeolite beta followed by extrusion with Bindzil binder [6].

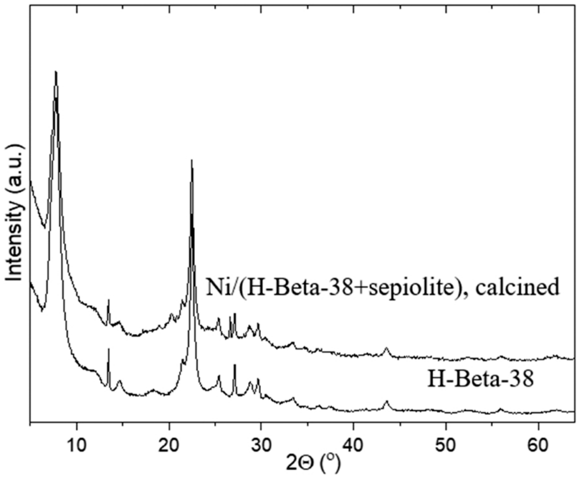

Fig. 6. XRD patterns of calcined, non-reduced Ni/(H-Beta-38 +sepiolite) extrudates compared to the initial Beta-38 zeolite [32].

synthesis). Interestingly the highest acidity was observed for Ru loaded on both Beta zeolite and bentonite, while the lowest acidity was measured for the extrudate in which Ru was loaded first on bentonite, mixed with H-Beta zeolite and extruded. Differences in total acidity for catalysts of the same composition and the metal loading were attributed to different synthesis procedures, in particular the step where the metal precursor was introduced onto supports of different acidity. In particular deposition of noble metals on zeolites led to changes in acidity compared to the pristine supports, affecting acidity of the final extrudates and the metal-to-acid site ratio.

Analogously to Pt- and Ru-Beta zeolite catalysts extruded with bentonite [4], the same procedure was applied for synthesis of Pt- Beta zeolite with Bindzil as a binder (Fig. 5) [6]. The characterization results revealed that when Pt was loaded by the method B (Fig. 5) it exhibited the lowest ratio between the metal to acid sites while the highest value was observed for the post synthesized catalyst when the metal was introduced onto the extrudates (method A, Fig. 5). The close vicinity of the metal and acid functions is crucial for selective skeletal isomerization reactions of hydrocarbons (see below).

The metal dispersion is also varied depending on the metal particle location [4,42]. For these extrudates the highest metal dispersion has been obtained when the metal is either located on the zeolite and on both zeolite and the binder, while if the metal is exclusively located on a mildly acidic binder, the metal particles are of a larger size [4,43]. Furthermore, it has been shown, that an organic binder can also increase the metal dispersion in extrudates. This was confirmed in [31], when methylcellulose used as an organic binder has increased the metal dispersion [31,41].

Typically, acidity of extrudates with addition of a binder decreased, for example, in Pt-Beta with alumina as a binder acidity decreased with an increasing content of alumina, which has only mild Lewis acidity [8]. It has also been reported, that addition of a binder does not change acidity [5], because the concentration of Brønsted acid sites in extrudates corresponded to the one for Pt/H-USY. It was also pointed out in [5] that due to the dilution of alumina in Pt/H-USY-Al_2O_3 extrudates with 17:83 ratio of the zeolite to boehmite, Brønsted acidity could not be reliably measured with the pyridine adsorption-desorption method. Subsequently *m*-xylene isomerization was taken as a model reaction to determine catalyst acidity, showing indeed that acidity was not affected by shaping [5].

Extruding Ni supported on Beta-zeolite powder with sepiolite as a binder did not affect the structural characteristics of the initial zeolite [32] (Fig. 6).

The X-ray diffraction pattern of the calcined non-reduced Ni/(H-Beta-38 +sepiolite) extrudates contains only reflexes from the Beta-zeolite (PDF No. 00–056–0487) without any additional lines characteristic for the crystallized nickel-containing phases. This may be due to a highly dispersed state of the nickel compounds when the crystallite size is lower than 2.5 nm. The zeolite structure was shown to be intact after extrusion, calcination as well as after subsequent impregnation with a nickel precursor followed by its decomposition at 450 °C for 6 h.

4. Catalytic results using extrudates

4.1. *Catalytic results with acidic/basic extrudates*

Mass transfer limitations were investigated in citronellal cyclization to isopulegol using H-Beta-25 powder and extrudate catalysts [27]. As expected, the effectiveness factor, defined as the ratio between the rate for extrudates and powder catalysts in trickle bed vs batch reactors in cyclisation of citronellal at the same conversion level, was ca. 0.15 indicating presence of mass transfer limitations [7]. The effectiveness factor was dependent on the extrudates diameter decreasing from 0.15 to 0.02 for 1.4 and 3.0 mm thick extrudates, respectively [27]. The effectiveness factor and the catalyst deactivation have been taken into account in mathematical modelling of continuous citral transformations to menthols [31].

