

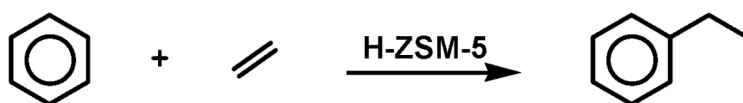
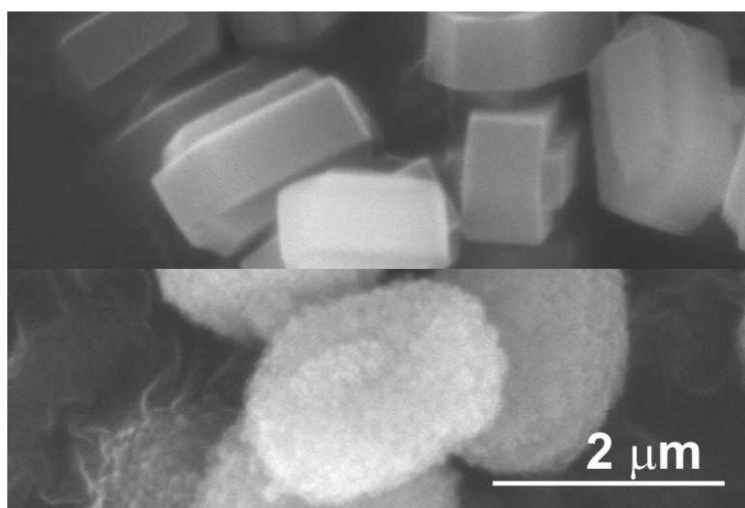
Communication

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 Improving Activity and Selectivity with a New Family of Porous Materials**

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Catalytic Benzene Alkylation over Mesoporous Zeolite Single Crystals: Improving Activity and Selectivity with a New Family of Porous Materials

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Zeolites and zeotype-materials have been found to catalyze a wide variety of chemical reactions.¹ In industry, zeolite catalysts are primarily used for catalytic fuel-upgrading in refineries and also for the production of various petrochemicals. When zeolite catalysts were first introduced in oil-cracking to replace the amorphous silica–alumina catalysts, it was estimated that the higher gasoline yield resulting from the zeolite catalyst corresponded to an added value of 40 billion U.S. dollars/year.² Much of the success of zeolite catalysis can be attributed to the presence of micropores (diameter < 20 Å) with well-defined structures that are responsible for the shape-selectivity exhibited by such catalysts. However, in many cases, the sole presence of micropores can also be a major limitation because mass transport to and from the active sites located within the micropores is slow, much slower than, for example, Knudsen diffusion, which is often limiting the performance of industrial catalysts. To overcome this limitation, there has been a long-standing drive either to minimize the crystal size of zeolite catalysts³ or to increase the pore size of available zeolites.^{4,5} Here, we show that a new family of zeolite catalysts, the mesoporous zeolite single crystals,⁶ exhibit significantly improved catalytic activities and selectivities as compared to conventional zeolite catalysts, in the alkylation of benzene with ethene. This is a major industrial process responsible for production of almost all ethylbenzene which in turn is the raw material for styrene manufacture. The mesoporous zeolite single crystals combine in each individual zeolite crystal, the crystallographic, intracrystalline micropore system typical of zeolites with a noncrystallographic, intracrystalline mesopore system. This is shown to dramatically improve mass transport in zeolite crystals.

Comparable samples of conventional⁷ and mesoporous⁶ zeolite powders were prepared according to published procedures. The resulting powders were pressed into catalyst tablets which were crushed and sieved to a particle size of 150–300 μm. Next, 150 mg of each catalyst was tested in an isothermal plug-flow reactor (4 mm inner diameter) at temperatures between 583 and 643 K and pressures of 2.5 and 5 bar. In the feed, the molar ratio of benzene to ethene was 5.1:1, and this limits the maximum conversion of benzene to ca. 20%. Flow rates corresponding to a weight-hourly space velocity (WHSV) (mass of feed/mass of catalyst/time) of 225 h⁻¹ were used, and the exit gas was analyzed on-line by GC.

