Benzene alkylation with 1-dodecene over H-mordenite zeolite

Bo Wang [a], Chul Wee Lee, Tian-Xi Cai [a] and Sang-Eon Park [*]

Catalysis Center for Molecular Engineering, KRICT, Taejon 305-600, Korea
E-mail: separk@pado.krict.re.kr
[a] *School of Chemical Engineering, DUT, 116012 Dalian, PR China*

Received 9 March 2001; accepted 21 June 2001

The alkylation of benzene with 1-dodecene was studied over solid-acid zeolites, such as H-mordenite, H-USY, HY, and H-ZSM-5, in a batch reactor at 140 °C and 10 atm. H-mordenite showed the highest selectivity of 78.2% for 2-phenyldodecane with 100% conversion. Depending on the catalyst amount (from 0.5 to 1.0 g) and the molar ratio of benzene to 1-dodecene (from 7 to 10), the conversion of 1-dodecene varied in the range from 63.8 to 100%. Furthermore, modification of H-mordenite by dealumination using nitric acid and by solid ion exchange with Mg^{2+} and Fe^{3+} ions led to the improvement of the selectivity for 2-phenyldodecane, and simultaneously reduction of the conversion of 1-dodecene is observed. In addition, it was found by pyridine adsorption FT-IR study that both strong Brønsted and Lewis acid sites are closely related to the conversion.

KEY WORDS: benzene; alkylation; 1-dodecene; H-mordenite; solid acid; modification

1. Introduction

The alkylation of benzene with higher *n*-alkenes, basically in the range of C_{10} to C_{13}, is performed industrially in the manufacture of linear alkylbenzene (LAB), an intermediate used in the production of linear alkylbenzene sulphonate (LAS). It is believed that the 2-phenyl isomer gives detergent of better emulsibility and biodegradability. The commercial process for LAB is based on alkylation of benzene with olefins using anhydrous HF as catalyst. Due to the hazardous nature of HF, efforts have been made to replace it with environmentally safer catalysts. Other solid acid catalysts reported for the alkylation of benzene with olefins include heteropolyacids [1], clays [2], ZSM-12 [3], HY [4], and pillared clays [5]. The alkylation of benzene with olefins goes through a carbonium ion mechanism. In the case of dodecene, six carbonium ions are possible. On the basis of the relative stabilities of the carbonium ions, one would expect the isomer content to increase with the carbon number (toward the center of the chain). This is found to be so in the case of HF, in which thermodynamic equilibrium is probably reached and six isomers are in the range from 16.7 to 25.3%. However, zeolitic materials, compared to other catalysts in this reaction, showed relatively higher selectivity for the 2-phenyl isomer, ranging from 20 to 35%. Young [3] reported alkylation of benzene with 1-dodecene over H-ZSM-12 and H-mordenite dealuminated by HCl. The conversions of 1-dodecene were 54 and 98%, respectively, with selectivities for phenyldodecane of 63 and 82%, respectively, of which the content of 2-phenyl isomer was 92% over H-ZSM-12 and 85% over dealuminated H-mordenite [3]. Recently, Wang *et al*. reported that the alkylation of benzene with 1-dodecene over a commercial mordenite, which contained 30% Al_2O_3 as the binder, was studied in a fixed-bed reactor at over 1.0 MPa, resulting that 95% conversion and 98% selectivity to linear phenylalkanes was achieved [6]. Besides, the mordenite exhibits very high selectivity for the 2-phenyl-substituted isomer, of 60% in the products. In addition, Anantaneni *et al*. patented a process of alkylation of benzene to form linear alkylbenzenes with selectivity for the 2-phenyl isomer in the range of 60.4–83.5% at different conversions using fluorine-containing mordenites [7–9]. It was believed that HF treatment induces reduction of the total Brønsted acid sites and increment of the strength of the remaining acid sites in the mordenite, which retarded coke build-up during LAB production.

In this study, much work was attempted for the preparation of 2-phenyldodecane with high selectivity in benzene alkylation with 1-dodecene over H-mordenite zeolite in a batch type reaction. In order to increase the selectivity for the 2-phenyl isomer, modification of H-mordenite was performed by dealumination using nitric acid and by solid ion exchange with Mg^{2+} and Fe^{3+} cations. Furthermore, it was evidenced by FT-IR that both strong Brønsted and Lewis acid sites are responsible for this reaction.

