Shape-selective alkylation of biphenyl over mordenites: effects of dealumination on shape-selectivity and coke deposition

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

Received 24 January 1994; accepted 1 March 1994

To understand the relationships between shape-selectivity and coke deposition in the alkylation of biphenyl over H-mordenite (HM), thermogravimetric analyses were examined for the catalyst after the reaction. The coke deposition during the catalysis was very severe over HM with low SiO_2/Al_2O_3 ratio, however, dealumination enhanced the decrease of coke deposition. Over highly dealuminated HM, volatile organic compounds, mainly biphenyl derivatives, were observed in addition to carbonaceous deposits. The deposits are produced from biphenyl derivatives on acid sites in the HM pore, and the ease of their formation is governed by acid site density and acid strength. The decrease of carbonaceous deposits and the increase of encapsulated biphenyl derivatives are related with the increase of both selectivity and yield of 4,4′-diisopropylbiphenyl (4,4′-DIPB). The increase of reaction temperature up to 250°C enhanced the catalysis over highly dealuminated HM, however, further increase of the temperature resulted in extensive decrease of the selectivity of 4,4′-DIPB. Coke deposition also increased with the temperature although its level was low. The composition of 4,4′-DIPB in encapsulated DIPB isomers remained as high as 80% in spite of a change of the distribution of bulk products.

Keywords: shape-selective catalysis; biphenyl; isopropylation; H-mordenite; carbonaceous deposits; encapsulated biphenyls

1. Introduction

Shape-selective alkylation of polynuclear aromatics is a promising way to introduce functional groups for synthesis of advanced materials [1–5]. We have found

---

[1] To whom correspondence should be addressed.

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

that H-mordenite is a highly potential catalyst for the shape-selective alkylation of biphenyl and naphthalene [1,3,4]. Severe coke deposition retards the catalysis using H-zeolites with low SiO_2/Al_2O_3 (Si/Al_2) ratio [6,7]. Coke deposition takes place at acid sites, and causes the catalyst deactivation. The dealumination of HM zeolite can modify acidic properties to decrease the formation of carbonaceous deposits and coke [8–11]. In this paper, we will report the effect of dealumination on coke deposition in the isopropylation of biphenyl over H-mordenite with various Si/Al_2 ratios.

2. Experimental

H-mordenites (Si/Al_2 = 10, 15, 20, 23, 30, 73, 110, and 220) were obtained from Tohsoh Corporation, Tokyo, Japan. All mordenites were calcined at 500°C just before use for the reactions. Biphenyl and propylene were purchased from Tokyo Kasei Co. Ltd., Tokyo, and used without further purifications. The reaction procedure was described in the previous paper [3].

Thermogravimetric analysis (TG) of the HM zeolite was performed after the reaction was carried out using Mac Science, TG-DTA 2000 in an air stream. The weight loss due to adsorbed water was corrected by the decrease in a blank measurement of the corresponding HM before the reaction. The compounds evolved during TG analysis using helium carrier gas containing 2% oxygen were identified by mass spectroscopy.

Biphenyl derivatives encapsulated in the pore were analyzed by GC after the destruction of HM using aqueous hydrofluoric acid solution.

3. Results and discussion

Fig. 1 shows the effect of the dealumination of HM zeolite on the isopropylation under 10 kg/cm^2 of propylene pressure. The yield of diisopropylbiphenyl (DIPB), especially 4,4′-DIPB, increased extensively with the increase of Si/Al_2 ratio. The selectivity of isopropylbiphenyl (IPBP) and DIPB isomers also changed significantly at Si/Al_2 ratio less than 20. The selectivities over HM10 [#1] were as low as ca. 60% for 4-IPBP and 52% for 4,4′-DIPB. The resultant low selectivities at low ratios suggest that the alkylation inside the pores is severely diffusion limited because of coke formation as discussed below, and that non-shape-selective alkylation and isomerization of 4,4′-DIPB occur at acid sites on the external surface. The selectivities of 4,4′-DIPB gradually increase with increasing ratio. Especially, over HM220, the selectivity of 4,4′-DIPB was up to ca. 90% with increasing of the conversion. These results suggest that the isopropylation occurs inside the HM

[#1] The number after HM expresses the Si/Al_2 ratio.

