Transformations of aromatic hydrocarbons over zeolites

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Abstract—Aromatic hydrocarbons represent an important group of starting materials, intermediates, as well as final products produced in the chemical industry in the range from large processes in petrochemistry up to the synthesis of fine chemicals. This short overview covers the recent achievements in acid-catalyzed transformations of aromatic hydrocarbons with a special focus on alkylation isomerization—disproportionation reactions in petrochemistry, and acylations or condensations used mainly in synthesis of chemical specialties. In the case of fine chemical synthesis, some zeolite applications in the preparation of important intermediates for pharmaceutical or fragrance products are presented. Advantages and disadvantages of the various types of zeolite are discussed in these reactions from the point of view of their (shape) selective properties, as well as the accessibility of acid sites.

Keywords: Aromatic hydrocarbons; zeolites; alkylation; isomerization; acylation; condensation; fine chemicals.

INTRODUCTION

Aromatic hydrocarbons represent about 30% of the total of 8–9 million known organic compounds and the amount of aromatic chemicals produced by organic chemical industry is of a similar order [1]. From this point of view the world overall demand for benzene was estimated to be around 33 million ton. The most important products starting from benzene are ethyl benzene, cumene, *p*-diethyl benzene, cymenes, *p*-di-isopropyl benzenes and linear C_{10} – C_{14} alkyl benzenes [2, 3], which are prepared by acid-catalyzed alkylations, most of them including zeolite catalysts [4].

The traditional technologies for petrochemical transformations of aromatic hydrocarbons used in the past and sometimes still in use employ harmful strong mineral or Lewis acids like HF or H₂SO₄, and AlCl₃, which exhibit severe corrosion

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and environmental drawbacks. Since the early 1980s zeolite-based catalysts [5-7]have been playing a dominant role in acid-catalyzed reactions, resulting in a development of new technologies for benzene alkylation with ethylene or propylene, toluene alkylation and disproportionation [8-13], ethyl benzene alkylation [14], xylene isomerization [15-17] and recently also some transalkylation reactions [2, 4]. In 2001 around 1.5 million metric ton of synthetic zeolites was produced in the world, of which ca 13% was applied as catalyst. Zeolite ZSM-5 is the most important zeolite catalyst for various petrochemical shape-selective transformations of di-alkyl aromatics [3, 4]. Simultaneously this zeolite serves as a extremely useful model zeolite for investigations on the role of shape-selectivity and transport on the activity and selectivity in these transformations [18]. Reaction mechanisms of transformations of aromatic hydrocarbons over zeolites are nowadays much better understood due to the substantial employment of *in situ* techniques like MAS-NMR or FT-IR spectroscopy [19, 20]. These techniques provide detailed information on the role of zeolites in these transformations and on the role of individual reaction steps. In addition, some zeolites exhibit interesting cage effects in alkylation reactions or with others the reactions can proceed almost exclusively on the "external" surface of zeolite crystals [21, 22].

While petrochemical reactions have been very frequently investigated over zeolites since the early 1980s, catalytic applications of zeolites in synthesis of fine chemicals have attracted increasing attention only over the last one or two decades [23]. In this respect zeolites offer several important advantages for, e.g., acylation reactions over "above-stoichiometric" initiators like AlCl₃ as "true" heterogeneous catalytic behaviour, possibility of regeneration and environmental tolerance. In addition, shape selective properties of zeolites can substantially increase the resulting selectivity to desired products [24, 25]. A real breakthrough in this area was announced by Rhodia [26]. Fix-bed technology processes for the acylation of anisole and veratrol were announced, leading to a significant simplification of the process, reduction of operating costs and a substantial decrease in an effluent volume [23].

The objective of this overview is to cover the recent advances in the application of zeolite-based catalysts in acid-catalyzed reactions of aromatic hydrocarbons, namely alkylations, isomerizations, disproportionations, as well as acylations or acetalization. The role of various zeolite structural types on the activity, transport and selectivity to desired products is discussed in the view of the differences in size and connectivity of their channels and the role of the "external" surface.

