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Catalysis with hierarchical zeolites

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ABSTRACT

Hierarchical (or mesoporous) zeolites have attracted significant attention during the first decade of the 21st century, and so far this interest continues to increase. There have already been several reviews giving detailed accounts of the developments emphasizing different aspects of this research topic. Until now, the main reason for developing hierarchical zeolites has been to achieve heterogeneous catalysts with improved performance but this particular facet has not yet been reviewed in detail. Thus, the present paper summaries and categorizes the catalytic studies utilizing hierarchical zeolites that have been reported hitherto. Prototypical examples from some of the different categories of catalytic reactions that have been studied using hierarchical zeolite catalysts are highlighted. This clearly illustrates the different ways that improved performance can be achieved with this family of zeolite catalysts. Finally, future opportunities for hierarchical zeolite catalysts are discussed, and the virtues of various preparation methods are outlined, including a discussion of possible pitfalls in the evaluation of new, potential hierarchical zeolite catalysts.

1. Introduction

During the last decade, the scientific literature on hierachical zeolites has dramatically increased, and several reviews highlighting various aspects of the recent developments have already appeared [1–7]. The term hierarchical zeolites refers to zeolites featuring at least one additional level of porosity besides the intrinsic micropore system characteristic of zeolites. In practice the term most often refers to mesoporous zeolites, i.e. hierarchical zeolites featuring additional porosity in the mesopore size region (pore diameters in the range 2–50 nm) because the major impact of auxiliary porosity on catalysis stems from porosity in this size region. Interestingly, it is difficult to trace the true origin of hierarchical zeolites, and their use as heterogeneous catalysts, since it is more or less hidden in the patent literature. However, with the current knowledge about these materials and their preparation methods there is no doubt that several early patents describe methods for preparing such zeolite materials, and also their use as heterogeneous catalysts in various reactions [8–11]. One reason that it is often not trivial to conclude when hierarchical zeolites were claimed in the patent literature is that the physical-chemical characterization reported originally does not provide direct evidence for the detailed structure of the materials studied. Thus, much of the recent interest in hierarchical zeolites can be ascribed to improved methods for visualization of the structure of these materials, and particularly to the wider availability of sufficiently elaborate electron microscopy techniques, such as high-resolution TEM and TEM tomography. With these methods, the structure of hierarchical zeolite catalysts can de deduced in impressive detail, and the observed catalytic performance can more easily be related to their structure. However, it is still necessary also to use various other physical–chemical characterization methods to establish that the structural modification of hierarchical zeolites has not lead to significant changes in other catalytically important properties of the zeolite, especially with respect to zeolite acidity. Only this way, reliable structure-activity relationships can be quantitatively established.

Here we present a review of the literature reporting the use of hierarchical zeolites as catalysts for different reaction types. The reactions types are divided into classes comprising alkylation, methanol-to-hydrocarbons (MTH) and olefin aromatization, isomerisation, cracking, condensation and other, more specific, reactions. The alkylation, isomerisation and cracking reactions share the same carbenium chemistry and could be viewed together. However, since the size of the substrates used and the operating temperature differs widely in these three categories, the effect of mesopores also differs and they are therefore treated separately.

One of the major limitations for the use of zeolites as catalysts is the limited access to the active sites within the individual crystals. This attribute serves as the material's strength (allowing for shape selectivity) as well as a weakness (mass transport limitations). It is predicted that mesoporous zeolites can contribute

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Table 1
Overview of the different reaction classes and the main effect of mesoporous zeolites.

Reaction type	Main observation
Alkylation reactions	Higher activity
Transalkylation reactions	Improved stability
Isomerisation reactions	Higher activity
Cracking of light substrates	No significant improvement
Cracking of heavy substrates	Substantially higher activity
MTH and aromatization reactions	Longer catalyst lifetime
Condensation reactions	Higher activity. Higher selectivity towards bulky products

to the field of catalysis in either of two ways. These hierarchical materials can potentially increase the number of reactions in which zeolites are used by allowing acceptable mass transport of larger reactants and products and allowing for reactions catalyzed by strong acidity to proceed on the mesopore surface and pore mouth. Alternatively mesoporous zeolites can simply serve by improving existing reactions/processes currently using zeolite catalysts. It is here illustrated how examples of both applications exist in literature. A summary of the major trends observed for hierarchical zeolites categorized by reaction type is shown in Table 1.

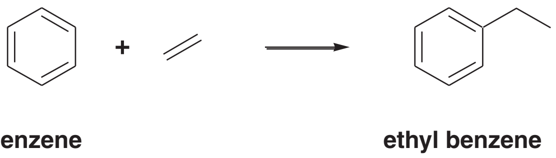
2. Alkylation reactions

Alkylations and acylations are important reactions in industry for which zeolites find use. Unfortunately, these processes are rarely operated at full potential due to mass transfer limitations within the zeolite catalysts; therefore, the advantages of applying mesoporous zeolites as catalysts for these transformations are obvious. In the literature, several reports are available dealing with mesoporous zeolites for such transformations, particular with alkylation of benzene. The general finding in these reports is the observation that mesoporous zeolites are more active for these transformations. This is expected due to shorter diffusion path length in mesoporous zeolites, however, what is perhaps not so obvious is why also an increased selectivity to monoalkylated products is observed.

2.1. Benzene alkylation

Christensen et al. [12] reported the use of mesoporous ZSM-5 prepared by carbon-templating for gas phase alkylation of benzene with ethylene (Scheme 1).

The authors used a molecular ratio of benzene:ethylene of 5.1:1, pressures from 2.5 to 5 bar and temperatures from 583 to 643 K. Undesired side reactions include the formation of di- and tri alkylated ethyl benzenes as well as numerous alkylated benzenes arising from transalkylation of the product. It was shown, that the mesoporous zeolite was significantly more active than the conventional zeolite catalyst. Moreover, it was shown that the selectivity towards ethyl benzene was significantly higher using the mesoporous zeolite and that the effect was even more pronounced at high conversions. The increased selectivtity towards the monoalkylated product, ethyl benzene, can be understood by looking at the schematic representation in Fig. 1 of the relative concentration profiles of benzene, ethylene and ethyl benzene [13].



Scheme 1.

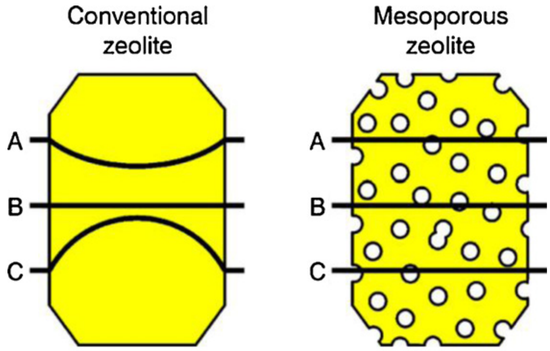


Fig. 1. Schematic of the relative concentration profiles (disregarding molecular adsorption) of benzene (A), ethylene (B) and ethyl benzene (C) in conventional and mesoporous ZSM-5 during alkylation of benzene with ethylene (figure reproduced from Ref. [13]).

The concentration profiles illustrated in Fig. 1 were derived from a classical evaluation of diffusion properties of the benzene, ethylene and ethylbenzene under actual operating conditions, showing that benzene and ethylbenzene are diffusion limited if the crystals are too large [13]. The concentrations of reactants and products in the zeolite and in the gas phase are likely different due to adsorption. However, as benzene is consumed in the alkylation reaction, a concentration gradient enriched in ethylbenzene and depleted in benzene is expected to be present in the conventional sample where diffusion restraints are pronounced. It is clear that if a relatively higher concentration of ethylbenzene exists in the interior of the crystal, this must lead to the formation higher levels of diethylbenzene. In other words, diffusion limitations in conventional crystals during alkylation of benzene with ethylene lead to higher levels of polyalkylated products than desired. On the contrary, in case of the mesoporous crystal, having a shorter average diffusion path length, the concentrations of ethylbenzene and benzene throughout the crystal will be much closer to the value strictly determined by gas phase concentration and adsorption affinity. In effect, successive alkylation of ethylbenzene is not as likely to occur in the mesoporous zeolite as in the case of the conventional one, and the monoalkylated product is predominant.

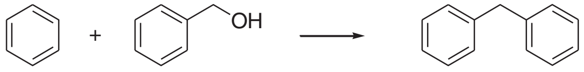
Dealumination of mordenite has been well understood for several decades but recently also base treatment (desilication) of mordenite, either alone or in combination with dealumination, has been successfully performed to obtain similar advantages.

In close relation to the previous example Groen et al. [14] compared a mesoporous mordenite catalyst obtained by desilication to a commercial sample with a smaller crystal size and higher acid density in the liquid phase benzene alkylation with ethylene. Despite the advantage with respect to crystal size and acidity, the hierarchical mordenite showed an initial higher activity in comparison with the commercial mordenite. Much more pronounced though was a remarkably slow deactivation of the mesoporous sample coupled with a slightly higher selectivity towards the desired ethyl benzene. The improved catalytic performance as discussed above was attributed to the enhanced mass transport. This report is a particularly interesting case where the authors chose to use the zeolite in the liquid phase where mass transport limitations pose much greater problems as compared to gas phase reactions. Nevertheless liquid phase reactions represent an interesting area in which mesoporous zeolites can find applications.

