Catalytic test reactions for the evaluation of hierarchical zeolites

Journal:	*Chemical Society Reviews*
Manuscript ID	CS-REV-12-2015-000935.R1
Article Type:	Tutorial Review
Date Submitted by the Author:	29-Feb-2016
Complete List of Authors:	Hartmann, Martin; University of Erlangen, Erlangen Catalysis Resource Center Machoke, Albert; University of Erlangen-Nürnberg, Institute of Chemical Reaction Engineering Erlangen Schwieger, Wilhelm; University of Erlangen-Nuremberg, Chemical Reaction Engineering

Tutorial review submitted to Chem. Soc. Rev.

"Catalytic test reactions for the evaluation of hierarchical zeolites"

Martin Hartmann[a]*, Albert Gonche Machoke[b] and Wilhelm Schwieger[b]

Erlangen Catalysis Resource Center (ECRC), Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

Chemical Reaction Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

*Corresponding Author:

Prof. Dr. Martin Hartmann

E-Mail: martin.hartmann@fau.de

Tel.: +49-9131-8528792

Abstract

Hierarchical zeolites have received increasing intention in the last decade due to their outstanding catalytic performance. Several types of hierarchical zeolites can be prepared by a huge number of different techniques. Hierarchical zeolites combine the intrinsic catalytic properties of conventional zeolites and the facilitated access and transport in the additional meso- or macropore system. In this tutorial review, we discuss several test reactions that have been explored to show the benefit of the hierarchical pore system with respect to their suitability to prove the positive effects of hierarchical porous zeolites. It is import to note that positive effects on activity, stability and less frequently selectivity observed for hierarchically structured catalyst not necessarily are only a consequence of the additional meso- or macropores but also number, strength and location of active sites as well as defects and impurities. With regard to these aspects, the test reaction has to be chosen carefully and potential changes in the chemistry of the catalyst have to be considered as well. In addition to the determination of conversion, yield and selectivity, we will show that calculation of the activation energy, determination of Thiele modulus and effectiveness factor are good indicators for the presence or absence of diffusion limitations in hierarchical zeolites compared to their parent materials.

Key learning points

- Hierarchical zeolites are an emerging technology in the mature field of industrial catalysts
- Several test reactions are suggested to prove the advantage of their hierarchical structure
- In addition to an increase in activity and selectivity suppression of coke formation is often observed
- Concept of Thiele modulus and effectiveness factor is required to judge the presence of diffusion limitation in hierarchical catalysts

Introduction

In recent years, hierarchical catalysts in particular based on microporous zeolites have received considerable attention.[1,2] Hierarchical zeolites include all microporous materials with at least two classes of pores. Here, the recent IUPAC classification of pores is used; micropores have a pore diameter below 2 nm, mesopores between 2 and 50 nm and macropores are pores with a diameter above 50 nm. The term "hierarchy" with respect to porosity in zeolites is often used in a very broad sense, namely for systems containing additional pores which can either be mesopores or macropores or both. Thus, hierarchical zeolites can have micropores and mesopores (also known as micro/mesoporous zeolites or mesoporous zeolites) or micropores and macropores (also known as micro/macroporous zeolites or macroporous zeolites) or micropores, mesopores and macropores. However, in hierarchical catalysts these different pore systems must be interconnected in order to classify the overall pore system as hierarchical and gain the full benefit in catalysis (for a good defenition of hierarchy see review of Schwieger et al. [3] or Perez-Ramirez et al. [6]).

It seems that the concept of hierarchically organizing the porosity in zeolite particles is relatively new, but catalysts with these characteristics, namely possessing at least two connected pore systems with pore sizes differing by at least one order of magnitude, have been used in industry for decades. The two most prominent examples are TS-1 (Enichem) and DDM, a deeply dealuminated mordenite (originally provided by DOW).[4] The later catalyst has been developed by DOW for use in its cumene process. Here, the intracrystalline mesopores are prepared by acid leaching and steaming, which results in fewer Brönsted acid sites with higher strength, which significantly improves the performance of the catalyst. Moreover, the one-dimensional channel system of mordenite is extended to a three-dimensional porous structure. Since the mesoporosity is mainly intracrystalline and not connected to the external surface of the crystals, however, its impact on the mass transport is limited.

In the case of TS-1, submicron particles are aggregated employing a mesoporous silica binder, which facilitates the diffusion through the aggregate particles. This first example of a hierarchically-ordered micro-mesoporous industrial catalysts has initiated the development of important industrial processes including the hydroxylation of phenol, the ammoximation of cyclohexanone and the epoxidation of propene.[4]

If only an improvement of mass transport efficiency is required, this can also be achieved by reducing the size of the zeolite crystals. An early industrial example is the zeolite beta-based catalyst for cumene and ethylbenzene processes employed by Polimeri Europa in the early 1990s. The key is the crystallization of blackberry-like aggregates of very small (10 - 20 nm) beta crystals. The presence of meso- and macropores in addition to the micropores of the zeolite results in efficient mass transport of reactant and product molecules within the aggregates.

In recent years, a number of new strategies have been developed, which allow the preparation of hierarchical catalysts in a more defined manner. Mainly zeolites with MFI topology, viz. ZSM-5, silicalite-1, TS-1 are studied, which have a medium sized pore system, i.e. pores with a circumference which is defined by rings consisting of 10 T-atoms. Straight channels (0.51 nm x 0.55 nm) are intersected by zigzag channels (0.53 nm x 0.56 nm), thus creating a three-dimensional network (Figure 1). However, some papers also deal with mordenite (MOR), zeolite beta (BEA) and MCM-22 (MWW). This topic has extensively been reviewed by a number of authors including Egeblad et al.[5], Perez-Ramirez et al.[6], Schwieger and co-workers [7], Chen et al.[8] and Serrano et al.[9].

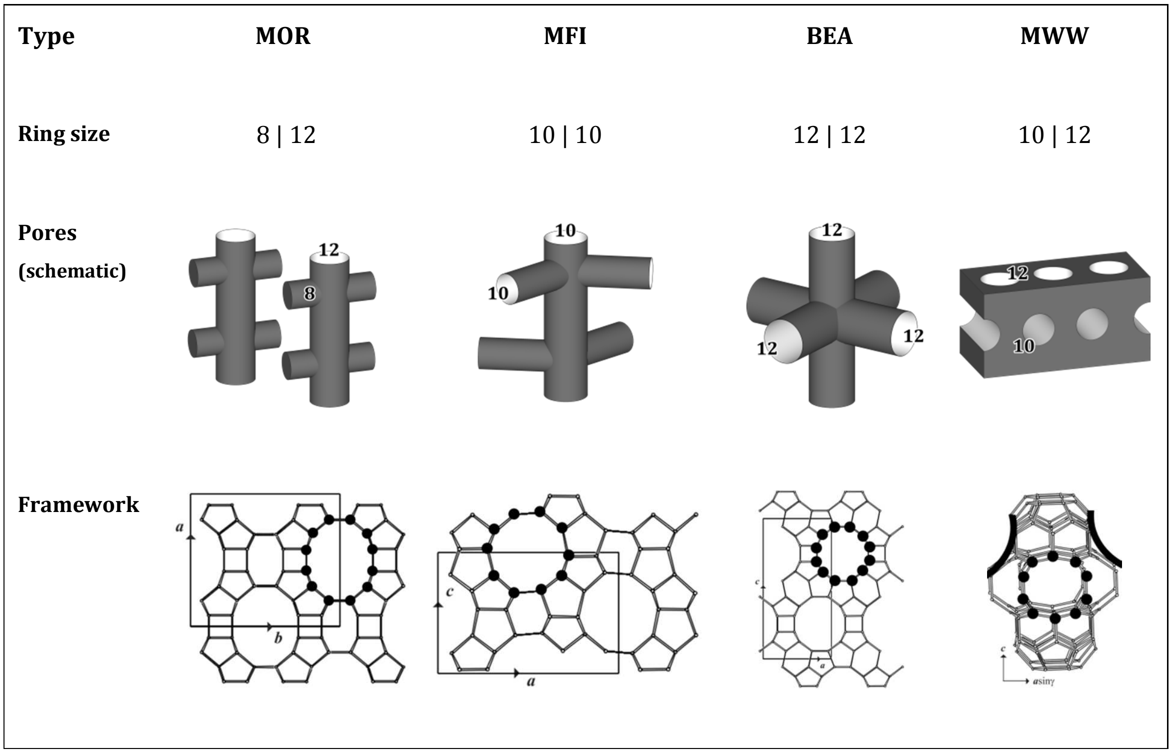

Figure 1: Schematic drawing of the structure of the zeolites used most commonly in zeolites-based hierarchical catalysts. Framework drawings adopted from: Ch. Baerlocher and L.B. McCusker, Database of Zeolite Structures: http://www.iza-structure.org/databases/.

The main interest to prepare hierarchical zeolites is to allow the transformation of large molecules, which cannot enter in the zeolitic micropores and to shorten the diffusion path length for molecules which tightly fit into these small pores. As a consequence, hierarchical materials have been used to achieve these tasks by increasing the external surface area, maximizing the rate of intracrystalline diffusion, and reducing the deactivation rate and thereby improving catalyst lifetime.[10] Despite all such promising applications and properties, the utilization of most of the hierarchical zeolites in large (industrial) scale is still a challenge. Laborious and very expensive synthesis procedures could be among the main reasons limiting the scale up of these materials into large scale production although hierarchical zeolites are described as industrial reality in a recent review.[11]

Apart from that, the preparation of hierarchical zeolites with significant amount of secondary porosity is still a challenge. As a consequence, many efforts have been devoted to developing more efficient strategies to prepare hierarchical materials with high degree of interconnected mesopores or macropores. Furthermore, the new methods should be simple, cheap and applicable to different zeolite structures.[6,12] Another trend is to develop methods which can be used to prepare hierarchical zeolites with wide range of Si/Al ratio. Last but not least, new methods should be able to prepare hierarchical zeolites with high zeolitic character. This means, the additional porosity should be introduced not at the expense of micropores. These efforts have resulted in the preparation of a huge number of hierarchical zeolites, which can be classified into few groups as discussed in a later chapter.

It is obvious that in addition to the development of novel synthetic strategies and thorough characterization of the resulting materials (as nicely discussed in ref.[13]), the evaluation of the novel catalysts in one or more suitable test reactions is required. While catalytic applications of hierarchical macroporous materials were covered by Parlett et al.[2] until 2012, in this tutorial review, we will look at the more recent literature devoted to catalysis over hierarchical zeolites and related (nanosized) materials and discuss the catalytic results with respect to their suitability to prove the positive effects of hierarchical porous zeolites. It is import to note that positive effects on activity, stability and less frequently selectivity observed for hierarchically structured catalyst not necessarily are only a consequence of the additional meso- or macropores but also number, strength and location of active sites as well as defects and impurities. With regard to these aspects, the test reaction has to be chosen carefully and potential changes in the chemistry of the catalyst have to be considered as well. Finally, although difficult and potentially debatable, we will give some recommendations for conducting relevant catalytic studies.

Diffusion and Reaction in Hierarchical Zeolites

Both success and limitations of zeolites as catalytic materials are associated with the small size of the micropores. On one side, these small pores enable shape selectivity (viz. reactant, product and transition state selectivity) and confinement effects on these materials. On the other side, the very presence of these small pores does not only prevent large molecules from accessing the active sites in zeolites, but it also slows down the transport of those molecules which are small enough to enter the zeolite micropores. As a consequence, large molecules can only be converted on external active sites and small molecules can access a small fraction of the zeolite crystal. The low utilization degree of zeolite crystals is due to the very long diffusion path lengths of molecules in large zeolite crystals.

