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Mesoporous zeolite single crystal catalysts: Diffusion and catalysis in hierarchical zeolites

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Abstract

During the last years, several new routes to produce zeolites with controlled mesoporosity have appeared. Moreover, an improved catalytic performance of the resulting mesoporous zeolites over conventional zeolites has been demonstrated in several reactions. In most cases, the mesoporous zeolites exhibit higher catalytic activity, but in some cases also improved selectivity and longer catalyst lifetime has been reported. The beneficial effects of introducing mesopores into the zeolites has in most instances been attributed to improved mass transport to and from the active sites located in the zeolite micropores. Here, we briefly discuss the most important ways of introducing mesopores into zeolites and, for the first time, we show experimentally that the presence of mesopores dramatically increases the rate of diffusion in zeolite catalysts. This is done by studying the elution of *iso*-butane from packed beds of conventional and mesoporous zeolite catalysts. Moreover, we discuss in detail the recent observation of improved activity and selectivity in the alkylation of benzene with ethene using mesoporous zeolite single crystal catalysts. For this reaction, we show by calculation of the Thiele modulus that this improved performance can be mainly attributed to a diffusional limitation of ethylbenzene in the zeolite pores. This is verified in new ethylbenzene dealkylation experiments where mesoporous zeolite catalysts show significantly improved activity over conventional zeolite catalysts.

Keywords: Carbon-templated zeolites; Mesoporous zeolites; Diffusion; Benzene alkylation

1. Introduction

Recently, the synthesis, characterization, and catalytic properties of mesoporous zeolites have attracted increasing attention, and several reviews [1,2] and research highlights [3,4] have appeared. Generally, the interest in mesoporous zeolites is motivated by the desire to improve the transport of reagents and products to and from the active sites located inside the zeolite micropores [5] as shown in Fig. 1.

Traditionally, mesopores have been introduced into zeolites and zeolite-like crystals mostly by dealumination [6]. However, recently several other schemes have appeared such as carbon templating [7,8], desilication [9–11], detitanation [12], zeolite seed assembly [13], resin templating [14], recrystallization [15], mesoscale cationic polymer templating [16] and by using amphiphilic organosilica zeolite precursors [17]. For some of these approaches, it has already been shown that catalysts with improved performance in various reactions can result. Specifically, mesoporous zeolites have shown superior performance over comparable conventional zeolites in various hydrocarbon conversion processes [18–22] and environmental processes [23–25]. Interestingly, the catalytic performance of mesoporous zeolites was most recently compared to that of mesoporous materials, such as MCM-41 and SBA-15, in the methanol-to-hydrocarbon reaction and in the synthesis of jasminaldehyde and vesidryl [17]. Not surprisingly, the mesoporous zeolites showed a dramatically improved performance over the mesoporous materials. The reason is that the mesoporous zeolites combine the presence of strongly acid sites and the hydrothermal stability characteristic of zeolites with the excellent mass transport properties of mesoporous materials. Therefore, it is expected that properly designed mesoporous

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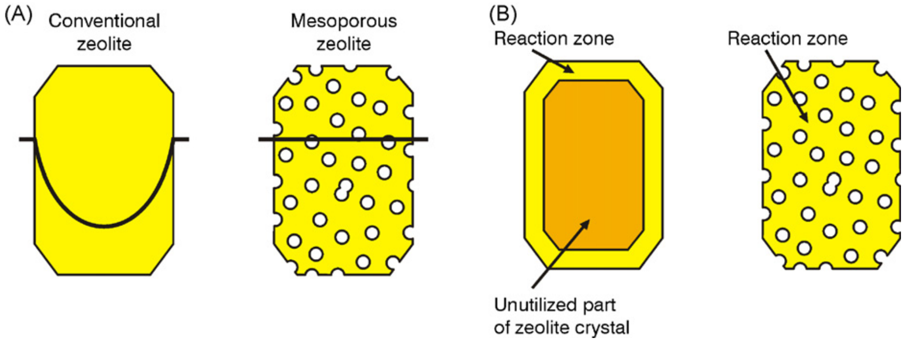

