Transactions of the Materials Research Society of Japan 29[5] 2179-2182 (2004)

ZSM-12 zeolite catalyzed shape-selective ethylation of biphenyl to 4,4'-diethylbiphenyl

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Ethylation of biphenyl with ethanol over zeolites (ZSM-12, SAPO-11, ZSM-5, MOR) was studied under fixed bed down flow conditions. The delaminated ZSM-12 gave the highest shape selectivity towards 4,4'-diethylbiphenyl (4,4'-DEBP) The catalysis is controlled by diffusion and restriction of transition states in the channels of ZSM-12. The selectivity of 4,4'-DEBP increased from 34 % to 40 % by the dealumination of ZSM-12: the non-selective reactions at the external acid sites were deactivated by the dealumination. Catalytic activity of MOR is the highest among the zeolites. Polyalkylation was observed over MOR and ZSM-12. ZSM-12 with small particle size enhanced the formation of polyethylated products; however, polyethylation decreased by the dealumination.

Molecular modeling study shows that 4,4'- and 3,4'-DEBP are least bulky and most stable isomers among the all DEBP isomers, respectively. Molecular fitting study revels that ZSM-12 pore is suitable for 4,4'-DEBP sieving. These results show that the formation of 4,4'-DEBP is the most favorable from aspects of diffusion and restriction of transition state in the channel of ZSM-12

Keywords: biphenyl, shape-selective ethylation, zeolites, dealumination, molecular modeling

1. INTRODUCTION

Shape selective alkylation of polynuclear aromatics using heterogeneous catalysts particularly zeolite catalysts has been the subject of interest for many researcher.[1-7] The isopropylation of BP is the shape-selective for the formation of 4,4'-diisopropybiphenyl (4,4'-DIPB) over MOR.[1] The ethylation of biphenyl (BP) with ethanol is important from manufacturing 4,4'-diethylbiphenyl (DEBP) which is key intermediate for advanced materials. We previously found that the ethylation of BP gave only 4,4'-DEBP in low yield because channel of MOR is not fit for the shape-selective formation of 4,4'-DEBP.[2-4] It is necessary to find new type of zeolites for shape-selective ethylation of BP to 4,4'-DEBP.

In present work, ethylation of BP with ethanol was examined over some zeolites to obtain information of steric interaction at transition state and diffusion in side their channels. The fitness of DEBP isomers inside channel of zeolites are also examine by molecular modeling.

2. EXPERIMENTAL

2.1. Catalyst preparation

ZSM-5 and MOR catalysts were obtained from Tosoh Corporation, Tokyo, Japan, whereas SAPO-11, ZSM-12L (large crystal) and ZSM-12S (small crystal) catalysts were prepared by reported procedures.[6-8] ZSM-12 is converted to H^+-form by using 1 M, 20 ml solution of ammonium nitrate per gram of catalyst stirring for 12 h at 80°C. This procedure is repeated thrice. The zeolites were calcined prior to use at 550°C for 7 h. Dealumination of ZSM-12L and ZSM-12S catalysts were carried out by using 1 M, 20 ml solution of EDTA per gram of catalyst for 12 h at 80°C. Then, zeolites were calcined at 550°C for 7 h.

2.2. Reaction procedures

The vapor phase ethylation is carried out in fixed bed, continuous, tubular down flow, Pyrex glass reactor (12 mm i.d.) in electrically heated furnace. 2.0 g of fresh zeolite (mesh size around 30) sandwiched between glass wool plugs was placed in the reactor. Catalyst is activated in O_2 (50 ml /min) at 550°C for 6 h and reaction was carried out in N_2 gas flow (20 ml /min). Feed prepared by using 1:5 molar ratios of BP and ethanol (EtOH) in 5.5 moles of cyclohexane (Cy), passed with help of pump. The products were identified using GC-MS (Shimadzu QP 5000) and analyzed by a Shimadzu Model 18A chromatograph (Ultra-1 capillary column (25 m x 0.3 mm). The yield of products was calculated on the basis of BP consumed for the reaction.

