Catal Lett (2009) 129:20–25
DOI 10.1007/s10562-008-9836-3

n-Heptane Hydroisomerization over Mesoporous Zeolites made by Utilizing Carbon Particles as the Template for Mesoporosity

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Received: 12 November 2008 / Accepted: 25 December 2008 / Published online: 30 January 2009

Abstract Mesoporous zeolites were successfully synthesized by utilizing carbon black particles during the sol–gel synthesis as a template for the network of mesopores. Mesoporous samples of ZSM-12, and Zeolite Beta were synthesized with this method with an average pore size about 400 Å. The size and the percentage of mesopores increases with the C/Si ratio. Our TEM investigations validate the formation of mesoporous networks and voids. This study proves that this method can be generalized for both high and low aluminum zeolites. Selected samples were tested for the hydroisomerization of *n*-heptane, a probe reaction of great importance for the upgrading of light naphthas. It was found that under identical operating conditions the mesoporous samples exhibited higher, almost fourfold, activity. The selectivity for C7 isomers was higher over the mesoporous samples in comparison with the regular ones. More specifically, the selectivities towards mono- and dibranched isomers increases monotonically with the degree of mesoporosity. The increase of branching over the mesoporous zeolite samples we observed is due to the combined effect of reduced residence times in the zeolite crystal for the reaction products, and the larger "average" pores of the mesoporous samples that allow the formation of bulkier reaction state intermediates. Moreover, the mesoporous samples resulted in generation of less light hydrocarbons (C3, C4). The above behavior is a testimony of the tremendous potential that mesoporous zeolite crystals offer and could be very beneficial for numerous refining processes.

Keywords Mesoporous zeolites · Carbon as template · *n*-Heptane hydroisomerization

1 Introduction

Modifying zeolites to achieve certain performance characteristics is a usual practice in catalysis involving zeolites. The advantageous characteristics of zeolites are described quite extensively in the open and patented literature [1–4]. However, the intracrystalline diffusion of species inside the pores of zeolites is severely limited, especially for cases of liquid phase reactions. This can have several negative implications for the success of the specific process, such as reduced selectivity and/or activity, need for higher or much higher operating pressure, or higher temperature. The increased diffusion limitations that zeolites impose are responsible for significant decreases of the product selectivities because of the increased residence time of the products in zeolite pores favoring undesired reactions such as overcracking. Moreover, the formation of mesopores can favor the production of more branched products which can be the desired ones for numerous applications. Evidently, generating a network of mesopores in zeolites crystals would offer numerous advantages for a large number of reactions.

In a recent study, the use of Carbon black as a template for mesoporosity was explored in ZSM-5 zeolites and found to be effective [5]. Our group built on this method in the past, utilizing carbon black particles mixed in the synthesis sol–gel to generate a network of mesopores for

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ZSM-12 after the burning of the occluded carbon [6]. This templating action of the carbon particles was very successful in generating a network of mesopores with a maximum of about 500 Å. Recently, we generalized this process for two other zeolites, namely Zeolite Beta and Zeolite Y, as well as MCM-41 and SBA-15 [7]. We found that mesoporous networks could be made in all samples, though the degree of mesoporosity and the corresponding parameter space are strongly related with each zeolite.

In this paper we report the performance of selected mesoporous samples of ZSM-12 and Zeolite Beta for the hydroisomerization of *n*-heptane in order to demonstrate the advantageous behavior of the network of mesoporous zeolites in comparison with the regular samples. This reaction was selected as a probe in view of its importance for upgrading light naphthas to more branched products with significantly higher research octane numbers.

2 Experimental

2.1 Synthesis of Mesoporous Zeolites

For synthesis of all mesoporous zeolites, carbon black particles with an average particle diameter of 12 nm (BP-2000 from Cabot Corp.) were used as the template for mesoporosity. The carbon black was dried at 150 °C for a minimum of 10 h prior to use. It was necessary to add the carbon black slowly to the samples during synthesis and to allow the samples to mix after carbon addition to ensure that the carbon had dissolved completely. The silica source used in the syntheses of the samples was Ludox HS-40 colloidal silica (40 wt%, DuPont), and deionized water was used throughout the work. The synthesis procedures followed for all samples are identical to those used in our earlier work [7].

