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Shape-selective alkylation of biphenyl over mordenite: cerium exchanged sodium mordenite and unmodified H-mordenite with low SiO_2/Al_2O_3 ratio

Y. Sugi [1], T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim [2]

National Institute of Materials and Chemical Research, AIST, Tsukuba 305, Japan

X. Tu and M. Matsumoto

Research and Development Center, Osaka Gas Co. Ltd., Osaka 554, Japan

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Liquid phase isopropylation of biphenyl with propylene was studied over a cerium exchanged sodium mordenite (Ce/NaM25) and a H-mordenite (HM25) with the same SiO_2/Al_2O_3 ratio of 25. Shape-selective catalysis occurred to give 4,4′-diisopropylbiphenyl (4,4′-DIPB) in high selectivity over Ce/NaM25 under any propylene pressures. HM25 gave 4,4′-DIPB shape-selectively under high propylene pressures. However, the reaction was severely deactivated at a conversion of ca. 60% under such a low pressure as 0.8 kg/cm^2 because of coke formation in the pore. The yields of 4-isopropylbiphenyl (4-IPBP) and 4,4′-DIPB decreased with the increase of those of 3-IPBP and 3,4′-DIPB because of non-selective alkylation and isomerization at external acid sites that are alive in spite of severe deactivation. No significant isomerization of 4,4′-DIPB over Ce/NaM25 was observed even at low propylene pressure. In the case of HM25, the isomerization of 4,4′-DIPB to 3,4′-DIPB occurred significantly under low propylene pressures, while it decreased under high pressure. These differences are ascribed to the differences of nature of acid sites between Ce/NaM25 and HM25 zeolites.

Keywords: Shape-selective catalysis; biphenyl; isopropylation; cerium exchanged sodium mordenite; H-mordenite; propylene pressure

1. Introduction

Shape-selective alkylation using zeolite is a useful way to introduce functional groups symmetrically to aromatic hydrocarbons [1]. H-mordenites have been found to be the most potential catalysts for the alkylation of polynuclear aromatics

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[1] To whom correspondence should be addressed.

[2] Present address: Department of Materials Engineering, Faculty of Engineering, Tottori University, Tottori 680, Japan.

such as biphenyl and naphthalene [2–6]. The design of acidic property is important to understand the shape-selective catalysis and to achieve improvement of catalyst performances. Sodium mordenite, which has originally no activity for acid catalysis, reveals Brønsted acid property by exchange of sodium cations with multivalent cations [7,8]. The exchange with rare earth cations is a well-known method to improve activity and life of zeolite catalysts [9–11]. We are much interested in solid acid catalysis of rare earth cation exchanged sodium mordenite. In this paper, we describe catalysis by cerium exchanged sodium mordenite (Ce/NaM25) in the isopropylation of biphenyl and compare it with unmodified H-mordenite (HM25) with the same SiO_2/Al_2O_3 ratio.

2. Experimental

H-mordenite (HM25, SiO_2/Al_2O_3 (Si/Al_2) = 25) was obtained from Tosoh Corporation, Tokyo, Japan. Sodium mordenite (NaM25) was prepared from HM25 by treatment with aqueous sodium hydroxide solution. Cerium exchanged sodium mordenite (Ce/NaM25) was obtained by cation exchange of NaM25 with cerium nitrate in aqueous solution at 90°C. Cerium to aluminum (Ce/Al) ratio of Ce/NaM25 was 0.27, as determined by XRF (Seiko Instruments Inc., SEA 2010). Surface areas of HM25 and Ce/NaM are 662 and 596 m^2/g, respectively. All mordenites were calcined at 500°C just before use. Biphenyl and propylene were purchased from Tokyo Kasei Kogyo Co. Ltd., Tokyo, and used without further purifications. Reactions were carried out at 250°C under 0.8–10 kg/cm^2 of constant pressure of propylene. Reaction and analytic procedures were described in the previous paper [3].

3. Results and discussion

Fig. 1 shows the catalytic activities of Ce/NaM25 and HM25 zeolites for the isopropylation of biphenyl under propylene pressure of 0.8–10 kg/cm^2. The rate of the reaction varied significantly with the change of pressure over Ce/NaM25.The activity under high pressure was much higher than that under such low pressures as 0.8 and 1.8 kg/cm^2. The low rate under low pressures is due to the limitation of propylene adsorbed on acid sites where the alkylation occurs. The initial rate over HM25 did not depend on pressures higher than 1.8 kg/cm^2, however, the reaction was severely deactivated after reaching 60% conversion under the low pressure of 0.8 kg/cm^2. The deactivation is ascribed to choking mordenite pores by coke deposition from biphenyl and its alkylated products [4].