Three different commercially available mordenite samples were desilicated and tested in liquid phase benzene alkylation with propene producing cumene (iospropylbenzene) in a study by de Jong and co-workers [15]. The mordenite samples were outside the optimal window with respect to Si/Al ratio for desilication [16] but with an increased concentration of sodium hydroxide mesopore formation proved possible. TEM imaging supported by additional characterization led the authors to conclude that the mesoporosity was mostly inter-particle, which lowers mass transport limitations between the nanosized particles. Indeed, for the alkylation of benzene with propylene over the alkali treated sample, an initial activity boost in the order of one magnitude was observed, while maintaining a similar cumene selectivity. The same authors [17] also used cumene synthesis to investigate whether a sequential post synthesis treatment using dealumination and desilication of commercially available mordenite could be advantageous. A comprehensive series of samples, dealuminated, desilicated or combinations thereof were prepared and compared to gain insight into the catalytic effects of Al-content, inter- and intracrystalline porosity, acid strength or the presence of extra-framework aluminum. Catalytically, the parent mordenite sample performed relatively poor, having a lower activity and selectivity towards cumene/di-isopropyl benzene as compared to reported literature values. Dealumination improved the performance only slightly, whereas a subsequent optimized desilication treatment resulted in a mesoporous catalyst having a significantly higher activity (up to 27-fold increase). Alas, the higher activity was accompanied by an increased selectivity towards di- and tri-isopropyl benzene. Interestingly, desilication of the parent sample gave an excellent combined cumene/di-isopropylenbenzene selectivity of >99% arising from suppressed propylene oligomerization which the authors attribute to the likely removal of weak Lewis acidic site present on the external surface. This observation highlights the complexity of interpreting catalytic data since mesopore formation occurs concurrently with a modification of the acidity of the samples. The use of thorough characterization methods (*e.g.* electron tomography, (MAS) NMR or FTIR using molecular probes) are thus needed in order to be able to discuss the full array of changes introduced during post synthesis treatment.

Commercial mordenite catalysts treated by desilication or dealumination have also been tested in transalkylation of alkylbenzenes (toluene and 1,2,4-trimethyl benzene) in a recent report [18]. Here an unchanged initial activity was observed; however, desilication was shown to improve the long term stability of the catalyst significantly. In line with the previous finding Yang et al. [19] tested a hierarchical beta zeolite prepared by dry gel conversion in the transalkylation of di-isopropylbenzene with benzene. The mesoporous beta sample showed a slightly lower initial activity compared to a solely microporous reference but deactivated only barely within the timeline of testing, in strong contrast to the reference. The improvements were attributed mainly to improved accessibility of the active sites and better diffusion properties in the hierarchical material.

Numerous patents from Dow Chemical [20–22] exist on the use of mesoporous (or 3-DDM) mordenite prepared by dealumination using mineral acids, and a recent review [23] highlights the catalytic properties of mesoporous mordenite in alkylation and cracking reactions. With respect to the former, mesoporous mordenite has been applied in alkylation of aromatic compounds such as biphenyl or phenol and transalkylation of alkylbenzenes. An interesting example from the open literature using mesoporous mordenite obtained by acid leaching is given by Garces and co-workers [24] The authors use the catalyst in the liquid phase alkylation of biphenyl with propylene, preferentially forming the para isomer 4,4'-diisopropylbiphenyl (DIPB). By performing the dealumination step once or twice, they elegantly introduce increasingly strong dealumination (SiO_2/Al_2O_3 ratio up to 2600) alongside mesopore formation occurring at the expense of the micropores. The best dealuminated catalyst showed a very good para selectivity of 73.5% and also had an improved stability towards deactivation. The authors discuss that the preferential removal of aluminum on the external surface could be the cause for both phenomena as non-shape selective isomerization of the products as well as pore blocking from crystal surface reactions were diminished.



Scheme 2.

In a similar study Kim and co-workers [25] studied the performance of dealuminated mordenite in the ethylation of biphenyl. Here, only moderate selectivity towards the para isomer could be observed and the authors attribute this to the lower steric restriction of the mordenite framework as compared to isopropylation.

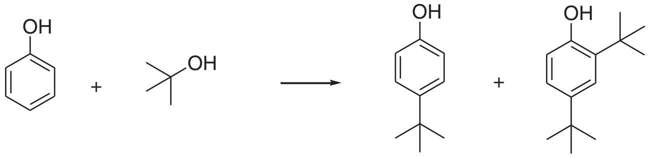
Xiao et al. [26] compared a mesoporous zeolite beta prepared by templating with mesoscale cationic polymers to conventional beta with a slightly smaller crystal size in the alkylation of benzene with 2-propanol. They operated the reaction at 473 K with a benzene/2-propanol ratio of 4:1. It was shown that the mesoporous sample exhibited higher activity than the conventional, and that the selectivity towards isopropyl benzene was also significantly higher.

Recently Sun and Prins [27] compared a mesoporous ZSM-5 prepared using amphiphilic organosilane as mesopore directing agent to a conventional ZSM-5 sample in alkylation of benzene with benzyl alcohol (Scheme 2). In this case, the mesoporous ZSM-5 exhibited dramatically improved catalytic activity in comparison with the conventional ZSM-5 sample.

Li et al. [28] also reported the use of a mesoporous zeolite for alkylation of benzene with benzyl alcohol. In this report, mesoporous mordenite was prepared by a combination of acid and base leaching procedures. It was shown that the activity of the mesoporous mordenite was much higher than that of the parent sample. To support the data from the benzene alkylation the authors used the isomerization of 2-methyl-2-pentene as a model reaction. The 2-methyl-2-pentene reaction is commonly used to probe the acidity of solid acids by evaluating the ratio of isomers formed. The model study identified the acid- and base leached mordenite as the most active catalyst as was found to be the case in the benzene alkylation.

Jin et al. [29] compared a mesoporous ZSM-5 sample obtained by desilication with a conventionally prepared ZSM-5 sample and showed that the hierarchical zeolite exhibits higher activity as well as longer lifetime in the alkylation of 2-methyl naphthalene with methanol to 2,6-dimethyl naphthalene. The reactants and products are of a similar size as the channels in the zeolite and therefore a large improvement in activity increasing from 5.3% to 37% after about 10 h at 673 K was seen. The authors argued that the mesoporosity and not a decreasing Si/Al ratio was the deciding factor determining the activity. This was investigated by comparing catalytic performance of the hierarchical ZSM-5 with that of a nanosized ZSM-5 having a significantly lower Si/Al ratio. The selectivity expressed as the ratio of 2,6-dimethyl naphthalene/2,7-dimethyl naphthalene was simultaneously affected. Selectivity towards the desired less sterically hindered product 2,6-dimethyl naphthalene was highest in the parent zeolite. From increasing mesoporosity the limiting mass transport was gradually relieved and the selectivity decreased for the most strongly desilicated samples. This example also illustrates that the activity of the catalyst can come at the cost of the selectivity due to partial loss of the shape selective properties of the zeolite, indicating that a compromise needs to be identified. In this specific case the authors were however able to address this problem using a different subsequent post treatment.

A recent study by Musilova et al. [30] have drawn similar conclusions with respect to selectivities when comparing a reference ZSM-5 with mesoporous samples prepared by carbon templating after catalytic testing of toluene disproportionation as well as toluene and *p*-xylene alkylation with isopropyl alcohol. In this study, thorough FTIR characterization was performed using



Scheme 3.

deuterated acetonitrile, pyridine and 2,6-di-tert-butyl pyridine as molecular probes. The authors were able to convincingly use a set of parent and mesoporous samples with insignificant differences in acid strength, concentration and type (Brønsted vs. Lewis) while showing that the amount of Brønsted acidic sites located at the external surface increased, correlating well with the introduced mesoporosity.

2.2. Alkylation and acylation of other substrates

Xu and co-workers [31] reported the use of a hierarchical ZSM-5 prepared by templating with polystyrene colloidal spheres in the alkylation of phenol with *t*-butanol. The authors investigated the activity as well as the selectivity towards 4-*tert*-butyl phenol and 2,4-di-*tert*-butyl phenol (Scheme 3). The hierarchical zeolite was much more active than the conventional sample, and apparently, the selectivity towards the highly bulky 2,4-di-*tert*-butyl phenol was also increased.

Nano-sized zeolite beta prepared by confined space synthesis by Derouane et al. was shown to be active for acylation of anisol by acetic anhydride [32]. The authors observed an improved catalytic performance at intermediate conversions when using the nano-crystals. This was attributed to the lowered mean diffusion length allowing for the easier egression of the bulky product *p*-methoxyacetophenone. Recently, nano-sized ZSM-5 was also used for acylation of anisol with acetic anhydride as well as acetyl chloride [33]. Also in this report, the mesoporous zeolite catalyst was more active than the conventional one.

3. Methanol to hydrocarbons and aromatization reactions

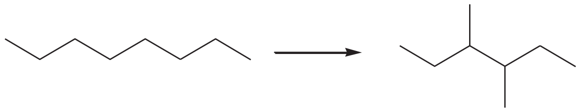
The methanol to hydrocarbons reaction (MTH) enables the use of gasified coal or biomass to form hydrocarbons and thus could play an important role in the future. The MTH reaction is an example of a reaction composed of multiple alkylation, cracking and isomerization steps, each catalyzed by the same strong Brønsted acidity sites. The aromatization of olefins resembles the MTH reaction to a great extent and zeolites are active catalysts in both cases. The general finding when using mesoporous zeolites is that an increased catalyst lifetime is observed. This effect could be attributed to an increased resistance towards coking of the mesoporous zeolites, however observations describing lower rates of coke formation as well as coke predominantly forming on the external surface have also been reported.