2.1.1 ZSM-12

For the synthesis, tetraethylammonium hydroxide (TEA-OH, Fluka, 40 wt% in water) was used as the template. In a typical synthesis, 0.227 g sodium aluminate (Alfa Aesar) was dissolved in a mixture of 17.5 mL TEAOH and 66.7 mL DI water. After the solid had dissolved, 3.733 g carbon black was added to the mixture and mixed vigorously for 10 min. 24.0 mL Ludox and 71.6 mL water were added, and the mixture was allowed to thoroughly mix for 30 min. The gel was transferred into a Teflon-lined autoclave and filled to 90% capacity. Crystallization was carried out at 160 °C under autogenous pressure for 10 days. Mesoporous ZSM-12 samples with differing C/Si ratios were synthesized during the work. After crystallization, the solid products were filtered and washed with DI water repeatedly, allowed to dry at room temperature, and finally calcined under air at 550 °C to burn the occluded template and the Carbon incorporated.

2.1.2 Zeolite Beta

For the synthesis, TEAOH was used as the template, and Ludox was used as the silica source. The synthesis order and ingredients are identical to that of ZSM-12, but with amounts corresponding to the products of the Zeolite Beta samples (5.688 g sodium aluminate, 48.7 mL TEAOH, 44.3 mL DI water, 4.167 g carbon black, 80.4 mL Ludox). Once the final gel was prepared, the gel was transferred into a Teflon-lined autoclave and filled to 90% capacity. Crystallization was carried out at 150 °C under autogenous pressure for 10 days. Mesoporous Zeolite Beta samples with differing C/Si were synthesized during the work. At the end of the crystallization step, the solid products were filtered, washed with DI water thoroughly, dried at room temperature, and finally calcined under air at 550 °C.

2.2 Preparation of Catalyst Samples

For all zeolite samples, it was necessary to perform a cation exchange procedure, followed by a platinum loading procedure for them to perform as catalysts in the hydroisomerization reaction. For the cation exchange, the zeolite samples were individually treated with 2N NH_4Cl solution at 90 °C for 4 h under agitation, which changed the zeolites to their ammonium forms. Once this was done, the samples were filtered and allowed to dry overnight. The zeolite samples were then converted to their protonated forms by calcination at 500 °C for 1 h. Platinum loading was done by wet impregnation using H_2PtCl_6 (Aldrich). The platinum loading weight percent was 0.5 wt% for all samples. The impregnated catalysts were dried overnight in an oven at 120 °C. Oxidation and reduction of the catalysts was done in situ before starting the reaction.

2.3 Catalyst Characterizations

2.3.1 XRD

XRD was used to identify the synthesized zeolites and their crystallinity. This was performed at the end of the zeolite synthesis step, before any catalyst preparation steps were performed. The XRD patterns for ZSM-12 and Zeolite Beta were recorded with a Siemens powder X-ray diffractometer using CuKα radiation. The 2θ values chosen for ZSM-12 ranged from 2° to 40°, and the 2θ values for Zeolite Beta ranged from 2° to 30°. The step size was 0.1° and the step time was 1 s.

2.3.2 *BET*

Nitrogen adsorption and desorption measurements for all sample types were performed at 77 K on a Micromeritics ASAP 2010. Prior to analysis, the samples were degassed at 300 °C for of 4 h. Micropore volumes and external surface areas were determined using t-plot analysis [8]. Pore size distribution was calculated from the adsorption isotherm according to the method developed by Barret–Joyner–Halenda [9].

2.3.3 *TEM*

High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) investigations were conducted in the University of Kentucky's Electron Microscopy Center, located in the Advanced Science and Technology Commercialization Center (ASTeCC). Samples were examined in a 200-keV JEOL-2010F field-emission high-resolution transmission electron microscope equipped with an Oxford energy-dispersive X-ray detector, a scanning TEM (STEM) unit and a Gatan imaging filter. TEM images were recorded with a Gatan 794 slow-scan CCD (charge coupled device) camera.