Aldol condensation of propanal was studied with two different extrudates, potassium modified USY-attapulgite and USY-bentonite. The latter catalyst with Lewis acid and basic sites was better than K-USY/Bent exhibiting Brønsted and Lewis acidity and thus resulting in pore blocking confirmed by diffusion of fluorescent microprobes (see above) [33]. A poor performance of K-USY-Bent was explained by a lack of basicity and low and uneven potassium loading. It was concluded, that the selection of a binder is crucial in scaling up this catalyst. Continuous synthesis of glycerol carbonate from glycerol and urea was studied using Mg-Al mixed oxide catalyst shaped using bentonite as a binder [19]. The results showed that the extrudates were relatively stable despite minor fouling and that the catalytic activity could be fully restored through calcination at 550 °C. As a comparison, it was observed that the pressure drop was rather high when using extrudates containing alumina, silica or montmorillonite as a binder.

Cracking of 1,3,5-triisopropylbenzene (Fig. 7) was investigated using hierarchical ZSM-5 derived extrudates containing silica as a binder [10]. The results revealed that less deactivation occurred with non-acidic silica as a binder. Furthermore, accumulation of carbonaceous materials decreased with decreasing acidity, while presence of large pores increased catalyst stability.

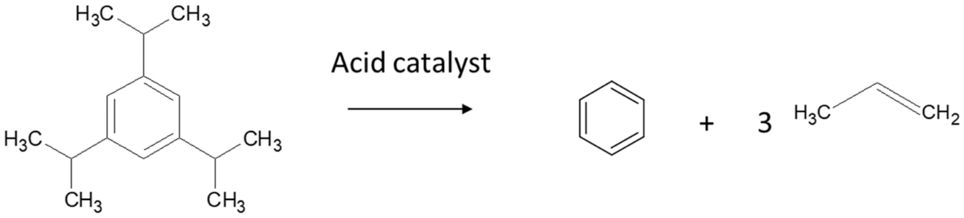

Fig. 7. Reaction scheme for cracking of 1,3,5-triisopropylbenzene.

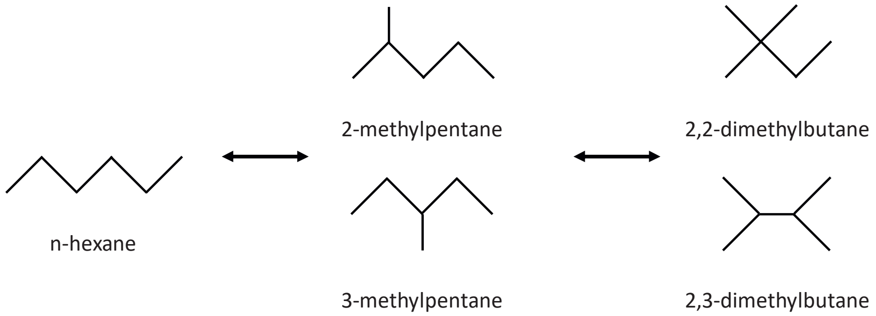

Fig. 8. Reaction scheme for hexane hydroisomerization [6].