The effect of propylene pressure on the formation of IPBP and DIPB isomers over Ce/NaM25 is summarized in figs. 2 and 3. The yields of IPBP and DIPB isomers are on the same curve under any propylene pressure. As shown in fig. 2, the

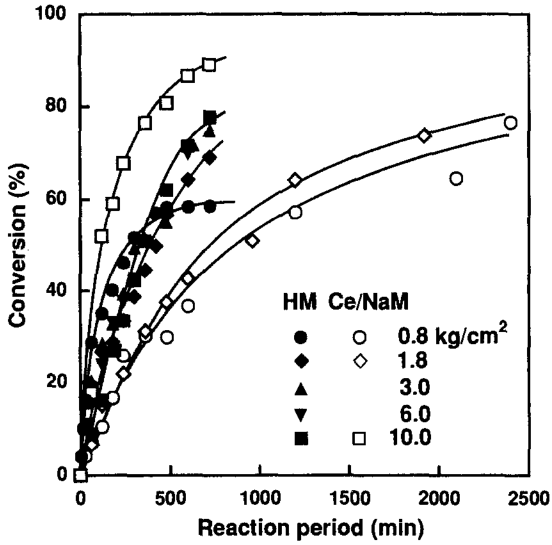

Fig. 1. Catalytic activity of Ce/NaM25 and HM25. Reaction conditions: biphenyl, 400 mmol; catalyst, 2 g; reaction temperature, 250°C.

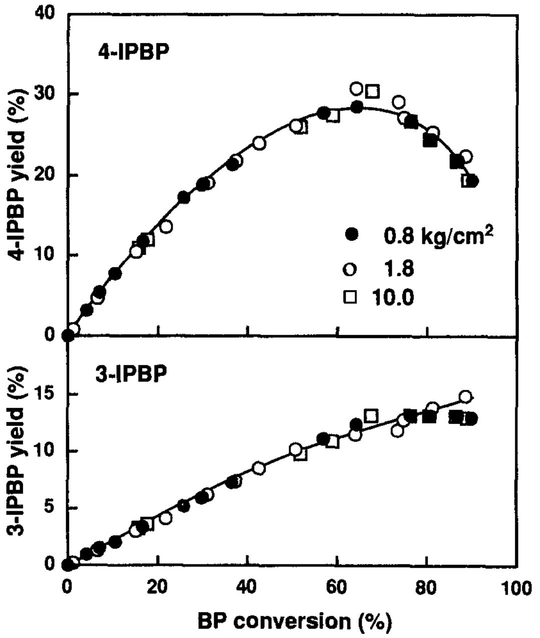

Fig. 2. Effect on IPBP yield of propylene pressure over Ce/NaM25. Reaction conditions: biphenyl, 400 mmol; Ce/NaM25, 2 g; reaction temperature, 250°C.

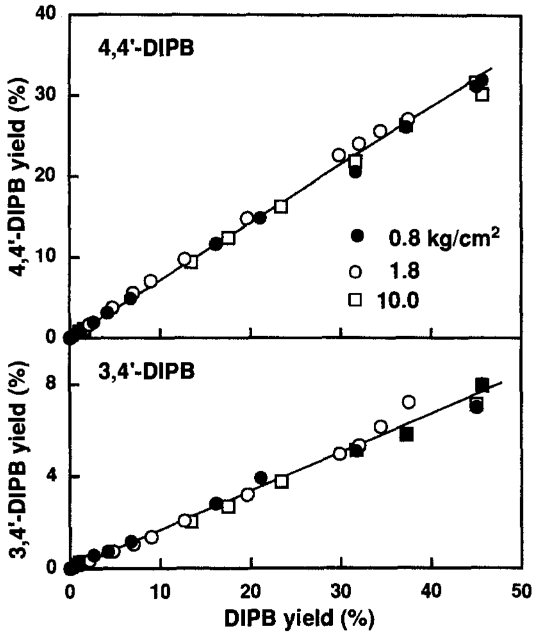

Fig. 3. Effect on DIPB yield of propylene pressure over Ce/NaM25. Reaction conditions are the same as for fig. 2.

yield of 4-IPBP increased to a maximum value of 30% with the increase of conversion, and decreased on further reaction. On the other hand, 3-IPBP increased monotonously with the conversion, although its formation was saturated at high conversion. The yields of 4,4′-DIPB and 3,4′-DIPB increased linearly with the increase of total DIPB yield during the reaction as shown in fig. 3. These results over Ce/NaM25 suggest that the reaction proceeds inside the pore by a consecutive reaction mechanism under any propylene pressure as previously proposed [3]. The first stage of the reaction to form IPBP isomers is governed by shape-selectivity by the mordenite pore to yield 4-IPBP as the principal isomer. 4,4′-DIPB and 3,4′-DIPB were formed only from 4-IPBP at the second stage of the reaction. 3-IPBP does not participate in the formation of 3,4′-DIPB, because it is bulkier than 4-IPBP.

