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SHORT COMMUNICATION

Shape-Selective Alkylation of Isopropylnaphthalene on MCM-22 Zeolite

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Abstract−An MCM-22 zeolite with an Si/Al ratio 13 was found to exhibit higher selectivity to β,β-diisopropylnaphthalene in the alkylation of isopropylnaphthalene with isopropylalcohol, as compared with other zeolites such as mordenite, Y and beta having similar Si/Al ratios. This high selectivity is ascribed to the specific pore shape of MCM-22 zeolite. The gradual increase in the selectivity with reaction time is due to its pore modification by coke deposit.

Key words: MCM-22 Zeolite, Shape-Selective Alkylation, Isopropylnaphthalene, β,β-Diisopropylnaphthalene, Specific Pore Shape

INTRODUCTION

Zeolites are the most promising microporous crystalline materials for achieving highly shape-selective catalysis. Recently, much attention has been paid to the shape-selectivity for the alkylation of polyaromatic compounds, such as the methylation and the isopropylation of naphthalene using zeolites in order to produce high-valued chemicals selectively. However, it is difficult to obtain a high yield of 2,6-dialkylnaphthalene using a continuous flow-type reactor over zeolite catalysts due to their low selectivity and fast deactivation by carbon deposit.

The MCM-22 (MWW) zeolite is composed of two channel systems, both of which are accessed through 10-membered (10-MR) windows [Leonowicz et al., 1994]. One system consists of two-dimensional, sinusoidal channels with 10-MR pore openings, while the other contains large cages consisting of 10-MR and 12-MR, with an internal space of 0.71×0.71×1.82 nm. The large cages may be shared by only one aromatic molecule, thus preventing the polymerization of aromatic molecules. Due to its specific pore shape, the MWW zeolite shows high stability and selectivity to the catalytic reactions involving aromatic compounds such as the disproportionation of toluene or ethylbenzene and the aromatization of n-butane [Corma et al., 1995a; Asensi et al., 1996; Kumar and Lindfors, 1996; Wu et al., 1998].

We examine here the shape-selective alkylation of 2-isopropylnaphthalene (2-IPN) using isopropylalcohol (IPA) over the MWW zeolite. The differences in the conversions of 2-IPN, the yields of diisopropylnaphthalene (DIPN) and the selectivities to 2,6-DIPN and β,β-DIPN of MWW, ZSM-5 (MFI), mordenite (MOR), Y (FAU) and beta (BEA) zeolites are discussed relating to their pore shapes.

EXPERIMENTAL

1. Sample

The hydrothermal synthesis of MWW zeolite was carried out in a stainless-steel autoclave over 65 h at 150 °C using hexamethyleneimine as a template, according to the reported procedure [Corma et al., 1995b]. The template was removed by calcination in air for 16 h at 550 °C. The calcined sample was ion-exchanged with 0.5 N NH_4NO_3 solution at 60 °C for 5 h to form the NH_4-MWW sample. The proton type of MWW zeolite was obtained by the calcination in air at 550 °C for 16 h. Zeolite samples with different pore shapes were selected to compare their conversions and selectivities. MFI (PQ Corp.), MOR (JRC-Z-HM20), FAU (PQ Corp.) and BEA (PQ Corp.) zeolites having similar Si/Al molar ratios were used in order to eliminate the effects of acidic properties.

2. Characterization

The Si/Al molar ratio of the synthesized MWW zeolite was determined by ICP (Inductively Coupled Plasma, Jobin Yvon Co., JY. 38 plus) after digestion of the sample using aqueous hydrofluoric acid. The Si/Al molar ratio of MWW zeolite was 13. The Si/Al molar ratios of MFI, MOR, FAU and BEA zeolites were 13, 10, 14 and 13, respectively.

The X-ray diffraction pattern of the calcined MWW zeolite was recorded by using an X-ray diffractometer (Rigaku, D/MAX-1200) with CuKα X-ray and Ni filter at 35 kV and 15 mA. The nitrogen adsorption isotherm on the MWW zeolite was obtained by using a conventional volumetric adsorption system at liquid nitrogen temperature after evacuation at 300 °C for 2 h under vacuum.

The temperature programmed desorption (TPD) profiles of ammonia from zeolites were recorded from 80 °C to 650 °C with a ramping rate of 10 °C/min under an He flow of 200 ml/min after activation in an He stream at 550 °C for 2 h. Ammonia was fully adsorbed on the sample at 80 °C by adding pulses of ammonia. The sample was then purged in an He stream at the same temperature for 2 h in order to remove physisorbed ammonia. The amount of ammonia desorbed from the sample was determined with a thermal conductivity detector.