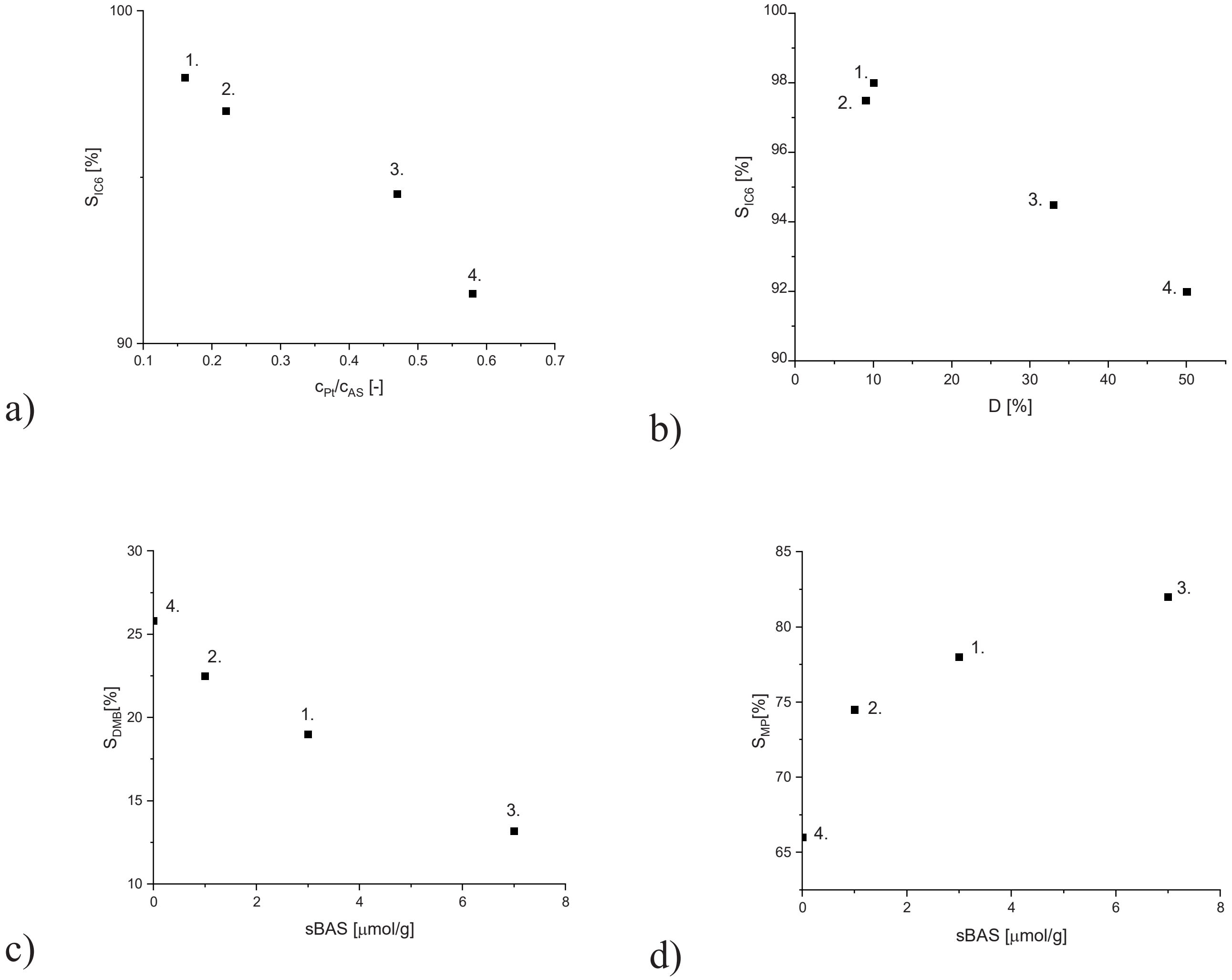

Fig. 9. Selectivity to C6 isomers as a function of a) metal- acid site ratio, b) Pt dispersion, c) selectivity to DMB and d) MP in *n*-hexane isomerization at 5 min time-on-stream at 250 °C [6]. Notation: iC6 - methylpentane, DMB – dimethylbutane, 1. In-situ synthesis, 2. Pt on zeolite, 3. Pt on binder and 4. Post synthesis. sBAS denotes the amount of strong Brønsted acid sites.

4.2. Catalytic results with metal modified extrudates

Metal modified extrudates have been intensively studied in *n*-hexane isomerization [6,7], hydroisomerization of hexadecane [38], transalkylation of benzene derivatives [8] and in one-pot transformation of citronellal and citral [4,37,43,44].

Different Pt extrudates supported on H-Beta-25 and extruded in the presence of Bindzil as a binder were tested in *n*-hexane hydroisomerization (Fig. 8) [6].

These extrudates had different metal location and proximity of metal-to-acid sites. The authors [6] concluded that catalyst deactivation was mainly influence by the metal location compared to the metal-to-acid site ratio or proximity of the active sites. The highest selectivity to C6 isomer was obtained with B-type extrudates (Fig. 5), in which Pt was located both on a binder and a support and its $c_{Pt}/c_{acid\ site}$ was the lowest among the studied catalysts (Fig. 9). Analogous results were obtained in hydroisomerization of hexadecane (Fig. 10) [38].

Although turnover frequency calculated per zeolite Al^{IV} site in

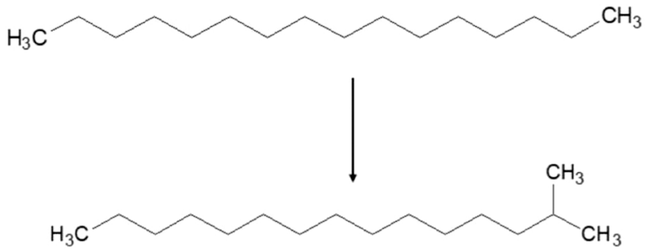

Fig. 10. Catalytic hydroisomerization of hexadecane to 1-methylpentadecane.

hydroisomerization of hexadecane was independent on the Pt location, the yield of the desired C16 isomer, 1-methylpentadecane was the highest when Pt was located on a zeolite [38]. This result was explained by a larger distance between Pt and the acid sites when Pt is on the alumina binder in comparison to Pt location on a zeolite. It was, however, also pointed out that both Pt-acid site intimacy and a proper balance between the metal and acid site concentration should be fulfilled [38].

The effect of the metal location in the extrudates was also studied for citronellal and citral transformations to menthol with Ru and Pt as metals (Fig. 11) [4,37,43,44].

It was interesting to observe that the metal location and the distance between the metal and acid sites were very prominent determining selectivity towards different products. The highest menthol yield, 32% was obtained in citronellal transformations at 70 °C under 10 bar hydrogen with the Ru extrudates when Ru was loaded directly on H-MCM-41 support after which the extrudates were made using Bindzil as a binder. This catalyst exhibited mild acidity, a rather high ratio between the ruthenium and acid sites, and the shortest distance between the metal and acid sites [37].