2. Experimental

Zeolite H-mordenite (Zeolyst, $SiO_2/Al_2O_3 = 35$), H-Y (Zeolyst, $SiO_2/Al_2O_3 = 4.8$), H-ZSM-5 (Zeolyst, $SiO_2/Al_2O_3 = 80$) and H-USY (Zeolyst, $SiO_2/Al_2O_3 = 80$) were used in this work. Mg–H-mordenite and Fe–H-mordenite were prepared by a solid-state ion exchange method according to [10,11]. 3 g H-mordenite was mixed with a desired amount of magnesium or ferric nitrate, respectively, and ground homogeneously, then calcined at 500 °C in a stream of dry inert gas for 5 h.

---

[*] To whom correspondence should be addressed.

1011-372X/01/0900-0099$19.50/0

Dealumination of H-mordenite is carried out based on [12]: 3 g H-mordenite was added into 250 ml 2 and 4 N HNO_3 solution and refluxed for 7 h, then filtered, washed with 10% HNO_3 and water, dried and calcined at 500 °C for 5 h. These dealuminated samples were denoted as H-mordenite (2 N) and H-mordenite (4 N) for H-mordenite treated with 2 N HNO_3 and 4 N HNO_3, respectively.

For the FT-IR study, a 12 mg sample was pressed into a self-supported wafer. This wafer was mounted in an infrared vacuum cell with calcium fluoride windows and degassed at 450 °C for 2 h. 1.5 Torr of pyridine vapor was introduced into the cell at room temperature. The cell was elevated to 200 °C and kept for 2 h. In order to investigate the acid strength, desorption of pyridine was performed by evacuation at 200 and 400 °C, respectively. The IR peak intensities were normalized with the 1882 cm^{-1} band assigned to the Si–O overtone of the zeolite framework [13]. The FT-IR spectra were recorded at room temperature, using a Nicolet Magna-IR 560 spectrometer over the range of 1000–4000 cm^{-1} with 2 cm^{-1} resolution.

The alkylation reaction was carried out in a batch reactor with a total volume of 150 ml at 140 °C. The reaction pressure was set at 10 atm by charging with N_2 to keep the reactants and products in the liquid phase. The typical composition of reaction mixture is benzene : n-decane : 1-dodecene (molar ratio) of 8.7 : 10.0 : 1, which is very similar to the commercial mixture used in the majority of industrial processes for the manufacture of LAB. Before reaction, the catalyst was activated at 500 °C for 3 h under flow N_2, cooled down in a dry box to 150 °C, then added into the reacting mixture. The products were analyzed by GC (HP 5890 series II) using FID furnished with a SE-30 30 m capillary column.

3. Results and discussion

The results of the alkylation of benzene with 1-dodecene over various catalysts, along with those over H-mordenite as a function of catalyst loading are presented in table 1. H-ZSM-5 shows no catalytic activity in this reaction. Among five different positional phenyldodecane isomers, as for the reaction product, isomer content decreases with the carbon number (toward the center of the chain) and a little higher selectivities for the 2-phenyl isomer of 30.7 and 25.5% are observed over H-Y and H-USY, respectively. However, only two different positional phenyldodecane isomers are formed over H-mordenite with the selectivity for 2-phenyl isomer up to 85%. In table 1, the isomer distribution in the dodecylbenzene fraction of a commercial sample of LAB manufactured using anhydrous HF as the catalyst is also included for comparison. It is observed that in contrast to H-Y, H-USY and H-mordenite, the isomer content increases with the carbon number (toward the center of the chain) with selectivities from 16.7% for the 2-phenyl isomer to 25.3% for the 6-phenyl isomer. It is also presented in table 1 that with increment of catalyst loading from 0.5 to 1.0 g, the conversion for 1-dodecene over H-mordenite goes up gradually from 63.8 to 100%, whereas the selectivity for 2-phenyldodecane decreases a little from 85.0 to 78.2%.