Zeolite catalysts are used in industry for a number of large-scale processes including Fluid Catalytic Cracking (FCC), conversion of aromatics such as xylenes, alkylation of benzene to form ethylbenzene and cumene and methanol to olefin conversion (MTO, MTP).[14] However, the current industrial utilization of these materials in catalysis is still far from exhaustion because of mass transport limitations imposed by the small size of the micropores. Figure 2 shows the impact of pore size on the diffusion of molecules with different dimensions.[11]

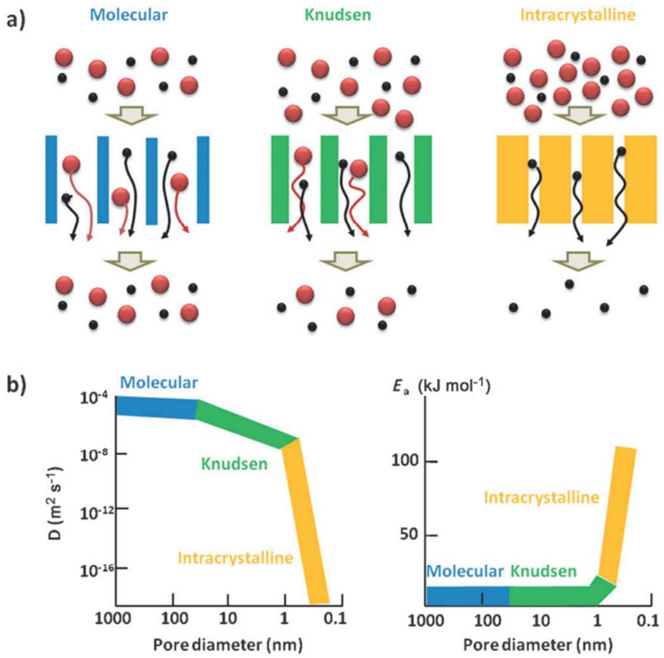

Figure 2: (a) Illustration of the diffusion of large (red) and small (black) molecules within macropores (in blue), mesopores (in green) and micropores (in yellow). (b) Magnitudes of diffusion coefficients (left) and activation energy (right) in different diffusion regimes as a function of pore sizes. The blue, green and yellow regimes correspond to diffusion in macropores, mesopores and micropores, respectively. Figure reproduced from ref. 11 with permission Wiley-VCH.

In the micropores, the configurational/activated diffusion regime dominates as a consequence of the tight fit of the molecules and the pore size. This diffusion regime is common in solids and is characterized by low diffusivities, which can be up to 2-3 order of magnitudes smaller than those observed in the Knudsen and molecular regimes (see Figure 2). These two diffusion regimes are typically observed for solid materials containing mesopores (Knudsen) and macropores (molecular) as shown in Figure 2. The low diffusivities in micropores have significantly reduced the transport of different reactants to and from the active sites. The delayed transport of reactants usually favors further conversion of these molecules into unwanted side products, which may also serve as coke precursors.[15] This will result in the accumulation of coke, which in turn blocks the micropores and result in deactivation of the zeolite catalyst. As a consequence, many zeolite catalyzed reactions suffer from deactivation due to coke formation, which significantly reduce the catalyst lifetime.[15]

In addition, the low diffusivities will result in poor utilization of the zeolite crystals, viz. only a small fraction of the zeolite crystal will be utilized during the chemical reaction as shown in Figure 3. As a consequence, very low effectiveness factors will be obtained in such systems. The effectiveness factor $\eta = r_{obs}/r_{intrinsic}$ relates the observed reaction rate with the intrinsic chemical rate, which can be represented graphically (Figure 3) as a function of the so-called Thiele modulus for an isothermal pellet (Table 1)

$$\phi = L\sqrt{\frac{k_m c_s^{n-1}}{D_{A,eff}}}$$

with k_m = rate constant of the reaction, c_s = concentration at the surface of the pellet, n = reaction order and $D_{A,eff}$ = effective diffusion coefficient. Interestingly, the particle geometry is of minor importance for the effectiveness factor (Figure 3). In order to maximize the effectiveness factor, the characteristic length of diffusion has to be minimized or the effective diffusion coefficient has to be maximized. Thus, a small Thiele modulus indicates that the reaction rate is low and the microkinetics limits the overall reaction, while a large Thiele modulus indicates a low diffusion rate and a diffusion limited reaction.

Since the observed rate constant, k_{obs}, is proportional to $(D_{A,eff})^{1/2}$, the observed activation energy is $E_{obs} = (E_D + E_A)/2$, where E_D is the activation energy for diffusion and E_A is the activation energy for reaction. Diffusional processes are weakly activated compared to chemical reactions, and the value of E_D can often be neglected compared to E_A. Thus, the observed activation energy for a severely diffusion-limited reaction is approximately one half the true value. The Arrhenius plot of the observed rate constant, shown in Figure 4, illustrates the effect of diffusion resistances on the observed activation energy. At low temperatures, the reaction rate is not limited by diffusion resistances and the observed activation energy is the true value. At high temperatures, the reaction rate is inhibited by diffusion resistances, and the activation energy is half the true value.

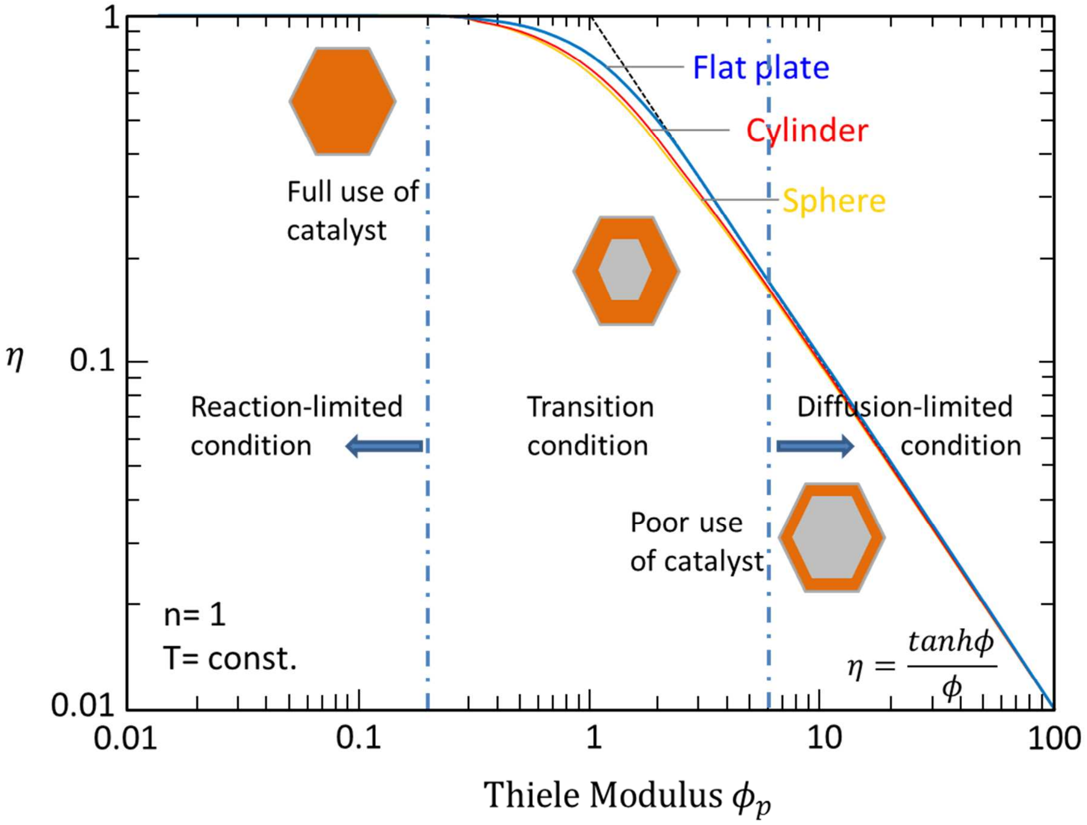

Figure 3: Effectiveness factor as a function of Thiele modulus for different geometries. At low effectiveness factors only a small portion of the crystal is effectively used during the reaction. By increasing the effectiveness factor, the crystal utilization can be maximized.

Table 1: Thiele modulus and effectiveness factor depending on different particle geometries (isothermal catalyst pellet, irreversible first-order reaction).

Geometry	**Thiele modulus ϕ**	**Effectiveness factor η_{pore}**
Flat plate (thickness 2L)	$\sqrt{\frac{k_m \rho_p}{D_{A,eff}}}$	$\frac{\tanh \phi}{\phi}$
Sphere (diameter d_p, radius r_p)	$\frac{d_p}{6}\sqrt{\frac{k_m \rho_p}{D_{A,eff}}}$	$\frac{1}{\phi}\left(\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi}\right)$
Cylinder (diameter d_{cyl}, length L, L>> d_{cyl})	$\frac{d_{cyl}}{4}\sqrt{\frac{k_m \rho_p}{D_{A,eff}}}$	$\frac{1}{\phi}\left[\frac{I_1(2\phi)}{I_0(2\phi)}\right]$ I = Bessel function
All geometries (approximation)	$\frac{V_p}{A_{p,ex}}\sqrt{\frac{k_m \rho_p}{D_{A,eff}}}$	$\frac{\tanh \phi}{\phi}$

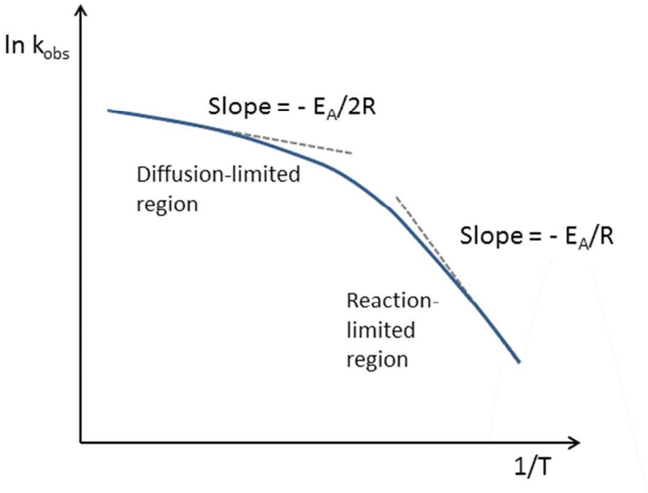

Figure 4: Temperature dependence of the observed rate constant of a reaction occurring in a porous catalyst pellet. Reproduced with permission from McGraw Hill Higher Education after ref. [16] .

The effectiveness factor is widely used in the field of heterogeneous catalysis to estimate the impact of transport processes on the rate of a catalyzed chemical reaction. From this, one way to maximize the effectiveness factor is to reduce the Thiele modulus, which can be achieved by either increasing the diffusivity or shortening the diffusion path length, the so-called correlation lenght, $L = V_p / A_{p,ex}$. This fundamental and simple approach has inspired researchers to prepare different zeolitic materials with better transport properties. Such advanced zeolites are characterized either by additional porosity levels (hierarchical zeolites),[9] or by small dimensions of the zeolite crystals, also known as nanosized zeolites.[17] As summarized in Figure 5, the preparation of hierarchical zeolites and nanosized zeolites has resulted in zeolitic materials with shorter diffusion path lengths due to the introduction of either mesopores or macropres to the microporous zeolite crystals.