In Table 1, the acidities of the two catalysts as determined by ammonia desorption,⁸ IR of adsorbed pyridine,⁹ and ²⁷Al MAS NMR⁸ are compared.

It is seen that an excellent agreement between the different experimental techniques for determining acidity exists for the zeolite catalysts. The conventional zeolite catalyst has almost twice as many acidic sites as the mesoporous zeolite catalyst.

Table 1. Zeolite Catalyst Acidity Expressed as Si/Al

catalyst	NH ₃	IR	²⁷ Al NMR
conventional	71	70	70
mesoporous	116	110	120

Table 2. Selected Properties of Zeolite Catalysts

catalyst	XRPD	SEM μm	pore volume ^a mL/g	mesopore size ^a nm
conventional	MFI	2.0	0.10	none
mesoporous	MFI	2.1	0.59	12

^a Mesopores were quantified by the BJH method. The conventional zeolite contains only micropores, whereas the mesoporous zeolite has both micropores and mesopores.

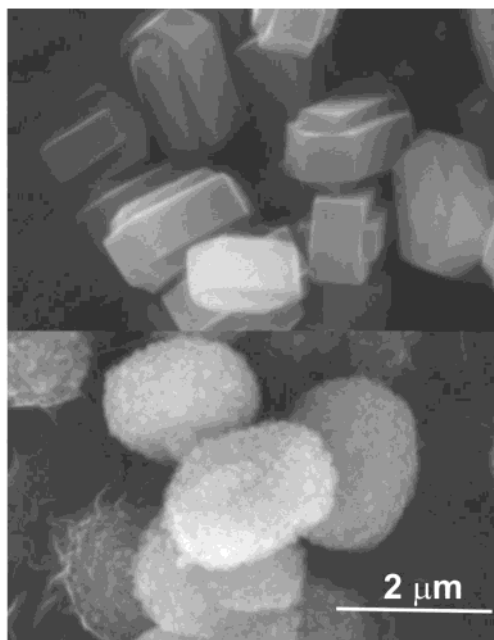


Figure 1. SEM images of the conventional and mesoporous zeolite catalysts used for alkylation of benzene with ethene.

Table 2 shows the results from scanning electron microscopy (SEM), X-ray powder diffraction (XRPD), and N₂ adsorption/desorption (at 77 K) studies.

Both catalysts are seen to contain exclusively zeolite ZSM-5 (with MFI structure). Moreover, the average crystal size as determined from SEM is almost the same, but the mesoporous zeolite crystals are slightly larger than the conventional zeolite crystals as shown in Figure 1. The typical coffin-shape of MFI crystals is observed for both samples, and the very different surface morphologies are easily seen.

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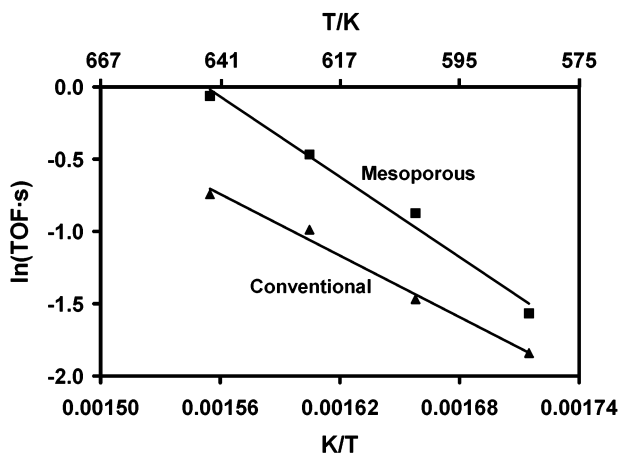


Figure 2. Arrhenius plot illustrating the activity difference between conventional and mesoporous zeolite catalysts. The activities are expressed as turn-over frequencies using the Si/Al ratios in Table 1 as a measure of the number of active sites.