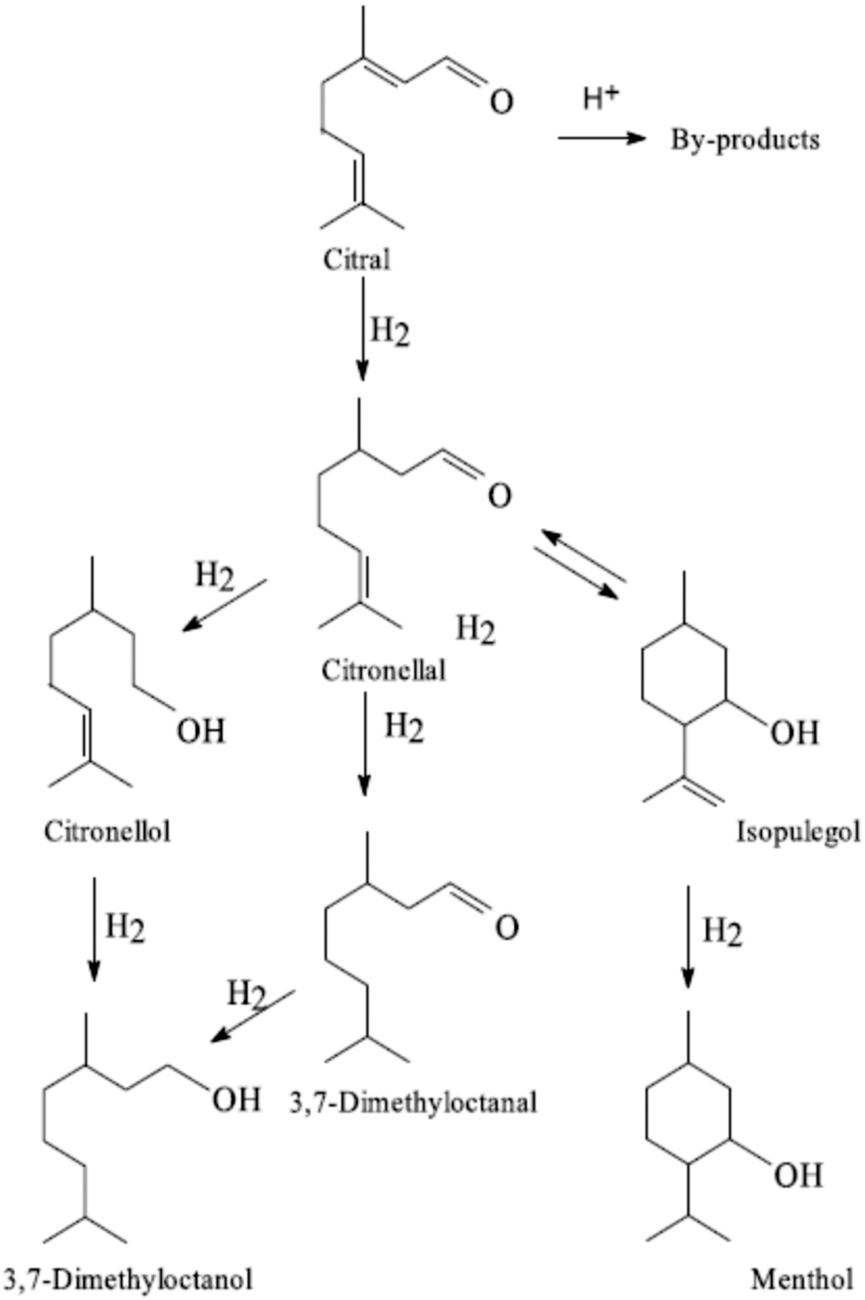

Fig. 11. Reaction scheme for one-pot synthesis of menthol from citral [31].

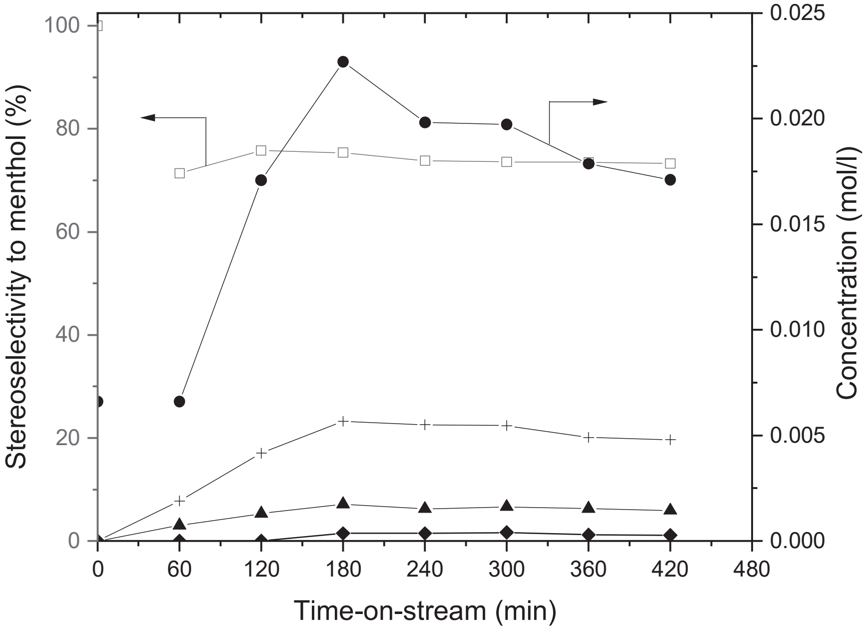

Fig. 12. Transformations of citral to menthol (●), neomenthol (+), isomenthol (◆) and neoisomenthol and stereoselectivity to menthol (□) in solution in cyclohexane (0.086 M) at 70 °C for 1 g catalyst, flow rate of citral solution 0.4 mL/min; H_2 flow rate 100 mL/min, 20 bar total pressure [32].