2.3. Characterization

The phase purity and crystallinity of the as-synthesized samples were determined by powder X-ray diffraction (XRD) (XRD-6000, Shimadzu) with Cu Kα radiation (λ=1.5418 Å). The surface area and porosity measurements were carried out by means of N_2 adsorption on a Belsorp 28SA apparatus (Bel Japan). Crystal size and morphology of the zeolites were determined by scanning electron microscopy (SEM) using a TOPCON ABT-60 microscope. Elemental analyses were performed by inductively coupled plasma (ICP) using (JICP-PS-1000 UV, Leeman Labs Inc.). The acidity of the catalyst was measured by temperature programmed desorption (TPD) of ammonia using BEL TPD-66 (Bel Japan): the catalyst was evacuated at 500 °C for 1 h, exposed to ammonia at 100°C for adsorption, and evacuated for a further 1 h. Samples were heated from 100°C to 600°C at 10°C/min under a constant helium flow at atmospheric pressure.

2.4. Molecular modeling studies

Computational studies were carried out using

Material Studio supplied by Accelrys Inc., UK. The force field energy minimization calculations were done using DFT theory with DMol module. The potential energies of the organic molecules were calculated using the double numerical plus polarization (DNP) basis set, using one local gradient-corrected exchange-correlation (LDA), Perdew-Wang (PWC) functional. Molecular graphics displays were obtained from Material Studio. The extents of the molecule in space were calculated for the energetically favorable conformation, their sizes and shapes were analyzed. The dimensions of molecules in three-dimensional space are measured according to the procedure detailed elsewhere.[10] Three largest dimensions (a x b x c) of EBP and DEBP isomers in mutually perpendicular directions were considered. Qualitative structural fitting of the molecules inside the zeolites were studied by molecular graphics (MG) as well as by comparing the dimensions of the molecules within the pore diameters of the zeolites. Zeolite lattices were generated from the library of MS studio.

3. RESULTS AND DISCUSSION

3.1. Properties of zeolites

The phase purity of samples was checked by powder XRD, exhibited high crystallinity. Peak intensity slightly decreases by conversion to H^+-form and the dealumination with EDTA. Surface area of ZSM-12Ssample is higher than ZSM-12L sampled (Table I). Dealumination of ZSM-12 samples show marginal increase of surface area as well as pore volume. The SEM analysis of ZSM-12L and ZSM-12S shows particle size ~7 and ~1 μm respectively (Fig.1).

Typical profiles of NH_3-TPD of zeolites are shown in Fig. 2. The ammonia desorption peaks are given in Table II, ammonia uptake increases in the following order: ZSM-12L-E > SAPO-11 ≈ ZSM-12S-E > ZSM-5 > MOR > ZSM-12L > ZSM-12S. Decrease of acid sites by the dealumination is reflected by the ammonia TPD profiles shown in Fig. 2. Peak temperatures are in the following order: SAPO-11 ≈ ZSM-12L-E> ZSM-12S-E > ZSM-12L > ZSM-5 > ZSM-12 > MOR.

3.2 Ethylation of biphenyl

Figure 3 shows the activity for the ethylation of BP. MOR is the most active catalyst for the ethylation of BP with ethanol. The activities are decreases in the order MOR > ZSM-12S > ZSM-12-L > ZSM-12S-E > ZSM-12L-E > SAPO-11 ~ ZSM-5. Conversion of BP increases with temperature up to 350°C and then decreases with further increase of temperature. The selectivity for 4,4'-DEBP decreases in the order: ZSM-12S-E > ZSM-12L-E > ZSM-12S > ZSM-12L > SAPO-11 > MOR > ZSM-5. ZSM-12 is the highest selective for 4,4'-DEPB among zeolites in this study. The dealumination of ZSM-12 enhanced the selectivity: the increase for ZSM-12S-E is higher than ZSM-12L-E. Shape selectivity of 4,4'-DEBP decreased with temperature.

Polyalkylation occurred significantly over MOR, whereas dialkylation products were obtained over ZSM-12, and dialkylated products decreased in the order: ZSM-12S-E > ZSM-12S > ZSM-12L-E > ZSM-12L > MOR > SAPO-11 > ZSM-5 (Fig. 5).