ALKYLATION AND ISOMERIZATION OF AROMATICS

Benzene, toluene and xylenes represent the most important raw materials for the production of various commodities like styrene and related polymers, nylon, polyurethane plastics, foams and polyesters [3]. Benzene is mainly used for alkylation with ethylene to ethyl benzene (for production of styrene monomer) and with propylene to cumene (for phenol production). Both of these processes originally employed ZSM-5 zeolite and were carried out in a gas phase. Further research resulted in new liquid phase processes using different structural types of zeolites applied by different companies [2, 4]. Toluene is mainly converted to benzene and a mixture of xylenes *via* toluene disproportionation, alkylated with propylene to cymenes for cresol production, chlorinated or nitrated. In the case of xylene different phthalic acids are prepared *via* oxidation of the respective xylene isomers and transformed further to resins. With regard to that xylene isomerization, frequently used as testing reaction for exploration of zeolite structures [27], increases the selectivity to the more desired *para-* and *ortho*-isomers [13].

Benzene alkylation

Alkylation of benzene with ethylene or propylene industrially represents the most important alkylation reactions leading to ethyl benzene and propyl benzene, respectively [3, 4, 8]. Originally, benzene alkylation with propylene was carried out using solid phosphoric acid, which was later on replaced by aluminium chloride. These two acids were employed industrially up to the 1980s when Mobil introduced new gas-phase technologies based on medium-pore zeolite ZSM-5 (Fig. 1). Since that time zeolites have dominated the market with benzene alkylation technologies, although a substantial improvement in their efficiency was achieved by shifting the reaction conditions from gaseous to liquid phase. Particularly in benzene alkylation with propylene several new technologies are offered by different companies using large-pore zeolites in contrast to previously utilized ZSM-5 in the gas phase [4]. During the last 15 years several companies introduced to the market new processes on cumene production and all of them provide cumene yields around 99%. This was achieved by applying liquid phase conditions for benzene alkylation and particularly large-pore zeolites, which decrease the formation of undesired *n*-propyl benzene to concentrations lower than 200–300 ppm. The zeolite catalysts include dealuminated (3-D) mordenite (Dow Chemicals [28]), non-disclosed zeolite cata-



Figure 1. Structure of zeolites ZSM-5 (A) and mordenite (B).



Figure 2. Structure of zeolites Beta (A) and MCM-22 (B).

lyst by UOP (Q-Max), zeolite Beta (Eni) and MCM-22 (Mobil). The schematic pictures of channel systems of zeolites Beta and MCM-22 are given in Fig. 2. All of these processes seemed to achieve a high maturity but still some improvements could be achieved, as it will be shown for benzene alkylation with ethylene (later in the text). Degnan *et al.* [29] reported that 14 industrial units for cumene production were under operation in 2001.

Xylene isomerization

The reaction mechanism of xylenes isomerization was investigated by a number of researchers, resulting in the proposal that zeolite structure controls the ratio between monomolecular and bimolecular mechanism [27, 30]. Corma and Sastre proposed that void reaction volume controls the mechanism of xylene isomerization. While a monomolecular mechanism operates in medium pore zeolites, large-pore zeolites and particularly those having large cavities, like zeolite Y, enable the bimolecular mechanism, leading also to the formation of trimethyl benzenes, as well as toluene as reaction intermediates. *m*-Xylene is usually used as the model reactant as both isomerization to *ortho*- and *para*-isomers, as well as transalkylation with another xylene molecule can proceed. The relative diffusion coefficients of these three xylene isomers are in the order *para/ortho/meta* = 1000:10:1 [15], which clearly emphasizes the role of transport with decreasing pore size of zeolites. In this respect, a particular interest in activities and selectivities in xylene isomerization is focused on zeolites possessing peculiar structures like SSZ-33 [31] or MCM-68 [32] combining 10- and 12-membered rings (Fig. 3). Catalytic and diffusion behaviour of all these zeolites is strongly influenced by the void reaction volume provided in zeolite intersections [33]. The larger this volume is, the larger intermediates can be formed inside, which can shift the ratio between monomolecular and bimolecular reactions towards the bimolecular ones. In the case of SSZ-33 Jones et al. [16] reported that at low flow rates of *m*-xylene the ratios *paralortho*, as well as isomerization/disproportionation are decreasing. The authors ascribed these results



Figure 3. Schematic pictures of channels of zeolites SSZ-33.