For the methanol to gasoline reaction Bjørgen et al. [34] and Lietz et al. [35] have tested mesoporous ZSM-5 obtained by desilication. In both studies, an increased lifetime of the mesoporous ZSM-5 zeolite compared to the conventional ZSM-5 is reported. Bjørgen and co-workers calculated the total methanol conversion capacity ($g_{\text{methanol converted}}/g_{\text{zeolite}}$ extrapolated from 50% deactivation) of the parent and the optimally desilicated sample and saw a significant increase by a factor of 3.3 when introducing mesoporosity. The initial activity of the hierarchical zeolite was observed to increase only slightly as a function of the desilication but the selectivity towards the gasoline fraction C_{5+} was on average improved by a factor of 1.7. Another pronounced difference was seen in a higher C_4 hydrogen transfer index (HTI-index) for the mesoporous samples which identify a more pronounced production of paraffinic and aromatic compounds. Presumably the high content of alkyl benzenes in the effluent is related to the increased ease with which these large compounds escape the mesoporous zeolite crystal. Interestingly, the authors also note that the mesopore formation leads to a decreased *p*-xylene selectivity over *o*-xylene which is in good correlation with other findings described in literature and discussed herein [36].

Recently Ryoo and co-workers published a synthesis approach using an elegantly designed bi-functional surfactant as the structure directing agent and were able to produce sheets of crystalline MFI with a thickness of only a single unit cell (2 nm) [37]. This remarkable material proved temperature stabile and contained conventional strong Brønsted acidity and was tested catalytically in several reactions including cracking of high density polyethylene (HDPE) and MTG. The single sheets possess little shape selectivity but exhibited a superior accessibility to the acidic sites seen by a substantially improved cracking performance of the large HDPE as compared to a conventional zeolite with similar Si/Al ratio. Catalytic results from the MTG reaction showed no initial activity difference due to the small size of methanol, but a significant increase in catalyst lifetime was found. The authors attributed this finding, in part to a slower coke deposition on the mesoporous material, together with the coke deposition predominantly taking place on the external surface since coke precursors readily could diffuse out of the zeolite. This study convincingly illustrates how the use of several catalytic reactions can be applied to highlight the different properties of a newly produced material versus a reference.

Another interesting study, published by the same laboratory, also reports how several mesoporous ZSM-5 samples prepared from different protocols were compared catalytically in the MTH reaction [38]. When plotting the external surface area as a function of the lifetime, until 50% conversion is reached, they observe a near linear correlation which highlights that mesoporosity can yield significantly higher conversion capacities for MFI catalysts in the MTH reaction. Further, a pronounced difference between the mesoporous and the purely microporous catalyst was seen in the distribution of the formed coke being located preferentially externally vs. internally, respectively.

For the methanol to propylene reaction, Mei et al. [39] used mesoporous ZSM-5 with the main findings that the important propylene/ethylene ratio as well as the propylene selectivity could be significantly increased by introduction of mesoporosity. The authors prepared mesoporous ZSM-5 by two different protocols, namely desilication and starch templating. Interestingly, they observe only an improved catalytic performance when using the desilicated zeolite. In part the authors attribute this to differences in the connectivity and location of the mesopores. In the case of desilication the mesopores are accessible from the external surface in contrast to starch templating where the mesopores are randomly distributed and occluded within the crystals. A mesoporous ZSM-5 reported by Sun et al. was also tested in the MTP reaction [40]. The material was prepared by carbonization of a precursor within the pores of SBA-15 followed by dissolution of the SBA-15 material and subsequently using the nanosized carbon as a hard template. In this study no initial selectivity improvement towards propylene was observed; however, a significant lifetime increase could be seen. In a recent study by Sommer et al., [41] SSZ-13 and desilicated SSZ-13 were compared in the methanol to olefins process. Here it was found that the desilicated SSZ-13 had a significantly shorter lifetime and contained less coke upon deactivation compared to conventional SSZ-13. The authors suggested that the cause behind this behavior were alterations in the acidity and surface area which illustrates that while the introduction of mesoporosity might be beneficial in some cases, side effects can have detrimental effects in the catalysis.



Scheme 4.

Furthermore, mesoporous ZSM-5 has been tested in butene [42] and 1-hexene [43] aromatization. Song et al. [44] investigated butene aromatization and the major finding was that the stability on stream was dramatically improved in the mesoporous zeolite obtained by desilication. As the catalysts deactivate, the xylene composition changes towards increased *p*-xylene selectivity in the case of the parent zeolite, whereas a continual composition close to the thermodynamic equilibrium was seen for the alkali treated samples. The coke deposited onto the zeolites was investigated and it was concluded that an equal amount of coke having similar properties was formed on the mesoporous as well as the conventional sample. Accessibility to the micropores was maintained in the mesoporous system which was explained by a significant amount of the coke being located in the mesopores where it is less detrimental to mass transport. In addition, the authors found that coke located in the mesopores was combusted at a lower temperature compared to coke situated in the micropores, as revealed by temperature programmed oxidation experiments.

In line with the previous report a similar improvement in the resistance towards deactivation by coking was reported in the case of 1-hexene isomerization and aromatization tested over a mesoporous ZSM-5 zeolite also obtained by desilication. Simultaneously, the relative amount of cracking over the mesoporous zeolite is observed to deteriorate which is explained by an unhindered access to the active sites in the micropores and good mass transport, both of which limits the residence time of the products in the micropores. These findings are validated by N_2 sorption–desorption measured on samples containing an equal amount of coke. It is seen that the accessible micropore volume decreases to a much larger extend in the conventional zeolite as compared to the mesoporous.

Upgrading of pyrolysis oil over a zeolite is one way to deoxygenate it and convert low value oxygenates into hydrocarbons and water. Park and co-workers have compared the use of ZSM-5 and hierarchical ZSM-5 prepared using organosilane templates for the upgrading of pyrolysis oil vapors [45]. It was found here that the mesoporous ZSM-5 was more active than the conventional catalyst. The authors ascribe this to the synergetic effect of the high acidity and high porosity of the mesoporous zeolite.

4. Isomerization reactions

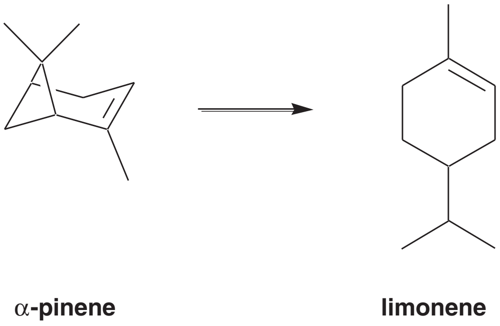
Zeolites are often used to isomerize hydrocarbon substrates into more valuable products. An important application of this is the upgrading of straight chained naphtha into highly branched products with high octane numbers and thus better gasoline properties (Scheme 4).

More than three decades ago, before the field of mesoporosity had matured in a field of its own, dealumination [46,47] was a known procedure to improve the performance of zeolite catalysts. An example is the use of dealuminated mordenite as a catalyst in the hydroisomerization of small paraffins into their branched isomers. In an early study by Koradia et al. [48] a series of Pt-loaded mordenite samples were prepared and dealuminated at varying levels and tested in *n*-pentane isomerization at 533 K. The authors identified an optimum dealumination level going from a parent SiO_2/Al_2O_3 ratio of 10.8–17.1. The authors discuss the effects of lower acid density and possible interaction of the loaded metal with the acidic site without addressing porosity. None the less, a large difference in the product selectivity is apparent and the optimal selectivity was found to coincide with the highest activity level.

Interestingly, with the standardization of characterization techniques such as TEM and N_2-physisorption, a new level of understanding could be obtained from analyzing dealuminated mordenite. In relation to the previous report Tromp et al. [49] studied dealuminated mordenite treated to a similar level. The Pt loaded mordenite samples were tested in *n*-hexane hydroisomerisation and the acid leaching increased the activity and shifted the selectivity towards primary products, i.e. mono-branched isomers while suppressing cracking. Results from TEM and N_2-physisorption showed that mesopores and/or cracks in the crystals were indeed formed and decomposition reactions using *n*- and isopropyl-amine showed an increased accessibility as a function of the dealumination treatment. Calculating the Thiele modulus concluded that the reaction was diffusion controlled in the parent sample. It was thus rationalized that the introduced mesoporosity effectively reducing residence time of the products on the catalyst along with better acid site accessibility were the reasons for the improved catalyst performance. Further, a thorough study regarding the diffusivity in dealumnated samples similar to the ones just described under “live” catalytic conditions have been made by van Donk et al. [50]. Using a tapered element oscillating microbalance (TEOM) the authors were able to obtain steady state diffusivities and uptake rates in untreated and dealuminated mordenite. Catalytic experiments showed a superior performance of the mesoporous sample and this activity increase could be assigned partly to decreased diffusion restrains arising from shorter intracrystal diffusion lengths as well as an improved intrinsic activity of the individual sites as aluminum is extracted from the framework.