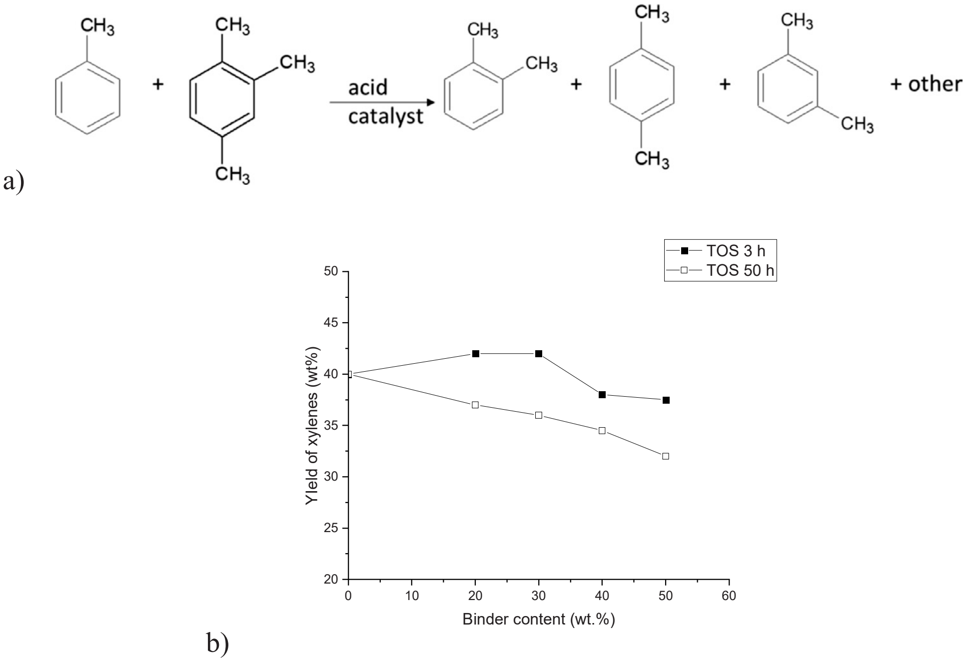

Fig. 13. a) Reaction scheme for transalkylation of 1,2,4-trimethylbenzene with toluene, b) Xylene yields in transalkylation of 1,2,4-trimethylbenzene with toluene at 400 °C under 10 bar with H_2/hydrocarbons ratio of 4 and WHSV of 5 h^{-1} [8].

In [4] citronellal transformations were performed over Pt containing extrudates, in which Beta-25 was used as a support and bentonite as a binder. Analogously to [37] the highest menthol yield was obtained at 35 °C under 10 bar hydrogen over in situ synthesized Pt/H-Beta-25 and bentonite extrudate [4]. The best catalyst contained the lowest concentration of weak acid sites as well as the Brønsted acid sites. As a comparison, Ru-extrudates were also used in citral transformation to menthols [43,44]. These Ru-MCM-41 [43] and Ru-H-Y-80 [44] extrudates both with Bindzil as a binder were not, however, selective to menthols in citral transformations at 70 °C under 10 bar hydrogen. In the former case, when experiments were performed in the presence of diffusional limitations, different location of Ru, being on a binder, on a support or on both, did not have any major effect on selectivity [42]. Analogously, differences in the product selectivity compared to [42] were suppressed for Ru/Bindzil extruded with 70 wt% H-Y-80 and for Ru/H-Y-80 extruded with 30 wt% Bindzil in the presence of internal mass transfer limitations [44].

High selectivity to menthol was recently obtained over Ni-mesoporous alumosilicate- sepiolite extrudates [31]. Rapid catalyst deactivation, however, occurred and menthol selectivity decreased linearly with decreasing conversion [31]. Catalyst deactivation was partially explained by leaching of Ni as well as pore blocking. In [31] also the effect of hydrogen pressure was investigated showing that the reaction order with respect to hydrogen was close to zero. However, under lower hydrogen pressure, catalyst deactivation was more prominent. It should also be pointed out that in [31] a kinetic model was developed being able to describe the effect of internal and external mass transfer. Ni supported on H-Beta-38-sepiolite composite catalyst in the form of extrudates was reported to provide relatively high menthols yield of 53% and 49% and stereoselectivity to menthol of 71–76% and 72–74% from citronellal and citral, correspondingly (Fig. 12) [32].

Transalkylation of 1,2,4-trimethylbenzene with toluene was investigated using Pt-Beta extrudates containing Al_2O_3 as a binder (Fig. 13) [8]. The catalytic activity decreased with increasing the amount of binder [45], while the yield of xylene decreased slightly with time-on-stream when the binder content was elevated. At 50 h time-on-stream major catalyst deactivation occurred at a higher binder content (Fig. 13). Another explanation for less efficient performance of extrudates with a large amount of alumina as a binder can be re-distribution of Pt particles due to migration of alumina into the framework and presence of Pt particles in the mesopores of the binder.

Extruded catalysts with cylindrical geometry based on K_2CO_3/γ-Al_2O_3/sepiolite containing magnetic particles (Fe_3O_4) were shown to be efficient in the transesterification of sunflower oil with ethanol reaching 88% yield in ethanolic biodiesel [9].