Fig. 1. (A) Schematic illustration of the concentration profile of a reactant through a conventional zeolite crystal when diffusion is limiting the zeolite catalyst performance. The concentration in the gas-phase is constant at a given position in the catalytic reactor under steady state conditions. In a mesoporous zeolite crystal, the diffusion is sufficiently fast to maintain the reactant concentration at the same level inside and outside the crystal during reaction. (B) For catalytic reactions involving reactants and products with relatively slow diffusion rates, it is not possible to fully utilize the entire zeolite crystal for catalysis unless intracrystalline mesopores are introduced.

zeolite catalysts will generally be superior to catalysts composed of mesoporous materials. It is noteworthy that despite the fact that the improved performance of the mesoporous zeolites has generally been ascribed to improved transport properties, there has so far not been any direct measure of this effect. Here, we first establish experimentally that the diffusion in mesoporous zeolites is significantly improved over that in comparable conventional zeolite catalysts. Then, we analyse in some detail the previously reported higher activity in alkylation of benzene with ethene using mesoporous zeolite catalysts, and also the simultaneous increase in selectivity to the desired mono-alkylated product. From this analysis, it is clear that it is the hindered diffusion primarily of ethylbenzene, but also to some extent benzene, that lowers productivity in this reaction. The analysis suggests that the effect of the introduced mesoporosity should be even larger in the dealkylation of ethylbenzene, a reaction which is important in xylene isomerization. This is verified experimentally in new catalytic experiments.

We have focused on the carbon templating method for introducing mesopores into zeolite crystals, since this method appears to be the most versatile approach to preparing hierarchical zeolites. Contrary to other methods, the carbon templating method is applicable to a wide variety of zeolite [7,19,24] and zeotype [26] structure types independent of their composition. Furthermore, it is the method that currently seems to yield the highest mesopore volumes (above 1.0 ml/g), and with the recent discovery of the in situ carbon templating method [27], it also appears to be the most practicable route to mesoporous zeolites.

2. Experimental

Conventional and mesoporous ZSM-5 zeolites were prepared according to published procedures [7]. The zeolite samples were characterized by scanning electron microscopy, transmission electron microscopy, elemental analysis, nitrogen adsorption/desorption, and ammonia-temperature programmed desorption (NH_3-TPD) as previously described [28]. The conventional ZSM-5 catalyst has a BET surface area of 370 m^2/g, a mesopore volume of <0.01 ml/g, an average crystal size of about 0.2–0.3 μm, and an acid capacity of 0.094 mmol/g (NH_3-TPD). The mesoporous ZSM-5 catalyst has a BET surface area of 350 m^2/g, a mesopore volume of 0.4 mm/g (average pore diameter 18 nm), an average crystal size of 1.0 μm, and an acid capacity of 0.119 mmol/g (NH_3-TPD).

The diffusion experiments were carried out in a custom-made multi-purpose micro-reactor setup with six gas lines, an U-shaped, glass-lined, stainless steel reactor, and an Inficon QMG 422 mass spectrometer to monitor the concentrations of the employed gases. About 90 mg sample of particle size 150–300 μm was loaded into the reactor, which had an inner diameter of 4 mm, giving a bed height of about 17 mm. Prior to the elution experiments the sample was dried at 350 °C for about 0.5 h in a stream of helium (Air Liquide, Alphagaz 2) at 100 Nml/min (100 ml/min at STP). While keeping the helium flow, the sample was cooled to 90 °C at which temperature the reactor was isolated, and the feed switched to a gas mixture of 1000 ppmv *iso*-butane in helium (Air Liquide, Alphamix 2) at 100 Nml/min. After a few minutes, the *iso*-butane signal of the mass spectrometer had stabilized and the valve to the reactor was opened. The uptake of *iso*-butane by the sample was monitored by the mass spectrometer, and after about two minutes the uptake was finished and the *iso*-butane signal returned to the 1000 ppmv level.

Catalytic experiments were conducted using a microreactor unit comprising a glass-lined U-tube reactor loaded with 0.17 g of tabletized zeolite catalyst, giving a bed height of about 25 mm. The temperature was varied between 350 and 450 °C at a pressure of 6 atm. A liquid mixture of 15 vol.% ethylbenzene and 85 vol.% meta-xylene was added to a preheated He carrier gas and flowed through the reactor, the aromatics/helium molar ratio being 1/5. Experiments were conducted at a WHSV of 6 h^{-1}. Products were analyzed on-line by gas chromatography assuming the following response factors (flame ionization detection) benzene: 1.12; toluene: 1.07; xylenes: 1.04; ethylbenzene: 1.08.