Table I. Physicochemical characterization of the catalysts

Zeolites	Pore diameter	SiO_2/Al_2O_3 ratio	Pore volume (cm^3/g)	Surface area (m^2/g)
ZSM-5	5.6	190.0	0.082	394
MOR	7.4	206.0	0.198	497
SAPO-11	6.3	0.3	0.041	189
ZSM-12L	5.9	92.3	0.089	214
ZSM-12L-E	5.9	105.4	0.106	262
ZSM-12S	5.9	93.0	0.096	272
ZSM-12S-E	5.9	155.0	0.119	293

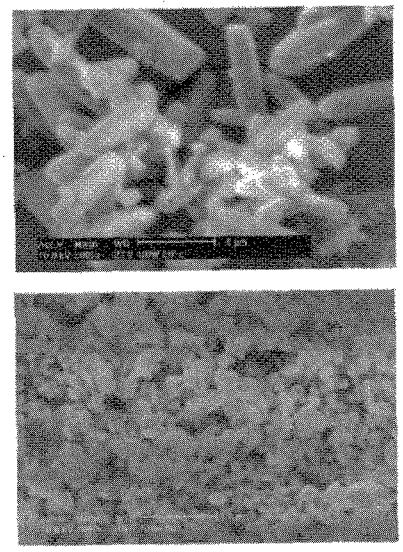

Fig. 1. SEM analysis of ZSM-12 samples. (a) ZSM-12L. (b) ZSM-12S.

Table II. TPD data obtained over different zeolites

Zeolites	Desorption temp. peaks (°C)		Moles of NH_3 m^3/g desorbed
ZSM-5	158	335	0.042
MOR	160	385	0.893
SAPO-11	175	237	0.039
ZSM-12L	175	321	0.916
ZSM-12L-E	203	267	0.027
ZSM-12S	182	335	1.073
ZSM-12S-E	210	275	0.039

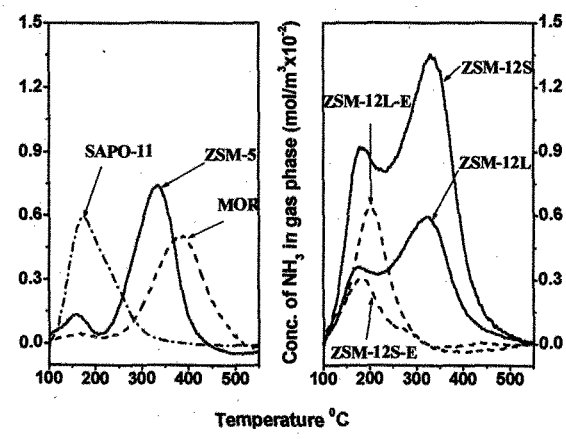

Fig. 2. NH_3-TPD profiles of zeolites

Table III. Catalytic activity and selectivity for alkylation of ethanol with BP over different zeolites

Zeolites	Conv.	Selectivity for EBP (%)			Selectivity for DEBP (%)				
		2-	3-	4-	2,4'-	2,4-	3,3'-	3,4'-	4,4'-
SAPO-11	4.7	45.2	23.1	31.7	24.7	17.3	1.8	12.5	13.1
ZSM-5	2.7	5.4	23.0	71.6	28.1	49.4	13.6	2.7	2.9
MOR	91.6	10.2	54.9	34.9	12.1	2.9	9.0	26.5	8.1
ZSM-12L	43.0	19.0	59.9	21.1	25.9	4.0	11.2	16.5	33.8
ZSM-12L-E	14.6	17.5	55.5	27.0	10.3	8.3	6.6	27.3	39.5
ZSM-12S	83.2	23.3	51.3	25.4	10.0	4.7	3.3	10.8	35.1
ZSM-12S-E	6.3	31.5	36.6	32.0	9.2	6.0	9.1	22.8	41.1

Reaction conditions: temperature= 300 °C, Feed= 1:5:5.5 moles, BP: EtOH: Cy, and WHSV = 1

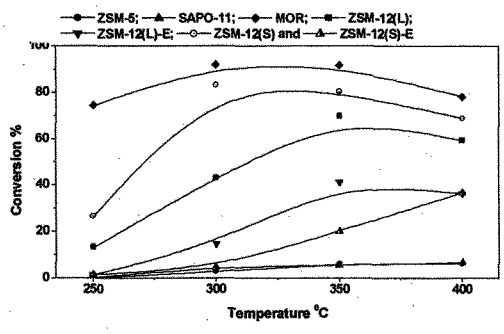

Fig. 3. Effects of reaction temperature on catalytic activity of zeolite. Reaction conditions: Feed=1:5:5.5 moles; BP: EtOH: Cy; WHSV = 1)

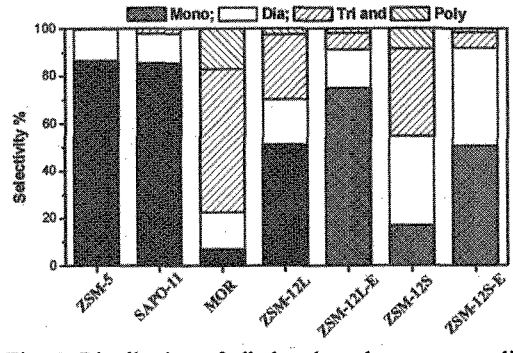

Fig. 5. Distribution of alkylated products over zeolites (Reaction conditions: temperature =300 °C and feed= 1:5:5.5 moles, BP: EtOH: Cy).