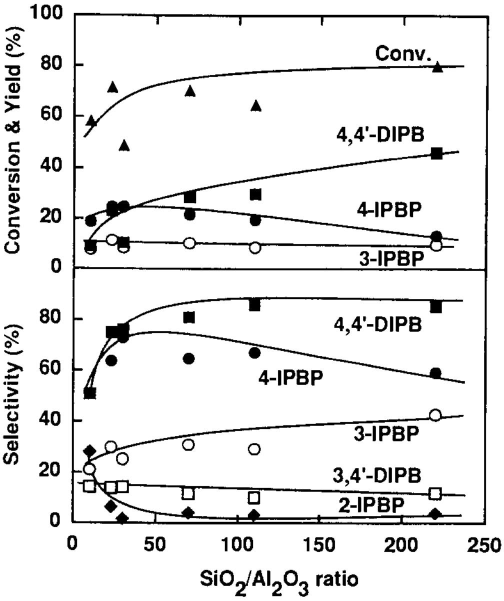

Fig. 1. Effect of SiO_2/Al_2O_3 ratio of H-mordenite on the isopropylation of biphenyl. Reaction conditions: biphenyl, 200 mmol; HM, 1 g; reaction temperature, 250°C, reaction period 4 h.

pores to form 4,4′-DIPB shape-selectively, and that the dealumination decreases the non-shape-selective alkylation and isomerization of 4,4′-DIPB because of the elimination of acid sites from the external surface. With the increase of the ratio, the selectivity of 4-IPBP decreased gradually, and that of 3-IPBP increased, because only 4-IPBP was consumed in further isopropylation to form DIPB isomers [3].

It has been known that the catalysis of zeolite with low Si/Al_2 ratio, such as HY, HL, and HM is severely deactivated by coke deposition, and that the dealumination enhances the decrease of coke deposition [6,7]. Acid density and strength are related to the coke deposition. Strong acid sites decrease preferentially by the dealumination in addition to the decrease of acid density [4,9–11]. To understand the relationships between shape-selectivity and acid property, we examined the analysis of coke deposition in the alkylation of biphenyl. TG profiles of HM zeolite after the reaction in an air stream are shown in fig. 2. The peaks around 600°C are produced from carbonaceous deposits in HM zeolite because carbon dioxide and water were found in the evolved gas. The amount of the deposits, calculated from weight loss, decreased with decreasing Si/Al_2 ratio of HM. These changes coincide with the decrease of the peak temperature of NH_3-TPD, which is considered to be an indicator of acid strength [4,11]. These results show that the deposition is enhanced by cooperation of the acid sites in the neighborhood, and that HM zeolites with low Si/Al_2 ratio enhance the coke deposition to choke the pore. The peak temperature also decreased with the increase of Si/Al_2 ratio. The change of the temperature reflects the degree of dehydrogenation of the deposits.

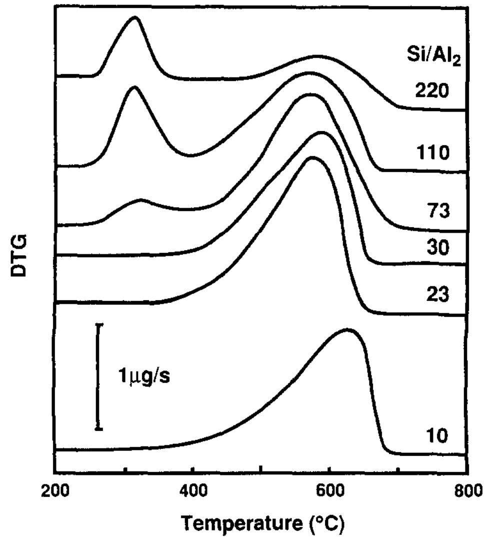

Fig. 2. TG profile of H-mordenite with various SiO_2/Al_2O_3 ratios used for the isopropylation. Sample: 10 mg. Temperature increase: 10°C/min.