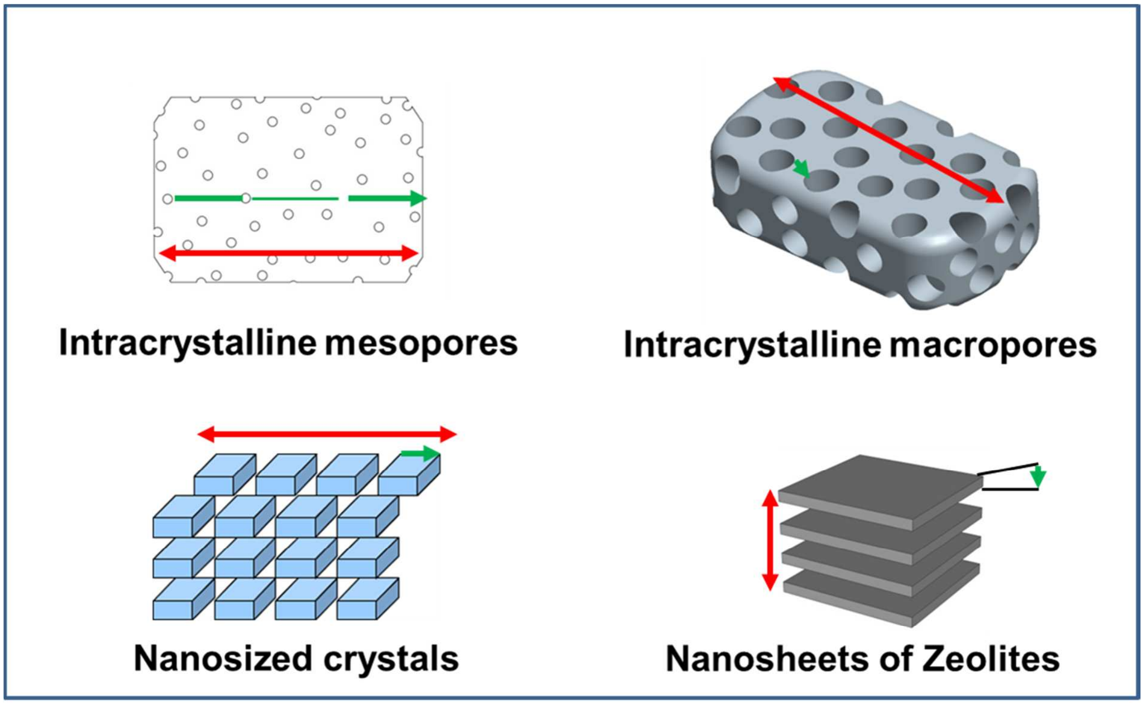

Figure 5: Schematic representation of different nanosized zeolites and hierarchical zeolites. Red arrows represent the characteristic diffusion length in a purely microporous crystal and green arrows show the reduced path lengths in nanosized or hierarchical systems.

Brief classification of hierarchical zeolites

Despite of the vast number of hierarchical zeolites available today, they can be broadly classified into pure zeolitic phases and composites, depending on the origin of the additional porosity (Figure 6). Pure zeolitic phases or true hierarchical zeolites are obtained when the additional porosity is located within the zeolite phase. In such cases, the secondary porosity is found either within the zeolite crystals or in the intercrystalline voids.

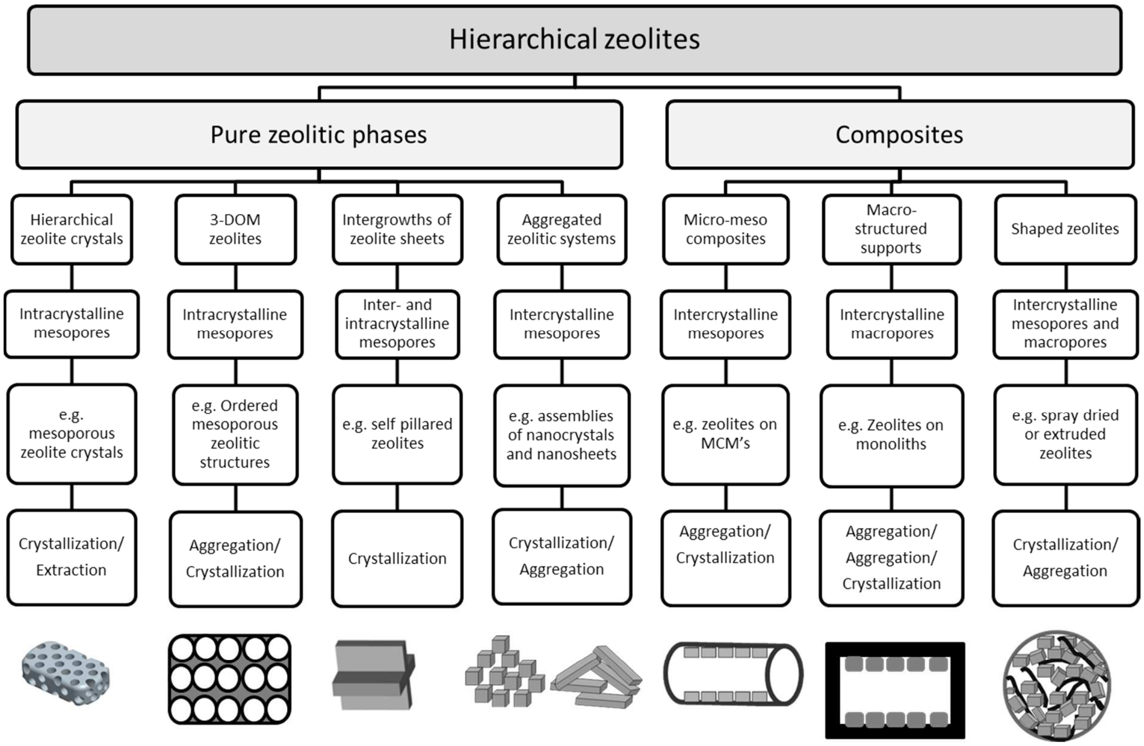

Figure 6: Classification of hierarchical zeolites according to the origin of the secondary porosity.

It is worth mentioning that apart from pure zeolitic phases, hierarchy in zeolites can also arise from additional phases. This is the case for composites, which may be composed of a zeolitic phase and a non-zeolitic phase. The non-zeolitic phase normally serves as a support or as a binder holding together the zeolite crystals.[18] When the non-zeolitic phase is a support, the secondary porosity originates from the macro- or mesopores of the support. On the other side, when binders are used to shape zeolites, the additional porosity originates from the intercrystalline voids due to the aggregation of the individual zeolite crystals and the binder.

In addition, the principles behind the preparation methods of these materials can be extracted from Figure 6. Despite the huge number of approaches available to prepare hierarchical zeolites,[8] the underlying principles are just three; aggregation, extraction and crystallization.[7] Some hierarchical zeolites utilize only one principle in their preparation, while others require a combination of two or even three of these principles.

Selected strategies to prepare hierarchical zeolites

Table 2 summarizes the advantages and limitations of the different strategies used to introduce additional porosity in microporous zeolites. These methods can be classified as either 'bottom-up' (hard templating, soft templating and non-templating) or 'top-down' (demetallation, delamination and recrystallization) approaches. In bottom up approaches, the secondary porosity is introduced during the synthesis of zeolites. This is achieved by the use of templates (templating approaches) or by simply relying on reaction conditions (non-templating approaches). In contrast to the bottom-up approaches, top-down approaches introduce secondary porosity on already existing crystalline zeolitic materials via post-synthetic modifications. Strategies like demetallation, delamination, recrystallization, shaping and coating of zeolite crystals on macroporous supports have been successfully employed to introduce secondary porosity in zeolitic materials.[7,22] From this, it is evident that much work has been done in preparing hierarchical zeolites and a detailed discussion of all available methods cannot be given in this review and only a brief introduction to some selected approaches will be provided here. A detailed discussion is found in a number of excellent reviews on this topic and the references cites therein.[9,19]

Table 2: Summary of the advantages and limitations of different methods used to prepare hierarchical zeolites (after ref. [19])

Method	Zeolitic character	Pore connectivity	Versatility to different zeolites	Preparation costs	Zeolites applied

Hard templating	High	Low to high	High	Medium to high	MFI, MTW
Soft templating	Low to medium	Low-medium	High	High	MFI, FAU
Non-templating	Low to medium	Medium	Medium	Medium	MFI
Demetallation	High	Low to high	Medium to high	Medium	Various
Delamination	High	Low	Low	High	MWW/ITQ-2
Recrystallization	Medium	Low	High	High	Various

Templating approaches are based on the addition of secondary templates to the synthesis mixture of microporous zeolites. Here, both hard templates as well as soft templates have been used to create secondary porosity. Hard templates like carbon nanotubes or nanoparticles, $CaCO_3$, metal oxide nanoparticles, biological materials, aerogels, polymers and resin beads have been used to direct the formation of either mesopores or macropores during zeolite synthesis. [9,20] In a typical synthesis procedure, a standard synthesis gel for obtaining a given microporous zeolite is prepared and then mixed with the hard template. Thereafter, the mixture is treated under hydrothermal conditions and the microporous zeolite network is formed around the hard template. Finally, the hard template is removed via either calcination or extraction with acids or bases. This method is superior for preparing hierarchical zeolites with high zeolitic character and a large fraction of either mesopores or macropores. In addition, it can be applied to different zeolite structures and it allows controlling the size of the obtained secondary pores.[19] However, this approach is still expensive due to the use of templates.

Furthermore, the mesopores or macropores formed via this method are poorly interconnected.

Alternatively, soft templating approaches can be used to introduce hierarchy in zeolites. Here, surfactants, organosilanes or macromolecular polymers are used to direct either the formation of only secondary porosity [21] or both micropores and mesopores.[30] When these molecules are used to direct the formation of the mesophase only, a microporogen must be added additionally.[21] In this technique, also known as dual templating, a soft template directs the formation of the mesophase, meanwhile a microporogen directs the formation of micropores. Although promising, the dual templating approach has quite often resulted in the formation of physical mixtures of an amorphous mesophase and the crystalline microporous zeolitic phase.[11]

To overcome such phase separation problems, bifunctional surfactants have been developed. Na et al. successfully utilized a bifunctional tertiary ammonium surfactant to direct the formation of both zeolitic microporous network as well as the mesophase.[30] In this approach, the hydrophilic surfactant head group, consisting of an ammonium group, directed the formation of the zeolite phase and the hydrophobic part of the template was used to direct the formation of the mesophase. As a consequence, a layered MFI-type zeolite material containing very thin zeolite nanosheets separated by an interlammellar spacing of about 4 nm was obtained. The thickness of the zeolite lamellar was reported to have a width of about the size of one unit cell of MFI-type zeolite along its b-axis. Although, the soft templating approach is a good strategy to prepare hierarchical zeolites with high degree of mesoporosity and can be applied to different zeolitic structures, most of the templates are not available commercially and must be synthesized. The preparation of such surfactants is very labor intensive and is still very expensive. In addition, the obtained zeolitic materials are characterized by low zeolitic behavior due to the high number of defects and low micropore volumes.[19]

In addition to the bottom-up approaches discussed above, post-synthetic approaches like demetallation, recrystallization, delamination and pillaring belong to the widely and most successful methods to prepare hierarchical zeolites. A detailed discussion on these techniques can be found in the literature.[12,22]

Frequently Employed Test Reactions

Over the years, hierarchical zeolites have been subjected to different classes of reactions namely alkylation and transalkylation reactions, isomerization reactions, cracking of light and heavy substrates, condensation reactions as well as the transformation of methanol or ethanol to hydrocarbons. In Table 3, prominent recent examples of the use of hierarchical zeolites in different reactions have been collected. While typically the observed increase in activity, stability and longer catalysts lifetime is ascribed to the presence of additional mesopores as a consequence of the employed synthetic strategy or post-synthetic modification, clear-cut evidence for this claim is rarely given. First of all, it is not evident from the beginning that the chosen reaction is really mass-transport limited. Moreover, the concentration of acid sites and their related strength has to be controlled carefully to make a valid comparison.