The uptake of *o*-xylene was measured by a quartz-spring gravimetric adsorption system. Samples were dehydrated at 300 °C

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under 1.33×10^{-4} Pa for 2 h. *o*-Xylene (Hayashi Chemical, 99%) vapor was introduced into the sample at 120 °C, and an increase in the mass was recorded for 180 min.

Thermogravimetric analyses of the zeolites after the isopropylation were performed on a DuPont 950 thermogravimetric analyzer. Approximately 20 mg of sample was heated in air to 800 °C with a ramping rate of 5 °C/min.

3. Reaction

The alkylation of 2-IPN was carried out at 275 °C, W/F of 0.37 g · h/mol, 2-IPN/IPA of 0.25 by using a continuous flow-type reactor under a vapor phase. The products were analyzed by GC with a TC-17 capillary column at 170 °C.

RESULTS AND DISCUSSION

1. Characterization of MWW(13) Zeolite

The X-ray diffraction pattern of the calcined MWW sample was consistent with that previously reported [Corma et al., 1995b]. The BET surface area of MWW zeolite obtained from the N_2 adsorption isotherm is 420 m^2/g.

Fig. 1 shows the result of the ammonia TPD obtained from the MWW, MFI, MOR, FAU and BEA zeolites. The TPD curve of MWW zeolite is characterized by two desorption peaks with maxima in the temperature regions of 210 °C and 450 °C, which correspond to weak and strong acid sites, respectively. Total areas of ammonia desorption from all zeolites used here are almost the same. The temperature at the maximum of the second desorption peak from the MWW zeolite is similar to that from the MFI zeolite. From the findings of the difference in the temperatures at the maxima, the order of acidic strength is obtained as MOR>MFI=MWW>BEA>FAU.

The uptake curves of *o*-xylene on the various zeolites are shown in Fig. 2. The uptake rate at the initial stage on the BEA or FAU zeolite is faster and the amount of *o*-xylene adsorbed at 180 min is also larger than those of the other zeolites. The uptake rates at the initial stage on MWW, MFI and MOR zeolites are slow. Since the adsorbed amount of *o*-xylene corresponds to the pore volume of zeolite, it is clear that the effective pore volume of the BEA or FAU zeolite is significantly larger than the other zeolites. The order of the effective pore volume of zeolite is found to be BEA>FAU>MWW≃MFI≃MOR.

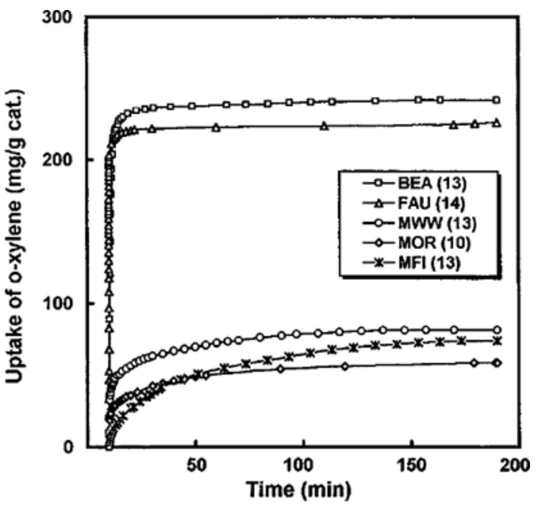

Fig. 1. Ammonia TPD profiles from various zeolite catalysts.

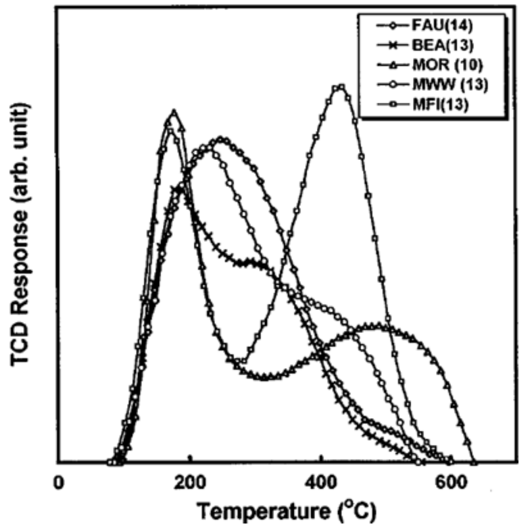

Fig. 2. Uptake curves of *o*-xylene on various zeolite catalysts at 120 °C.