Table 1
Benzene alkylation with 1-dodecene over various catalysts and as a function of the weight of catalyst.[a]

Catalyst, weight	Conversion[b] (%)	Selectivity for positional isomers of phenyldodecanes				
		2-Ph	3-Ph	4-Ph	5-Ph	6-Ph
HF[c]	100	16.7	16.4	17.5	24.1	25.3
H-ZSM-5, 0.5 g	0	–	–	–	–	–
H-USY, 0.5 g	100	25.5	20.3	16.5	18.8	18.7
H-Y, 0.5 g	76.0	30.7	21.6	16.8	16.0	14.8
HF-treated mordenite[d]	99.7	79.9	16.6	0.8	1.3	1.3
H-mordenite, 0.5 g	63.8	85.0	15.0	–	–	–
H-mordenite, 0.6 g	81.0	84.7	15.3	–	–	–
H-mordenite, 0.7 g	88.2	83.2	16.8	–	–	–
H-mordenite, 0.8 g	98.5	79.5	17.4	1.5	1.6	–
H-mordenite, 1.0 g	100	78.2	18.0	1.9	1.9	–

[a] Reaction conditions: 140 °C, 10 atm, 3 h, benzene : n-decane : 1-dodecene (molar ratio) = 8.7 : 10.0 : 1.

[b] Conversion is calculated based on 1-dodecene. See [7].

[c] C_{12} – alkyl benzene fraction from commercial LAB: liquid phase reaction, WHSV indeterminate.

[d] Benzene : 1-dodecene (molar ratio) = 28, from [8].

The absence of conversion over H-ZSM-5 indicates that its channel structure (0.53 × 0.56 nm and 0.51 × 0.55 nm) does not provide enough space for the formation of the bulky intermediate which would result from the electrophilic attack of the benzene ring with a secondary dodecylcarbenium ion. de Almeida *et al.* observed the same phenomenon when they applied H-ZSM-5 and H-ZSM-12 to this reaction [14]. H-ZSM-5 and H-ZSM-12 did not promote alkylation at 100 °C. At 180 °C, they exhibited a very low activity. H-ZSM-5 gave rise to 2-, 3-, 4-, 5- and 6-phenyldodecane, but only 2-phenyldodecane was formed over H-ZSM-12. The low performance of these catalysts occurred despite the presence of acid sites with number and strength at least comparable with a dealuminated H-Y zeolite, as was characterized by NH_3-TPD. The H-Y zeolite, however, exhibited a higher activity, even at 100 °C. It was suggested that the very low activity of H-ZSM-5 was due to its small pore size (0.53 × 0.56 nm and 0.51 × 0.55 nm). The channel system did not provide enough space for the formation of the bulky transition state and the alkylation was hindered. The low conversion observed was attributed to the reaction on the external surface of the zeolite crystals and this also explained why all possible isomers were found. In the case of H-ZSM-12, the alkylation reaction appeared to be not over the external surface of the particle but in the H-ZSM-12 pore system with non-connecting unidimensional pores of cross sections of dimension of 0.57 × 0.62 nm due to the absence of 3-, 4-, 5- and 6-phenyldodecane. It was suggested that product or transition state intermediate selectivity prevailed over H-ZSM-12, resulting in only the 2-phenyldodecane, the least bulky isomer.

In comparison with H-ZSM-5, the pore openings of H-mordenite, H-Y and H-USY are much bigger. It is known that H-mordenite has only unidirectional pores (0.67 ×

0.70 nm), while the H-Y and H-USY have large cavities (1.3 nm diameter) along with 3D pore systems (0.73 nm and 0.76 × 0.73 nm, respectively). With the same catalyst loading of 0.5 g, the conversions of 1-dodecene over H-USY, H-Y, and H-mordenite are 100, 76.0, and 63.8%, respectively, which is proportional to the pore aperture. So the pore aperture of a zeolite is an important factor in controlling the catalytic activity. It is believed that compared to H-USY, the relatively smaller pore size of H-mordenite restricts the diffusion of reactants and products, as well as the formation of a bulky transition state, which leads to decrease of the conversion.