5. Conclusions and future outlook

Shaping of the catalysts started to be intensively studied during the recent years, because of a lack of systematic knowledge about catalyst properties and their changes during extrusion for different types of binders and additives. Furthermore, interconnectivity of pores, which has a large impact on catalytic properties, has been recently investigated with advanced characterization methods including pulse field gradient NMR spectroscopy and the fluorescent probe analysis.

The special emphasis has been put on the effect of metal location in the extrudate, namely on the support or on a binder. In acid/base catalyzed reactions few model reactions have been investigated with extrudates, e.g. aldol condensation, isomerization of citronellal and cracking of benzene derivatives. Several extrudate properties are crucial in performing these reactions resulting in differences in catalyst stability and pressure drop for different binders. For bifunctional catalysts the metal location has a large impact on the metal particle size, proximity of the metal and acid sites and acidity, especially in hydroisomerization of hydrocarbons or in one-pot synthesis of menthol from citronellal and citral.

The recent results obtained from systematic studies with extruded catalysts prepared by different methods and covering synthesis, characterization and testing are very valuable, giving more in depth knowledge of the applicability of extrudates and defining the challenges, which remain to be solved for their efficient industrial use. One important question, requiring further research, is how interactions between the additives and active species affect the catalyst properties. Furthermore, a need to investigate interconnectivity of pores, amounts of the metal and acid sites, their location and mutual influence has been identified. Furthermore, academic research focusing on potentially attractive catalytic materials should also explore the effect of the mass transfer on activity and selectivity by calculating for example the effectiveness factor. The above-mentioned studies are, however, very scarce in the academic literature being often limited to few specific reactions, like hydrocracking or hydroisomerization of alkanes. It should also be emphasized here that laboratory scale extrudates do not necessarily exhibit the same properties as industrial scale extrudates, especially in terms of rheology or mechanical strength, etc. The authors strongly encourage continuation of research and systematic studies on the exciting topic of shaped catalysts to provide a better control on the active metal/acid site location despite an apparent lack of glamour in doing this compared with e.g. synthesis of catalytically active phases per se.

CRediT authorship contribution statement

Päivi Mäki-Arvela: Conceptualization, Writing first draft. ***Irina Simakova:*** Investigation, Writing – review & editing. ***Zuzana Vajglová:*** Investigation, Writing – review & editing. ***Narendra Kumar:*** Investigation, Writing – review & editing. ***Dmitry Yu Murzin:*** Supervision, 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.

Data availability

Data will be made available on request.

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References

[1] D.Yu Murzin. Engineering catalysis, 2d edition.,, deGruyter,, Berlin, 2020.
[2] D.Yu Murzin, Mesolevel bifunctional catalysts, Kinet. Catal. 61 (1) (2020) 80–92.
[3] R. Bingre, B. Louis, P. Nguyen, An overview on zeolite shaping technology and solutions to overcome diffusion limitations, Catalysts 8 (2018) 163.
[4] M. Azkaar, P. Mäki-Arvela, Z. Vajglová, V. Fedorov, N. Kumar, L. Hupa, J. Hemming, M. Peurla, A. Aho, D.Yu Murzin, Synthesis of menthol from citronellal over supported Ru-and Pt-catalysts in continuous flow, React. Chem. Eng. 4 (2019) 2156–2169.
[5] P.S. Mendes, J.M. Silva, M.F. Ribeiro, A. Daudin, C. Bouchy, From powder to extrudate zeolite-based bifunctional hydroisomerization catalysts: on preserving zeolite integrity and optimizing Pt location, J. Ind. Eng. Chem. 62 (2018) 72–83.
[6] Z. Vajglová, N. Kumar, M. Peurla, L. Hupa, K. Semikin, D.A. Sladkovskiy, D. Yu Murzin, Deactivation and regeneration of Pt-modified zeolite Beta–Bindzil extrudates in *n*-hexane hydroisomerization, J. Chem. Techn. BioTechn. 96 (6) (2021) 1645–1655.
[7] Z. Vajglová, N. Kumar, P. Mäki-Arvela, K. Eränen, M. Peurla, L. Hupa, M. Nurmi, M. Toivakka, D.Y. Murzin, Synthesis and physicochemical characterization of shaped catalysts of β and Y zeolites for cyclization of citronellal, Ind. Eng. Chem. Res. 58 (2019) 18084–18096.
[8] F.M. Almulla, S.A. Ali, M.R. Aldossary, E.I. Alnaimi, V.I. Zholobenko, A. bin Jumah, A.A. Garforth, On the influence of alumina as a binder on the performance of Pt-beta catalyst during the transalkylation of toluene and 1, 2, 4-trimethylbenzene, Micro Mesop. Mat. 320 (2021), 131095.
[9] E. Garcia Silveira Jr., O. Rodriguez Justo, V. Haber Perez, I. Reyero, A. Serrano-Lotina, L. Campos Ramirez, D.F. dos Santos Dias, Extruded catalysts with magnetic properties for biodiesel production, Adv. Mater. Sci. Eng. 2018 (2018) 3980967.
[10] S. Zhao, D. Collins, L. Wang, J. Huang, Influence of ZSM-5 porosity and binder introduction on the coke formation in the cracking of 1,3, 5-triisopropylbenzene, Catal. Today 368 (2021) 213–216.
[11] Z. Vajglová, I.L. Simakova, K. Eränen, P. Mäki-Arvela, N. Kumar, M. Peurla, S. Tolvanen, A. Efimov, L. Hupa, J. Peltonen, D.Yu Murzin, The physicochemical and catalytic properties of clay extrudates in cyclization of citronellal, Appl. Catal. A Gen. 629 (2021), 138426.
[12] J. Lefevere, L. Protasova, S. Mullens, V. Meynen, 3D-Printing of hierarchical porous ZSM-5: the importance of the binder system, Mater. Des. 134 (2017) 331–341.
[13] U.N.S. Hareesh, R. Anantharaju, P. Biswas, K. Rajeswari, R. Johnson, Colloidal shaping of alumina ceramics by thermally induced gelation of methylcellulose, J. Am. Ceram. Soc. 94 (2011) 749–753.
[14] D.P. Serrano, R. Sanz, P. Pizarro, I. Moreno, P. de Frutos, S. Blazquez, Preparation of extruded catalysts based on TS-1 zeolite for their application in propylene epoxidation, Catal. Today 143 (2009) 151–157.
[15] N.E. Kiratzis, P.F. Luckham, The rheology of aqueous alumina suspensions in the presence of hydroxyethylcellulose as binder, J. Eur. Cer. Soc. 19 (15) (1999) 2605–2612.
[16] A. Ozcan, H. Kalipcilar, Preparation of zeolite A tubes from amorphous aluminosilicate extrudates, Ind. Eng. Chem. Res. 45 (2006) 4977–4984.