Thus, the major difference in this comparison between the conventional and the mesoporous zeolite catalysts is the presence of noncrystallographic intracrystalline mesopores resulting in a very high porosity and a large average pore size for the mesoporous zeolite. The mesoporous zeolites are members of a new family of materials characterized by a high porosity attributed to a network of mesopores introduced into each individual crystal. Recently, similar materials have been reported for other compounds.¹⁰ However, the mesoporous zeolite single crystals are unique in the sense that they contain interconnected micropores and mesopores inside each individual single crystal. In Figure 2, the importance of such a bimodal pore size distribution in the catalytic alkylation of benzene with ethene is clearly shown. The activity measurements are conducted at conditions that are comparable to those used in industrial processes but generally at somewhat lower conversions. Therefore, the effect of the enhanced mass transport with the mesoporous zeolite catalyst could be even larger than shown here.

First of all, it is seen that the mesoporous zeolite catalyst is significantly more active than the conventional zeolite catalyst. Furthermore, it appears reasonable to conclude that this activity difference can be ascribed to improved mass transport in the mesoporous zeolite because the presence of a diffusional limitation is manifested by a lower apparent activation energy. For the conventional and mesoporous zeolite catalysts, we find apparent activation energies of 59 and 77 kJ/mol, respectively. This is in the same range as those previously reported.¹¹ By use of established diffusion theory and published values for the diffusion coefficients of benzene and ethylbenzene,¹² the global Thiele modulus for reactants and products was calculated under the assumption of activated diffusion and a first-order reaction rate expression. This clearly shows that, at the experimental conditions, the diffusion of ethylbenzene is limiting the reaction rate while diffusion of benzene is not. At industrial conditions, diffusion of benzene can also be limiting. Attributing the higher activity to improved mass transport is also substantiated by the different selectivities to ethylbenzene seen for the two catalysts and shown in Figure 3. The selectivities are measured between 583 and 643 K and at 2.5 bar. Comparable conversions were achieved by adjusting the feed flow. In all

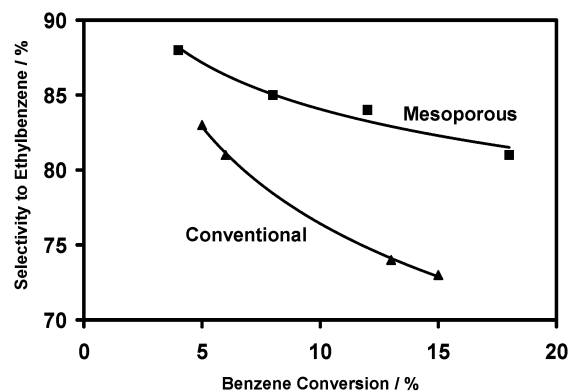


Figure 3. Selectivity to ethylbenzene for mesoporous zeolite and conventional zeolite catalyst obtained at 583–643 K and 2.5 bar.

experiments, the major byproduct was dialkylated benzene, and less than 0.5% was converted into polyalkylated products that were not further analyzed.

The higher selectivities to ethylbenzene observed with mesoporous zeolite catalyst can be understood in simple terms. Whenever a benzene molecule is ethylated, it can either be transported into the product stream or undergo further ethylation. In the mesoporous zeolite catalyst, the diffusion path is significantly shorter than that in the conventional zeolite catalyst, and further ethylation is suppressed. Hence, it is possible with the mesoporous zeolite catalysts to obtain both a higher activity and a higher selectivity to the desired product. Recently, several other successful attempts to overcome the transport limitation with zeolite catalysts in various processes have been reported,^{13,14} and there has also been much focus on establishing new synthetic routes to mesostructured zeolite catalysts.^{15,16} Most industrial zeolite catalysts are operated at conditions where the reaction rate is limited by diffusion rates. This suggests that use of mesoporous zeolite single crystals can lead to improvements in existing processes or allow entirely new applications of zeolite catalysts.

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