The alkylation of benzene with olefins goes through a carbonium ion mechanism. In the case of dodecene, six carbonium ions are possible. The relative stabilities of carbonium ions increase as the C-number increases, for example, the least stable being the primary ion (1-position). In fact, due to its very low stability, the 1-phenyl isomer is not detected in the product. On the basis of the relative stabilities of the other carbonium ions (all secondary), it is expected that the isomer content will increase with the carbon number (toward the center of the chain). This is found to be so in the case of HF, in which thermodynamic equilibrium is probably reached. However, in the cases of H-Y, H-USY, and H-mordenite, the content of 2-phenyl isomer is greater, suggesting the non-attainment of thermodynamic equlibrium. It is pronounced in the case of H-mordenite with selectivity for the 2-phenyl isomer of up to 85.0%, due to its relatively smaller pore openings, while H-mordenite behaves so shape selective that the 4-, 5-, and 6-phenyl isomers are not formed at all. With increment of the catalyst loading from 0.5 to 1.0 g, the opportunity for reaction of reactants over external surface acid sites is increased, so selectivity for the 2-phenyl isomer decreases a little from 85.0 to 78.2%. At the same time, 4- and 5-phenyl isomers are also detected. However, the conversion for 1-dodecene over H-mordenite is improved clearly from 63.8 to 100% when the catalyst is loaded from 0.5 to 1.0 g, respectively. It is deserved to point out that even at 100% conversion, selectivity for 2-phenyl isomer is 78.2%, much higher than that over H-USY of 25.5% due to their different structural characteristics. High selectivity for the 2-phenyl isomer and high conversion over H-mordenite make it applicable to selective production of the 2-phenyl isomer, the most desirable product in detergency sector.

On the other hand, it is observed that with the increase of benzene to 1-dodecene ratios from 7 : 1 to 10 : 1, the conversion increases from 56.2 to 98.0%. Meanwhile, the selectivity for the 2-phenyl isomer decreases from 88.0 to 83.3%. As this reversible reaction reaches equilibrium state, the increase of the amount of benzene leads to the increase of conversion for 1-dodecene. At the same time, the isomerization of 2-phenyl isomer to 3-phenyl isomer results in a little decrease of its selectivity.

In order to understand the relationship between acidic properties and catalytic activities and to improve the selectivity for the 2-phenyl isomer, H-mordenite is modified by Mg^{2+} and Fe^{3+} ion exchange. As seen in table 2, Mg^{2+} and Fe^{3+} ion exchange leads to a decrease of conversion from 63.8 to 4.0 and 21.4%, respectively, but they favor formation of 2-phenyldodecane, with selectivity of 100 and 90.3%, respectively. It is expected that Mg^{2+} and Fe^{3+} ion exchange reduces acid strength and decreases its number as well, which leads to the decrease of conversion and lowers the opportunity for 2-phenyldodecane to isomerize to other isomers. The clogging effect of MgO and Fe_2O_3, which seem to be formed during solid-state ion exchange at high temperature, in the zeolite channel is also probably attributed to the increase of selectivity for less bulky 2-phenyldodecane.

Table 2
Benzene alkylation with 1-dodecene over dealuminated H-mordenite and Mg^{2+}- and Fe^{3+}-ion-exchanged H-mordenite.[a]

Catalyst	Conversion[b] (%)	Selectivity for positional isomers of phenyldodecanes (%)				
		2-Ph	3-Ph	4-Ph	5-Ph	6-Ph
H-mordenite	63.8	85.0	15.0	–	–	–
Mg–H-mordenite (1 wt% Mg)	4.0	100	–	–	–	–
Fe–H-mordenite (1 wt% Fe)	21.4	90.3	9.7	–	–	–
H-mordenite (2 N)[c]	57.3	86.1	13.9	–	–	–
H-mordenite (4 N)[c]	22.7	89.4	10.7	–	–	–

[a] Reaction conditions: 140 °C, 10 atm, 3 h, benzene : n-decane : 1-dodecene (molar ratio) = 8.7 : 10.0 : 1.

[b] Conversion is calculated based on 1-dodecene.

[c] H-mordenite (2 N) and H-mordenite (4 N) represent that H-mordenite is dealuminated by 2 and 4 N HNO_3.

Compared to H-Y and H-USY, the relatively smaller pore openings of H-mordenite restrict the formation of bulky intermediate and limit its catalytic activity in benzene alkylation with 1-dodecene. So H-mordenite was dealuminated by HNO_3 to widen the pores in order to increase the conversion of 1-dodecene [12]. As we could see in table 2, after dealumination by 2 and 4 N HNO_3, the conversions over these two dealuminated H-mordenite zeolites decrease to 57.3 and 22.7%, respectively. Micropore analysis shows that the pores of dealuminated H-mordenite (2 N) and H-mordenite (4 N) increase a little from H-mordenite's 0.65 to 0.67 and 0.68 nm, respectively. Also it is characterized by XRD that the crystallinities of the samples before and after dealumination by 2 and 4 N HNO_3, respectively, have no apparent difference. So, it is interpreted that it is the removal of acid sites by dealumination with HNO_3 which causes the decrease of conversion.