[17] G.T. Whiting, S.H. Chung, D. Stosic, A.D. Chowdhury, L.I. Van Der Wal, D. Fu, J. Zevevic, A. Travert, K. Houben, M. Baldus, B.M. Weckhuysen, Multiscale mechanistic insights of shaped catalyst body formulations and their impact on catalytic properties, ACS Catal. 9 (2019) 4792–4803.

[18] G.T. Whiting, N. Nikolopoulos, I. Nikolopoulos, A.D. Chowdhury, B. M. Weckhuysen, Visualizing pore architecture and molecular transport boundaries in catalyst bodies with fluorescent nanoprobes, Nat. Chem. 13 (2019) 23–31.

[19] G.M. Lari, A.B. de Moura, L. Weimann, S. Mitchell, C. Mondelli, J. Pérez-Ramírez, Design of a technical Mg–Al mixed oxide catalyst for the continuous manufacture of glycerol carbonate, J. Mater. Chem. A 5 (2017) 16200–16213.

[20] Y.V. Vatutina, K.A. Nadeina, O.V. Klimov, M.O. Kazakov, I.G. Danilova, S. V. Cherepanova, D.F. Khabibulin, E.Yu Gerasimov, I.P. Prosvirin, P.P. Dik, A. S. Noskov, Peptization of alumina by ammonia to adjust catalytic properties of NiMo/B-Al_2O_3 hydrotreating catalysts, Catal. Today 375 (2021) 377–392.

[21] V.V. Zhivonitko, Z. Vajglová, P. Mäki-Arvela, N. Kumar, M. Peurla, D.Yu Murzin, Diffusion measurements of hydrocarbons in zeolites with pulse-field gradient nuclear magnetic resonance spectroscopy, Russ. J. Phys. Chem. A 95 (2021) 547–557.

[22] V.V. Zhivonitko, Z. Vajglová, P. Mäki-Arvela, N. Kumar, M. Peurla, V.V. Telkki, D. Yu Murzin, Diffusion measurements of hydrocarbons in H-MCM-41 extrudates with pulsed-field gradient nuclear magnetic resonance spectroscopy, Phys. Chem. Chem. Phys. 24 (2022) 8269–8278.

[23] N.L. Michels, S. Mitchell, J. Perez-Ramirez, Effects of binders on the performance of shaped hierarchical MFI zeolites in methanol-to-hydrocarbons, ACS Catal. 4 (2014) 2409–2417.

[24] L. Gueudré, M. Milina, S. Mitchell, J. Pérez-Ramírez, Superior mass transfer properties of technical zeolite bodies with hierarchical porosity, Adv. Funct. Mater. 24 (2014) 209–219.

[25] S.P. Verkleij, G.T. Whiting, S. Parres Esclapez, S. Li, M.M. Mertens, M. Janssen, A. J. Bons, B.M. Weckhuysen, High-pressure operando UV-Vis micro-spectroscopy of coke formation in zeolite-based catalyst extrudates during the transalkylation of aromatics, ChemCatChem 13 (2020) 5465–5475.

[26] E.J.W. Verwey, Theory of the stability of lyophobic colloids, J. Phys. Chem. 51 (1947) 631–636.

[27] Z. Vajglová, N. Kumar, P. Maki-Arvela, K. Eranen, M. Peurla, L. Hupa, D. Yu Murzin, Effect of binders on the physicochemical and catalytic properties of extrudate-shaped beta zeolite catalysts for cyclization of citronellal, Org. Proc. Res. Dev. 23 (2019) 2456–2463.

[28] K.Y. Lee, H.K. Lee, S.K. Ihm, Influence of catalyst binders on the acidity and catalytic performance of HZSM-5 zeolites for methanol-to-propylene (MTP) process: single and binary binder system, Top. Catal. 53 (2010) 247–253.