to external diffusional limitations at low flow rates. Simultaneously, the decrease in *paralortho* and isomerization/disproportionation ratios could be explained by a longer contact time, which shifts the concentrations of individual products more to thermodynamic equilibrium ones. Deactivation of the "external" surface of SSZ-33 enhances the differences between diffusion coefficients of xylene isomers, which lead to higher *paralortho* ratios. In a similar way Zheng *et al.* [20] described the selectivities to xylene isomers investigating the rate of diffusion and rate of the isomerization of individual xylenes over ZSM-5 zeolite with surface modified by silylation. Surface modification suppressed acid sites located in the pore entrances and increased the role of transport compared with parent zeolite. This led to the increasing concentration of *m*-xylene, as the most bulky isomer, in the pores and enhanced selectivity to *p*-xylene.

Very recently, Corma's group has shown the catalytic behaviour of *m*-xylene over ITQ-13, the first synthesized zeolite [34], exhibiting intersected 9- and 10-membered ring channels (Fig. 4) [35]. In the structure of this zeolite, the 9-membered ring is 0.40×0.48 nm and this channel is perpendicular with the 10-membered ring channel (they are interconnected) having a cross-section of 0.48×0.53 nm. At the conversion level of about 20% ITQ-13, similar to ZSM-5, discriminated disproportionation of *m*-xylene while monomolecular isomerization proceeded very easily. Trimethyl benzene product distribution and docking calculations indicated that all three trimethyl benzene isomers can be formed in channel intersections, while only the smallest one (1,2,4-trimethyl benzene) can diffuse from the zeolite crystals through 10-membered rings (not in 9-membered rings). *Ortho-* and *meta*-xylenes also cannot diffuse in 9-membered rings, in contrast to *para*-xylene, however, it is much restricted than in the 10-membered ring channel [35].

From the comparison of the reaction rates in toluene, *m*-xylene and 1,2,4-trimethyl benzene transformations it is evident that the reaction rate increases in the sequence toluene < m-xylene < 1,2,4-trimethyl benzene [36]. This clearly indicates that diffusion is not the only parameter that controls the rate of the transformation reaction as a higher diffusivity does not necessarily translates to a higher reactivity, as toluene with the highest diffusivity was found to be the least reactive.



Figure 4. Structure of the 9- (A) and 10-membered (B) ring of zeolite ITQ-13.

Advanced zeolite-based catalysts

The exploitation of zeolites in petrochemical reactions is attributed to their microporous character, which is responsible for the shape-selectivity being advantageously used to achieve high selectivities to especially *para*-isomers [4]. However, practically all petrochemical applications of zeolites suffer from the low transport of reactants and products in the zeolite channel systems. In this respect, two challenging approaches were recently proposed: (i) application of mesoporous zeolite single crystals synthesized in the presence of carbon particles or nanotubes as secondary templates [37, 38], (ii) utilization of micro/mesoporous composites prepared from zeolite nanoparticles assembled into the mesoporous structure [39, 40]. Mesoporous ZSM-5 exhibited superior catalytic activity in benzene alkylation with ethylene; selectivity to ethyl benzene, particularly at higher conversion levels was also much higher compared with conventional ZSM-5. Scanning electron micrograph images of conventional ZSM-5 and mesoporous ZSM-5 show a difference in the roughness of the external surface due to the addition of carbon black particles to the synthesis mixture (cf., Fig. 5). In the case of m-xylene isomerization a substantial increase in the activity of this zeolite was observed after inducing mesoporous structure, which was related to a decrease in the selectivity to *para*-isomers probably due to a shorter contact time [38]. As an example of oxidation reaction with hydrogen peroxide, styrene was converted to styrene oxide [38]. Micro/mesoporous composite consisting of Beta/MCM-41 reached comparable conversion with industrial Beta zeolite in toluene alkylation with isopropyl alcohol [41]. Further increases in catalytic activity of Beta/MCM-41 composite materials were reported for cyclization of citronellal to (\pm) -isopulegol [42], benzene long-chain alkylation with 1-dodecene [43] and ethyl benzene alkylation [44].



Figure 5. SEM images of zeolite ZSM-5 (A) and mesoporous zeolite ZSM-5 (B).