Table 3: Test reactions employed over hierarchical zeolites.

Zeolite structure	Method(s) employed to introduce hierarchy	Comments	Reference
Methanol to hydrocarbons			

MFI	Desilication by NaOH and TPA$^+$, carbon templating (CT) and seed-silanization (SS)	Demonstration of the critical impact of mesopore topology on the performance of hierarchically organized zeolite catalysts	Milina et al. (2015) [23]
MFI	Desilication; dry-gel conversion with nanocarbon templates; addition of organosilane templates	Generation of mesopores results in increased lifetime of the catalyst; conversion decreases with amount of external coke formed.	Kim et al. (2010) [24]
MFI	Desilication with NaOH solutions of different concentration	Only slightly longer catalyst lifetime was observed on the desilicated catalysts treated with differently concentrated NaOH solution due to similar total pore volume.	Bjørgen et al. (2008) [25]
MFI	Soft templating with two different surfactants (TPAOAC and CTAB)	Hierarchical MFI zeolite prepared by TPAOAC exhibited a much longer catalyst lifetime compared to the CTAB-templated materials. Interconnectivity of the mesopores is required in order to make the best use of the additional porosity	Wang et al. (2014) [26]
MFI	Desilication; soft (hard) templating with starch	Desilication leads to interconnected and accessible mesopores, while starch templating leads to more randomly oriented mesopores surrounded by micropores The desilicated catalysts exhibited the longest lifetime and the highest propylene/ethylene ratio owing to their open mesoporosity	Mei et al. (2008) [27]
CHA	Soft templating with organosilane	Rare example of hierarchical	Sun et al.

(SAPO-34)		silicoaluminophoshate, which exhibits increased catalyst lifetime and increased selectivity to ethene and propene.	(2014) [28]
MFI	(Non-templating) Conversion of silica gel in a fluoride medium	Hierarchical MFI with reduced thickness along the b axis exhibited prolonged lifetime and higher selectivities to propene and butene.	Zhang et al. (2015) [29]
MFI	Soft templating with diquartenary ammonium surfactants	Formation of MFI nanosheets - introduction of mesopores results in better resistance to coke formation.	Choi et al. (2009) [30] and Hu et al. (2012) [31]
Ethanol to hydrocarbons			
MFI	Dry-gel conversion	The catalytic activity of nano-sized hierarchical and conventional zeolites with similar Si/Al ratios are studied in the ETH reaction. Hierarchical zeolites exhibited a longer catalyst lifetime although more coke was formed over this catalyst.	Ramasamy et al. (2014) [32]
MFI	Fluoride leaching, alkaline leaching, nano-sized crystals	Lifetime of the catalyst is not related to the coking rate but to the number of the pore mouth. Clear advantage of nano-sized hierarchical catalyst with respect to lifetime is reported.	Lakiss et al. (2015) [33]
Benzene alkylation with ethene			
MFI	Carbon templating	Gas phase reaction, increase in activity, selectivity and apparent activation energy observed.	Christensen et al. (2003) [34]
Friedel-Crafts alkylation of aromatics with benzylalcohol			

MFI	Amphiphilic organosilane is used	Liquid phase reaction, hierarchical mesoporous MFI was about nine times more active than a standard ZSM-5 with the same Si/Al ratio. The higher activity was related to the reduced diffusion limitations in the mesoporous MFI samples.	Sun et al. (2008) [35]
BEA	Desilication and desilication with subsequent acid treatment	In the benzylation of benzene no significant difference was observed between a desilicated catalyst and the standard materials. After a subsequent acid treatment, the catalytic activity improved significantly. Thus, desilication caused partial loss of the acidity, which can be recovered by adding a subsequent acid washing step In the benzylation of mesitylene a clear gain in activity for the modified catalysts was observed.	Wang et al. (2015) [36]
MFI	Self-pillared zeolite nanosheets by repetitive branching	Alkylation of mesitylene with benzyl alcohol occurs on the external active sites, while self etherification of benzyl alcohol proceeds on the acid sites in the MFI micropores.	Zhang et al. (2012) [37]
MOR	Demetallation; acid-treatment; acid-base treatment; acid-base-acid treatment	Hierarchical zeolites showed clearly better catalytic performance than the parent material. The catalytic activity of the hierarchical zeolites differed in the following order: Acid-base-acid leached > acid–leached > acid-base leached. This performance trend is related to	Leng et al. (2013) [38]

		the degree of mesoporosity which decreases in the same order. All catalysts had similar selectivities.	
MOR	Demetallation, carbon templating and soft templating	One of the few examples that the methods for the preparation of hierarchical catalysts can be extend to zeolites other than ZSM-5. Only base treated catalysts with subsequent acid treatment exhibited excellent catalytic performance. The performance of the modified MOR depends on the method used to prepare the parent catalyst.	Li et al. (2009) [39]
Methane dehydroaromatization to benzene			
MFI	Zeolitization of mesoporous materials/self-assembly of nanocrystals	Hierarchical zeolites gave higher methane conversion and stronger resistance to coke compared to standard ZSM-5.	Chu et al. (2009) [40]
MWW and MFI	Aggregation of small crystallites	Mesopores provided easier access to the active sites resulting in high methane conversion and very strong coking resistance and thus exceptional catalyst stability.	Chu et al. (2010) [41]
MWW	Nestlike hollow hierarchical microspheres	Higher external surface due to mesopores resulting in improved benzene yield and catalyst lifetime.	Chu et al. (2010) [42]
Synthesis of methylenedianiline			
FAU /Hierarchical USY MWW/ITQ-2	Combination of alkali and acid treatment Delamination	Liquid phase reaction; Creation of mesoporosity by post-synthetic modifications led to: (i) an enhanced activity, (ii) a high isomer ratio, (iii) an increased oligomer fraction, and (iv) an	Keller et al. (2015) [43]

		improved resistance to fouling. Hierarchical USY outperformed delaminated catalysts.	
Beckmann rearrangement of oximes			
Silicalite-1	Hard templating with polyvinyl alcohol (PVA)	Hierarchical porosity led to facile mass transport of reactants and products which resulted in better catalytic performance (higher activity and selectivity).	Yin et al. (2015) [44]
Silicalite-1	Soft templating with special designed surfactants	MFI nanosheets exhibited higher conversion and selectivities compared to bulk MFI. The advantages of auxiliary porosity decreased as the dimensions of the oximes were decreased The exceptional catalytic performance was linked to the presence of the large number of silanol groups located on the external surface of the nanosheets.	Kim et al. (2011) [45]
Direct oxidation of benzene to phenol			
MFI	Soft templating with special designed surfactants	Nanosheet morphology results in different agglomeration behavior of iron species (i.e. more isolated species were observed on nanosheets compared to the bulk MFI). The formation of isolated iron species resulted in poor catalytic performance of nanosheets in N_2O decomposition, but in better catalytic performance in the oxidation of benzene to phenol. Coke was deposited mainly on	Koekkoek et al. (2013) [46]

		the external surface of nanosheets, whereas more coke was deposited in the micropores of the bulk ZSM-5 catalyst.	
MFI	Desilication	Alkali treated catalysts produced more phenol than the standard catalyst and had longer lifetime. Post-synthetic modifications did not result in any modification of the iron sites. The better catalytic performance was linked to the presence mesopores, which reduce the diffusion path for phenol	Gopalakrischnan et al. (2008) [47]
Dehydration of glycerol to acrolein			
MFI	Salt-aided seed-induced route	Goal: To study the effect of mesopore architecture (size, amount, distribution and connectivity) on the performance and lifetime of the catalyst. Catalysts with more open and interconnected mesopore architecture display high activity, long lifetime and improved selectivity. Closed and small mesopores resulted in poor catalytic performance and short catalyst lifetime	Zhang et al. (2015) [29]
Methylcyclohexane cracking			
MFI	Fluoride leaching, alkaline leaching, nano-sized crystals	The presence of mesopores close to the active sites improves the stability of the catalysts by favoring desorption of products.	Ngoye et al. (2014) [48]

		While light coke (alkylbenzenes) has no impact on catalyst stability, heavy coke (alkylphenantrenes and alkylpyrenes) poisons the active sites probably remote from the mesopores.	

Methanol to gasoline or olefins

A frequently conducted test reaction is the conversion of methanol to either gasoline (Methanol To Gasoline), olefins (Methanol To Olefins, Methanol To Propylene) or aromatics (Methanol To Aromatics). This group of processes is considered to provide promising alternative routes for the production of hydrocarbons (viz. gasoline, aromatics, ethylene and propylene) from non-petroleum sources such as natural gas, coal and biomass via methanol and synthesis gas as intermediate products. The reaction is complex and results in the formation of a large number of products in the sequence light olefins → n/iso-paraffins, higher olefins, aromatics and napthenes → coke. The mechanism of deactivation and coke formation is still under debate. However, the formation of naphthene derivates during the co-reaction of methanol and different methyl benzenes was observed over zeolite beta. The rate of coke formation varies among the different zeolites and zeotypes (viz. the silicoaluminophophate SAPO-34) used and the topology as well as acid site density and strength play major roles. As coke formation results in rapid deactivation of the catalyst, suppression of catalyst deactivation has been attempted by employing hierarchical zeolites prepared via different routes (Table 3).