The peaks at lower temperature below 400°C appeared in the TG profile of HM with Si/Al$_2$ ratio higher than 72 as shown in fig. 2. The latter peaks were volatile organic compounds by MS analyses. They consist of biphenyl derivatives encapsulated in HM pores. The peak area increased with the increase of Si/Al$_2$ ratio. These results show that biphenyl derivatives accommodated in the pore are precursors of carbonaceous deposits. The biphenyl derivatives are easily dehydrogenated to form the deposits in HM pore with low Si/Al$_2$ ratio, and the dehydrogenation is not a rapid reaction in highly dealuminated HM pore, because high acid density and strength are essential for the reaction.

The decrease of carbonaceous deposits and the increase of encapsulated biphenyl derivatives are related to the increase of both selectivity and yield of 4,4′-DIPB as shown in fig. 1. The yield and the selectivity of 4,4′-DIPB increased with decreasing acid strength. The low selectivity of 4,4′-DIPB over HM with low Si/Al$_2$ ratio is due to the participation of non-shape-selective alkylation over external acid sites which are alive in spite of severe coke deposition.

Fig. 3 shows the effect of reaction temperature on the product distribution in the isopropylation of biphenyl over highly dealuminated HM220. The conversion was increased with reaction temperature. The yield of 4,4′-DIPB increased with reaction temperature up to 300°C, and decreased at the higher temperatures. The yield of 3,4′-DIPB increased at higher temperatures corresponding to the decrease of 4,4′-DIPB. For yields of IPBP isomers, 4-IPBP decreased with reaction temperature, while 3-IPBP increased at higher temperature. Corresponding to the changes of the yields, the decrease of the selectivities of 4,4′-DIPB and 4-IPBP and the increase of those of 3-IPBP and 3,4′-DIPB occurred extensively at the temperatures

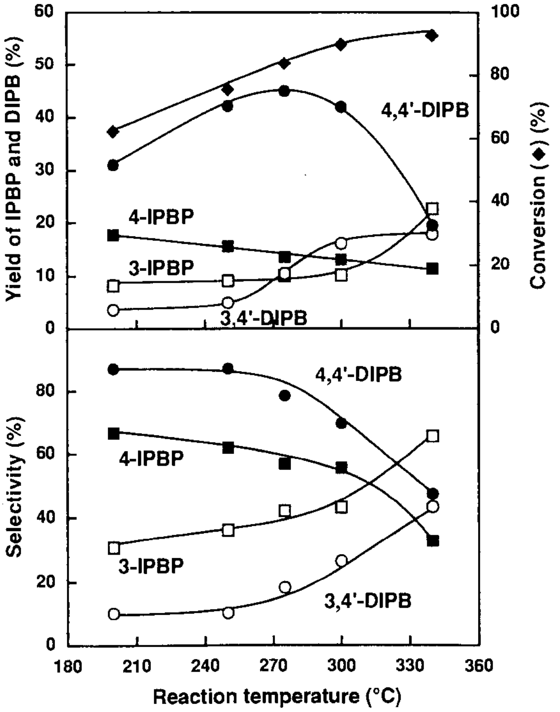

Fig. 3. Effect of reaction temperature on the isopropylation over HM220. Reaction conditions: biphenyl, 200 mmol; HM220, 1 g; reaction time 4 h.

higher than 300°C. The analysis of DIPB isomers encapsulated in the pore shows that the composition of 4,4′-DIPB remained almost constant at the level of 80% in spite of a significant change of bulk products. These results strongly support highly shape-selective catalysis in the HM pore, and the decrease of selectivity of 4,4′-DIPB and 4-IPBP at high temperatures is due to the isomerization at the external surface as observed over HM220 under low propylene pressures [3].

The amounts of carbonaceous deposits and volatile biphenyl derivatives measured by TG analysis are shown in fig. 4. The deposits increased with the increase of reaction temperature. The dehydrogenation of biphenyls enhanced the formation of the deposits at such a high temperature as 340°C, although the level of the deposits was much lower than those for HM with low Si/Al_2 ratio. Biphenyl derivatives encapsulated in HM pore decreased at higher temperatures. Their change with high temperature is related to the increase of the deposits. These results indicate the effectiveness of HM pore for shape-selective isopropylation of biphenyl.