SYNTHESIS OF CHEMICAL SPECIALTIES

Aromatic hydrocarbons also play an extremely important role as intermediates and products in the fine chemical industry or production of specialty chemicals. Although the amount of aromatic hydrocarbons used in this area is only 2–3% of the overall production of aromatic hydrocarbons, they include hundreds and hundreds of extremely important substances extensively applied in the pharmaceutical, flavour and fragrance industry or in agriculture. These aromatic hydrocarbons can be synthesized by various reactions like, e.g., alkylations, isomerizations, condensations or even metathesis reactions [45]. This chapter briefly discusses some recent achievements in the application of zeolites for acid catalyzed acylation reactions of aromatic hydrocarbons in the synthesis of fine chemicals, more details can be found in a recent review paper [46].

Acylations for pharmaceutical intermediates

Naproxen and Ibuprofen are well-known pharmaceuticals, the synthesis of which includes one or even two acylation steps, respectively. Although industrially they are still synthesised using aluminium trichloride or hydrofluoric acid, zeolite-based catalysts offer particular advantages over conventional acylation catalysts due to their environmental tolerance, no waste problems and lack of aggresive medium for running of the reactions.

Naproxen (2-(6-methoxy-2-naphthyl)propionic acid) is an important antiinflammatory drug, the intermediate of this synthesis is 2-acetyl-6-methoxy naphthalene. Acylation of 2-methoxy naphthalene is kinetically preferred to the 1-position. Selective formation of 2-acetyl-6-methoxy naphthalene gaves an interesting potential for application of zeolites with proper channel sizes (Scheme 1).

Screening of different structural types of zeolites resulted in the conclusion that the large-pore zeolite Beta with a three-dimensional channel system is the highly



Scheme 1. Acylation of 2-methoxy naphthalene with acetic anhydride to 2-acetyl-6-methoxy naphthalene and 1-acetyl-2-methoxy naphthalene.



Figure 6. Channels of Beta polymorph C.

active catalyst in this acylation reaction [24, 47–50]. Heinichen and Hölderich shown that catalytic activity of zeolite Beta is enhanced due to the formation of extraframework aluminium species while acid treatment increases the activity of the "external surface" due to the extraction of aluminium species out of the micropores [47]. The slightly smaller diameter of polymorph C of zeolite Beta [51, 52] resulted in a decrease in the catalytic activity compared with zeolite Beta; however, the selectivity to 2-acetyl-6-methoxy naphthalene was higher. This result was explained by different diffusivities of individual isomers in zeolite Beta is shown in Fig. 6. Further increase in the selectivity to 2-acetyl-6-methoxy naphthalene can be achieved by a passivation of the external surface of zeolite Beta by coating with amorphous silica [49]. Comparing the reaction behaviour in liquid and gas phase, it can be concluded that the contribution of undesirable reactions leading to the formation of organic deposits strongly increases with increasing reaction temperature.

Hoechst-Celanese and Boots processes are used for the synthesis of Ibuprofen [53] and they include the acylation of benzene with isobutyric acid derivatives to isopropylphenyl ketone followed by hydrogenation to isobutyl benzene, with another consecutive acylation with acetic anhydride to p-isobutyl acetophenone. Klisáková *et al.* modelled the first acylation step using toluene instead of benzene as a substrate (Scheme 2) [54, 55]. All three isomers of isopropyltolyl ketones were found among reaction products with a preferential selectivity for the *para*-isomer due to the shape-selective effect of the zeolite channel system.

Acylation of toluene was investigated in a liquid phase with a number of different structural types of zeolites and with isobutyric anhydride or isobutyryl chloride as acylating agents in batch mode. The highest selectivities (around 90%) for the *para*-isomer were achieved with H-ZSM-5 and H-mordenite; however, the conversion of acylating agents did not substantially exceed 20%. The highest conversion of acylating agents (60–70%) was observed for H-Beta (Si/Al = 12, 37 and 75) and H-USY (Si/Al = 15 and 40). In this case, the selectivity for isopropyltolyl ketones reached *ca*. 80%. In general, the selectivity decreases with increasing conversion due to the formation of di-acylated species and some amount of cymenes. The increase in the conversion of acylating agents was found at higher tolueneto-acylating agent molar ratio and with decreasing concentration of acid sites (increasing Si/Al ratio), probably due to a better balanced adsorption/desorption. The initial acylation rate of isobutyric anhydride with toluene was about twice higher than that of isobutyryl chloride. Finally, step-wise addition of acylating agent led to a more efficient consumption of acylating agent and to a higher reaction rate [54].