3. Results and discussion

The interest in introducing mesopores in zeolite catalysts can primarily be attributed to the possibility of improving the transport of reactants and products to and from the active sites located in the zeolite micropores, and thereby improving the catalyst performance. Today, there are several examples that this approach can actually result in an increased catalytic activity and/or selectivity. However, there has been no attempt to directly establish that the superior catalytic performance is a result of the improved mass transport. Therefore, we decided to independently assess how the presence of mesopores influences the diffusion properties of the conventional and mesoporous zeolite samples. Since the main difference between these two samples is the presence of a significant amount of intracrystalline mesopores in the mesoporous sample, the direct comparison of the elution behaviour of these two samples should give a clear indication of any significant difference in diffusion rates. Prior to the elution experiment, the zeolite samples were charged with *iso*-butane. As an example of the uptake, the *iso*-butane trace for a sample of mesoporous ZSM-5 is displayed in Fig. 2.

After another few minutes, the stream was changed to pure helium at 100 Nml/min, and the elution of *iso*-butane was monitored by the mass spectrometer. In Fig. 3, data for the mesoporous ZSM-5 and the conventional ZSM-5 are displayed together with the data for an empty reactor. The latter is included as reference. The data is plotted as the logarithm of the *iso*-butane concentration versus time and only the part which decreases exponentially is included.

Gorring and DeRosset [29] developed a technique to experimentally determine the effective diffusivity of porous catalyst materials, using a single catalytic pellet (sphere) as sample. They expressed the slope *S*, and the intercept *I*, of the linear part of the trace when plotting the logarithm of the elute concentration versus time as

$$S = \frac{D\pi^2}{\varepsilon(R+1)a^2} \tag{1}$$

$$I = \frac{D8C_0\pi a}{\varepsilon V} \tag{2}$$

where D is the overall effective diffusivity, ε the fraction of voids in the sphere, R the adsorption coefficient for the adsorption of the elute at the pore walls, a the radius of the sample sphere, C_0 the mole of elute in void space of sphere per unit volume of sphere at $t = 0$, and V is the volumetric flow rate of the eluant. From these two equations the overall effective diffusivity, D, can be calculated independently, and when they give the same value the theory is valid. In our case, the sample is a packed bed of particles instead of a single pellet and it is not straightforward to use the analysis of Gorring and DeRosset. However, assuming that the macropores ‘‘between’’ the particles of the packed bed are much larger than the meso- and micropores of the particles, then contribution of the macropores to the effective diffusivity will be small. Assuming further that the adsorption coefficient, void fraction, and an ‘‘effective’’ radius, a, are similar for our two ZSM-5 samples, we write:

$$\frac{D_{\mathrm{Meso}}}{D_{\mathrm{Conv}}} \approx \frac{I_{\mathrm{meso}}}{I_{\mathrm{Conv}}} \tag{3}$$

and

$$\frac{D_{\mathrm{Meso}}}{D_{\mathrm{Conv}}} \approx \frac{S_{\mathrm{meso}}}{S_{\mathrm{Conv}}} \tag{4}$$

By fitting the data of Fig. 3, we get: $I_{\mathrm{Meso}} = -5.41$, $I_{\mathrm{Conv}} = -6.39$, $S_{\mathrm{Meso}} = -7.39 \times 10^{-2}\ \mathrm{s}^{-1}$ and $S_{\mathrm{Conv}} = -2.53 \times 10^{-2}\ \mathrm{s}^{-1}$, which give $D_{\mathrm{Meso}}/D_{\mathrm{Conv}} \approx \exp(-5.41)/\exp(-6.39) \approx 2.7$ and $D_{\mathrm{Meso}}/D_{\mathrm{Conv}} \approx 2.9$, for the intercepts and slopes, respectively.