In summary, the dealumination of H-mordenite enhanced the shape-selective alkylation of biphenyl. TG analyses of HM zeolite after the reaction show severe coke deposition during the catalysis over HM with low Si/Al_2 ratio, however the dealumination enhanced the decrease of coke deposition. Over highly dealuminated HM, volatile organic compounds, mainly biphenyl derivatives were

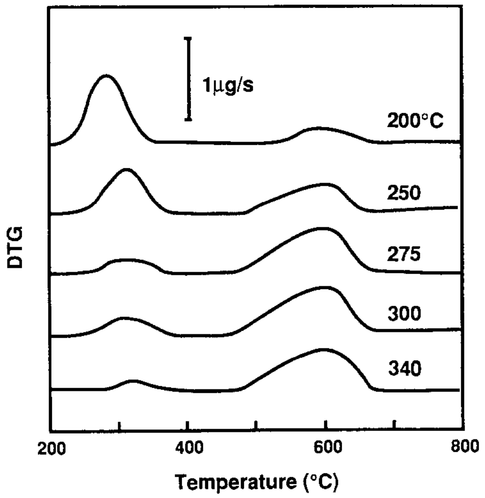

Fig. 4. Effect of temperature on TG profile of H-mordenite used for the isopropylation. Conditions are the same as for fig. 2.

observed in addition to carbonaceous deposits. The deposits are produced from biphenyl derivatives, and the ease of their formation is governed by acid density and strength. The decrease of carbonaceous deposits and the increase of encapsulated biphenyl derivatives are related with the increase of both selectivity and yield of 4,4′-DIPB.

The increase of reaction temperature below 250°C enhanced the catalysis over highly dealuminated HM, however, the shape-selectivity decreased extensively at temperatures higher than 300°C. The formation of carbonaceous deposits also increased with temperature although the level was low. The composition of 4,4′-DIPB in encapsulated DIPB isomers was as high as 80% at 340°C in spite of a significant change of bulk products.

These results indicate the effectiveness of HM pore for shape-selective isopropylation of biphenyl.

Acknowledgement

The authors thank Mr. H. Asahina and T. Sakai of Mitsubishi Petrochemical Co. for the identification of compounds in TG analysis.

References

[1] Y. Sugi, T. Matsuzaki, T. Hanaoka, K. Takeuchi, T. Tokoro and G. Takeuchi, Stud. Surf. Sci. Catal. 60 (1991) 303.

[2] A. Katayama, M. Toba, G. Tekeuchi, F. Mizukami, S. Niwa and S. Mitamura, J. Chem. Soc. Chem. Commun. (1991) 39.

[3] X. Tu, M. Matsumoto, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim and Y. Sugi, Catal. Lett. 21 (1993) 71.
[4] J.-H. Kim, T. Matsuzaki, T. Hanaoka, Y. Kubota, Y. Sugi, X. Tu and M. Matsumoto, submitted.
[5] G.S. Lee, J.J. Maj, S.C. Rocke and J.M. Garces, Catal. Lett. 2 (1989) 243.
[6] O. Dejaifve, A. Aurox, P.C. Gravelle, J.C. Vedrine, Z. Gabelica and E. Derouane, J. Catal. 70 (1981) 123.
[7] N. Neuber, H.G. Karge and J. Weitkamp, Catal. Today 3 (1988) 11.
[8] H.G. Karge and J. Weitkamp, Chem. Ind. Techn. 58 (1986) 946.
[9] K. Segawa, M. Sakaguchi, S. Nakata and S. Asaoka, Nippon Kagaku Kaishi (1988) 528.
[10] M. Sawa, M. Niwa and Y. Murakami, Appl. Catal. 53 (1989) 169.
[11] J.-H. Kim, S. Namba and T. Yashima, Zeolites 11 (1991) 59.