The dependence on propylene pressure of the isomerization of 4,4′-DIPB over Ce/NaM25 is quite different from that over the highly dealuminated H-mordenite HM220. No significant isomerization of 4,4′-DIPB over Ce/NaM25 was observed even under the low propylene pressure of 0.8 kg/cm^2. We previously described that the isomerization during the isopropylation over HM220 under low propylene pressure occurs at external acid sites, and that preferential adsorption of propylene prevents the isomerization [3]. These differences indicate that Ce/NaM25 has no acid sites on its external surface to isomerize 4,4′-DIPB.

Figs. 4 and 5 summarize the effect of propylene pressure on the yield of IPBP

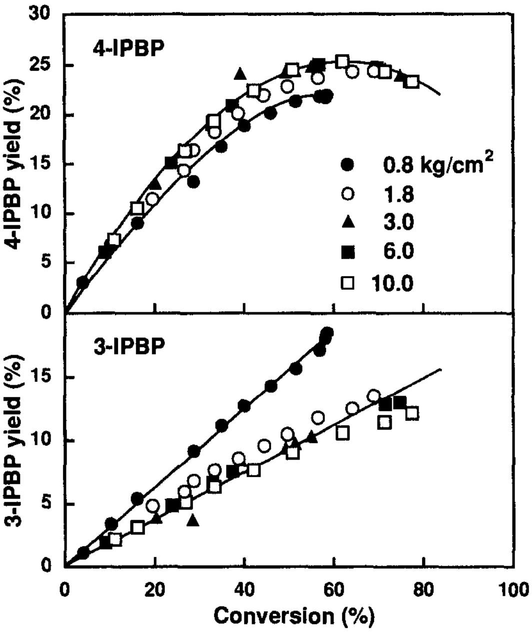

Fig. 4. Effect on IPBP yield of propylene pressure over HM25. Reaction conditions: biphenyl, 400 mmol; HM25, 2 g; reaction temperature, 250°C.

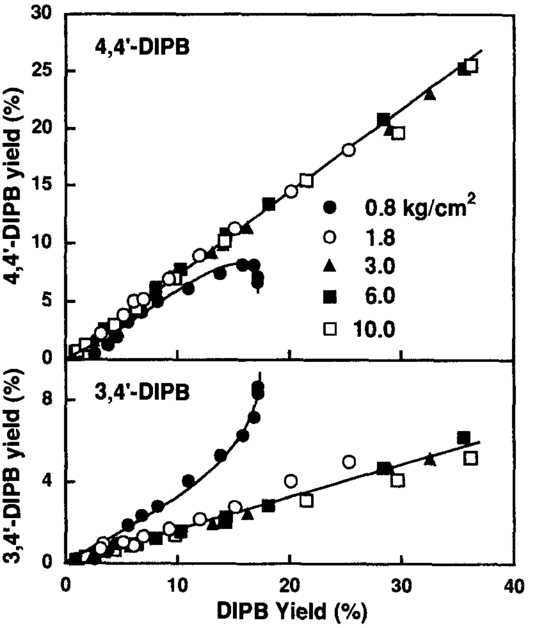

Fig. 5. Effect on DIPB yield of propylene pressure over HM25. Reaction conditions are the same as for fig. 4.

and DIPB isomers over HM25. The product distribution varied with propylene pressure corresponding to catalytic activity as shown in fig. 1. The yields of IPBP and DIPB isomers are on the same curve under pressures higher than 1.8 kg/cm^2. The yield of 4-IPBP has a maximum value at a conversion of 40–60%, whereas that of 3-IPBP increased linearly with the conversion. The yields of 4,4′-DIPB and 3,4′-DIPB under the pressures of 1.8–10 kg/cm^2 increased linearly against total DIPB yield. These results under high pressures indicate that the alkylation over HM25 occurs predominantly inside the pore to give the most slim isomers, 4-IPBP and 4,4′-DIPB, and that the isomerization of 4,4′-DIPB is not significant. However, the selectivity of 4,4′-DIPB over HM25 was lower than that over HM220 [3]. This low selectivity over HM25 is probably due to the participation of non-shape-selective alkylation catalyzed by external acid sites.