The fact that the ratios are about the same, indicates that our analysis is sensible, and it is reasonable to conclude that the effective diffusivity of the mesoporous ZSM-5 is about three times larger than of the conventional one. This is a noteworthy result since the mesoporous ZSM-5 crystals are about three times larger than the conventional ZSM-5 crystals and because *iso*-butane is not a particularly large probe molecule. However, more experimental data, using other molecules, as well as a more thorough analysis is necessary to make general conclusions. Nevertheless, it appears reasonable to assume that for molecules larger than *iso*-butane there could easily be a

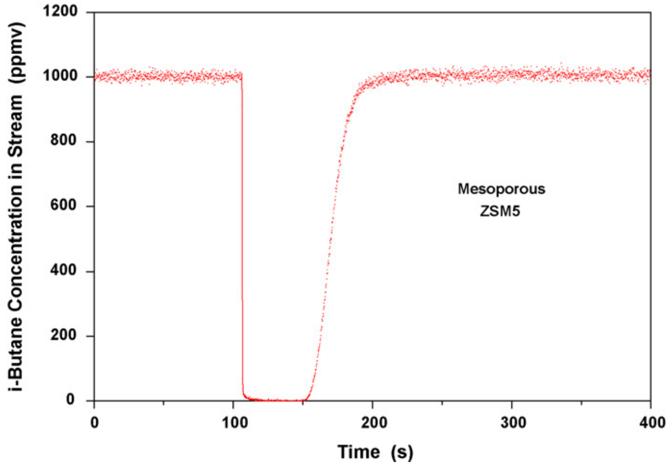

Fig. 2. Uptake of *iso*-butane in a sample of mesoporous ZSM-5. At about 100 s the valve to the reactor is opened. After another 100 s the uptake is finished.

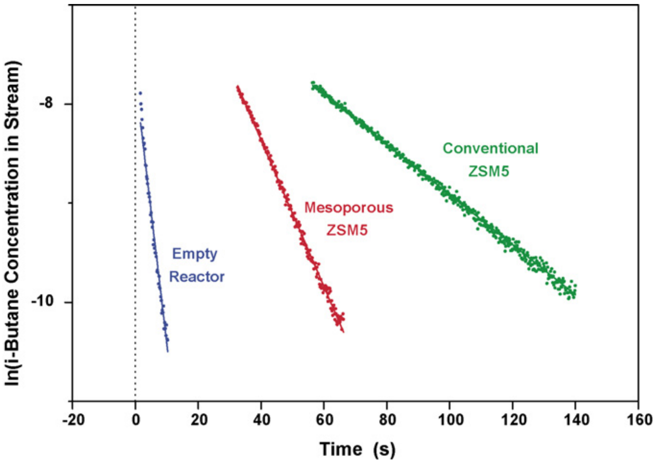

Fig. 3. Elution of *iso*-butane in mesoporous and conventional ZSM-5. The result of an empty reactor is shown as reference. The average crystal size is about 1 and 0.3 μm for the mesoporous and the conventional ZSM-5, respectively. At time = 0, the feed is changed to pure helium.

significant effect of the improved diffusion in the mesoporous zeolite that would translate into a superior performance.

Recently, it was shown that in the ethylation of benzene *both* an improved activity *and* an improved selectivity to the monoethylated product was observed with the mesoporous zeolite [18] and this was ascribed to faster mass transport due to the presence of the intracrystalline mesopores. Here, we investigate this observation and the interpretation in detail. The possible existence of diffusion limitations in zeolite catalysts can be calculated using the equations for diffusion in small pores (see e.g. [30]). Due to the small pore size, it is assumed that the diffusion mechanism in the pores is *activated diffusion*. For activated diffusion, the diffusion coefficient is calculated at any temperature given a reference value D' as shown in Eq. (5) [31]:

$$D(T) = D' \exp\left(\frac{-E_a}{RT}\right) \tag{5}$$

The so-called *Thiele modulus* φ and the *effectiveness factor* η are defined as shown in Eq. (6). The Thiele modulus can be used to calculate the effectiveness factor, which will tell if there is a diffusion limitation for a given reaction:

$$\eta \equiv \frac{\text{measured activity}}{\text{activity without diffusion limitation}}, \qquad \varphi \equiv \sqrt{\frac{\text{intrinsic rate}}{\text{diffusion coefficient}}} \tag{6}$$

For a reaction with an *n*th order reaction rate, the Thiele modulus can be calculated using Eq. (7) with R being the typical particle size, k the intrinsic reaction rate constant and C the reactant concentration inside the particle, which is lower than the bulk concentration, if diffusion limitation occurs. The relationship between φ and η is given by Eq. (8):

$$\varphi = \sqrt{\frac{R^2 k C^{n-1}}{D}} \tag{7}$$

$$\eta = \frac{3}{\varphi}\left(\frac{1}{\tanh(\varphi)} - \frac{1}{\varphi}\right) \Rightarrow \eta = 1 \quad \text{for } \varphi < 1 \quad \text{and} \qquad \eta = \sqrt{\frac{2}{n+1}} \times \frac{3}{\varphi} \quad \text{for } \varphi > 10 \tag{8}$$