In a recent study by Chao et al. mesoporous MFI was prepared using a procedure involving base treatment and re-crystallization [51]. This mesoporous MFI material was found to have decreased *n*-hexane and 2-methylpentane sorption capacity while the sorption capacity for 2,2-dimethylbutane was increased. This higher capacity for bulky hydrocarbons is also reflected in a higher selectivity of the bulky isomers for the isomerisation of *n*-hexane at 600 K when using the platinum modified versions. For the hydroisomerisation of *n*-heptane Moushey and Smirniotis [52] compared the activity of ZSM-12 and Beta with those of their mesoporous analogues prepared by carbon templating. In this study, the mesoporous ZMS-12 material was found to exhibit a four times higher activity than the conventional ZSM-12 zeolite at 533 K. A comparison of the product selectivity at 593 K shows that the mesoporous ZSM-12 gives 86% isomerisation product as compared to 72% for the conventional ZSM-12 zeolite. A similar trend was observed for the Beta zeolite. The increased selectivity towards the isomerisation products is attributed by the authors to the shorter residence time of the substrate in the mesoporous zeolite crystal. In a similar study, the hydroisomerisation of *n*-octane using Pt/MOR and Pt/Beta as well as their mesoporous analogues was examined at 503–523 K [53]. The mesoporosity was introduced by partially destroying the parent mordenite and Beta zeolites using sodium hydroxide, followed by a hydrothermal treatment in the presence of cetyltrimethylammonium bromide. Varying degrees of mesoporosity are introduced in this way by changing the amount of sodium hydroxide. The study shows that the mesoporous zeolites in all cases exhibit higher activity than their parent samples (1.3-2 fold increase).

Isomerisation of larger hydrocarbons has also been studied. Delamination of layered zeolite precursors with the FER-type structure can lead to the ITQ-6 material which contains mesoporosity. In a study by Corma and co-workers, this material was used for the hydroisomerisation of *n*-hexadecane at 673 K and compared to ferrierite [54]. Here it was found that ITQ-6 is more active than ferrierite and gives a higher isomerisation to cracking ratio. In addi-



Scheme 5.

tion, the isomerisation products are more highly branched than the isomerisation products formed from using ferrierite.

A comparison of various commercial Beta zeolites for the isomerisation of fatty acids (C_{18}) at 523 K has been carried out by Zhang and Zhang [55]. In this study, zeolites having different Si/Al ratios and mesoporosities are compared. It was found that the mesopore surface area is the most important parameter for increasing the conversion of fatty acids. This observation is well rationalized by the large size of the reactants presumably only allowing the isomerisation reactions to take place on the external/mesopore surface.

The isomerisation of *o*-xylene to *p*-xylene has been studied by Fernandez et al. using a mesoporous ZSM-5 prepared by desilication [36]. The finding here was that the mesoporous ZSM-5 displayed higher activity than the parent ZSM-5, resulting in a higher conversion of *o*-xylene. However, the improved activity comes at the cost of a loss in shape selectivity and more *m*-xylene is formed. This negative side effect was reduced by an acid wash treatment of the desilicated zeolite, removing some of the aluminum in the mesopores that caused the non-shape selective isomerisation reaction.

Hydrocarbons such as monoterpenes are known to readily isomerize. Thus, these have also been studied using hierarchical zeolites [56,57]. Here, ZSM-12 was desilicated using sodium hydroxide to produce a mesoporous ZSM-12 zeolite. This mesoporous material was found to have enhanced activity relative to the conventional ZSM-12 zeolite for the isomerisation of α-pinene as presented in Scheme 5.

A similar result was obtained for the desilication of ZSM-5. In terms of product selectivity, however, the difference between the desilicated and the parent zeolites is less pronounced as a mixture of various monoterpenes with a similar composition is formed in all cases.

5. Cracking reactions

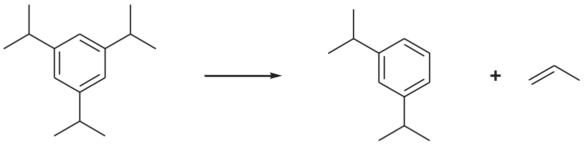
Cracking reactions constitute one of the most important uses of zeolites due to their strong Brønsted acidity. Since mesoporous zeolites combine benefits of strong acidity, high thermal stability and enhanced surface area they have been studied for the cracking of hydrocarbons of sizes ranging from C_6 to hydrocarbons containing thousands of carbon atoms, which is the case for substrates such as polyethylene. Particularly, the fluid catalytic cracking (FCC) and hydrocracking processes are extremely important industrially since huge amounts of heavy hydrocarbon feedstocks are cracked into more valuable fractions on a daily basis in refineries all over the world. These processes apply mesoporous zeolite Y as the catalyst, and the effect of mesopore modification on this zeolite is well known and has been reviewed earlier [1,58]. One particular important point regarding the use of zeolite Y as a cracking catalyst is made by Kung et al. [59]. It is well known that dealumination by steaming or acid treatment enhances the cracking activity of zeolite Y; however, as a function of dealumination a substantial modification of the acidic properties occur, creating entirely new types of acidic sites and the exact origin of the improved activity can thus be rather hard to pinpoint. Interestingly, the authors argue that minimizing diffusion restraints by the introduction of mesoporosity could be critical with respect to increasing rates of bimolecular and oligomeric cracking reactions and thus serve as an alternative explanation to highly active single sites. This example illustrates a major challenge which lies in separating the effects of acid site modification vs. porosity introduction which is of relevance in most of the hierarchical zeolite material described throughout this review. Concerning exactly this Haag et al. [60] have previously demonstrated the ability to isolate catalytic effects from mass transport limitations in ZSM-5 by using crystallites with increasing sizes in the cracking of numerous either linear or branched paraffins.

Recenly, also other zeolites have been studied in various types of hydrocarbon cracking reactions. The general finding here is that mesoporous zeolites are comparable in activity to conventional zeolites for the cracking of small substrates (C_8). However, the mesopores lead to a tremendous activity increase due to the enhanced accessible surface area for larger substrates.

5.1. Naphtha

The cracking of naphtha over mesoporous zeolites has been studied by several groups. Jung et al. prepared mesoporous MFI zeolites by alkali treatment and studied their activity for the cracking of *n*-octane at 773 K [61]. Here it was found that the mesoporous MFI displays a lower activity than the conventional MFI while the product selectivity remains largely unaffected. This decrease in activity is ascribed to the decrease in the number of highly acidic sites due to the alkaline treatment. The effect of mesopores thus does not seem to affect this type of cracking reaction particularly. In a similar study by Niwa and co-workers, mesoporous ZSM-5 synthesized by the use of organosilane templates was used for the cracking of *n*-octane and compared to conventional ZSM-5 [62]. These cracking experiments were also carried out at 773 K and the activity of the mesoporous zeolites was found to be comparable to or slightly lower than the activity of the conventional zeolites. Unfortunately, the product composition was not investigated in this study. A feed of refinery derived naphta was cracked over carbon templated ZSM-5 by Bari Siddiqui et al. [63]. Comparable activities for non-mesoporous references were reported but significantly higher propene and ethylene yields were found from the mesoporous sample attributed to a shorter residence time suppressing secondary reactions. Mesoporous ZSM-5 has also been studied for the cracking of 1-hexene by Xu and co-workers [43]. In this study the mesoporosity is introduced by alkali treatment to produce zeolites containing varying degrees of mesoporosity. Here, the alkaline treated zeolites were found to display a slightly higher activity than the parent ZSM-5 zeolite. The largest difference here is the product selectivity, as the alkaline treated zeolites are reported to be more selective towards aromatics (15–20%) than the parent ZSM-5 zeolite (5%) whereas the latter shows a higher selectivity for C_4–C_{10} olefins (623 K). A biphasic zeolite composite consisting of a core of Y zeolite and an outer layer of Beta nano-crystals was prepared by Zheng et al. and tested for the cracking of *n*-octane [64]. This composite material has a micropore volume comparable to the two parent zeolites (0.19 ml/g), and also a mesopore volume of 0.13 ml/g that is much larger than that of a physical mixture of Y and Beta. For the cracking of *n*-octane at 773 K the composite was found to be more active than pure H-Y (6% conversion) and a physical mixture of H-Y and H-Beta (48% conversion) giving a conversion of 76%. The cracking products were not identified in this study.

It thus appears that for the cracking of small substrates, the acidity of the zeolite is the dominant factor in determining the overall catalyst activity. This observation indicates that only minor, if any,



Scheme 6.

mass transport limitations exist at the high temperatures typically employed for hydrocarbon cracking.

5.2. *Aromatic compounds*

Hierarchical ZSM-5 prepared from a macroporous silica gel has been used for the cracking of triisopropylbenzene (Scheme 6) [65].

Since triisopropylbenzene is too large to enter the microporous system of the ZSM-5 it is not surprising that the hierarchical zeolite achieves a much higher conversion (98%) compared to the conventional zeolite (14%). For the cracking/isomerisation of 1,2,4-trimethylbenzene, mesoporous Beta and ZSM-11, synthesized by the use of polyvinylbutyral as the mesopore directing agent, have been tested and compared [66]. The authors showed that the mesoporous ZSM-11 is more active and *e.g.* shows the same activity at 623 K as the conventional ZSM-11 shows at 663 K. The product selectivity is quite different in the two cases, though. While the conventional ZSM-11 zeolite exhibited a 31% selectivity to xylenes, the selectivity for the mesoporous analogue was only 12%. Instead, the mesoporous ZSM-11 primarily leads to mesitylene isomerisation (79% selectivity) which is lower for the conventional zeolite (57%). This selectivity difference can be explained by the slow diffusion of the bulky mesitylenes in the conventional zeolite leading to increased retention times and also an increased chance of cracking to form smaller products that can easily diffuse out of the zeolite crystal. The mesopores have the opposite effect and serve to reduce the substrate retention time in the zeolite and thus minimizes the chance for cracking.

A study from Weiss and co-workers [67] (and references therein) presents early work using dealuminated mordenite in cracking of cumene into benzene and propylene. Acid leaching is seen to deplete the active sites within the catalyst and the intrinsic activity is lowered but a substantial lifetime increase is simultaneously observed making the dealuminated catalyst superior after prolonged reaction times. This is attributed to an increased rate of product desorption, effectively lowering the tendency to form high molecular weight condensates.