Acylation of phenol is another reaction of a high interest, as *para*-hydroxy acetophenol is used for the synthesis of paracetamol (*para*-acetoaminophenol), another important pharmaceutical product, while *ortho*-hydroxy acetophenol (Scheme 3) is a key intermediate for the synthesis of *para*-hydroxy coumarin and warfarin, which are used as anticoagulant drugs in the therapy of thrombotic disease [56]. Gas-phase acylation of phenol with acetic acid was investigated on different mesoporous molecular sieves and also on zeolites Y and ZSM-5. Both zeolites produced efficiently *ortho*-hydroxy acetophenol with parallel O-acylation to phenyl acetate. ZSM-5 was found to be highly stable against coke formation, probably due to shape selective behaviour of its micropores [56]. Acetic acid not active in other acylations of aromatic hydrocarbons [54] was found highly active in gas-phase phenol acylation.



Scheme 2. Toluene acylation with isobutyryl chloride.



Scheme 3. Acylation of phenol to hydroxyl acetophenones.

Acylations for flavour intermediates or products

Acylation of fused aromatic rings focused mainly on the acylation of naphthalene to 2-acetonaphthone (2-acetyl naphthalene) and the acylation of 2-methoxy naphthalene to 2-acetyl-6-methoxy naphthalene. In the former case 2-acetyl naphthalene is a well-known fragrance, as well as important intermediate, while 2-acetyl-6-methoxy naphthalene is an important reaction intermediate for the synthesis of the anti-inflammatory drug Naproxen. Both of these compounds are of a high commercial interest.

In the homogeneous phase naphthalene acylation to the 1-position is electronically favoured for electrophilic substitution (Scheme 4). Using a conventional acylation catalyst, aluminium chloride, and acetyl chloride as acylating agent a mixture of 1- and 2-acetyl naphthalene is produced [57]. The solvent employed usually controls the ratio of 1-/2-acetylnaphthalene obtained, which ranges from 91:9 in 1,2-dichloroethane to 25:75 in nitrobenzene. It was reported that nitrobenzene is the only solvent providing a high selectivity to 2-acetylnaphthalene, which has been explained by the formation of a bulky complex among acetyl chloride, naphthalene, catalyst and nitrobenzene. Of course, elimination of such solvent is very challenging.

With respect to the results of acylation in the liquid phase, particularly large-pore zeolites were proposed for naphthalene acylation, as some shape-selectivity effects were expected, which could lead to an increase in the selectivity to 2-acetyl isomer. Liquid-phase acylation of naphthalene with acetic anhydride was investigated over various large-pore zeolites [25], namely faujasite, mordenite and Beta, in the temperature range 100–140°C, employing *trans*-decalin as the solvent. The highest activity and long term stability of zeolite Beta was achieved with Si/Al ratio equal to 37. At lower Si/Al ratios a rapid deactivation of zeolite Beta was observed, while at Si/Al ratios higher than 60 the activity was very low. Also with zeolite Y a maximum activity was observed with a medium concentration of acid sites (Si/Al = 25), indicating a critical importance of adsorption/desorption equilibria to obtain a high activity of the catalyst. Zeolite Beta was found to exhibit selectivity to 2-acetyl naphthalene over 80% at 35% naphthalene conversion. Excess of naphthalene in the reaction mixture and stepwise addition of acetic anhydride improved the naphthalene conversion [25].

2-Acetyl naphthalene is not only an important component of flavour compositions but also an intermediate in further upgrading. Propylene glycol can react with



Scheme 4. Acylation of naphthalene to acetyl naphthalenes.

2-acetylnaphthalene to produce 2-methyl-2-naphthyl-4-methyl-1,3-dioxolane possessing orange blossom fragrance (Scheme 5) [58]. While 2-acetyl naphthalene can be formed inside the channel system of zeolite Beta, it is clear that 2-methyl-2-naphthyl-4-methyl-1,3-dioxolane is too large to fit into the channel systems of any zeolite. However, the successful application of delaminated zeolite ITQ-2 can serve for this reaction as nice evidence on the efficiency of zeolite "external" acid sites. While the yield of this product was only 4% over Beta zeolite, a substantial increase in the yield (20%) was obtained with MCM-22 having much higher external surface. Particular improvement in the yield was obtained using ITQ-2, the "external" surface area of which is 2–3-times larger than that of MCM-22. In this case the yield of 2-methyl-2-naphthyl-4-methyl-1,3-dioxolane reached 63% [58]. A schematic drawing of randomly oriented layers in ITQ-2 is provided in Fig. 7. Another example of the efficient catalytic behaviour of ITQ-2 is acetalization of vanillin with propylene glycol to vanillin propylene glycol acetal.