Minute quantities of powdered sample material were dispersed onto copper grids equipped with lacey carbon support structures prior to the TEM investigations.

2.4 Catalytic Tests

The catalytic tests were performed in a fixed bed flow reactor hosted in a temperature controlled oven. For each run, 50 mg of catalyst on dry basis were loaded in the reactor on top of a quartz wool. For every run reported in this study fresh catalysts were used. The catalyst was activated in situ with high purity O_2 at 450 °C for 1 h, followed by purging of the catalyst with helium for 15 min, both at atmospheric pressure. Finally, the catalysts were reduced with high purity H_2 at 450 °C for 1 h, and then they were brought to the reaction temperature. The reactor operated at 100 psig total pressure with H_2/n-C7 molar ratio equal to 16; conversion was varied by altering the temperature or the space velocity. The analysis of the catalyst was performed after 1 h on stream, and repeat experiments confirmed that the data obtained were closely reproducible. The rate of deactivation is insignificant under the present experimental conditions as we have proven in numerous of our earlier studies. The analyses of the reactor effluent was accomplished using a gas chromatograph (Hewlett-Packard, 5890 Series II) equipped with a mass spectrometer (Hewlett-Packard, 5972 Series II). Separation was achieved using a capillary column (SUPELCO Petrocol DH50.2). The concentrations of the products were calculated by using a calibration factor for each product.

3 Results and Discussion

XRD was used to confirm the identity and crystallinity of the samples. The samples were highly crystallized and that the addition of carbon black in the compositions described in this paper did not reduce the crystallinity of the samples as shown from the XRD analyses (the spectra are not presented in this study). The nominal compositions of the synthesis gels for our mesoporous samples of both ZSM-12 and Zeolite Beta are presented in Table 1.

Other than varying the water amount, the only variable altered for a given zeolite type was the amount of carbon added to the synthesis mixture. The change in water was necessary to adjust the viscosity of the synthesis gel to allow for mixing. Based on their Si/Al values, the samples of Zeolite Beta should expected to be more active that those of ZSM-12.

Figures 1 and 2 show the pore size distributions for ZSM-12 and Zeolite Beta, respectively. In all cases, the generated mesopores falls in the range of 20–70 nm. For both zeolites studied in this work the increase of the C/Si ratio results in both an increase of the size and the percentage of mesopores, at least in this range of C/Si ratios. It is remarkable to note that the use of carbon black as template, does indeed assist the formation of mesopores of significantly larger average diameter, namely about two orders of magnitude larger than the actual pore of the zeolites without any loss of crystallinity.

The generated mesoporosity can be confirmed by our TEM investigations. Figures 3 and 4 show the high resolution TEM images for ZSM-12 without any carbon and with C/Si = 2.0, respectively. One can observe that the incorporation of carbon during synthesis results in the formation of mesoporous voids (Figs. 4, 5). These mesopores are clearly identified on the surface of the crystal in the form of cavities. In the main part of the crystal (lower

Table 1 Nominal composition of the synthesis gel for the zeolite samples used in this work

Samples[a]	Si/Al	TEAOH/Si	C/Si	H_2O/Si
ZSM12(0.0)	75	0.242	0.000	10.0
ZSM12(0.5)	75	0.242	0.500	10.0
ZSM12(1.0)	75	0.242	1.000	45.0
ZBeta(0.0)	10	0.200	0.000	11.0
ZBeta(0.5)	10	0.200	0.500	11.0
ZBeta(1.0)	10	0.200	1.000	14.2