The effects of weight hourly space velocity (WHSV) are studied over ZSM-12S-E. As WHSV increases, the conversion of BP and the selectivity of 4-ethylbiphenyl (4-EBP) and 4,4'-DEBP decreased.

The 12-member channel (5.9 Å) system of ZSM-12 is expected as shape-selective catalytic sites for the ethylation of BP to 4,4'-DEBP. As previously discussed, steric environment of MOR pores is too loose for the restriction of transition state to 4,4'-DEBP. Small pore zeolites with 10-member channels, particularly ZSM-5 (5.6 Å) and SAPO-11 (5.5 Å) may not emerge as a shape selective catalyst, because BP can not easily enter and the products can not accommodate in their pores.

3.4. Influence of particle size

Diffusion of reactant and products in zeolite pores is important for efficient catalysis. Here, we studied the ethylation of BP over ZSM-12 with different particle size as shown in Fig. 1. The catalytic activity of ZSM-12S is higher than that of ZSM-12L. These

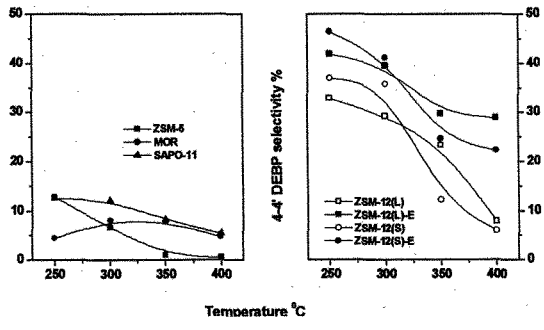

Fig. 4. Effects of reaction temperature on the selectivity for 4,4'-DEBP. Reaction conditions: Feed=1:5:5.5 moles; BP: EtOH: Cy; WHSV = 1)

differences are not due to the Al content of the samples because both samples have almost same Al contents. These results show that the reaction is controlled by diffusion through the channels of the zeolites (Table III and Fig. 1). The difference in surface area is also reason of the higher activity of ZSM-12S because high accessibility to acid sites enhanced the catalysis. Thus the observed differences in activity have to be related with differences in the amount of strong acidity sites present in the samples (Fig 2). Similar results are obtained by Aguilar *et. al* for alkylation of BP with methanol over beta zeolites.[11]

3.5. Dealumination of zeolites

It is essential to understand what occurs at acid sites in the pore and on the external surface. The dealumination by EDTA is effective method for reduction of external acid sites. The selectivity for 4,4'-DEBP was enhanced by the dealumination of both ZSM-12. Polyalkylation also decreased with increase of the shape selective formation of 4,4'-DEPB as shown in Fig. 3. The enhancement of the selectivity of 4,4'-DIPB can be explained by preferential deactivation of external acid site by the dealumination. The selectivity of the 4-EBP increased with the increase of 4,4'-DEBP over dealuminated ZSM-12.

3.6. Molecular modeling studies

The potential energies of energetically favorable conformation among all isomers shows that 3,4'-DEBP is the most stable. Molecular dimensions of some DEBP isomers are shown in Table IV. Molecular dimension of energetically favorable conformation shows that 4,4'-DEBP is the least bulky among DEBP isomers, and 3,4'-DEBP and 3,3'-DEBP isomers are bulkier than 4,4'-DEBP. 4,4'-DEBP (5.2 Å) can diffuse selectively

Table IV. Kinetic dimensions and potential energies of the monoalkylated and dialkylated BP isomers