Early studies by Björgen et al. [25] and Mei et al.[27] in 2008 were conducted on MFI zeolites prepared by alkaline leaching. After treatment with 0.20 M NaOH, the total conversion given in grams of methanol converted per gram catalyst until complete deactivation, increased by a factor of 3.3, and the selectivity towards the gasoline fraction increased by a factor of 1.7. While the Si/Al ratio was reduced from 46 for the parent ZSM-5 to 36 and 27 after leaching with 0.05 or 0.20 M NaOH, the total acidity as evident from ammonia TPD measurements seems to be unchanged. However, the number of Lewis acid sites appears to be larger as evident from IR studies in the diffuse reflectance mode (DRIFTS).[25] High propylene selectivity (42.2%) and propene/ethene ratio (10.1) were observed by Mei et al.[27] on a high silica H-ZSM-5 catalyst modified by alkaline desilication. The enhanced catalytic performance was attributed to the newly created open mesopores on the surface of the zeolite crystals together with the lower Brønsted acidity compared to the parent sample. A larger amount of mesopores was formed in H-ZSM-5 crystals via the soft template route by adding 5 wt.-% of starch. However, the mesopores formed via this method are randomly distributed in the zeolite crystals and play only a minor role in the molecular transport of the reactants, so the improvement in propylene selectivity and propylene/ethylene ratio of the catalyst is less evident. The higher propylene selectivity and propylene/ethylene ratio on modified H-ZSM-5 (especially by alkaline treatment) compared to unmodified H-ZSM-5 could be also related to different contributions of the methylaromatics route and olefins methylation/cracking route in MTP reaction. The work by Mei et al. demonstrates that the creation of open mesopore cavities or channels in H-ZSM-5 zeolite is as important as the right adjustment of its Brønsted acidity in the design and preparation of stable and selective H-ZSM-5 catalysts for the methanol to propene (MTP) reaction. MFI nanosheets also exhibit a significantly better performance compared to a standard MFI zeolite with a Si/Al ratio around 50. Again, the build-up of coke is significantly smaller in the hierarchical material.[30] Under relevant conditions (T = 450 °C, p = 0.1 MPa (p_{MeOH} = 20 kPa) and WHSV = 1.5 h^{-1}) a high propylene selectivity of 51.0 % and high propylene/ethylene (P/E) ratio of 12.1 as well as long catalytic lifetime in methanol to propylene (MTP) reaction. The excellent catalytic performance of MFI nanosheets is mainly ascribed to the unique morphology and textural properties of the catalyst. The ultrathin nanosheets are believed to enormously shorten the diffusion path length and thus remarkably improve the molecular diffusion. As a result, the product molecules could easily escape from the zeolite channels, and secondary reactions like aromatization and hydrogen transfer are suppressed drastically, leading to high propylene selectivity and a low deactivation rate.[31] Moreover, the considerably larger specific surface area and higher mesopore volume of the MFI nanosheet zeolite compared to a standard ZSM-5 enable the catalyst to accommodate a larger quantity of coke, which contributes to the notable improvement in catalytic lifetime. Subsequent studies attempt to derive at a correlation between mesoporosity and coke formation. In a study by Kim et al. [24], a roughly linear correlation between the mesoporosity (i.e. external specific surface area) and the catalyst lifetime was confirmed. The origin of catalytic longevity was explained in terms of the facile diffusion of coke precursors from the micropores to the external surfaces (or the surfaces of the mesopore walls) owing to a large external surface area and short diffusion path lengths. Catalytic deactivation under the present reaction conditions occurred almost as a result of the formation of internal coke, that is, as a result of coke inside micropores. Selective dealumination at the surface of the mesopore walls caused no significant change in the coke generation ratio between internal and external locations. Removal of internal Al led to a marked increase in the catalyst lifetime.

It has been reported that ethanol transformation to hydrocarbons is more sensitive to changes in the textural properties of zeolites than other model reactions such as methylcyclohexane cracking.[33,48] However, the results are similar to those reported for methanol conversion. During ethanol to hydrocarbon conversion at 623 K and 3 MPa, carbonaceous material is formed due to unwanted side reactions. The composition of the coke is strongly related to the shape and the dimension of the ZSM-5 catalyst employed. Lakiss et al. reported that the structure of the molecules trapped is limited to polyalkyl-benzenes, -naphthenes, -anthracenes and –pyrenes. In general, coking occurs mainly due to poisoning and to a much lesser extent by pore blocking.[33]

As visualized in Figure 7, data obtained so far indicate that the shortening of the diffusion path length by reducing the crystal dimensions (preparation of either nanocrystals or zeolite nanosheets) results in enhanced catalyst lifetime. The introduction of additional (macro)porosity by different synthetic strategies also reduces the diffusion paths and, thus, potentially also catalyst deactivation. However, it becomes clearer in recent studies that in the case of methanol or ethanol to hydrocarbons (MTH, ETH), different aspects have also to be considered including density and strength of the Brönsted acid sites, location of the coke formed, temperature of the catalyst bed etc.[33,48] In addition, coke formation may be promoted by defects and is not only a consequence of diffusion limitations of the coke precursors.

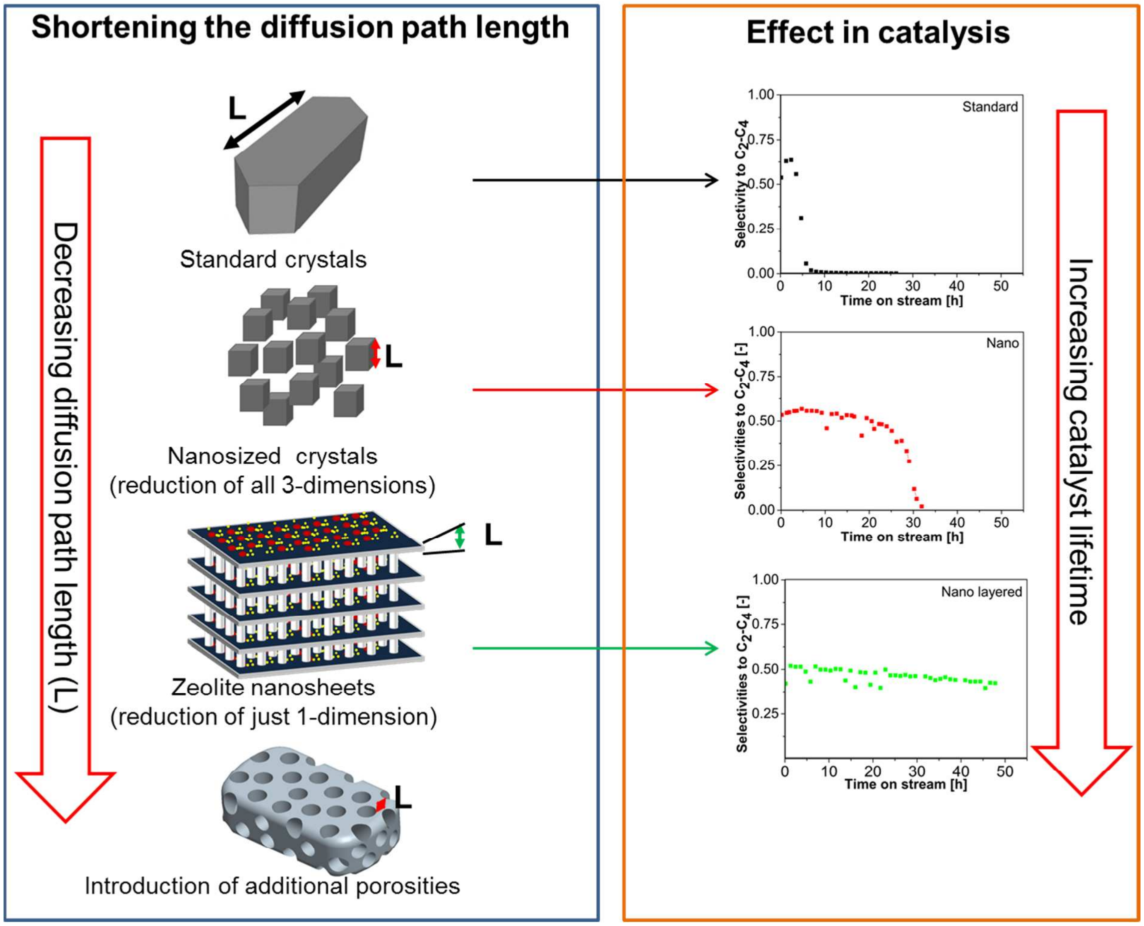

Figure 7: Summary of the influence of reduced diffusion path length. On the left side, the different strategies used to reduce the diffusion path lengths are visualized, and the impacts of different diffusion path lengths in catalysis are displayed on the right side.

Alkylation of benzene with ethene

In order to compare the catalytic performance of carbon-templated mesoporous MFI zeolites with a standard MFI-type catalyst, alkylation of benzene with ethene to form ethylbenzene was chosen as an industrially relevant test reaction.[34] The world-wide demand for ethylbenzene, which is the raw material for styrene production, is roughly

$22 \cdot 10^6$ t per year and is almost exclusively produced by this reaction. The alkylation of benzene with ethene over the H-ZSM-5 catalyst constitutes the heart of the Mobil–Badger process, which was first brought on stream in 1980. With the industrially-employed H-ZSM-5 catalyst, an excellent selectivity for ethylbenzene of more than 98% is obtained at a benzene conversion level of about 20%. The uniform channels of zeolite ZSM-5 permit the entrance of the feed molecules as well as departure of the product molecules ethylbenzene and diethylbenzene isomers, while higher alkylated products are restricted from leaving.[20]

Any of the higher alkylated products formed within the ZSM-5 channels are forced to undergo transalkylation or dealkylation to facilitate their diffusion back to the bulk. Steric hindrance of the necessary transition states is also believed to inhibit the formation of poly-alkylated products. Although these are the clear advantages of using a shape-selective microporous catalyst, the problems of catalyst deactivation by coke formation and low reaction rates owing to mass transport limitations are major obstacles to overcome.

Christensen et al. showed that the zeolite catalyst with the hierarchical pore architecture is significantly more active than the conventional zeolite catalyst under the reaction conditions employed ($T = 583$ to 643 K; $p = 0.25$MPa), which are sufficiently close to the conditions employed in the industrial process ($T = 700$ K; $p = 2$ to 5MPa).[34] Moreover, the selectivity to ethylbenzene increases by 5 to 10 % depending on the benzene conversion. The increased activity is ascribed to the improved mass transport in the mesoporous zeolites which is indicated by an increase of the apparent activation energy from 59 to 77 kJ mol^{-1}.

Attributing the higher activity to improved mass transport is further substantiated by the differences in selectivities observed for the two catalysts. The higher selectivity to ethylbenzene is explained by Christensen et al. in the following way: Whenever an ethylbenzene molecule is formed, it can either be transported into the product stream or undergo further alkylation. However, in a mesoporous zeolite the diffusion path is significantly shorter than in the conventional zeolite and further alkylation is suppressed. In addition, the determined activation energy is larger when the hierarchical catalyst is employed compared to the standard zeolite which is in line with the expectation in case of pore diffusion limitation.

Friedel-Crafts-Alkylations of aromatics

The Friedel–Crafts alkylation is an important class of reactions in petrochemistry. Among these alkylations, the liquid-phase benzylation of aromatic compounds by benzyl alcohol is of significance for the production of diphenylmethane and substituted diphenylmethanes which are key industrial compounds used as pharmaceutical intermediates and fine chemicals. Thus, Friedel-Crafts alkylation of aromatics such as benzene, toluene or mesitylene with benzyl alcohol (Figure 8) is a frequently employed test reaction in the liquid phase.[35,36,38,39] Due to the presence of bulky intermediates or substrates, the additional (meso-)porosity is expected to booster the performance of the zeolite-based catalyst.

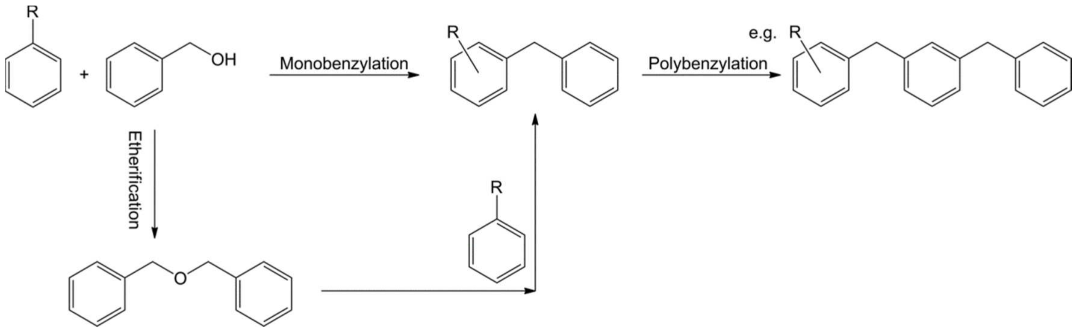

Figure 8: Alkylation of aromatics (R = H, CH_3 or alkyl) with benzyl alcohol.