FT-IR spectra of four different samples (H-mordenite, Fe–H-mordenite, Mg–H-mordenite and H-mordenite (4 N)) in the range of the hydroxyl group are shown in figure 1(A). The spectrum of H-mordenite contains two main bands at 3610 and 3745 cm^{-1}. The band at 3610 cm^{-1} is associated with the acidic OH group (–Si–OH–Al–) and the 3745 cm^{-1} band with the terminal, non-acidic OH group bound to the silicon framework [12]. In the cases of Fe–H-mordenite and H-mordenite (4 N), the intensity of the band at 3610 cm^{-1} is reduced and new bands at 3665 cm^{-1} in both cases and

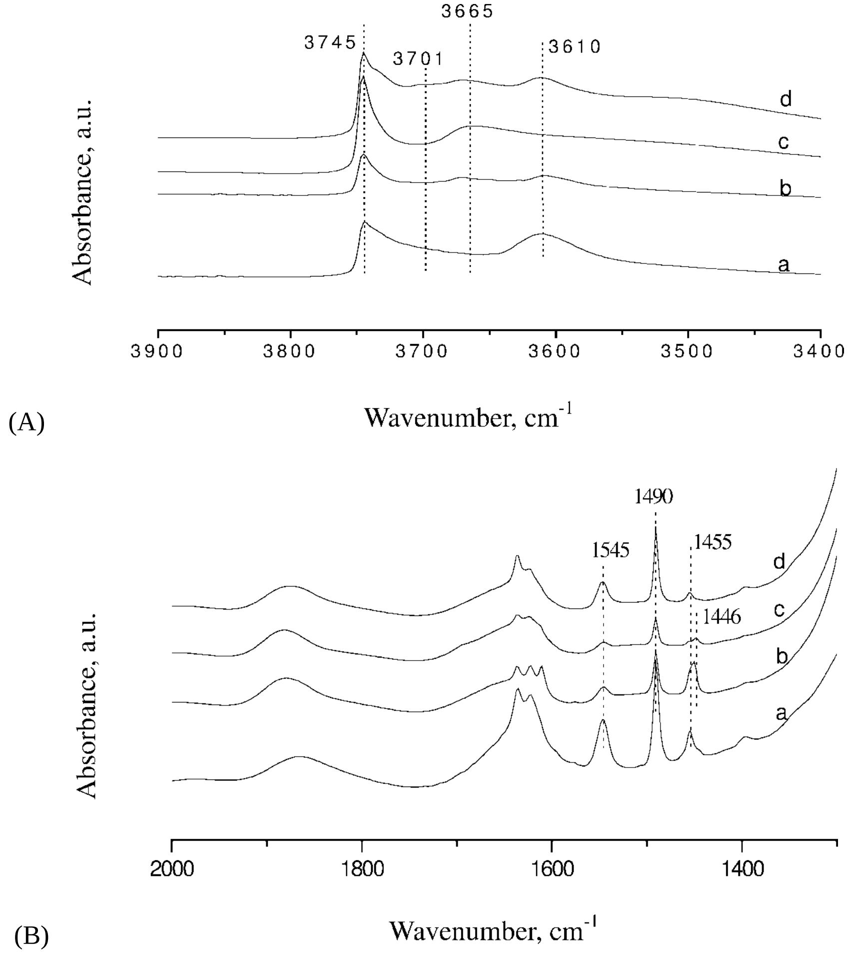

Figure 1. (A) FT-IR spectra of the hydroxyl vibration region for (a) H-mordenite, (b) Fe–H-mordenite, (c) Mg–H-mordenite, and (d) H-mordenite (4 N). (B) FT-IR spectra of pyridine adsorbed (a) H-mordenite, (b) Fe–H-mordenite, (c) Mg–H-mordenite, and (d) H-mordenite (4 N).

3701 cm^{-1} only in the case of H-mordenite (4 N), assigned to hydroxyls linked to aluminum atoms dislodged from the framework, are also detected. It is exhibited in figure 1(A) that after Mg^{2+} ion exchange, the band at 3610 cm^{-1} totally disappears and the band at 3665 cm^{-1}, assigned to hydroxyls linked to aluminum atoms dislodged from the framework, appears. It is reported that OH vibration at 3610 cm^{-1} represents strong acid sites and the intensity of this band is proportional to strong acid site [2]. When H-mordenite is exchanged by Mg^{2+} and Fe^{3+} ions, or dealuminated by HNO$_3$, this band disappears, or the intensity of this band is reduced, respectively, which indicates the above modification methods cause the loss of strong acid sites. However, the above modification methods do not influence the non-acidic OH band at 3745 cm^{-1} apparently.