5.3. *Hexadecane*

The cracking of hexadecane using mesoporous zeolites has also received a lot of attention. In one study, mesoporous HZSM-5 zeolite prepared by carbon templating was compared to conventional HZSM-5 [68]. Here it was found that the mesoporous HZSM-5 had a significantly increased activity, leading to 52% *n*-hexadecane conversion compared to 17% for the conventional zeolite. When the zeolites were impregnated with platinum their cracking activity increased significantly and the mesoporous HZSM-5 was again found to display higher activity. In addition to this, a fourfold increase in *n*-hexadecane isomerisation was achieved for the mesoporous zeolites. This large difference in product selectivity was explained in terms of shorter retention time of the substrates in the zeolite crystals, leading to less cracking and more isomerisation. In a different study, mesoporous silicalite-2 and HZSM-11, both of MEL structure type, were compared to conventional HZSM-5 for the cracking of *n*-hexadecane at 553 K [69]. Here a large difference in *n*-hexadecane conversion was observed. Whereas mesoporous silicalite-2 is almost inactive due to its lack of acidity, mesoporous HZSM-11 gave almost complete (94%) conversion, while the conventional HZSM-5 gave a modest 38% conversion under identical conditions. It should be noted that the mesoporous HZSM-11 used in this study has a lower acid density than the conventional HZSM-5, thus illustrating that the mesopores play a crucial role in the catalyst activity. In a similar study, mesoporous and conventional HZSM-12 are compared and the diffusion of *n*-hexadecane out of the zeolite was studied as well as the effect of coking [70]. For the cracking of *n*-hexadecane the mesoporous zeolite again exhibited superior activity compared to the conventional HZSM-12 zeolite. The mesoporous HZSM-12 was found to contain more coke deposits than the conventional zeolite and yet it maintains a higher activity. The coking resistance phenomena was explained by the effect of the mesopores to increase the number of entry points to the microporous system as well as the overall surface area, and thereby increase the amount of coking needed to restrict its accessibility.

Scheme 7.

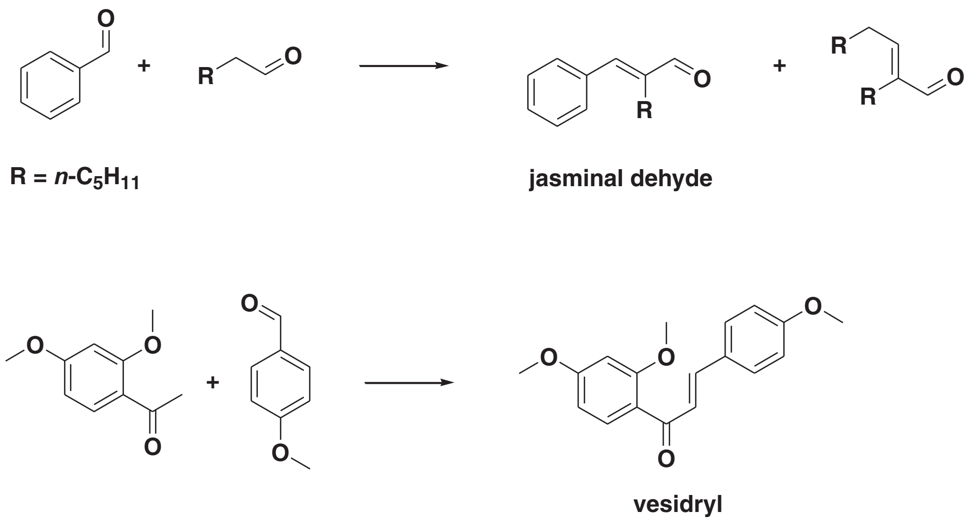
5.4. *Vacuum gas–oil*

Cracking of VGO is an important refinery process. Recently, Triantafyllidis and co-workers have studied the cracking of VGO using hierarchical MFI zeolites synthesized using organosilane templates [71]. This procedure results in a material having a very narrow set of mesopores, depending on the size of the template used (2.2 nm or 5.2 nm). These two hierarchical zeolites were compared to conventional ZSM5 and found to display much higher activity and selectivity towards gasoline. The gasoline yield improved from 12% to 19% when using the mesoporous zeolites at one set of conditions (823 K) where the VGO conversion also was improved from 33% to 48%.

5.5. *Polyethylene/polypropylene*

The recycling of plastic waste such as polyethylene and polypropylene is a challenging task since the carbon chain length is typically in the range of tens of thousands. Cracking over a zeolite catalyst to produce light olefins is one option (Scheme 7).

Obviously, the large polymer molecules cannot enter the microporous system of a zeolite. As a consequence, zeolites containing large mesopores and a large external surface area have been studied intensively in the recent years. Serrano et al. have synthesized ZSM-5 nano-crystals (~10 nm) by the addition of an organosilane compound during the zeolite synthesis [72]. This material has a very large external surface area (314 m^2/g) and total surface area (586 m^2/g). In the cracking of polypropylene at 633 K (50/50 wt% of catalyst and polypropylene), this material achieves complete conversion in 3 h compared to 27% for the conventional ZSM-5 zeolite. A similar catalyst was also used by the same group to crack actual agricultural plastic film waste consisting of LDPE (low density polyethylene) and ethylene-vinyl acetate co-polymer [73]. Here the nanocrystalline HZSM-5 again proved to be superior to other zeolites and mesoporous materials. Using a similar approach, hierarchical Beta zeolite having a large external surface area (145 m^2/g) and total surface area (857 m^2/g) was synthesized and used for the cracking of LDPE [74]. Here it was shown that the TOF increases by a factor of 18 when compared to a conventional Beta zeolite. Additionally, while the conventional zeolite exclusively leads to the formation of C_1–C_5 products the hierarchical zeolite only has 50% selectivity to these small products while forming 50% of the larger C_6–C_{40} compounds. This selectivity difference was attributed to the mesoporous nature of the material



Scheme 8.

which allows the large products to exit the zeolite before they are converted into smaller cracking products. In a separate study by Pérez-Ramírez et al., the mesoporosity was introduced into Beta zeolite by desilication using NaOH [75]. By varying the amount of template still present in the zeolite during desilication, different degrees of mesoporosity can be introduced. In this study, the temperature needed to reach 50% LDPE conversion was compared for the various zeolites and the study shows a good trend between the mesopore volume of the zeolite, and the required temperature. For the conventional Beta zeolite, a temperature of 703 K is required, whereas a temperature of 623 K is required in one case when using a mesoporous sample. This corresponds to a TOF that is ∼10 times higher per aluminum for the mesoporous Beta zeolite. MFI containing micro/mesoporosity synthesized by the use of an organosilane surfactant was thoroughly studied by Ryoo and co-workers for the cracking of polyethylene [76]. The hierarchical MFI zeolite was found to display a significantly higher activity than conventional MFI, achieving an 88% PE conversion opposed to 10% for the conventional at 653 K. In order to substantiate that the increase in activity is caused by the mesoporosity of the MFI, selective dealumination of the aluminum in the mesopores was achieved using tartaric acid. Testing of the mesopore-dealuminated MFI zeolite revealed an activity comparable to that of the conventional MFI zeolite (12% conversion), thus supporting the conclusion that the mesopores are the source of the increased activity for the PE cracking reaction.

Catalytic testing showing an improved performance is solid documentation for relevance of a given protocol introducing mesoporosity. It is however often not enough to comprehensively describe the catalyst. Relatively few reports perform actual diffusion or uptake experiments but an example where thorough characterization is coupled with uptake and adsorption data using several probes, as well as catalytic performance is given by Verboekend et al. [77]. The 1-dimensionel zeolite ITQ-4 was desilicated and increasing levels of mesoporosity were introduced as a function of desilication strength. Cracking of LDPE was chosen as test reaction and indeed an optimally desilicated sample was able to operate at lower temperatures; the temperature where a 10% conversion was reached was lowered by 353 K compared to the parent sample. Elution studies using *n*-butane and neopentane reveals a faster desorption from the mesoporous crystals indicating a faster molecular transport within this sample. Interestingly, when adsorbing selected molecules from the gas phase, a pronounced difference between the adsorption behavior of propane and propene is seen. The authors correlate this observation with the introduction of Lewis acidity evidenced by infrared spectroscopy (using pyridine and collidine) and are thus able to discuss the mesoporosity and acidity changes in the proper context.

6. Condensation reactions

Hierarchical zeolites have found application as catalysts for several different types of acid catalyzed condensation reactions. These range from aldol-type reactions, over esterications to protection of aldehydes and ketones by acetalization. These reactions represent illustrative examples of how hierarchical zeolites can be applied in reactions which are traditionally beyond the scope of purely microporous zeolites due to the large molecular size of the reactants or products compared to the dimensions of the zeolite channels.

6.1. Aldol condensation reactions

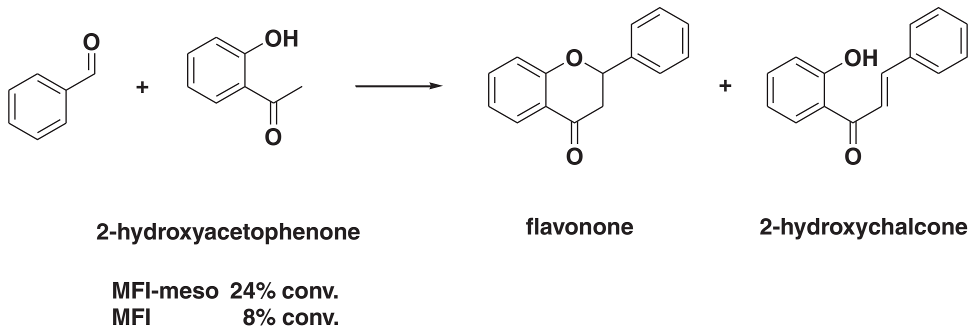
An example of the application of hierarchical zeolites for condensation reactions is in the syntheses of jasminaldehyde and vesidryl reported by Ryoo and co-workers as shown in Scheme 8 [78].