The improved performance of the hierarchical zeolites compared to the respective parent materials is ascribed to the introduced mesoporosity, facilitating the transport to the active sites.[49] A clear linear trend is observed between benzyl alcohol conversion and secondary mesoporosity, viz. specific mesopore surface area.

Zhang et al.[37] compared the catalytic properties of self-pillared pentasil (SPP) zeolite nanosheets with those of pillared MFI, three-dimensionally ordered mesoporous-imprinted (3DOm-i) MFI, and three conventional MFI catalysts with different crystal sizes of 17, 1.4, and 0.2 µm, respectively. As a result of the increase in number of accessible acid sites, the pseudo–first-order rate constant for the liquid-phase alkylation of mesitylene, which is not able to enter the micropores of the MFI zeolite, by benzyl alcohol was found to vary by more than two orders of magnitude. However, when normalized per number of external acid sites, the rate constant varies only slightly (Figure 9A). This shows that the strength of the external acid sites is similar for all samples tested regardless of their different morphology, crystal dimensions and porosity..

The self-etherification of benzyl alcohol in the presence of 2,6-di-tert-butylpyridine (used in order to deactivate the external sites) was further employed as a test reaction in the liquid phase. The plot of the effectiveness factor versus the Thiele modulus shows excellent agreement with the experimental data (Figure 9B). Thus, it can be concluded that Brønsted acid sites in the micropores of SPP and pillared MFI have similar strength to those in conventional and nanocrystalline MFI. As a consequence, the observed differences in apparent reaction rates can be fully accounted for by diffusion limitations. The paper is considered exemplary for the importance of the location of acid sites (micropores v. external mesoporoisty) and the validity of the Thiele concept even for hierarchical zeolite catalysts.

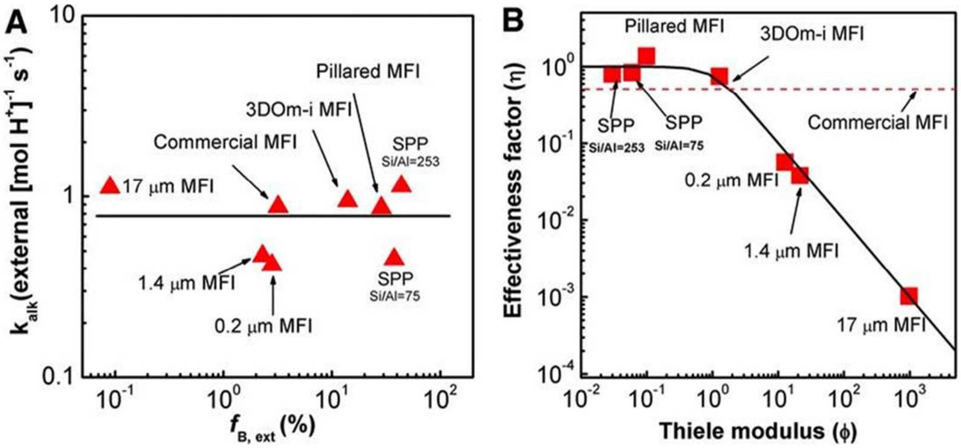

Figure 9: Comparison of the catalytic performance of self-pillared pentasil (SPP) zeolite, pillared MFI, 3DOm-i, and and commercial and conventional MFI zeolites with different particle size. (**A**) Pseudo–first-order rate constant divided by the number of external Brønsted acid site for mesitylene alkylation by benzyl alcohol; $f_{B,ext}$ gives the fraction of external Brönsted acid sites (**B**) Effectiveness factor versus Thiele modulus plot (solid line) with respect to selected experimental data in the self-etherification of benzyl alcohol. The effectiveness factor of commercial MFI is indicated by the dashed line because its Thiele modulus cannot be determined due to the broad particle size distribution of the commercial zeolite. (reproduced with permission from ref. 37)

Methane dehydroaromatization

Methane dehydroaromatization (MDA) to benzene and H_2 under non-oxidizing conditions is studied in a continuous flow reactor over Mo/H-ZSM-5 catalysts. Up to date, Mo/H-ZSM-5 is the most promising catalyst where near equilibrium conversion of CH_4 can be achieved with high selectivity to aromatics at 973 K. However, methane conversion decreases drastically with time-on-stream due to the heavy carbonaceous deposits on the catalyst, which is a big drawback for the reaction. Over a conventional Mo/H-ZSM-5 catalyst, coke deposition leads to rapid decrease of the methane conversion with time-on-stream. In contrast, a Mo/H-ZSM-5-MS catalyst exhibited higher CH_4 conversion up to 24 h.[41] Novel hierarchical ZSM-5 microspheres (named ZSM-5-MS) of about 3 μm in diameter, which are assembled from "French fries"-like crystals (i.e. in shape of French fries) of about 100 nm in width, were synthesized by using SBA-15 as the silica source. Thus, ZSM-5-MS exhibited a unique geometrical shape which was entirely distinct from the conventional MFI shape. The N_2 adsorption isotherm of the ZSM-5-MS shows a clear hysteresis loop at about relative pressure $p/p_0 = 0.5$ to 0.9, indicating the presence of mesopores which is reasonably assigned to intercrystalline voids between the French fries-like crystals. Correspondingly, the pore size distribution gives a sharp peak at about 15 nm with a tail up to 45 nm; these mesopores are believed to be important for the practical application of the zeolite. The catalytic tests demonstrate that the mesopores in the Mo/ZSM-5-MS provide easier access to the active sites located in the micropores resulting in higher CH_4 conversion. Due to its mesopores, Mo/ZSM-5-MS is more resistant to coking, which improves the catalyst durability.

Nestlike hollow hierarchical Mo/H-MCM-22 microspheres are found to be superior catalysts compared to a conventional Mo/H-MCM-22 catalyst with respect to benzene yield (9.3 vs. 6.8 % at 973 °C at ca. 400 min time-on-stream).[42] Although deactivation by coke formation is observed for both catalysts, the decline in activity is much more pronounced for the conventional catalyst. It is suggested by the authors that the hollow and hierarchical structure results in the formation of more active sites and the improved diffusion of large product molecules away from the active sites result in the improved performance observed. However, no explicit evidence for improved transport is presented.

Synthesis of methylene dianiline

Another industrially relevant example is the synthesis of methylene dianiline (MDA), the precursor for the most common isocyanate used in the production of polyurethanes (ca. 15×10^6 t per year in 2012). MDA is industrially synthesized from a condensate of aniline and formaldehyde, viz. called aminal, via a series of rearrangements catalyzed by acid sites (Figure 10). As the composition of an MDA mixture is directly related to the quality of the obtained polyurethanes, a heterogeneous catalyst is required that allows the synthesis of MDA fulfilling the specifications of the commercially established products. Besides the achievement of a high ratio of 4,4 –MDA to 2,4 -MDA (referred to as the ”isomer ratio”), a substantial oligomeric fraction (>20%) is required, which ensures a high melting point, sufficient flame resistance and mechanical stability of the resulting polyurethanes due to long polymer chains and extensive cross-linking.

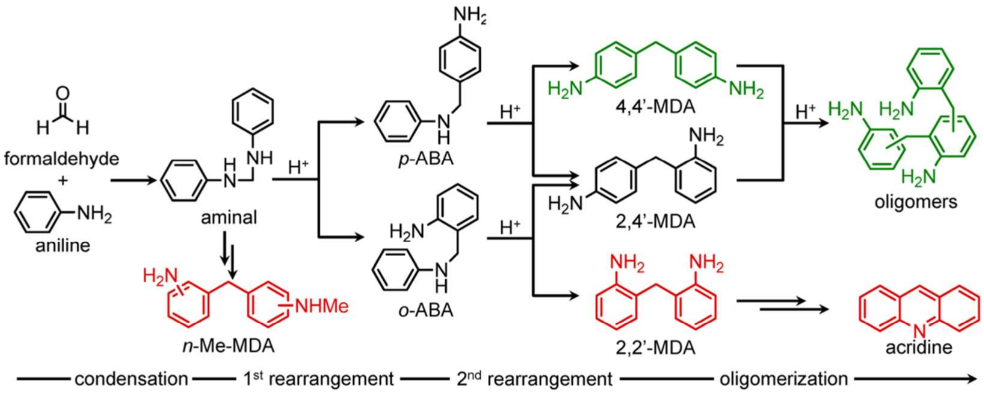

Figure 10: Reaction network for the synthesis of MDA mixtures. Desired products are colored green and undesired by-products are colored red. Reproduced with permission from the American Chemical Society from ref.[49]

Keller et al. reported a successful strategy to design hierarchically-structured zeolite catalysts for the synthesis of methylendianiline (MDA) by liquid-phase reaction of aniline and formaldehyde. The controlled generation of intracrystalline mesopores within commercial zeolite crystals by affordable postsynthetic treatment (alkaline leaching in the presence of TPABr at 65 °C for 30 min) is highly beneficial, leading to (a) enhanced activity by a factor of seven for the best catalyst (b) a high isomer ratio around 6 ± 0.5, (c) an increased oligomer fraction, and (d) an improved resistance to fouling (factor of 3). The observed linear dependence of the 4,4'-MDA as well as the 2,4'-MDA yield from the product of specific mesopore surface area and concentration of Brönsted acid stresses the importance of both influence factors. The authors demonstrate that mesoporosity, acidity, and crystallinity have to be carefully balanced to attain a superior faujasite-based catalyst. Among the different zeolites studied (FAU, BEA, MFI, MOR, HEU) hierarchical USY (faujasite structure) outperforms all other zeolite topologies evaluated, as well as other state-of-the-art catalysts such as delaminated zeolites and mesoporous aluminosilicates.

Beckmann rearrangement

The Beckmann rearrangement of cyclohexanone oxime to e-caprolactam (Figure 11) is an important step in the industrial production of Nylon 6 fibers and resins. A dry gel conversion method has been developed to produce a hierarchical porous silicalite-1 catalyst containing both micropores and mesopores (V_{meso} = 0.19 cm^3/g) by using polyvinyl alcohol (PVA) as a mesopore template. The synthesized hierarchical porous silicalite-1 exhibited hierarchical porosity and higher catalytic activity in the vapor phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam compared to a conventional silicalite-1 catalyst (Conversion X = 83 vs. 63 % at 2h time-on-stream).[44] The higher activity is attributed by the authors to the hierarchical porosity, which might facile the mass transport of reactants and products in this reaction and a higher amount of silanol nests.

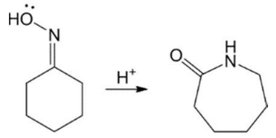

Figure 11: Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam.

Although activity and selectivity are higher on the hierarchical silicalite-1 catalyst, an influence of particle morphology and particle size (the presence of nanocrystals is evident from TEM micrographs) cannot be ruled out from the data reported so far.