However, since the intrinsic reaction rate constant k is often unknown, the *global Thiele modulus* Φ (defined in Eq. (9)) can be calculated instead and used to estimate the effectiveness factor η. When looking at an isothermal reactor bed with bed voidage ε, reactant space velocity SV, reactant conversion $x = C_{in}/C_{out}$ and overall reaction rate r_p, Φ for a first order reaction is given by Eq. (9):

$$\Phi \equiv \frac{R^2}{D} \times \frac{r_p}{C} \approx \frac{R^2}{D} \times \frac{\mathrm{SV} \ln(x)}{1-\varepsilon}, \qquad \Phi = \varphi^2 \times \eta \tag{9}$$

The limiting cases for η as a function of Φ are given by Eq. (10):

$$\eta = 1 \quad \text{for } \Phi < 0.1; \qquad \eta = \frac{9}{\Phi} \quad \text{for } \Phi > 100 \tag{10}$$

Table 1
Activated diffusion parameters for benzene and ethylbenzene in silicalite-1 (from Ref. [31])

	D' (m^2/s)	E_a (kJ/mol)	D (370 °C) ($\times 10^{-11}$ m^2/s)
Benzene	6.9×10^{-9}	28.8	3.15
Ethylbenzene	1.9×10^{-8}	34.4	3.00

Hence it is possible to set $\Phi = \Phi_{lim} = 0.1$ and given a specific catalytic experiment determine the minimum particle size R_{lim}, at which diffusion limitations will occur (Eq. (11)). And if $\Phi > 100$ the effectiveness factor can be calculated using Eq. (10).

$$R_{lim}^2 = \frac{\Phi_{lim} \times D \times (1-\varepsilon)}{\mathrm{SV} \times \ln(x)} \tag{11}$$

Using this approach, it is possible to analyse the catalytic activity measurements reported for alkylation of benzene with ethylene to form ethylbenzene. Values for the activated diffusion of benzene and ethylbenzene in MFI-zeolites can be found in the literature [31] and are shown in Table 1.

In a typical experiment, ethylene and benzene was reacted in gas phase in a plug flow reactor with SV = 15, $\varepsilon = 0.8$ and $T = 370$ °C over a ZSM-5 catalyst. With the typical size of the conventional zeolite (Si/Al = 71) of 2 μm and the mesoporous zeolite (Si/Al = 116) of 0.04 μm (corresponding to the average distance between mesopores; the crystal size was about 2 μm) used in that study, the results are as shown in Table 2.

The results in Table 2 shows that the mass transport of both benzene and ethylbenzene in the conventional zeolite is diffusion limited ($\Phi > 0.1$), and the maximum crystal size needed to avoid such diffusion limitation is <0.5 μm. In the case of the mesoporous zeolite, the mass transport of neither benzene nor ethylbenzene is diffusion limited ($\Phi \ll 0.1$). Thus, the concentration profiles of benzene, ethylene and ethylbenzene in the conventional and mesoporous zeolites during catalysis can be illustrated as shown in Fig. 4.

Thus, the increased activity in the ethylation of benzene over the mesoporous zeolite can be explained by the fact that the entire mesoporous zeolite crystal is effectively utilized for catalysis with both reactants present in their optimal concentrations throughout the crystal. This is not the case for the conventional catalyst where the interior is partly depleted for benzene. On the other hand, the improved

Table 2
Results from alkylation of benzene with ethylene over ZSM-5 zeolite at 370 °C and SV = 15

	Conventional zeolite	Mesoporous zeolite
Typical size (μm)	2	0.04
Conversion/selectivity to ethylbenzene	15%/73%	18%/81%
$\Phi_{benzene}$	0.41	2.02×10^{-4}
$R_{lim,benzene}$ (μm)	0.49	0.44
$\Phi_{ethylbenzene}$	0.43	2.11×10^{-4}
$R_{lim,ethylbenzene}$ (μm)	0.48	0.43