A different feature of the catalysis was observed in the isopropylation under the low propylene pressure of 0.8 kg/cm^2. The isopropylation was almost stopped at the conversion of ca. 60%. This severe deactivation is due to choking the pores by coke deposition. The product distribution was also different from those under higher pressures. The yields of 3-IPBP and 3,4′-DIPB deviated upward from those under higher pressures. On the other hand, downward deviations occurred for the yields of 4-IPBP and 4,4′-DIPB, although they were not so much for 4-IPBP. The yield of 4,4′-DIPB increased up to the maximum value of 7–8% at a total DIPB yield of ca. 15%, and then decreased because of the isomerization to 3,4′-DIPB. Change of product distribution under low pressures is ascribed to the decrease of shape-selective reaction inside the pore and the increase of non-shape-selective reactions. The latter reactions are considered to occur predominantly on external acid sites that are still alive in spite of severe deactivation. Under high pressures, preferential adsorption of propylene on the acid sites not only reduces coke deposition inside the pore, but also prevents the isomerization of 4,4′-DIPB similarly to HM220 [3]. On the other hand, preferential adsorption of biphenyl on the acid site prompts coke deposition under low propylene pressures.

Fig. 6 shows the isomerization of 4,4′-DIPB over Ce/NaM25 and HM25 in absence and presence of propylene. No significant isomerization occurred over Ce/NaM25 even in absence of propylene. On the other hand, 4,4′-DIPB was isomerized extensively to 3,4′-DIPB over HM25 under the same condition. On the other hand, the isomerization over both Ce/NaM25 and HM25 was less than 4% under 10 kg/cm^2 of propylene. These differences indicate that acid properties are quite different between these two zeolites. Acid sites over Ce/NaM25 do not act as active sites for the isomerization, whereas external acid sites of HM25 are active for the reaction. Under high pressures, the isomerization of 4,4′-DIPB and 4-IPBP on external acid sites over HM25 are prevented by preferential adsorption of propylene as discussed in a previous paper [3]. These features correspond with the difference of catalytic behavior between Ce/NaM25 and HM25 zeolites in the isopropylation of biphenyl.

In summary, cerium exchanged sodium mordenite (Ce/NaM25) acts as a shape-

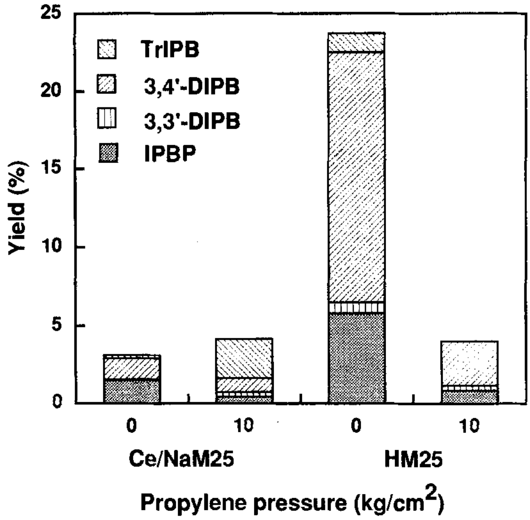

Fig. 6. The isomerization of 4,4'-DIPB over Ce/NaM25 and HM25 under propylene pressure. Reaction conditions: biphenyl, 200 mmol; catalyst, 1 g; reaction temperature, 250°C.

selective catalyst for the isopropylation of biphenyl. The active sites are Brønsted acid sites produced by cerium cation exchange. No external acid sites on Ce/NaM25 act as active sites for the isomerization of 4,4'-DIPB. The shape-selective catalysis over H-mordenites with low Si/Al_2 ratio such as HM25 occurred under high propylene pressures similar to the case of Ce/NaM25. However, severe deactivation occurred under low pressure of 0.8 kg/cm^2 because of choking mordenite pores by coke deposition, and the reaction was stopped at the conversion level of ca. 60%. The isopropylation and the isomerization occur with low shape-selectivity over external acid sites that are still alive in spite of severe coke deposition. The differences of catalytic behavior between Ce/NaM25 and HM25 are due to the differences of acid properties between these two zeolites.

Further aspects of the catalyses and characterization of the catalysts are under investigation.

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