The important breakthrough in applications of zeolites for the synthesis of fine chemicals has been achieved by Rhodia, applying zeolites Beta and Y for acylation of anisole (Scheme 6) and veratrole (Scheme 7). In the case of anisole acylation considerable simplification of the technological process and higher *para*-selectivity were reached [23].



Figure 7. Schematic picture of organization of layers of ITQ-2.



Scheme 5. Condensation of 2-acetyl naphthalene with propylene glycol to 2-methyl-2-naphthyl-4-methyl-1,3-dioxolane.



Scheme 6. Acylation of anisole (methoxy benzene) with acetic anhydride.



Scheme 7. Acylation of veratrole (1,2-dimethoxy benzene) with acetic anhydride.



Scheme 8. Acylation of ferrocene.

As for veratrole it was reported that further reduction of the deactivation rate is still desirable [59]. A detailed analysis of reaction products and organic compounds retained in the zeolite catalyst after the reaction revealed that di-acylated and tri-acylated benzenes are formed with further condensation products. All these undesired products contribute to the deactivation of the zeolite and some of them cannot be removed by a Soxhlet extraction.

Acylation of ferrocene

Ferrocene derivatives or their complexes are used as catalysts for asymmetric synthesis of a wide number of optically active organic compounds [60, 61]. Acetyl ferrocenes are used as intermediates for the production of a variety of functional materials such as functional polymers, charge transfer complexes, chiral catalysts, combustion catalysts for propellants, pharmaceutical treatment, etc. [62, 63]. As for other acylations discussed in this paper the conversion of ferrocene in acylation with acetic anhydride (Scheme 8) was significantly influenced by the zeolite structure, Si/Al ratio and by the molar ratio of ferrocene to acetic anhydride.



Figure 8. Time-on-stream dependence of ferrocene conversion over different zeolites in ferrocene acylation with acetic anhydride.

The lowest ferrocene conversion was observed for medium-pore zeolite ZSM-5. On the other hand, the most active catalyst for ferrocene acylation was large-pore three-dimensional zeolite Beta (Fig. 8), exhibiting nearly 100% conversion of ferrocene after 180 min reaction. At least under the reaction conditions applied it seems that the first acylation step leads to the deactivation of the second cyclopentadiene ring, which prevents its further acylation. The comparison of zeolite Beta differing in the Si/Al ratio (12.5, 37.5 and 150) clearly revealed that with increasing concentration of acid sites the conversion of ferrocene increased as well.

Other examples of transformations of aromatic hydrocarbons over zeolites like hydroxy alkylations or various re-arrangements can be found in a recent overview by de Vos and Jacobs [64].

SUMMARY AND OUTLOOK

Zeolites, without any doubt, are the most important catalysts in the chemical industry for transformation of aromatic hydrocarbons, starting from petrochemical applications up to fine chemical synthesis. Future interesting areas of the research should cover:

1. Application of new types of micro/mesoporous "hierarchic" systems, which will benefit from acidity of zeolites, as well as from improved transport properties of mesoporous materials.

- 2. Further improvements of shape-selectivity resulting in higher selectivities for the desired products can be achieved by synthesizing new structural types of zeolites and particularly those combining "even" and "odd" numbers of T-atoms in the channels.
- 3. Better utilization of the "external" surface of zeolites in reactions that do not require shape selectivity to reach high selectivities for the desired products.
- 4. Investigation of new reactions, especially in fine chemical synthesis. There is a huge number of reactions which has not been tested yet.
- 5. New experimental approaches like *in situ* MAS-NMR and FT-IR will help us to understand in more detail the reaction mechanisms of aromatic transformations and to better acknowledge the benefits of zeolites both in gas, as well as liquid-phase reactions.