Here the reactants are relatively bulky and therefore have difficulties in penetrating into the bulk of the crystals. This is evidenced by the low conversion of the substrates when using conventional ZSM-5 as the catalyst, namely 4% in the synthesis of jasminaldehyde and 3% in the synthesis of vesidryl. However, when using mesoporous ZSM-5 as the catalyst, conversions of 98% and 60% are observed, respectively. Thus, here it seems that the added mesoporosity serves to enhance the accessible surface area and thereby increase the activity of the zeolite catalyst dramatically.

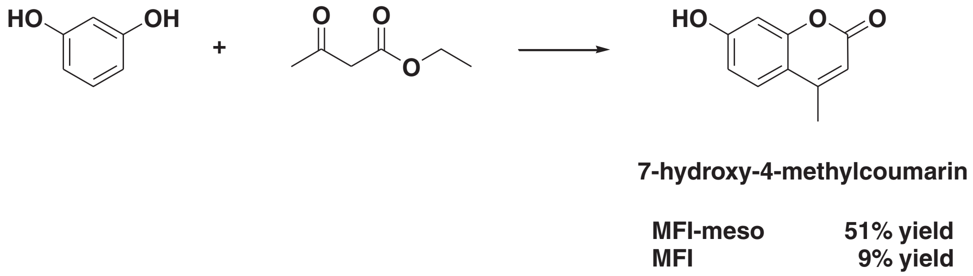
In a recent work, the same authors have also prepared a series of nano-sized ZSM-5 zeolites by addition of different alkylalkoxysilanes during the synthesis and tested the zeolites in various reactions [79]. One of these reactions, where a positive effect from mesoporosity can be seen in the conversion, is the condensation of benzaldehyde and 2-hydroxyacetophenone yielding a mixture of flavanone and 2-hydroxychalcone (Scheme 9).

6.2. Esterification reactions

Another reaction investigated was the condensation of resorcinol and ethylacetoacetate to give 7-hydroxy-4-methylcoumarin as the bulky condensation product (Scheme 10).



Scheme 9.



Scheme 10.

Here the product yield was reported to increase from 9% to 51% when using the mesoporous MFI zeolite. Again, this exemplifies that mesoporous zeolites might find application as catalysts for reactions beyond traditional petrochemical industry.

Condensation of a carboxylic acid and an alcohol giving an ester is another type of condensation reaction which has been carried out using mesoporous MFI zeolites (Scheme 11) [76,79].

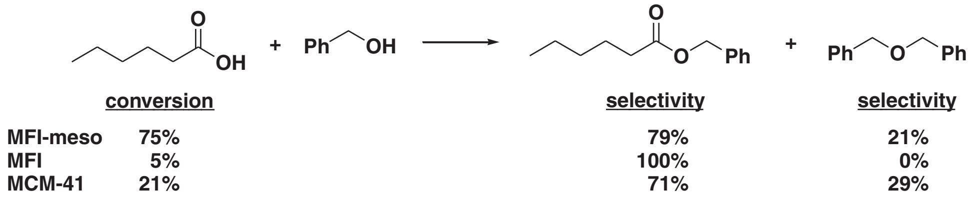
For this reaction, in terms of hexanoic acid conversion, the hierarchical MFI catalyst is more active than a conventional MFI catalyst as well as an Al-MCM-41-type catalyst. After five experimental runs, the hierarchical MFI catalyst still exhibited 78% benzyl alcohol conversion whereas the other catalysts were completely deactivated. This exemplifies that hierarchical zeolites are more stable than amorphous mesoporous materials even though the initial activities of the catalysts, i.e. conversion after a single run, are comparable. However, this example also illustrates that mesopores can facilitate undesired effects since the benzyl hexanoate selectivity drops from 100% to 79% when using the mesoporous MFI instead of the conventional MFI. This decrease in selectivity is caused by the formation of dibenzylether, a bulky by-product which is too large to be formed in the micropores but which is easily formed in the larger mesopores. Thus, the increased activity in this case again comes at the cost of a decrease in shape selectivity.

6.3. Acetalisation reactions

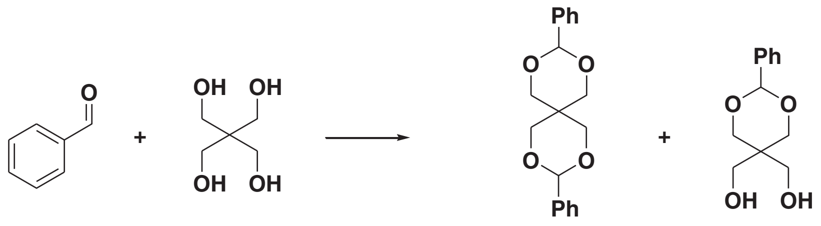
Reactions involving condensation of aldehydes and ketones with an alcohol yielding an acetal or a ketal, respectively, have also been studied using mesoporous zeolites as the catalyst [76]. These were reported for the condensation of cyclohexanone with methanol forming a relatively small condensation product as well as for the condensation of benzaldehyde with pentaerythritol to give a much bulkier product.

For the condensation of benzaldehyde and pentaerythritol (Scheme 12) using a conventional MFI zeolite, no conversion was observed. In contrast, mesoporous MFI as well as MCM-41 were much more efficient catalysts, leading to near complete conversion under similar conditions (393 K). Both catalysts exhibited high selectivity towards the diacetal product. The reaction was shown to be catalyzed by the exterior acid sites as opposed to the acid sites in the micropores by the observation that no conversion was seen when a catalyst was subjected to preferential dealumination of the exterior acid sites by treatment with tartaric acid. The dealuminated zeolite was inactive for the condensation reaction and it is thus plausible to conclude that the bulky acetal product is preferentially formed in the mesopores of the zeolite and not in the micropores. In contrast, the condensation reaction between cyclohexanone and methanol was found to be much less affected by the use of a catalyst containing mesopores [76]. Here, a 50% yield of 1,1-dimethoxycyclohexane was achieved by the use of a conventional MFI zeolite, while a 58% yield was obtained for the mesoporous analogue under identical conditions. Thus, for this reaction involving small molecules there is not much benefit in applying a mesoporous as opposed to a conventional MFI zeolite.

The use of a hierarchical zeolite obtained by desilication and its use as a catalyst in the Chichibabin condensation of formalde-



Scheme 11.



	conversion	selectivity	selectivity
MFI-meso	100%	95%	5%
MFI	0%	-	-
MCM-41	95%	100%	0%

Scheme 12.

hyde, acetaldehyde and ammonia to form pyridine and 3-picoline at 723 K has also been reported [80]. The mesoporous zeolite was found to be slightly more stable than the conventional zeolite. However, the yields of pyridine and 3-picoline were comparable for the parent and desilicated zeolite, suggesting that this reaction involving small reactants and products does not benefit significantly from the use of a mesoporous zeolite. Additionally, it should be noted that the desilication treatment was found by FT-IR studies to lead to the formation of extra framework aluminum species, i.e. the introduction of Lewis acidity. Thus it should be kept in mind that the introduction of mesoporosity by chemical post treatment methods such as desilication inevitably will bring about changes to the zeolite in addition to introducing mesoporosity.

7. Other reactions

Aside from alkylation, isomerisation, cracking and condensation reactions, hierarchical zeolites have also found application as catalysts in several other reactions involving organic substrates. These include the Beckmann rearrangement reaction as well as oxidations and epoxidations. In many of these cases, the reactants are too bulky to penetrate into the interior of the crystals, thus the reaction takes place in the pore mouths or on the external/mesopore surface of the zeolite. Although the specific micropore system of the zeolite for such applications is perhaps not so important, there are still good reasons for choosing a zeolite catalyst as opposed to other types of solid acid catalysts. One of the main reasons is their crystalline nature which makes them more acidic and more stable than amorphous materials of similar chemical compositions.

7.1. Beckmann rearrangement

The use of hierarchical zeolites have been reported for the Beckmann rearrangement reactions of cyclohexanone oxime [81,82] and cyclododecanone oxime [83]. For Beckmann rearrangement of cyclohexanone oxime, silicalite-1 as well as TS-1, i.e. pure silicate MFI and titanosilicate MFI, respectively, were applied as catalysts. The hierarchical silicalite-1 catalyst was made by an approach resembling carbon-templating which involved impregnation of a zeolite gel onto an organic aerogel followed by crystallization and carbonization. The zeolite–carbon material was then calcined to produce a hierarchical zeolite monolith or subjected to a second impregnation and crystallization step. In both cases, the resulting materials were at least twice as active in terms of $(g_{\text{caprolactam}})/(g_{\text{catalyst}} \cdot h)$ as compared to a hieararchical zeolite reference sample consisting of nanosized crystals. The same reaction was studied using nanosized TS-1 samples prepared in the absence as well as presence of different amounts of crosslinking agent (1,7-dichloro-octamethyl-tetrasiloxane) added to the synthesis gels. After 1 h reaction time at 553 K the caprolactam productivity in terms of $(\text{mmol}_{\text{caprolactam}})/(g_{\text{catalyst}} \cdot h)$ were about the same for the non-crosslinked nanosized catalyst and the catalyst prepared using 0.65 mmol linker. However, after 4 h reaction time, the caprolactam productivity observed for the non-crosslinked sample decreased by 85% whereas it increased by 28% for the sample crosslinked using 0.65 mmol linker. Still more active was the sample prepared using 1.3 mmol linker, and this catalyst did not even exhibit deactivation after 30 h on stream at 633 K. Thus, addition of crosslinker in the synthesis of nanosized TS-1 leads to more active and more stable catalysts.