2. Isopropylation of 2-IPN over Various Zeolites

The isopropylation of 2-IPN was investigated on the MWW, MFI, MOR, FAU and BEA zeolites by a flow method. Fig. 3 shows the changes in the conversion of 2-IPN, the yield of DIPN, and the selectivities to 2,6-DIPN and β,β-DIPN as a function of time on stream. The conversion of 2-IPN and the yield of DIPN were highest over FAU zeolite, while a very low conversion was obtained over MOR zeolite. The FAU zeolite has supercages forming large intermediates as well as achieving fast diffusion, resulting in the highest conversion. The large cavity may be effective in the reaction of polyaromatic compounds due to low restriction. On the other hand, the MOR zeolite has linear pores, which can be blocked easily with large polyaromatic molecules. The MFI zeolite with a narrow pore structure did not exhibit the activity for the isopropylation of 2-IPN under these reaction conditions.

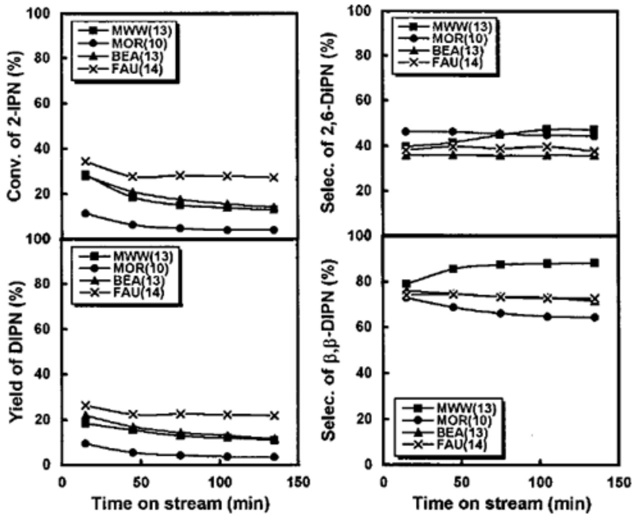

Fig. 3. Isopropylation of 2-IPN over zeolite catalysts with various pore structure as a function of time on stream.

Table 1. Catalytic properties of various zeolites at 105 min of reaction time

Catalyst	Conv. (%)	Yield (%)			Distributions of DIPN isomers		
		DIPN	Naphthalene	poly-IPN	α,α-	α,β-	β,β-
BEA(13)	15.6	12.9	0.4	2.3	9.3	17.6	73.1
FAU(14)	28.0	22.3	1.2	4.5	5.9	21.4	72.7
MOR(10)	3.9	3.3	0.3	0.3	10.2	25.1	64.7
MWW(13)	13.8	12.0	1.3	0.5	6.2	5.7	88.1
MFI(13)	0	-	-	-	-	-	-

The selectivity to 2,6-DIPN at an early stage was high over the MOR zeolite, and that of the MWW zeolite increased with the lapse of reaction time. The selectivity to β,β-DIPN at an early stage was almost the same value of 75-79% on both catalysts. The selectivity to β,β-DIPN of MOR zeolite decreased with the stream of reaction time, while that of MWW zeolite increased with the reaction time, achieving 90% at 120 min. This selectivity of MWW zeolite was the highest value in this study. The enhancement of the shape-selectivity of MWW zeolite with the lapse of reaction time can be explained in terms of its pore modification by coke deposit.

The conversion of 2-IPN, yields of products and the distributions of DIPN isomers at 105 min of reaction time are summarized in Table 1. Generally, catalytic properties on zeolites vary with their acidity and structure. The concentration of acid sites of zeolites cannot be concerned with in the activity for this reaction, due to their similar Si/Al molar ratios of zeolites used here. The FAU and BEA zeolites with a large pore volume exhibit the highest conversion of 2-IPN, the highest yields of poly-IPN and DIPN isomers including α-isopropyl group. The MWW zeolite shows high selectivity to β,β-DIPN. The low selectivities to β,β-DIPN on the BEA and FAU zeolites compared to that of MWW zeolite under these conditions suggest that the non-shape selective alkylation occurs at the large inner cavity. Furthermore, the low selectivity of the MOR zeolite is due to non-selective catalysis at the acid sites on the external surfaces [Kim et al., 1995]. These facts indicate that if this alkylation occurs inside the zeolite pore, the selectivity for the β-position may be significantly higher than that of the α-position. Furthermore, the formation of DIPN isomers with α-isopropyl group in the zeolite pore is prevented because the corresponding transition state has a bulky conformation. The high selectivity to β,β-DIPN on MWW zeolite reveals that its pillow-type pore prefers to form the long linear-shape products of alkylation.