During the last decade many examples of technological relevant reactions of aromatic hydrocarbons related to the synthesis of fine chemicals were described in the open literature. Some of them already reached industrial applications. There is no doubt that, due to the complexity of advantages of zeolites compared with conventional catalysts, we can expect an increasing number of their applications in the near future.

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REFERENCES

- 1. H.-G. Frank and J. W. Stadelhofer, Industrial Aromatic Chemistry. Springer, Berlin (1988).
- 2. C. Perego and G. Ingallina, Green Chem. 6, 274 (2004).
- 3. G. Bellussi, Stud. Surface Sci. Catal. 154, 53 (2005).
- 4. J. Čejka and B. Wichterlová, Catal. Rev. 44, 375 (2002).
- 5. D. H. Olson and W. O. Haag, ACS Symp. Ser. 248, 275 (1984).
- 6. T. F. Degnan Jr., Top. Catal. 13, 349 (2000).
- 7. C. R. Marcilly, Top. Catal. 13, 357 (2000).
- 8. W. W. Kaeding, G. C. Barile and M. M. Wu, Catal. Rev.-Sci. Eng. 26, 597 (1984).
- 9. J. Čejka, B. Wichterlová and S. Bednářová, Appl. Catal. 79, 215 (1991).
- 10. B. Wichterlová, N. Žilková and J. Čejka, Microporous Mater. 6, 405 (1996).
- 11. J. Čejka, A. Vondrová, B. Wichterlová, G. Vorbeck and R. Fricke, Zeolites 14, 147 (1994).
- 12. J. Čejka and B. Wichterlová, J. Catal. 146, 523 (1994).
- 13. T. Tsai, S. Liu and I. Wang, Appl. Catal. A 181, 355 (1999).
- 14. B. Wichterlová and J. Čejka, Catal. Lett. 16, 421 (1992).
- 15. G. Mirth, J. Čejka and J. A. Lercher, J. Catal. 139, 24 (1993).
- 16. C. W. Jones, S. I. Zones and M. E. Davis, Microporous Mesoporous Mater. 28, 471 (1999).
- 17. F. J. Llopis, G. Sastre and A. Corma, J. Catal. 227, 227 (2004).
- 18. J. Čejka, N. Žilková, B. Wichterlová, G. Eder-Mirth and J. A. Lercher, Zeolites 17, 265 (1996).