Also hierarchical ITQ-2 zeolites made by delamination of MCM-22 were reported active in the Beckmann rearrangement reaction [83]. In this reaction, involving rearrangement of cyclododecanone oxime, the lactam yield at 403 K was significantly higher when ITQ-2 was applied as catalysts than when either MCM-41 or conventional zeolite Beta were used. The lower activity and selectivity of the conventional zeolite Beta catalyst was attributed to the substrate being simply too bulky to penetrate into the bulk of the crystal. Thus, the reaction takes place on the surface where no shape selectivity is possible. On the other hand, the lower activity of the MCM-41 catalyst was shown to be caused by the material having fewer sites with weaker acidity.

7.2. Epoxidation and hydroxylation reactions

Hierarchical TS-1 catalysts have also found application as catalysts for epoxidation and hydroxylation reactions. In fact, epoxidation was one of the first reactions reported in which a hierarchical zeolite was used as catalyst [84]. In the report, a carbon-templated TS-1 catalyst was compared to a conventional TS-1 catalyst in the epoxidation of 1-octene and cyclohexene with hydrogen peroxide at a reaction temperature of 313 K. By plotting the product concentration ratios for the mesoporous and conventional catalysts ($C_{\text{mesoporous}}/C_{\text{conventional}}$) it was shown that epoxidation of 1-octene is not diffusion-limited under the reaction conditions, since $C_{\text{mesoporous}}/C_{\text{conventional}}$ is close to unity during the entire experiment, whereas for the epoxidation of cyclohexene there is a clearly improved catalytic activity for the mesoporous sample. Very recently, epoxidation of cyclohexene was reported using mesoporous TS-1 prepared by assembly of seeds [85]. Also hierarchical TS-2, i.e. MEL-structured titanosilicate, has been applied for epoxidation reactions [86].

Recently, also nanocrystalline TS-1 was studied as catalyst for the epoxidation of 1-octene using the bulky organic tertbutylhydroperoxide as the oxidant [87]. The hierarchical catalysts were prepared by adding a silanization agent to hinder the growth and agglomeration of zeolitic seeds during crystallization. Comparing the catalytic performance of a small series of samples with decreasing crystal size and thus increasing inter-particle porosity it was observed that the epoxide selectivity in all cases was 100%. However, large differences, ranging from 6% to 42% conversion at 373 K after 3 h were observed. The authors argued that the high external surface area and the increased accessibility to the active Ti-sites were the source of the catalytic improvements.

Hydroxylation of benzene with nitrous oxide forming phenol was recently reported using hierarchical ZSM-5 catalysts prepared by desilication [88]. The most pronounced difference seen in the catalytic tests was a dramatic deactivation of the parent zeolite which was avoided in the case of the hierarchical zeolite. ICP-OES and EPR measurements showed that the state and amount of iron in the two samples were similar, thus the improved catalytic performance is most likely due to the interconnected mesopore system, which effectively lowers the average diffusion length for reactants and products. Very recently, also hydroxylation of phenol with hydrogen peroxide was reported using carbon-templated mesoporous TS-1 [89]. The mesoporous TS-1 was almost twice as active as the conventional TS-1.

7.3. *Hydrotreating reactions*

Hierarchical zeolite supported noble metal catalysts were recently reported as catalysts for hydrogenation of bulky aromatic molecules [90,91] as well as for hydrodesulfurization of 4,6-dimethyldibenzothiophene [91,92]. Concerning hydrogenation of pyrene, ion exchange of $Pd(NH_3)_4^{2+}$ onto mesoporous zeolite Beta afforded a catalyst (Pd/Beta-meso) which was more active than similarly prepared conventional Beta, Al-MCM-41 and γ-Al_2O_3 based catalysts. The improved activity of the Pd/Beta-meso sample in comparison with Pd/Al-MCM-41 and Pd/γ-Al_2O_3 was attributed to the higher amount and strength of acid sites. However, the improved activity of the Pd/Beta-meso sample in comparison with Pd/Beta must be attributable to the additional mesoporosity since the acid amount and strength distribution of these samples are quite similar. In addition to exhibiting higher conversion of pyrene, the content of deep hydrogenation products (hexahydro-, decahydro- and perhydropyrenes) in the reaction liquids was also considerably higher for Pd/Beta-meso than for the other catalysts. This is important, since it is well known that the intermediately hydrogenated products become increasingly refractory towards further hydrogenation. This observation is apparent from a similar hydrogenation study in which it was shown that hydrogenation of naphthalene proceeded with similar activity over Pd/Beta-meso and Pd/Al-MCM-41, but where Pd/Beta-meso was considerably more active than Pd/Al-MCM-41 in the hydrogenation of tetralin [91]. Moreover, the Pd/Beta-meso catalyst showed much greater tolerance than the Pd/Al-MCM-41 sample when carrying out hydrogenation of naphthalene as well as pyrene in the presence of 200 ppm thiophene.

Another hydrotreating reaction which has been studied using hierarchical zeolites recently is hydrodesulfurization of 4,6-dimethyldibenzothiophene [91,92]. This reaction has been studied using the Pd/Beta-meso catalyst mentioned above, as well as with mesoporous Pt/ZSM-5, Pd/ZSM-5 and Pt-Pd/ZSM-5 catalysts. In one of the reports, Pd/Beta-meso was shown to be able to reduce the sulfur content of the reaction liquid more than the Pd/Al-MCM-41 catalyst it was compared to [91]. For instance, the sulfur content after 3 h at 523 K was 165 ppm using the Pd/Beta-meso catalyst in comparison with 226 ppm for the Pd/Al-MCM-41 catalyst. This finding was attributed to the increased acidity of the Beta-meso support in comparison with the Al-MCM-41 support. Concerning the mesoporous ZSM-5 supported catalysts, comparison of Pt and Pd samples on these supports with reference catalysts of the same metals on conventional ZSM-5 and γ-Al_2O_3 showed that mesoporous Pt/ZSM-5 (63%) and, particularly, mesoporous Pd/ZSM-5 (83%) were considerably more active than the reference catalysts [92]. Very recently, mesoporous zeolite L prepared by assembly of zeolite L nanocrystals was reported as support for more classic CoMo and NiMo type catalysts for hydrodesulphurization (HDS) [93] In this report it was shown, that the mesoporous L material was a better support for the active material than purely microporous zeolite L as well as the Al_2O_3. The excellent performances of the mesoporous zeolite L supported catalysts were attributed to high amounts and strengths of acid sites as well as a highly porous structure.

7.4. *Reactions involving inorganic substrates*

Hierarchical zeolites have also found application as catalysts for conversion of inorganic molecules such as NO and N_2O. Concerning these molecules the application of hierarchical zeolite catalysts has proceeded along two different avenues. One strategy is the selective catalytic reduction (SCR) of NO with NH_3, another is the direct decomposition of NO or N_2O. At any rate, the key issue is the conversion of NO or N_2O to N_2 (and H_2O/O_2).

One strategy for NOx removal in stationary as well as automotive applications is the selective catalytic reduction (SCR) of nitrogen oxides with NH_3. For this application, conventional Fe and Cu zeolites are currently attracting much attention [94]. Also mesoporous iron-containing zeolites have been studied as catalysts for NO SCR with NH_3 [95,96]. It was shown, that mesoporous Fe-ZSM-5 as well as mesoporous Fe-ZSM-12 catalysts were more active than the conventional analogues at all temperatures in the studied interval (573–773 K) and that they were both more active than the reference 3% V_2O_5/TiO_2 catalyst above 723 K [96]. Moreover, it was shown that the NO conversion activity is increased when increasing the iron loading of the samples until a maximum is reached. For the mesoporous Fe-ZSM-5 sample a maximum of ca. 30% conversion at 623 K is achieved at an iron loading of 6–7%, whereas for the conventional Fe-ZSM-5 sample, a maximum of ca. 15% is reached at an iron loading of 2–3% [95]. Similarly, a maximum of ca. 60% conversion at ca. 6% loading is reached over mesoporous Fe/ZSM-12 in comparison with 35% at 4% loading for the conventional Fe/ZSM-12 [96]. This suggests that a better dispersion of the iron species is possible in the mesoporous samples in comparison with the conventional samples.

Another strategy for NO removal is the direct decomposition of this molecule to N_2 and O_2. This reaction has also been studied using mesoporous zeolite catalysts, in this case Cu-ZSM-5 and Cu-ZSM-11 [97]. It was shown that both mesoporous Cu-ZSM-11 and mesoporous Cu-ZSM-5 were more active than their conventional references. These observations were shown to correlate with the accessibilities of the active Cu species in the zeolite samples. Moreover, EPR (electron paramagnetic resonance) investigations revealed that mesoporosity in the zeolites facilitate the formation of dimeric or oligomeric Cu-species in contrast to the monomeric Cu-species dominating in the conventional samples. Another observation apparent from the experimental data was that the mesoporous Cu-ZSM-11 catalyst was twice as active as the mesoporous Cu-ZSM-5 catalyst. This was attributed to preferential formation of active Cu-sites in the straight channels of ZSM-11 rather than in the sinusoidal channels of ZSM-5.