Fig. 4 shows the TG profiles of the catalysts used in the isopropylation of 2-IPN. The amount of coke deposited on MFI or MOR zeolite with low conversions for the alkylation, was very small as compared with other zeolites. On the other hand, a high level of the coke was formed on the MWW zeolite, which showed a high selectivity to β,β-DIPN. Since the extent of alkylation is small on MFI and MOR zeolites due to their pore shape, the amount of carbon deposited on the catalyst is small. The high extent of the alkylation on FAU and MWW zeolites brings about a large amount of coke deposition. The increased spatial constraints of the MWW zeolite by coke deposition may be responsible for the enhancement of the selectivity to β,β-DIPN with the lapse of reaction time.

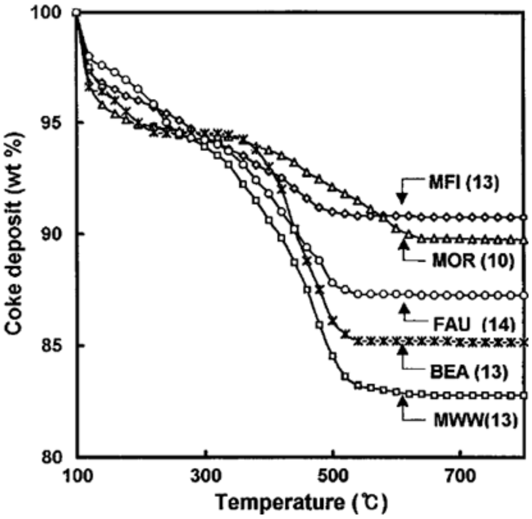

Fig. 4. TG profiles of the catalysts used for the isopropylation of 2-IPN.

In conclusion, a pillow-type pore of MWW zeolite prefers to form linear-shaped reaction intermediates and to keep only one aromatic molecule per a cage, resulting in the high yield of β,β-DIPN. In addition, the MWW zeolite shows a noticeable increase in β,β-DIPN selectivity during the reaction time, which can be attributed to the increased spatial constraints inside the pores by coke deposition. These findings show that MWW zeolite has a great potential as a catalyst for the shape-selective reaction involving aromatic molecules.

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REFERENCES

Asensi, M. A., Corma, A. and Martinez, A., "Skeletal Isomerization of 1-Butene on MCM-22 Zeolite Catalyst," *J. Catal.*, **158**, 561 (1996).

Corma, A., Gonzales-Alfaro, V. and Orchilles, A. V., "Catalytic Cracking of Alkanes on MCM-22 Zeolite. Comparison with ZSM-5 and Beta Zeolite and its Possibility as an FCC Cracking Additive," *Appl. Catal. A: General*, **129**, 203 (1995a).

Corma, A., Corell, C. and Perez-Pariente, J., "Synthesis and Characterization of the MCM-22 Zeolite," *Zeolites*, **15**, 2 (1995b).

Kim, J.-H., Sugi, Y., Matsuzaki, T., Hanaoka, T., Kubota, Y., Tu, X. and Matsumoto, M., "Effect of SiO_2/Al_2O_3 Ratio of H-mordenite on the Isopropylation of Naphthalene with Propylene," *Microporous Materials*, **5**, 113 (1995).

Kumar, N. and Lindfors L.-E., "Synthesis, Characterization and Application of H-MCM-22, Ga-MCM-22 and Zn-MCM-22 Zeolite Catalysts in the Aromatization of n-Butene," *Appl. Catal. A: General*, **147**, 175 (1996).

Leonowicz, M. E., Lawton, J. A., Lawton, S. L. and Rubin, M. K., "MCM-22: A Molecular Sieve with Two Independent Multidimensional Channel Systems," *Science*, **264**, 1910 (1994).

Wu, P., Komatsu, T. and Yashima, T., "Selective Formation of p-Xylene with Disproportionation of Toluene over MCM-22 Catalysts," *Microporous and Mesoporous Materials*, **22**, 343 (1998).