[a] The number in parentheses represents the atomic ratio of C to Si

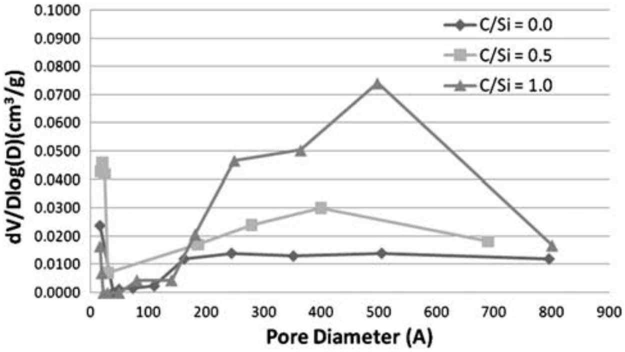

Fig. 1 Pore size distributions for ZSM-12 samples for various C/Si atomic ratios

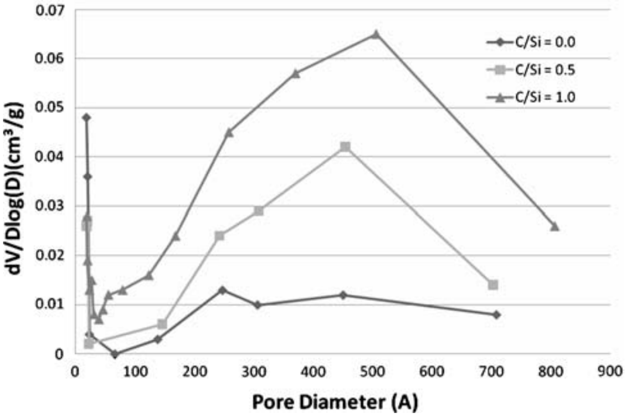

Fig. 2 Pore size distributions for Zeolite Beta samples for various C/Si atomic ratios