Generally, the acidity of a catalyst influences product distribution as well as catalytic activity. Using pyridine as a probe molecule, we can discriminate between Brønsted and Lewis acid sites and calculate the number of each acid center. Figure 1(B) shows the FT-IR spectra of pyridine adsorbed H-mordenite, Mg^{2+} and Fe^{3+} ion exchanged H-mordenite and dealuminated H-mordenite (4 N), respectively. For pyridine adsorbed samples, the acidic OH bands disappear; however, the non-acidic OH bands retain the same intensity. In the region 1400–1600 cm^{-1} three sharp bands due to C–C stretching vibrations of pyridine are observed. The band at 1490 cm^{-1} is due to the pyridine adsorbed on both Brønsted and Lewis acid sites. The IR bands at 1545 and 1455 cm^{-1} assigned to pyridinium ions and coordinatively bound pyridine, respectively, were used to calculate the relative bulk concentrations of Brønsted and Lewis acid sites, based on the integrated absorbances [15]. The Mg^{2+} ion in the zeolite shows a characteristic infrared band at 1446 cm^{-1} after pyridine adsorption. And also, in order to investigate the acid strength, desorption of pyridine was performed by evacuation at 200 and 400 °C. It is assumed that the stability of pyridine complexes in zeolites is consistent with the order of the strength of acid sites [16]. So it is designated that acid centers evacuated at 200 and 400 °C represent weak and strong acid sites, respectively. The relative concentration of each type of acid site determined by pyridine adsorption/desorption FT-IR is calculated in table 3, based on the relative concentration of the sum of Brønsted and Lewis acid sites of H-mordenite, which is adopted as the standard and normalized to 100.

As regards the active sites in alkylation of aromatics or substituted aromatics with olefins, either Brønsted acid sites/Lewis acid sites or a combination of them are believed

Table 3
Relationship between the conversion and the relative concentration[a] of Brønsted and Lewis acid sites for pyridine adsorbed catalysts in terms of the evacuation temperature.

Catalyst	Conversion (%)	Weak, 200 °C[b]			Strong, 400 °C[b]		
		B	L	B + L	B	L	B + L
H-mordenite	63.8	72	32	104	73	27	100
Mg–H-mordenite (1 wt% Mg)	4.0	22	3	25	3	3	6
Fe–H-mordenite (1 wt% Fe)	21.4	46	28	74	3	46	49
H-mordenite (4 N)	22.7	105	22	127	31	6	37

[a] The numbers are the relative values normalized by strong B + L of H-mordenite as 100. (B = Brønsted acid sites, L = Lewis acid sites.)
[b] Evacuation temperature.

as active sites [17,18]. As shown in table 3, the conversions over H-mordenite and H-mordenite (4 N) are 63.8 and 22.7%, respectively. However, the number of weak Brønsted acid sites of H-mordenite (4 N) is 105, higher than 72 of H-mordenite, and this is in contradiction with the conversion. As regards the Lewis acid sites, the numbers of weak Lewis acid sites in H-mordenite, Fe–H-mordenite and H-mordenite (4 N) are 32, 28 and 22, respectively. The difference among them does not correlate well with the difference of conversion over these catalysts of 63.8, 21.4, and 22.7%, respectively. As it is the same case, in regard of strong Brønsted or Lewis acid sites, separately, the contradiction between number of acid centers and conversion is apparent. However, if both strong Brønsted and Lewis acid sites are assumed as active sites, the sum of the numbers of these two kinds of acid centers exhibits a most similar trend with the conversion. So, it can be suggested that both strong Brønsted and Lewis acid sites are favorable for this reaction. For H-mordenite with SiO_2/Al_2O_3 of 35, the concentration of aluminum ions as potential acid sites is theoretically estimated about 83×10^{-5} mol/g. By assuming charge balance between AlO_2^-, Fe^{3+} and Mg^{2+}, one Fe^{3+} ion should substitute three protons and one Mg^{2+} ion substitute two protons during the solid state ion exchange. The degrees of exchange by Mg^{2+} and Fe^{3+} are about 100 and 66%, respectively. Certainly, the solid-state reaction cannot proceed completely. But Mg^{2+} ion exchange results in much decrease of acid sites of parent zeolites and this leads to drastic decrease of conversion. Furthermore, the two main reasons attributed for the differences in product distributions in benzene alkylation with 1-dodecene are: (1) the existence of two equilibration steps, one for the olefin (1-dodecene) and another for the phenyldodecanes, and (2) the differences in the rates of the two reactions (olefin isomerization and alkylbenzene isomerization) [19]. Much loss of strong acid sites in Mg–H-mordenite reduces the opportunity for 1-dodecene isomerization and phenyldodecane isomerization, which leads to the higher selectivity for the 2-phenyl isomer. It is also observed that Fe^{3+} ion exchange induces the formation of many strong Lewis acid sites, which could overcome its loss of strong Brønsted acid sites to some extent.