No.	Isomers	Dimensions (a x b x c) Å	Potential Energy (au)
1	2-EBP	5.4 x 7.0 x 10.2	-537.1163
2	3-EBP	5.8 x 7.2 x 10.2	-537.1200
3	4-EBP	5.0 x 5.2 x 12.0	-537.1202
4	2,4'-DEBP	5.1 x 7.1 x 10.2	-614.3379
5	2,4-DEBP	5.4 x 7.5 x 10.2	-615.0338
6	3,3'-DEBP	5.4 x 7.1 x 11.0	-615.0363
7	3,4'-DEBP	5.7 x 6.7 x 12.2	-615.0366
8	4,4'-DEBP	5.0 x 5.2 x 14.4	-615.0365

in ZSM (5.9 Å). Molecular graphics (MG) picture shows the fitting of 3,4'-DEBP, 3,3'-DEBP and 4,4'-DEBP (CPK model) inside ZSM-12 pores (cross-section of the 12-MR) shown in Fig. 6 (upper). The diffusion of 4,4' DEBP through ZSM-12 is possible, but 3,4'- and 3,3'-DEBP are not easy diffused through the channel (Table. IV). The diffusion of 4,4'-DEBP isomer is very freely, but slight reduction of pore diameter should be required for the shape-selective formation. MG picture in Fig. 6 (middle) shows the fitting of 3,4'-DEBP, 3,3'-DEBP and 4,4'-DEBP inside the MOR pores (cross-section of the 12-MR). MG picture in Fig. 6 (bottom) shows that all isomers not possible to diffuse through 10-MR channels of ZSM-5.

3.7 Mechanistic aspects

The selectivity of 4,4'-DEBP was the highest over ZSM-12. This is explained by the restricted transition state mechanism. 4,4'-DEBP at transition state is more favorable than the other bulkier isomers, and can easily diffuse through channel because its least bulkiness among all isomers. The slight reduction of pore diameter should be required for the shape-selective formation of 4,4'-DEBP.

All isomers are easily accommodated and freely diffused in the channel of MOR to result in low selectivity for 4,4'-DEBP, and in the formation of polyalkylated products. However, ZSM-5 pores are too small for all DEBP isomers to accommodate and diffuse in them.

None-selective reactions at external acid sites occurs significantly; however, they were reduced by dealumination, and improved the selectivity for 4,4'-DEBP, although the catalytic activity decreased.

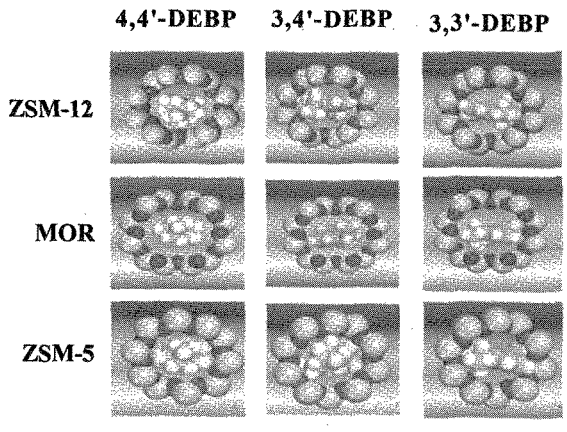

Fig. 6 The MG picture shows the fitting of DEBP isomers (CPK model) inside ZSM-12, MOR and ZSM-5 pores (cross-section of the 10 and 12-MR).

4. CONCLUSIONS

The ethylation of BP was studied over zeolites (ZSM-12, SAPO-11, ZSM-5, MOR) under vapor phase conditions. The delaminated ZSM-12 gave the highest selectivity for 4,4'-DEBP. This is explained by the restricted transition states mechanism to form 4,4'-DEBP isomer selectively, which is the least bulky among all isomers, can easily diffuse through channel. Other zeolites gave lower selectivity for 4,4'-DEBP. Polyalkylation was observed over MOR and ZSM-12. ZSM-12 with small particle size enhanced the formation of polyethylated products; however, polyethylation decreased by the dealumination.

Molecular modeling study shows that 4,4'-DEBP are the least bulky and most stable isomers among the all DEBP isomers, respectively. Molecular fitting study revels that ZSM-12 pore is suitable for 4,4'-DEBP sieving. These results show that the formation of 4,4'-DEBP is the most favorable from aspects of diffusion and restriction of transition state in the channel of ZSM-12. However, the slight reduction of pore diameter should be required for the improvement of shape-selective formation of 4,4'-DEBP.

Further aspects of these catalyses are under investigation.

Acknowledgement

S. B. W. thanks to Japan Society for the Promotion of Science (JSPS) for fellowship.

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(Received October 10, 2003; Accepted October 31, 2003)