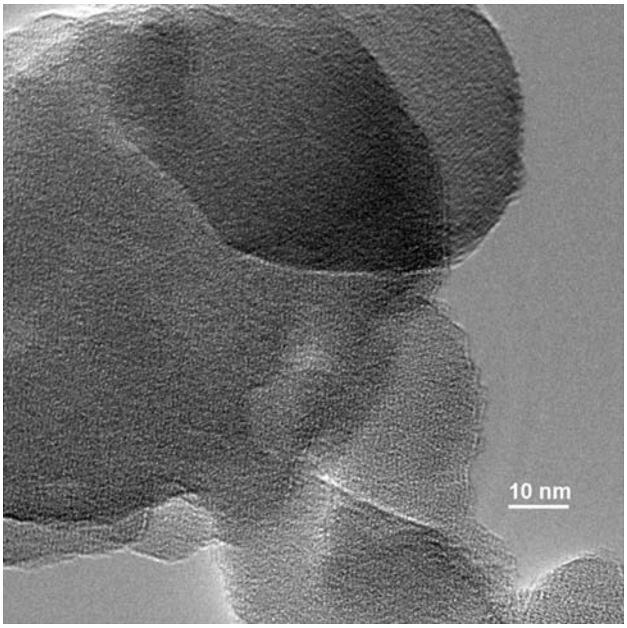

Fig. 3 TEM of the as synthesized ZSM-12 without any use of carbon {ZSM12(0)}

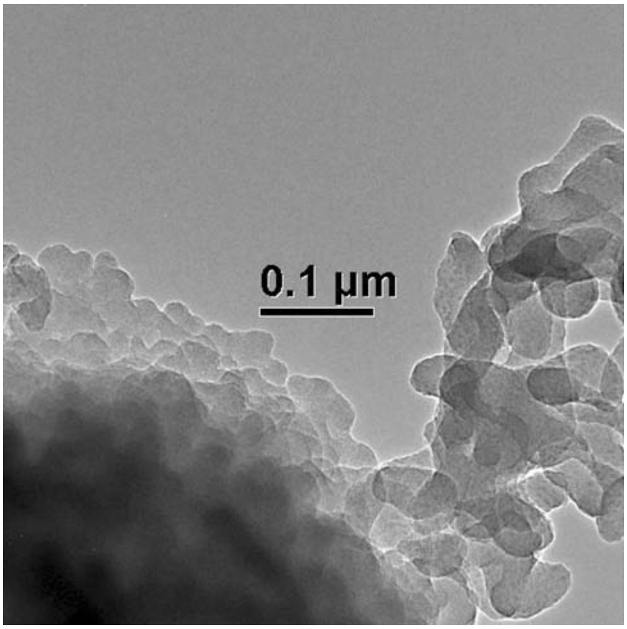

Fig. 4 TEM of ZSM-12 with C/Si = 2.0 {ZSM12(0)}

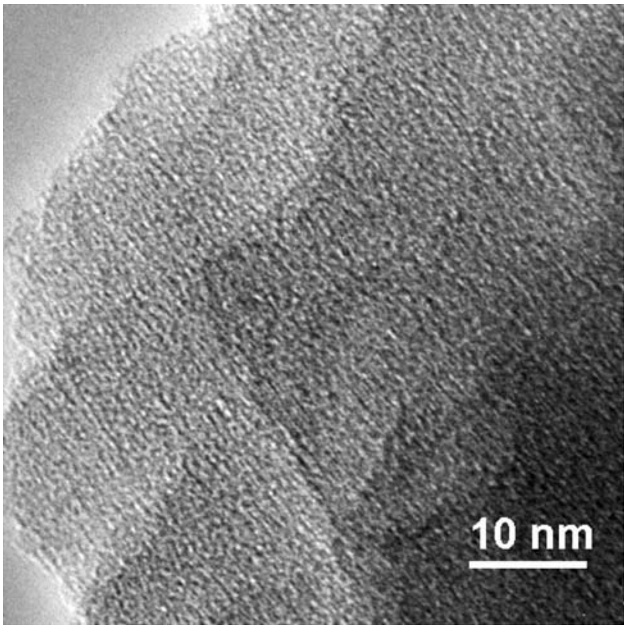

Fig. 5 TEM of the as synthesized Zeolite Beta without any use of carbon {ZBeta(0)}

left part of the photo) the networks of mesopores are distinguished by regions of lower density material (brighter areas). Moreover, the use of carbon during synthesis can lead into regions like that shown on the right part of the photo where there are large voids and empty spaces. A similar situation is observed with the beta zeolite sample with C/Si = 1.0 (Fig. 6). The surface of the crystal has numerous domains with mesopores and intracrystalline channels. These TEMs offer a clear proof that

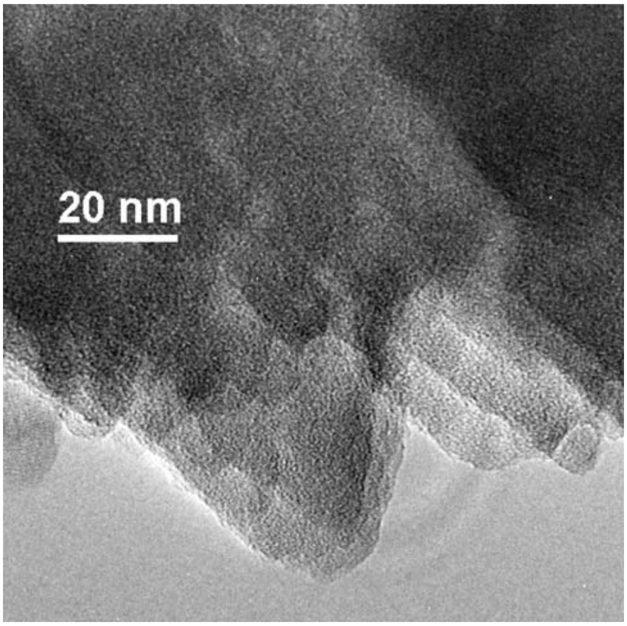

Fig. 6 TEM of Zeolite Beta with C/Si = 1.0 {ZBeta(1)}

mesoporosity is generated in the samples and confirms the results of the nitrogen physisorption tests.

3.1 Catalytic Experiments

The hydroisomerization of *n*-heptane was chosen as the test reaction to demonstrate the beneficial role of forming mesopores. The performance of the zeolite types was tested by varying the space velocity under otherwise identical operating conditions. The results of these experiments are presented in Figs. 7 and 8.