Oxidation of benzene to phenol

Phenol is an important industrial intermediate for the production of various chemicals such as bisphenol A, phenolic resins, caprolactam, alkylphenols, and adipic acid. The cumene hydroperoxide process is currently the preferred industrial method to produce phenol. One of the alternative routes involves the direct oxidation of benzene with nitrous oxide. A promising catalyst for this process is Fe/ZSM-5 zeolite, but the strong catalyst deactivation due to formation of carbonaceous by-products remains an obstacle in its commercialization.[46]

An alkali treatment of a commercial ZSM-5 zeolite induces substantial intracrystalline mesoporosity through desilication. The resulting mesoporous H-ZSM-5 zeolite has been tested for the hydroxylation of benzene and it was found to increase the lifetime of the catalyst by suppressing the catalyst deactivation and enhancing the phenol yield and selectivity with time on stream. It is suggested that the improvements in the catalytic performances are due to the presence of mesopores in the crystals, which likely reduce the lengths of remaining micropores and improve the transport of the phenol molecule out of the zeolite crystal.[47]

It is reported that a sheet-like ZSM-5 zeolite deactivates much slower than bulk Fe/ZSM-5, which is attributed to the much lower probability of secondary reactions of phenol in the short straight channels of the sheets. It is found that carbonaceous materials are mainly deposited in the mesopores between the nanosheets and to a much lesser extent in the micropores. This contrasts the strong decrease in the micropore volume of bulk Fe/ZSM-5 due to rapid clogging of the continuous micropore network. The formation of coke deposits is limited in the nanosheet zeolites because of the short molecular trafficking distances. It is argued that at high Si/Fe content, coke deposits mainly form on the external surface of the nanosheets.[46]

The higher activity of nano-sized catalysts is believed to be caused by the increased mass transport in the smaller crystalline domains, which is most important for the removal of the phenol product from the micropore space. The lower rate of deactivation should be the result of the increased ratio of the external surface over the micropore volume. As a consequence, the residence time of phenol in the micropores will be lower, thus deactivating reactions such as overoxidation and condensation reactions are limited. It has been suggested that the formation of phenolate may also block the micropores and precede coke formation.

Since the performance of the Fe/ZSM-5 catalyst significantly depends on the state of iron in those catalysts, the influence of the hierarchical support cannot easily be separated from the state of iron, which is most difficult to determine by e.g. ESR spectroscopy. As a consequence, the results of this reaction have to be analyzed with care.

Dehydration of glycerol to acrolein

Biodiesel formation results in the co-production of glycerol, which can be converted to a number of valuable platform chemicals. Dehydration of glycerol is one of the most interesting catalytic processes because of its perspective to provide a sustainable route for acrolein production for industrial and agricultural applications (Figure 12). However, up to now, it is still unclear and controversial what type of hierarchical porosity is suitable for the glycerol dehydration. Jia et al.[50] investigated the catalytic performances of nanosized H-ZSM-5 (d_p = 20-60 nm) and compared to a conventional H-ZSM-5 (d_p = 0.2-2 μm) with similar Si/Al ratios of ≈ 65 and illustrated that the zeolites with short micropores were more suitable for glycerol dehydration confirming that mass transport limitations indeed play a role in this reaction. Conversely, Possato et al.[51]

performed a systematic study on the gaseous phase dehydration of glycerol using microporous MFI zeolites and alkaline-desilicated mesoporous ones, in which all of the samples showed rather similar catalytic performance if the Si/Al ratio is similar. A slight decrease in deactivation is found although the coke contents of the different catalysts increased with mesopore volume.

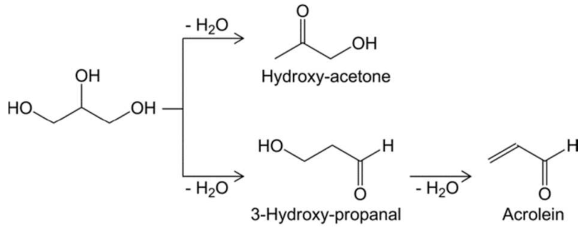

Figure 12: Pathway of glycerol dehydration leading to acrolein or hydroxyl-acetone.

A simplified microscopic picture (Figure 13) was developed by Possato et al.[51] in order to explain the deactivation of the ZSM-5 catalyst. In case of a standard microporous material, the coke is deposited in the straight and sinusoidal micropores and its effect on catalytic performance is more pronounced even for low coke content, caused by pore blockage obstructing the access of glycerol to the narrow channels located deep in the crystals. In the case of hierarchical zeolites, the coke is not deposited in narrow micropores as confirmed from the insignificant changes in crystallographic parameters of the zeolite, but is preferentially located in the intracrystalline pockets created by means of desilication. This behavior originates from the change of location of most of the active sites as well as from the easier retention of coke molecules in non-confined environments, typical of purely microporous zeolites.

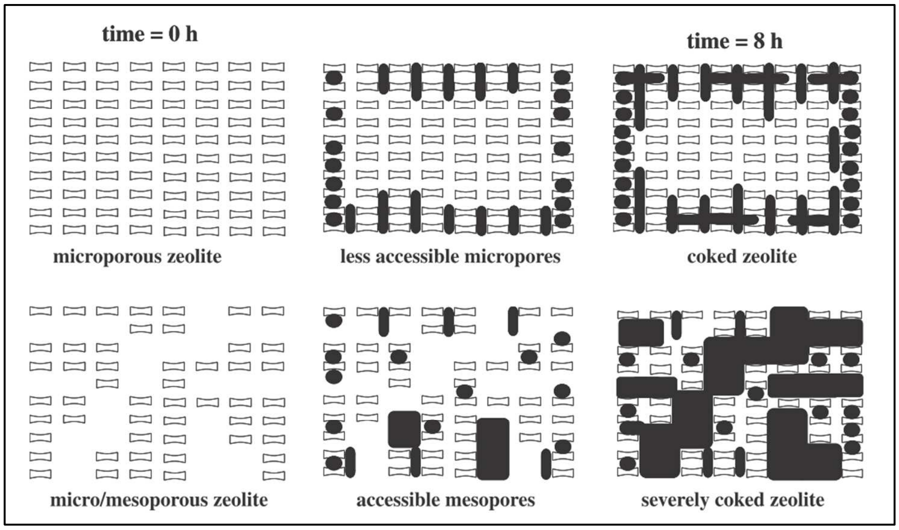

Figure 13: Schematic representation of the domains of coke deposition and location in the pores of a microporous zeolite during glycerol dehydration. Reproduced with permission from Elsevier B.V. from ref. [51].

In a recent paper by Zhang et al.[29], four different typical hierarchical ZSM-5 catalysts with diverse mesoporosity and similar microporosity/acidity are prepared by the salt-aided seed-induced route. By systematically studying their catalytic performances, the effect of various mesopore types on glycerol dehydration are studied, including pore size, pore volumes, distribution, and connectivity. The sample with open and interconnected mesopore architecture display high activity, longer lifetime, and improved selectivity compared to catalysts with closed and small mesopores. This findings are attributed by the authors to the mass transfer limitations and/or the in-pore condensation of the reactant or its heavier derivatives. Moreover, the combined effect of acidity and hierarchical structure was also explored by changing the framework Si/Al ratio. When the Si/Al ratio is decreased from ca. 100 to ca. 36, the deactivation rate is reduced and the acrolein selectivity is slightly increased due to the higher density of acid sites. This example shows nicely that both mesopore structure and Si/Al ratio have to be considered when assessing the performance of hierarchical catalysts.

Catalytic cracking

The kinetics of the catalytic cracking of the (model) naphtha compounds cyclohexane, methylcyclohexane and *n*-heptane over ZSM-5 has been studied by Konno et al.[52] The catalytic cracking was found to follow first-order kinetics with respect to the alkane concentrations and the activation energies for cyclohexane, methylcyclohexane and n-hexane cracking over nano-ZSM-5 (crystal size = 100 nm) were determined to be 119, 116 and 126 kJ mol^{-1}, respectively, which are significantly higher compared to the conventional catalyst (macro-ZSM-5; crystal size = 2 μm). In order to elucidate the rate-limiting step in the cracking process, Thiele modulus and effectiveness factor were determined. Cracking with nano-ZSM-5 proceeded under reaction-limiting conditions, whereas the reaction over macro-ZSM-5 at 923 K took place under transition conditions between reaction- and diffusion-limiting. Nano-ZSM-5 was also applied to the catalytic cracking of a model naphtha feed compared to the macro-ZSM-5 demonstrating that the former catalyst was both more effective and stable and generated a higher yield of light olefins. The paper is considered a fine example for the usefulness of the concept of Thiele modulus and effectiveness factor also not applied here to a hierarchical catalyst where the characteristic length would be more difficult to determine precisely.

Finally, the potential of hierarchical zeolites as catalysts for the production of fuels and chemicals from biomass and the pyrolysis of polyethylene has been explored.[53] Notable recent examples are works on glucose and lactose isomerization by Tsapatsis and co-workers[54] and epoxidation of biodiesel by Gläser and co-workers.[55] These reactions are very complex and a challenging topic and not well suited as a standard test reaction system for the evaluation of hierarchical zeolites although certainly of practical importance.

In Table 4, the results of the discussed test reactions are summarized. In all cases, improved hierarchical zeolite-based catalysts with respect to activity (conversion) and selectivity are reported. However, in the majority of the tested reactions coke formation is severe, which prohibits clear-cut conclusions. Only in rare cases activation energies or the thiele modulus are determined which would allow a more direct assessment of the presence of mass transport limitation in the hierarchical zeolite compared to a standard zeolite.

Table 4: Comparison of selected test reactions with respect to different performance indicators.

Test reaction	Activity	Selectivity	Activation energy or Thiele modulus	Deactivation by coke formation	Indicator for benefit of mesopores
MTG / MTO /ETO	Already 100 % for standard catalyst	Improved	not determined	Reduced significantly	+
Alkylation of benzene with ethene	Increases	Improved	Increases	Not dominant at technically relevant reaction conditions	+
Friedel-Crafts Alkylation of aromatics with	Significantly increased	Not much different	Only determined for the hierarchical	Does not play a significant role	++

benzylalcohol			material		
Synthesis of methylene dianiline	Linear increase with product of mesopore surface area and concentration of Brönsted sites	Increased for carefully balanced catalyst	Not reported	Does not play a significant role in this liquid phase reaction.	++
Dehydration of glycerol	Already 100 % for standard catalyst	Improved	Not determined	Reduced	+
Beckmann rearrangement	Increased	Significantly improved	Not determined	Occurs, no significant improvement	-
Oxidation of phenol	Increased	Improved	Not determined	Increase lifetime of the hierarchical catalyst	-
Catalytic cracking of naphtha	Increased	Improved with respect to	Determined for nano-sized	Reduced	++

compounds		light olefins	zeolites		

Legend: (-) not well suited, (+) suitable, (++) recommended.

Conclusions and recommendations for meaningful catalytic experiments

In order to improve the degree of utilization of zeolite crystals in catalytic transformations, the dimensions of zeolite crystals should be reduced from few micrometers to few nanometers, by preparing nanodimensioned or layered zeolites. An alternative strategy to reduce transport limitations in zeolites is to introduce additional inter or intracrystalline mesopores or preferentially macropores. Both nanosized zeolites and hierarchical zeolites have their success and limitations as discussed above and the selection of the right material depends on the reaction system, preparation method as well as the preparation costs and stability of the formed material.

The literature discussed in this tutorial review clearly confirms that predominantly test reactions with industrial relevance such as methanol to olefins or gasoline, alkylations, oxidations and cracking of model substrates have been selected to characterize the catalytic performance of hierarchical zeolite catalyst. With respect to a "standard" catalyst with similar topology – and not always comparable Si/Al ratio, particle size, morphology etc., - higher activity and selectivity, increased resistance to coke formation and other advantages are reported. Although always "improvement of mass transport resistance" or "shortening of diffusion path length" is cited as origin of improved catalytic performance, suitable tests to prove the presence of mass transport limitations are typically not performed. Thus, the chemical engineering concepts of effectiveness factor and Thiele modulus are only rarely explored.