- 19. I. I. Ivanova, N. S. Nesterenko and C. Fernandez, Catal. Today 113, 115 (2006).
- 20. S. Zheng, A. Jentys and J. A. Lercher, J. Catal. 241, 304 (2006).
- A. Corma, V. Fornes, L. Forni, F. Marquez, J. Martinez-Triguero and D. Mascotti, J. Catal. 179, 451 (1998).
- J. Čejka, A. Krejčí, N. Žilková, J. Kotrla, A. Weber and S. Ernst, *Microporous Mesoporous Mater.* 53, 121 (2002).
- 23. P. Métivier, in: *Fine Chemicals through Heterogeneous Catalysis*, R. A. Sheldon and H. van Bekkum (Eds), p. 161. Wiley-VCH, Weinheim (2001).
- 24. P. Botella, A. Corma, M. T. Navarro, F. Rey and G. Sastre, J. Catal. 217, 406 (2003).
- 25. L. Červený, K. Mikulcová and J. Čejka, Appl. Catal. A 223, 65 (2002).
- 26. M. Spagnol, L. Gilbert, E. Benazzi and C. Marcilly, Patent WO 96/35655 (1996).
- 27. A. Corma and E. Sastre, Chem. Commun., 173 (1991).
- 28. G. R. Meima, Cattech 3, 5 (1998).
- 29. T. F. Degnan, C. M. Smith and C. R. Venkat, Appl. Catal. A 221, 283 (2001).
- 30. A. Corma and E. Sastre, J. Catal. 129, 177 (1991).
- 31. S. I. Zones, US Patent 4,963,337 (1990).
- 32. G. Košová, Stud. Surface Sci. Catal. 158, 59 (2005).
- 33. A. Corma, Microporous Mesoporous Mater. 21, 487 (1998).
- 34. T. Boix, M. Puche, M. A. Camblor and A. Corma, US Patent 6,471,941 B1 (2000).
- 35. F. J. Llopis, G. Sastre and A. Corma, J. Catal. 242, 195 (2006).
- 36. S. Al-Khattaf, N. M. Tukur, A. Al-Amer and U. A. Al-Mubaiyedh, Appl. Catal. A 305, 21 (2006).
- C. H. Christensen, K. Johannsen, I. Schmidt and C. H. Christensen, J. Am. Chem. Soc. 125, 13370 (2003).
- I. Schmidt, C. H. Christensen, P. Hasselriis, M. Yu. Kustova, M. Brorson, S. Dahl, K. Johannsen and C. H. Christensen, *Stud. Surface Sci. Catal.* 158, 1247 (2005).
- 39. Y. Liu, W. Zhang and T. J. Pinnavaia, J. Am. Chem. Soc. 122, 8791 (2000).
- 40. P. Prokešová, S. Mintova, J. Čejka and T. Bein, Microporous Mesoporous Mater. 64, 165 (2003).
- 41. P. Prokešová, N. Žilková, S. Mintova, T. Bein and J. Čejka, Appl. Catal. A 281, 85 (2005).
- 42. Y. Zhu, Y. Nie, S. Jaenicke and G.-K. Chuah, J. Catal. 229, 404 (2005).
- 43. A. Bordoloi, B. M. Derassy, P. S. Niphadkar, P. N. Joshi and S. B. Halligudi, *J. Mol. Catal. A* **253**, 239 (2006).
- 44. A. Sakthivel, W.-H. Chen, S.-H. Liu, S.-J. Huang, A.-Y.- Lo, Y.-H. Hsu, S. D. Lin and S.-B. Liu, *Catal. Lett.* **108**, 173 (2006).
- 45. T. J. Donohue, A. J. Orr and M. Bingham, Angew. Chem. Int. Edn. 45, 2664 (2006).
- 46. G. Sartori and R. Maggi, Chem. Rev. 106, 1077 (2006).
- 47. H. K. Heinichen and W. F. Hölderich, J. Catal. 185, 408 (1999).
- 48. M. Casagrande, L. Storato, M. Lenarda and R. Ganzerla, Appl. Catal. A 201, 263 (2000).
- P. Andy, J. Garcia-Martinez, G. Lee, H. Gonzalez, C. W. Jones and M. E. Davis, *J. Catal.* 192, 215 (2000).
- M. L. Kantam, K. V. S. Ranganath, M. Sateesh, K. B. S. Kumar and B. M. Choudary, J. Mol. Catal. A 225, 15 (2005).
- 51. A. Corma, M. T. Navarro, F. Rey, J. Rius and S. Valencia, *Angew. Chem. Int. Edn.* **40**, 2277 (2001).
- 52. A. Corma, M. T. Navarro, F. Rey and S. Valencia, Chem. Commun., 1486 (2001).
- 53. R. A. Sheldon, Chem Tech. 24, 38 (1994).
- 54. J. Klisáková, L. Červený and J. Čejka, Appl. Catal. A 272, 79 (2004).
- 55. J. Klisáková and G. Šťávová, Stud. Surface Sci. Catal. 158, 1637 (2005).
- 56. C. L. Padró and C. R. Apesteguía, J. Catal. 226, 308 (2004).
- 57. P. H. Gore, Chem. Rev. 55, 229 (1955).
- 58. M. J. Clement, A. Corma and A. Velty, Appl. Catal. A 263, 155 (2004).

- 59. C. Giugnard, V. Pedron, F. Richard, R. Jacquot, M. Spagnol, J. M. Coustard and G. Perot, *Appl. Catal. A* 234, 79 (2002).
- 60. M. D. Vukicevic, Z. R. Ratkovic, A. V. Teodorovic, G. S. Stojanovic and R. D. Vukicevic, *Tetrahedron* 58, 9001 (2002).
- 61. S. Taudien, O. Riant and H. B. Kagan, Tetrahedron Lett. 36, 3513 (1995).
- 62. R. J. Hu and B. G. Li, Catal. Lett. 98, 43 (2004).
- 63. T. J. Brunker, C. Arisandy, A. R. Cowley, L. H. Rees, S. Barlow and D. O'Hare, *J. Organomet. Chem.* 689, 252 (2004).
- 64. D. E. de Vos and P. A. Jacobs, Microporous Mesoporous Mater. 82, 293 (2005).

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