For both zeolites, under relatively low WHSV the conversion of *n*-heptane is almost comparable. The highest difference is observed with the Zeolite Beta samples, where the conversion difference is about 13% for the lowest value of WHSV. However, as the WHSV increases, the mesoporous zeolite samples demonstrated far better performance in terms of activity. For the ZSM-12 samples, the difference grows from 4% at the lowest value of WHSV to a nearly 10% increase at WHSV of 50 h^{-1}. The Zeolite Beta samples show a bit better improvement in performance, namely with a 13% difference in conversion for the lowest space velocity which grows to about 30% difference at highest space velocity. In other words, under the highest space velocity the mesoporous sample {ZBeta(1.0)} sample is nearly twice as active as the non-mesoporous one {ZBeta(0.0)}. Moreover, as the space velocity increases, the mesoporous zeolite samples both for ZSM-12 and Zeolite Beta show less decrease in conversion which approaches a plateau. From these trends, it is apparent that forming mesoporosity in the zeolite particles improves the intracrystalline mass transfer to a significant extent in comparison with the conventional zeolites. This enhances the reactant accessibility to more active sites located away from the surface of the crystal.

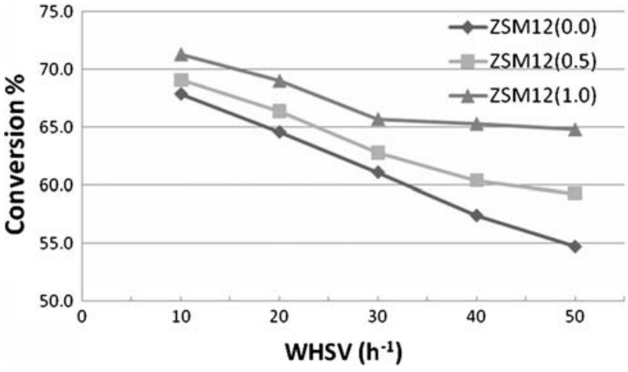

Fig. 7 Conversion of *n*-heptane over ZSM-12 samples at 300 °C, H_2/n-C7 = 16

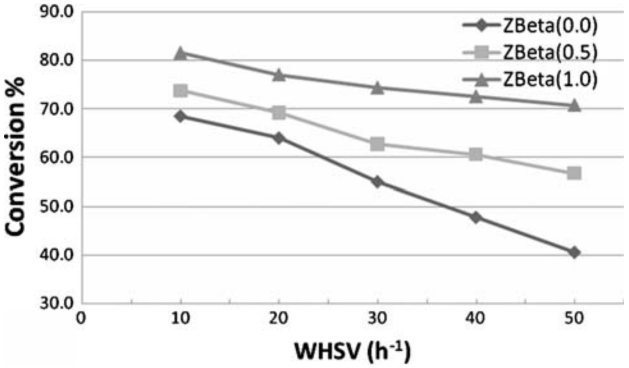

Fig. 8 Conversion of *n*-heptane over Zeolite Beta samples at 230 °C, H_2/n-C7 = 16

The product distributions of *n*-heptane isomerization were obtained over the mesoporous samples at a WHSV of 7 h^{-1} and at a temperature such that the overall conversion was in the vicinity of about 75% for all zeolite samples. The results of this study are presented in Tables 2, 3 and 4. In these tables, the percentage isomerization sum is defined as ratio of C-7 isomers over all products. For all samples the overall isomerization increased monotonically with the increase of the mesoporosity. Moreover, higher amount of short chain alkanes, namely C3 and C4s, were formed over the conventional zeolites compared to the mesoporous samples. This is indeed a unique characteristic since minimizing the generation of hydrocarbons with smaller molecular weight is very beneficial for numerous refining processes. On the other end, selectivities towards single and double branched isomers of are higher over the mesoporous zeolite samples than the case of the regular ones. This type of behavior is attributed to the lower diffusion limitations exerted in the mesoporous samples, which favors the outwards diffusion of products thus minimizing

Table 2 Product distributions of *n*-heptane isomerization and cracking over ZSM-12 samples at 320 °C under H_2/n-C7 = 16, and WHSV = 7 h^{-1}