4. Conclusions

Benzene alkylation with 1-dodecene was carried out over H-ZSM-5, H-USY, H-Y, H-mordenite, and modified H-mordenite zeolites. The conclusions are as follows:

(1) It is observed that the conversion of 1-dodecene is proportional to the pore apertures of the zeolites, which evidences that pore size of zeolite is an important factor in controlling activity. Furthermore, among all the catalysts applied in this study, H-mordenite shows the highest selectivity for 2-phenyldodecane, of over 78.2%, owing to its medium pore size and one-dimensional pore opening system. Meanwhile, the conversion over H-mordenite could be enhanced by increasing the catalyst amount and the molar ratio of benzene to 1-dodecene.

(2) It is characterized by FT-IR that both strong Brønsted and Lewis acid sites are favorable for this reaction. Mg^{2+} ion exchange results in much decrease of strong acid sites of parent zeolites, and this leads to drastic decrease of conversion and higher selectivity for the 2-phenyl isomer. However, it is observed that Fe^{3+} ion exchange induces the formation of some strong Lewis acid sites, which could overcome its loss of strong Brønsted acid sites to some extent. Dealumination with nitric acid has no apparent influence on the aperture of H-mordenite, but decreases the number of strong Brønsted and Lewis acid sites, which leads to decrease of conversion.

References

[1] R.T. Sebulsky and A.M. Henke, Ind. Eng. Chem. Process Des. Dev. 10 (1971) 272.
[2] T.J.L. Berna and D.A. Moreno, Eur. Pat. Appl. EP 0 353 813 (1991).
[3] L.B. Young, US Patent 4 301 317 (1981).
[4] Y. Cao, R. Kessas, C. Naccache and Y. Ben Taarit, Appl. Catal. A 184 (1999) 231.
[5] M.Y. He, Z.H. Li and M. Enze, Catal. Today 2 (1988) 321.
[6] I. Wang, S.J. Li and J.Y. Liu, in: *Int. Symp. Zeolites and Microporous Crystals*, Sendai, Japan, 2 LC 01, 6–9 August 2000.
[7] J.F. Knifton, P.R. Anantaneni and M. Stockton, US Patent 5 770 782 (1996).
[8] P.R. Anantaneni, US Patent 6 133 492 (2000).
[9] P.R. Anantaneni, US Patent 6 166 281 (2000).
[10] H.G. Karge, Stud. Surf. Sci. Catal. 105 (1997) 1901.
[11] H.G. Karge and H.K. Beyer, Stud. Surf. Sci. Catal. 69 (1991) 43.
[12] P. Wu, T. Komatsu and T. Yashima, J. Phys. Chem. 99 (1995) 10923.
[13] C.D. Chang, C.T.-W. Chu, J.N. Miale, R.F. Briger and R.B. Calvert, J. Am. Chem. Soc. 106 (1984) 8143.
[14] J.L.G. de Almeida, M. Dufaux, Y.B. Taarit and C. Naccache, Appl. Catal. A 114 (1994) 141.
[15] R. Borade, A. Sayari, A. Adnot and S. Kaliaguine, J. Phys. Chem. 94 (1990) 5989.
[16] J. Datka and E. Tużnik, J. Catal. 102 (1986) 43.
[17] K. Zhang, C.H. Huang, H.B. Zhang, S.H. Xiang, S.Y. Liu, D. Xu and H.X. Li, Appl. Catal. A 166 (1998) 89.
[18] V.C. Hand and G.K. Williams, Envirron. Sci. Technot. 9 (1990) 1245.
[19] H.R. Alul, Ind. Eng. Chem. Prod. Res. Dev. 7 (1968) 7.