With respect to the question of the most suitable test reaction, a clear-cut answer cannot be given. The reaction should be diffusion-limited over standard zeolite crystals (as evident from Thiele modulus and effectiveness factor) and the influence of coke formation on the activity should be moderate. The use of bulky reactants is preferred, but should be adapted to the pore size of the zeolite employed. Thus, a one fits all reaction is currently not in sight. Cracking of methyl cyclohexane, cumene and other similar substrates may provide information on the influence of textural properties on coke formation. Another option is the alkylation or dealkylation of aromatics such as toluene or cumene. Preferably, a defined mixture of different sized substrates may be used.

In any case, comparison to a standard zeolite catalyst with similar Si/Al ratio, particle size, number and strength of active sites is required for comparison. Thus, thorough characterization of both the hierarchical zeolite and the parent catalysts is mandatory for a valid assessment of the benefit of a hierarchical pore system. Often, nano zeolites are performing equally well but are not hierarchical. Therefore, it is important to compare catalysts with similar particle size and (if possible) morphology.

In addition to the determination of conversion, yield and selectivity, calculation of the activation energy, determination of Thiele modulus and effectiveness factor are good indicators for the presence or absence of diffusion limitations in hierarchical zeolites compared to their parent materials.

With respect to the properties of the hierarchical zeolite, the literature available so far indicates that interconnected hierarchical pore systems which are accessible from the outer surface of the crystal by the additional meso- or even better macropores are preferred.

Acknowledgements

Part of this work was inspired by discussions in the catalysis commission of the International Zeolite Association (IZA). Our work in this area was generously supported by the German Science Foundation (DFG) in the frame of the Cluster of Excellence “Engineering of Advanced Materials” at the FAU Erlangen-Nürnberg and the priority program SPP 1570.

References

---

[1] M.S. Holm, E. Taarning, K. Egeblad and C.H. Christensen, *Catal. Today*. 2011, **168**, 3-16.
[2] C.M.A. Parlett, K. Wilson, A.F. Lee, *Chem. Soc. Rev*. 2013, **42**, 3876-3893.
[3] W. Schwieger, A.G. Machoke, T. Weissenberger, A. Inayat, T. Selvam, M. Klumpp and A. Inayat, Chem. Soc. Rev. 2016, **45**, **DOI:** 10.1039/C5CS00599J
[4] G. Bellussi, A. Carati and R. Millini, in Zeolites and Catalysis, J. Cejka, A. Corma and S. Zones (eds.), Wiley-VCH, Weinheim (2010), pp. 449-492
[5] K. Egeblad, C.H. Christensen, M. Kustova, C.H. Christensen, *Chem. Mater*. 2008, **20**, 946-960.
[6] J. Perez-Ramirez, C.H. Christensen, K. Egeblad, C.H. Christensen and J.C. Groen, *Chem. Soc. Rev*. 2008, **37**, 2530-2542.
[7] S. Lopez-Orozco, A. Inayat, A. Schwab, T. Selvam and W. Schwieger, *Adv. Mater*. 2011, **23**, 2602-2615.
[8] L.-H. Chen, X.-Y. Li, J.C. Rooke, Y.-H. Zhang, X.-Y. Yang, Y. Tang, F.S. Xiao and B.-L. Su, *Chem. Mater*. 2012, **22**, 17381-17403.
[9] D.P. Serrano, J.M. Escola, P. Pizarro, *Chem. Soc. Rev*. 2013, **42**, 4004-4035.
[10] Y. Yan, X. Guo, Y. Zhang and Yi Tang, *Catal. Sci. Technol*. 2015, **5**, 772-785.
[11] K. Li. J. Valla, and J. Garcia-Martinez. *ChemCatChem* 2014, **6**, 46-66.
[12] V. Valtchev, G. Majano, S. Mintova and J. Pérez-Ramírez, *Chem. Soc. Rev*. 2013, **42**, 263-290.
[13] S. Mitchell, A. B. Pinar, J. Kenvin, P. Crivelli, J. Kärger and J. Perez-Ramirez, *Nat. Com*m. 2015, 6: 8633, DOI: 10.1038/ncomms9633.
[14] J. Shi, Y. Wang, W. Yang, Y. Tang and Z. Xie, *Chem. Soc. Rev*. 2015, **44**, 8877-8903.
[15] M. Guisnet and F.R. Ribeiro, Catal. Sci. Ser. 2011, **9**, 3-18.

---

[16] M.E. Davis: Fundamentals of Chemical Reaction Engineering, McGraw-Hill Higher Education, New York, NY (2003).

[17] S. Mintova, J.-P. Gilson and V. Valtchev, *Nanoscale* 2013, **5**, 6693-6703.

[18] J. Cejka and S. Mintova, *Catal. Rev. Sci. Eng*. 2007, **49**, 457-509.

[19] J. Vernimmen, V. Meynen and P. Cool, *Beilstein Journal of Nanotechnology* 2011, **2**, 785-801.

[20] M. Hartmann, *Angew. Chemie Int. Ed*. 2004, **43**, 5880-5882.

[21] M. Choi, H.S. Cho, R. Srivastava, C. Venkatesan, D.-H. Choi and R. Ryoo, *Nat. Mater*. 2006, **5**, 718-723.

[22] I.I. Ivanova and E.E. Knyazeva, *Chem. Soc. Rev.* 2013, **42**, 3671-3688

[23] M. Milina, S. Mitchell, P. Crivelli, D. Cooke and J. Perez-Ramirez, *Nat. Commun*. 5:3922 DOI: 10.1038/ncomms4922 (2014).

[24] J. Kim, M. Choi and R. Ryoo, *J. Catal.* 2010, **269**, 219–228.,

[25] M. Bjørgen, F. Joensen, M. Spangsberg Holm, U. Olsbye, K.-P. Lillerud and S. Svelle, *Appl. Catal. A: General* 2008, **345**, 43–50.

[26] Q. Wang, S. Xu, J. Chen, Y. Wei, J. Li, D. Fan, Z. Yu, Y. Qi, Y. He, S. Xu, C. Yuan, Y. Zhou, J. Wang, M. Zhang, B.-L. Su and Z. Liu, *RSC Adv.* 2014, **4**, 21479-21491.

[27] C. Mei, P. Wen, Z. Liu, H. Liu, Y. Wang, W. Yang, Z. Xie, W. Hua and Zi Gao. *J. Catal*. 2008, **258**, 243–249.

[28] Q. Sun, N. Wang, D. Xi, M. Yang and J. Yu, *Chem. Commun*. 2014, **50**, 6502-6505.

[29] L. Zhang, Y. Song, G. Li, Q. Zhang, S. Zhang, J. Xu, F. Deng and Y. Gong, *RSC Adv*., 2015, **5**, 61354-61363.

[30] M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki and R. Ryoo, *Nature* 2009, **461**, 246-249.

[31] S. Hu, J. Shan, Q. Zhang, Y. Wang, Y. Liu, Y. Gong, Z. Wu, T. Dou, *Appl. Catal. A: General* 2012, **445-446**, 215-220

[32] K.K. Ramasamy, H. Zhang, J. Sun, Y. Wang, *Catal. Today* 2014, **238**, 103-110.

[33] L. Lakiss, F. Ngoye, C. Canaff, S. Laforge, Y. Pouilloux, Z. Qin, M. Tarighi, K. Thomas, V. Valtchev, A. Vicente, L. Pinard, J.-P. Gilson and C. Fernandez, *J. Catal*. 2015, **328**, 165-172.

[34] C. Hviid Christensen, K. Johannsen, I. Schmidt, and C. Hviid Christensen, *J. Am. Chem. Soc*. 2003, **125**, 13370 - 13371

[35] Y. Sun and R. Prins, *Applied Catal. A: General* 2008, **336**, 11-16.

[36] Y. Wang, Y. Sun, C. Lancelot, C. Lamonier, J.-C. Morin, B. Revel, L. Delevoye and A. Rives, *Microporous Mesoporous Mater*. 2015, **206**, 42–51.

[37] X. Zhang, D. Liu, D. Xu, S. Asahina, K.A. Cychosz, K.V. Agrawal, Y. Al Wahedi, A. Bhan, S. Al Hashmi, O. Terasaki, M. Thommes and M. Tsapatsis, *Science* 2012, **336**, 1685-41687.

[38] K. Leng, Yi Wang, C. Hou, C. Lancelot, C. Lamonier, A. Rives and Y. Sun, *J. Catal*. 2013, **306**, 100-108.

[39] X. Li, R. Prins and J. A. van Bokhoven, *J. Catal*. 2009, **262**, 257-265.

[40] N. Chu, J. Yang , C. Li, J. Cui, Q. Zhao, X. Yin, J. Lu and J. Wang, *Microporous Mesoporous Mater.* 2009, **118**, 169–175

[41] N. Chu, J. Yang, J. Wang, S. Yu, J. Lu, Y. Zhang and D. Yin, *Catal. Commun.* 2010, **11**, 513-517.

[42] N. Chu, J. Wang, Y. Zhang, J. Yang, J. Lu and D. Yin, *Chem. Mater*. 2010, **22**, 2757-2763.

[43] T.C. Keller, J. Arras, S. Wershofen and J. Perez-Ramirez, *ACS Catal.* 2015, **5**, 734-743.

[44] C. Yin, R. Ni, X. Bao and Y. Chen, *Microporous Mesporous Mater*. 2015, **202**, 133-137.

[45] J. Kim, W. Park and R. Ryoo, *ACS Catal.* 2011, **1**, 337 – 341.

[46] A.J.J. Koekkoek, W. Kim, V. Degirmenci, H. Xin, R. Ryoo and E.J.M. Hensen, *J. Catal*. 2013, **299**, 81-89.

[47] S. Gopalakrishnan, A. Zampieri and W. Schwieger, *J. Catal.* 2008, **260**, 193–197.

[48] F. Ngoye, L. Lakiss, Z. Qin, S. Laforge, C. Canaff, M. Tarighi, V. Valtchev, K. Thomas, A. Vicente, J.P. Gilson, Y. Pouilloux, C. Fernandez and L. Pinard, *J. Catal*. 2014, **320**, 118-126.

[49] D. Verboekend, S. Mitchell, M. Milina, J.C. Groen and J. Perez-Ramirez, *J. Phys. Chem. C* 2011, **115**, 14193-14203.

[50] C.-J. Jia, Y. Liu, W. Schmidt, A.-H. Lu and F. Schüth, *J. Catal.* 2010, **26**, 71-79.

---

[51] L.G. Possato, R.N. Diniz, T. Garetto, S.H. Pulcinelli, C. V. Santilli and L. Martins, *J. Catal.* 2013, **300**, 102-112.

[52] H. Konno, R. Ohnaka, J. Nishimura, T. Tago, Y. Nakasaka and T, Masuda, *Catal. Sci. Technol*. 2014, **4**, 4265-4273.

[53] K. S. Triantafyllidis, E.F. Ilopoulou, S. A. Karakoulia, C. K. Nitsos and A.A. Lappas, in Mesoporous Zeolites, J. Garcia-Martinez and K. Li (eds.), Wiley-VCH (2015), pp. 497-540.

[54] L. Ren, Q. Guo, P. Kumar, M. Orazov, D. Xu, S.M. Alhassan, K.A. Mkhoyan, M.E. Davis and M. Tsapatsis, *Angew. Chem. Int. Ed*. 2015, **54**, 10848-10851.

[55] N. Wilde, M. Pelz, S.G. Gebhard and R. Gläser, *Green Chem.* 2015, **17**, 3378-3389.