Conversion (%)	ZSM12(0.0) 74.2	ZSM12(0.5) 75.3	ZSM12(1.0) 77.6
Product dist. (mol %)			
Propane	14.1	13.3	6.7
Isobutane	11.2	10.5	5.3
Butane	3.0	2.6	1.7
2,2-Dimethyl pentane	0.0	0.0	0.0
2,4-Dimethyl pentane	3.6	3.8	3.8
2-Methylhexane	28.9	29.2	35.9
2,3-Dimethyl pentane	5.8	5.6	6.2
3-Methylhexane	33.3	34.9	40.4
% Isomerization	71.6	73.5	86.3

Table 3 Product distributions of *n*-heptane isomerization and cracking over Zeolite Beta samples at 230 °C under H_2/n-C7 = 16, and WHSV = 7 h^{-1}

Conversion (%)	ZBeta(0.0) 69.4	ZBeta(0.5) 75.4	ZBeta(1.0) 83.9
Product dist. (mol %)			
Propane	29.1	26.4	21.4
Isobutane	29.2	26.3	21.4
Butane	0.0	0.0	0.0
2,2-Dimethyl pentane	1.1	1.4	1.8
2,4-Dimethyl pentane	2.5	2.8	3.1
2-Methylhexane	15.4	18.0	22.5
2,3-Dimethyl pentane	3.0	3.4	3.6
3-Methylhexane	19.9	21.7	26.2
% Isomerization	41.9	47.3	57.2

Table 4 Product distributions of *n*-heptane isomerization and cracking over ZSM-12 and Zeolite Beta samples under H_2/n-C7 = 16, and WHSV = 7 h^{-1}

Sample	Temperature (°C)	Conversion (%)
ZSM12(0.0)	260	9.7
ZSM12(0.5)	260	15.4
ZSM12(1.0)	260	38.4
ZBeta(0.0)	180	22.5
ZBeta(0.5)	180	36.2
ZBeta(1.0)	180	55.4

the cracking of the produced isomers. One could appreciate more this beneficial behavior if we consider that the branched isomers crack much faster than the linear ones. Finally, we performed tests at lower temperature in order to examine how significantly the mesoporosity increases the activity. Table 4 shows the conversion data obtained for ZSM-12 and Zeolite Beta. The ZSM-12 samples were tested at 260 °C, and the Beta samples at 180 °C. ZSM-12 shows nearly fourfold increase in conversion from ZSM12(0.0) to ZSM12(1.0) under these conditions, while Zeolite Beta shows a similarly impressive change in conversion, with the conversion percentage more than doubling.

4 Conclusions

Mesoporous zeolites with differing geometries were successfully synthesized using carbon black as the template for mesoporosity. The synthesized mesoporous samples were found to exhibit better activity in the hydroisomerization of *n*-heptane, which was attributed to the generation of mesoporosity in the crystals, which eases the accessibility of reactants to the active sites. Over the mesoporous crystals, the increased selectivity towards production of isomers versus cracking validates the beneficial role of reduced diffusional limitations for the outwards diffusion of products. Moreover, the mesoporous samples result in less light hydrocarbons (C3, C4), a property that could be of unique value for numerous processes.

References

1. Szostak R (1989) Molecular sieves: principles of synthesis and identification. Van Nostrand Reinhold, New York
2. Kuehne MA, Babitz SM, Kung HH, Miller JT (1998) Appl Catal A 166:293
3. Maselli JM, Peters AW (1984) Catal Rev Sci Eng 26:525
4. Liu Y, Zhang WZ, Pinnavaia TJ (2000) J Am Chem Soc 122:1255
5. Jacobsen CJH, Madsen C, Houzvicka J, Schmidt I, Carlsson A (2000) J Am Chem Soc 122:7116
6. Wei X, Smirniotis PG (2006) Microporous Mesoporous Mater 97:97
7. Moushey D, Graham U, Davis BH, Smirniotis PG (2008) Microporous Mesoporous Mater (to be submitted for publication)
8. Lippens BC, Linsen BG, de Boer JH (1964) J Catal 3:32
9. Barret P, Joyner LG, Halenda PP (1951) J Am Chem Soc 73:373