Also decomposition of N_2O has been studied using hierarchical zeolite catalysts [98–100]. In a thorough study, it was shown that steam activation of Fe, Ga and "normal" Al-ZSM-5 samples improved the catalytic activity in N_2O decomposition, whereas merely calcining the samples prior to the catalytic experiments had a detrimental effect on the activity [98]. Moreover, the authors showed that alkaline treatment of the steam-activated samples further increased their catalytic activity. One reason for this was further touched upon in a more recent report, where it was shown that alkaline treatment enhanced the iron uptake capacity during ion exchange [99]. In fact, it was shown that the Fe ion exchange capacity of as-received ZSM-5 was limited to 0.9 wt% whereas the alkaline treated sample could contain up to 1.98 wt% Fe. The increased iron uptake capacity was also evident from the catalytic experiments, however, it appears that only a fraction of the extra Fe becomes active in the reaction, since the activity was only slightly increased. However, this relatively low activity increase might perhaps be explained by the observation that acidity is important for the reaction as was shown earlier [98]. In fact, this might explain why a subsequent NH_4NO_3 ion exchange treatment of alkaline treated ZSM-5 improves the N_2O conversion significantly [100].

8. Summary and discussion

The most important reason for using a mesoporous zeolite is its large external surface area that enables easy diffusion of substrates and products in and out of the zeolite. Unlike mesoporous materials such as MCM-41, mesoporous zeolites are crystalline and thus have much stronger hydrothermal stability and also much higher acidity which often makes them preferable for use in catalysis and also viable alternatives to conventional solid acid catalysts such as clays and solid phosphoric acids. However, introducing mesoporosity in zeolites simultaneously dictates that an increasing portion of the acidity will be available for molecules too large to actually enter the micropore structure. In order to analytically describe this important issue Pérez-Ramírez and co-workers have introduced an accessibility index (ACI) and the hierarchy factor (HF). The accessibility index is a characterization tool using bulky bases (pyridine, 2,6-lutidine and 2,4,6-collidine) in combination with infrared spectroscopy, to directly measure the effective mesoporosity of any zeolite system. It was shown that 2,4-lutidine probes approximately half the Brønsted acidic sites in a commercial ZSM-5 sample vs. all after a strong desilication and 2,4,6-collidine can access only 6% of the Brønsted acidic sites in the reference sample contrasted by almost 40% post desilication. This observation further supports the need to consider non-shape selective reactions in highly mesoporous zeolites in order to fully understand the properties of these materials in which the ACI can be a helpful tool [101]. The hierarchy factor [102] is an analytical tool intended to make comparison of mesoporosities possible independent of sample preparation. If considering a shape selective reaction taking place within the micropores, the micro- and mesopores will serve a distinctly different purpose, i.e. confining the active sites and facilitate mass transport, respectively. The authors thus argue that an optimum between the relative distributions is important in identifying the best catalyst for a given reaction. The hierarchy factor is defined as the product of (V_{micro}/V_{pore}) and (S_{meso}/S_{BET}) and can be conceptualized as a measure of how large a fraction of the micropore volume is advantageous to sacrifice in order to produce mesoporosity while still improving the catalytic performance. A linear correlation between productivity and the HF could be seen for benzene alkylation with ethylene [102] which very interestingly shows that not simply the most mesoporous sample performed best in this reaction but rather a sample having a pronounced mesoporosity as well as a (relatively) preserved microporosity. It must be noted that the HF does not take account for changes in acidity and should thus naturally be used supplemented by additional characterization. It does however, give an improved understanding of the porosity introduced allowing for a discussion of at which point a zeolite is in fact mesoporous enough. Supposedly a high HF is beneficial with respect to catalytic applications but this further depends on the reaction investigated. The same authors [77] have presented an illustrative example where the cracking of LDPE was tested over zeolite ITQ-4 desilicated to increasing levels. As the cracking reaction proceeds on the mesopore surface and pore openings the catalytic optimum was seen after the HF had reached its maximum. On the other hand considering a reaction with only a slight diffusion restraint one could expect the catalytic optimum to occur before a maximum in HF was reached. The HF is nonetheless an excellent tool for analyzing mesoporosity in zeolites, especially if porosity obtained by different protocols is to be compared.

8.1. Effect of mesopores on different reactions

Despite the different conditions and materials reported throughout literature, some generalizations on the effect of mesoporous zeolites in different reaction categories can be made though. Most of these can be classified into one of following two groups: reactions which take place in the micropores of the zeolite and reactions that take place on the external surface or in the pore mouths. For reactions taking place in the micropores, the mesopores effectively enhance the rate of diffusion in the bulk catalyst. For reactions taking place outside the microporous system, the mesopores dramatically increase the external surface area. The overall feature for both groups is that an increased catalytic activity is observed. This is especially the case for the cracking of large molecules such as polyethylene and hexadecane [68–76] but also in the condensation of large molecules and in the alkylation of aromatic compounds [12,76,78].

The effect of mesoporosity on selectivity is often a result of the increased diffusion of products out of the zeolite, thereby reducing the retention time of the product in the zeolite and thus the chance of it undergoing a second reaction. This effect causes an increase in the selectivity of most isomerisation reactions over that of cracking and in some cases an increase in the amount of large products formed in the cracking of *e.g.* polyethylene is seen. However in some cases a loss in selectivity of a desired product is observed. This is often caused by a loss of shape selectivity, leading to the formation of bulky by-products outside of the zeolite micropore system [76]. If a reaction benefits from the shape selective feature of a conventional zeolite, this effect is likely to be diminished using a mesoporous analogue and a decrease in selectivity is thus likely to occur unless measures are taken to deactivate the acid sites of the external surface of the crystals.

8.2. Effect of mesopores on the catalyst

The lifetime of the catalyst has in many cases been shown to increase by the introduction of mesoporosity. The main cause of deactivation in most cases relates to the effects of pore blocking by coke deposition in the zeolite. Numerous reports have argued that the positive effect on lifetime is caused not by a decreased rate of coke formation but rather from an enhanced resistance to the effects of coking. Shorter mean diffusion lengths coupled with more pore entrances in the mesoporous crystals render the crystal harder to block and this could very well account for the decreased effects of coking. This simple argument may however not describe the full picture. Authors have reasoned that as a consequence of the mesoporosity the products formed will have a lower retention time in the micropores which can suppress secondary reactions (coking). Naturally these considerations are very reaction specific but in this way the increased stability would be an effect derived of the improved mass transport.

9. Outlook

There are many methods of introducing mesoporosity into zeolites and these methods allow a high degree of fine-tuning to take place, enabling mesoporous zeolites containing a high degree of complexity to be synthesized. However, this also has the inherent drawback that a vast amount of unique mesoporous materials are reported in the literature, making comparison across research groups a difficult task. Therefore a large proportion of the work effort related to mesoporous zeolites is spent on material preparation, leaving less room for more thorough characterization and catalytic testing. However, the use of mesoporous zeolites in catalysis is certainly gaining momentum and comparison across research groups is now possible as the volume of literature usable for comparison increases and generalized tools such as the ACI and HF have been introduced. The present review is focused on the catalytic use of hierarchical zeolites. The field combines multiple disciplines bringing together advanced material preparation, sophisticated and equipment-demanding characterization, as well as careful catalytic testing. From the reviewed literature it is clear that some of the best scholarly studies come from scientific groups which are well founded within all three categories and have dedicated time to perform in-depth characterization and demonstrate detailed knowledge of the catalytic reactions tested, while following the general recommendations for catalytic testing [103]. Reports preparing exciting materials but lacking the catalytic aspect have thus not been described in this contribution.

At present it is clear that many reactions indeed can benefit from the use of a mesoporous zeolite. A challenge within the field lies in the evaluation of the level and type of mesoporosity introduced into the zeolite crystal. Some of the protocols used for manufacturing the mesoporous zeolites can fairly easily be tuned into generating a series of zeolites with increasing levels of mesoporosity. This is especially true for desilication [104] but has also been shown valid by changing the carbon source in carbon-templating [105], varying the amount of cationic-polymer [26], *etc.* From comparing a series of zeolites with increasing levels of mesoporosity it could prove possible to extrapolate which level of mesoporosity is sufficient for the specific reaction. In this context it is naturally very important to consider whether the reaction is taking place within the micropores, in the pore mouths or solely on the external/mesopore surface. Evidently all three types of reactions will benefit from introducing mesoporosity into the zeolite. However, for a reaction that is proceeding within the micropores the level of mesoporosity at which diffusion is no longer a limiting factor is presumably different from a reaction proceeding in the pore mouths or on the mesopore walls. Further, in cases where a balance between activity and shape selectivity is sought, insight into the catalytic evolution using a series of hierarchical samples could contribute to understanding the reaction and the effect of mesoporosity in the zeolite catalyst.

Another challenge is connected to the need of comparing the hierarchical zeolite to a zeolite with physical-chemical properties differing only in the absence of mesoporosity. Indeed zeolites are complicated materials and often when a reference material is produced it can be problematic to claim that it is representative of a perfect non-mesoporous counterpart with exactly similar Si/Al ratio, crystal size, elementary distribution, defect density, *etc.* This problem can be negligible in most cases but for example in the case of desilication extra-framework aluminum can form on the external surface during the procedure [42,80,106]. The extra-framework aluminum sites thus represent an alien non-shape selective reactivity in the otherwise shape selective catalyst. This exemplifies why caution should be exercised in the interpretation of the catalytic data, since the mesoporosity introduced is presumably the most significant difference between the conventional/parent and the hierarchical sample, but potentially not the only one.

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