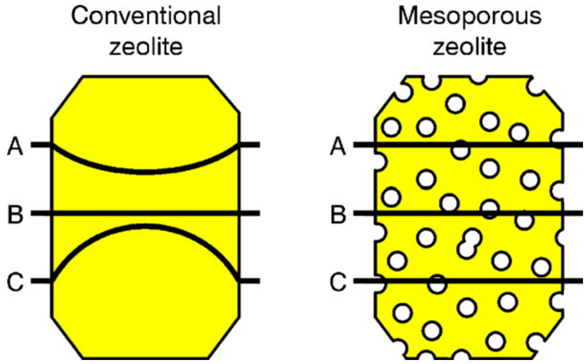

Fig. 4. Schematic illustration of concentration profiles of (A) benzene, (B) ethylene, and (C) ethene during ethylation of benzene with conventional and mesoporous zeolite single crystal catalysts, respectively.

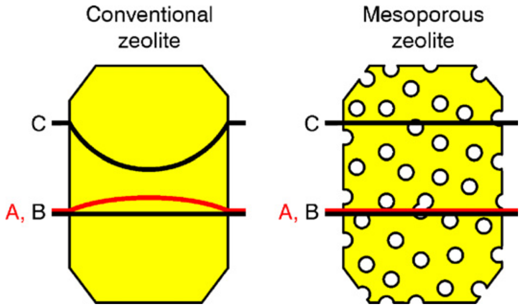

Fig. 5. Schematic illustration of concentration profiles of (A) benzene, (B) ethylene, and (C) ethene during dealkylation of ethylbenzene with conventional and mesoporous zeolite single crystal catalysts, respectively.

selectivity to the mono-ethylated product is attributed to the concentration profile of ethylbenzene. In the conventional sample, the ethylbenzene concentration is relatively high in the interior of the crystals, thereby favouring dialkylated products. In the mesoporous sample, diffusion is so fast that the ethylbenzene concentration throughout the crystal is kept very close to that of the gas phase and thus dealkylation is suppressed relatively to that in the conventional zeolite sample.

This analysis suggests that the beneficial effect of the mesopores should also be observed in the dealkylation of ethylbenzene. This reaction is of importance in the technical isomerization of xylenes to suppress build-up of ethylbenzene in the product stream. Here, the analysis would be completely analogous to that presented for the ethylation of benzene resulting in concentration profiles through conventional and mesoporous zeolite catalysts as sketched in Fig. 5. Again, the concentration gradient of ethylbenzene in the interior of the conventional zeolite would result in lower catalytic rate. To establish this experimentally, the activity difference between the conventional and mesoporous ZSM-5 samples were determined. The catalytic performance was evaluated at conditions relevant for xylene isomerization. Table 3 shows the activity data at three different temperatures.

At conditions far from equilibrium, it is seen that the mesoporous zeolite exhibits more than twice as high reaction rate even though the acidity of the two samples are comparable, and the crystal size of the mesoporous zeolite is about three to four times larger than that of the conventional zeolite sample.

Table 3
Activity of conventional and mesoporous zeolite catalysts in dealkylation of ethylbenzene

Temperature (°C)	Conventional ZSM-5 conversion (%)	Mesoporous ZSM-5 conversion (%)
350	22.4	44.7
400	51.3	68.4
450	80.1	83.8

4. Conclusion

It is shown experimentally that the diffusion of *iso*-butane is significantly faster in mesoporous zeolite single crystal catalysts than in conventional zeolite crystal catalysts. This provides independent support to the proposal that the beneficial effect of mesopores in numerous catalytic reactions can be attributed to improved mass transport, in particular with larger reactant molecules. This conclusion is also supported by a classical evaluation of the diffusion properties of ethylbenzene, benzene and ethylene during catalytic ethylation of benzene. The analysis provides a semi-quantitative explanation for the observed increase in both activity and selectivity with the mesoporous zeolite catalysts. Finally, it is shown that beneficial effect of mesopores should also be apparent in the dealkylation of ethylbenzene and this is verified experimentally. Thus, it appears that for many reactions mesoporous zeolites are expected to show superior performance over conventional samples. With the methods shown here, it should be possible not only to rationalize experimental observation but also to predict the possible improvement in catalyst performance, and even to tailor the mesoporous zeolite for optimal activity and selectivity. So far, such tailoring of the zeolite catalyst appears only to be possible with the carbon templating method.

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