[29] P.S. Mendes, A.L. Taleb, A.S. Gay, A. Daudin, C. Bouchy, J.M. Silva, M.F. Ribeiro, Nanoscale insights into Pt-impregnated mixtures of zeolites, J. Mater. Chem. A 5 (2017) 16822–16833.

[30] Z. Vajglová, N. Kumar, M. Peurla, J. Peltonen, I. Heinmaa, D.Y. Murzin, Synthesis and physicochemical characterization of beta zeolite-bentonite composite materials for shaped catalysts, Catal. Sci. Technol. 8 (2018) 6150–6162.

[31] I.L. Simakova, Z. Vajglová, P. Mäki-Arvela, K. Eränen, L. Hupa, M. Peurla, E. Mäkilä, J. Wärnå, D.Yu Murzin, Citral-to-menthol transformations in a continuous reactor over Ni/mesoporous aluminosilicate extrudates containing a sepiolite clay binder, Org. Proc. Res. Dev. 26 (2022) 387–403.

[32] I. Simakova, P. Mäki-Arvela, M. Martinez-Klimov, J. Muller, Z. Vajglova, M. Peurla, K. Eränen, D.Y. Murzin, Continuous synthesis of menthol from citronellal and citral over Ni-beta-zeolite-sepiolite composite catalyst, Appl. Catal. A: Gen. 636 (2022), 118586.

[33] M. Hernández-Giménez, L.M. de Kort, G.T. Whiting, H. Hernando, B. Puértolas, J. Pérez-Ramírez, C.A.J. Bruijnincx, B.M. Weckhuysen, Upscaling effects on alkali metal-grafted ultrastable Y zeolite extrudates for modeled catalytic deoxygenation of bio-oils, ChemCatChem 13 (2021) 1951–1965.

[34] L. Lakiss, J.P. Gilson, V. Valtchev, S. Mintova, A. Vicente, A. Vimont, R. Bedard, S. Abdo, J. Bricker, Zeolites in a good shape: catalyst forming by extrusion modifies their performances, Micro Mesop. Mat. 299 (2020), 130134.

[35] G.T. Whiting, A.D. Chowdhury, R. Oord, P. Paalanen, B.M. Weckhuysen, The curious case of zeolite–clay/binder interactions and their consequences for catalyst preparation, Far. Disc. 188 (2016) 369–386.

[36] B. Wang, X. Yan, H. Zhang, Interaction between phosphorus and zeolite/binder: a realumination study on beta zeolites, Micro Mesop. Mater. 313 (2021), 130735.

[37] Z. Vajglová, N. Kumar, M. Peurla, K. Eränen, P. Mäki-Arvela, D.Yu Murzin, Cascade transformations of (±)-citronellal to menthol over extruded Ru-MCM-41 catalysts in a continuous reactor, Catal. Sci. Techn. 10 (2020) 8108–8119.

[38] P.S. Mendes, J.M. Silva, M.F. Ribeiro, A. Daudin, C. Bouchy, Bifunctional intimacy and its interplay with metal-acid balance in shaped hydroisomerization catalysts, ChemCatChem 13 (2020) 4582–4592.

[39] B. de Lucas, P. Sánchez, A. Fúnez, M.J. Ramos, J.L. Valverde, Liquid-phase hydroisomerization of n-octane over platinum-containing zeolite-based catalysts with and without binder, Ind. Eng. Chem. Res. 45 (2006) 8852–8859.

[40] A. Aranzabal, D. Iturbe, M. Romero-Sáez, M.P. González-Marcos, J.R. González-Velasco, J.A. González-Marcos, Optimization of process parameters on the extrusion of honeycomb shaped monolith of H-ZSM-5 zeolite, Chem. Eng. J. 162 (2010) 415–423.

[41] Z. Vajglová, N. Kumar, M. Peutia, L. Hupa, K. Semikin, D.A. Sladkoyskiy, D. Yu Murzin, Effect of the preparation of Pt-modified zeolite beta-bentonite extrudates on their catalytic behavior in n-hexane hydroisomerization, Ind. Eng. Chem. Res. 58 (2019) 10875–10885.

[42] F. Ribeiro, C. Marcilly, Étude de la technique d′échange ionique avec compétition. Cas du dépôt de platine sur support solide acide par échange cationique, Rev. l′Inst. Fr. Pétr 34 (1979) 405–428.

[43] Z. Vajglová, P. Mäki-Arvela, K. Eränen, N. Kumar, M. Peurla, D.Y. Murzin, Catalytic Transformations of citral in a continuous flow over bifunctional Ru-MCM-41 extrudates, Catal. Sci. Technol. 13 (2021) 2873–2884.

[44] Z. Vajglová, M. Navas, P. Mäki-Arvela, K. Eränen, N. Kumar, M. Peurla, D. Y. Murzin, Transformations of citral over bifunctional Ru-H-Y-80 extrudates in a continuous reactor, Chem. Eng. J. 429 (2022), 132190.

[45] Y. Zhang, Y. Zhou, A. Qiu, Y. Wang, Y. Xu, P. Wu, Effect of alumina binder on catalytic performance of PtSnNa/ZSM-5 catalyst for propane dehydrogenation, Ind. Eng. Chem. Res. 45 (2006) 2213–2219.