Catalysis Letters 59 (1999) 55–60

Synthesis of 1-phenyl-1-xylyl ethane by Friedel–Crafts alkylation of xylene with α-methylbenzyl alcohol over mordenite

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Received 9 November 1998; accepted 16 March 1999

In the Friedel–Crafts alkylation of xylene to prepare 1-phenyl-1-xylyl ethane (PXE), α-methylbenzyl alcohol was used as an alkylating agent over a mordenite catalyst. The catalyst was characterized by MAS-NMR, N_2 adsorption/desorption, NH_3-TPD, and various other techniques and was found to possess strong Brønsted acid sites. When temperature was low, the main product was bis-(α-methylbenzyl) ether. However, as the temperature went up, PXE and heavies, styrene trimers and heavier oligomers, became main products. The formation of PXE, occurring on strong acid sites, is favored by raising temperature, space velocity, pressure, and xylene/MBA ratio within the experimental ranges. As the catalyst deactivates, the selectivities to PXE and heavies decrease and those to linear dimer and styrene increase. A reaction mechanism is proposed.

Keywords: Friedel–Crafts alkylation, 1-phenyl-1-xylyl-ethane, α-methylbenzyl alcohol, mordenite

1. Introduction

1-phenyl-1-xylyl ethane (PXE) is a colorless synthetic liquid with many excellent properties suitable for various applications, e.g., a solvent for pressure-sensitive record materials, plasticizer, heating medium, electric-insulating oil, and high-boiling solvent. For years it has been synthesized by the alkylation of xylene with styrene over sulfuric acid [1,2] sulfated zirconia [3], silica–alumina [4], and zeolites [5]. When the mineral acid is used as a catalyst, low temperatures (about 0 °C) should be employed to suppress the oligomerization of styrene. In this case, the process always is accompanied by serious waste disposal problems. One alternative to avoid these nuisances is to use solid acid catalysts. When solid acid catalysts are used, higher ratios of xylene to styrene ($\geqslant 10$) and low space velocities ($<1\ \mathrm{h}^{-1}$) should be adopted to minimize the deactivation of the catalysts and to achieve higher yields at elevated temperatures [4]. However, even under these controlled reaction conditions, the catalysts deactivate rather rapidly; a frequent regeneration is unavoidable to remove heavy byproducts formed by the oligomerization of styrene.

Recently, several studies on the Friedel–Crafts alkylation of hydrocarbons by using aromatic alcohols as alkylating agents have been reported [6–9]. For example, Sun et al. [7] studied the alkylation of benzene and xylene with p-methylbenzyl alcohol over various acid catalysts. Over a Nafion resin/silica nanocomposite catalyst in p-xylene, a remarkable alkylate yield of 97% was obtained at 100 °C after 1 h in a batch reactor. This high chemoselectivity to the desired products and relatively higher stability of aromatic alcohols than their olefin counterparts under severe reaction conditions make them substitutes for olefins [6,9]. We, in this paper, investigated a novel heterogeneous reaction system where α-methylbenzyl alcohol (MBA) instead of styrene was reacted as an alkylation agent with xylene in the synthesis of PXE. As a solid catalyst, a proton form of commercial mordenite was used since it has relatively strong acid sites and 12-membered ring large pores that facilitate the transport of bulky reaction products. The acid nature as well as other properties of the catalysts were characterized with temperature-programmed desorption of ammonia (NH_3-TPD), ^{27}Al and ^{29}Si MAS-NMR, FTIR spectroscopy of adsorbed pyridine, nitrogen adsorption/desorption and various other techniques and were correlated with catalytic performance.

2. Experimental

An H form of mordenite, HMOR, as cylindrical extrudates ($1/8''$) was obtained from UOP and was used as received.

^{27}Al and ^{29}Si spectra were recorded by using magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR, Bruker AVANCE DRX 500 with a Bruker 7 mm CP/MAS probe), as reported elsewhere [10]. Acidic properties were characterized with NH_3-TPD (Altamira AMI-1 with an AMETEK quadrupole mass spectrometer) following the method of Kwak and Sachtler [11,12] and with FT-IR spectroscopy (Nicolet, Magna-IR 750) of adsorbed pyridine. Before taking the IR spectra at 350–450 °C, the sample was calcined at 400 °C for 1 h under Ar flow followed by cooling to room temperature. Then the pyridine vapor was introduced to a high-pressure transmittance sample cell at the same temperature. The catalyst was

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further characterized with XRD (MAC M03XHF, Cu Kα at 40 kV and 40 mA), XRF (Philips, type 9430), and ICP (GBC, model 1250).

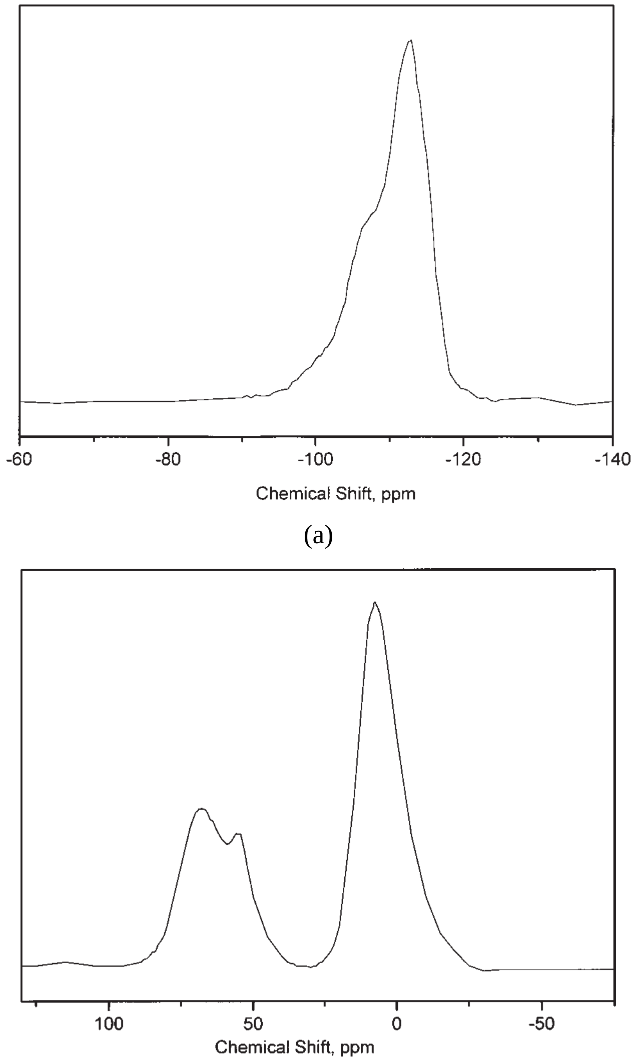
Reaction tests were carried out at reaction temperatures between 100 and 200 °C, volumetric ratios of m-xylene (Yakuri Pure, 99%) to MBA (Aldrich, 98%) between 5 : 3 and 7 : 1, and weight hourly space velocities (WHSV) between 1.8 and 4.5 h^{-1} using a full automatic continuous fixed-bed reaction system (AMI-1000, Altamira). The reaction pressure was also varied between 30 and 670 psig. Argon was used as a carrier gas with the volume ratio of argon (gas volume) to hydrocarbons (MBA + xylene, liquid volume) set at 100. Products were analyzed with a Hewlett–Packard 5890A gas chromatograph equipped with a FID (PONA column, 50 m × 0.32 μm × 0.3 mm ID). Chemical structures of the products were identified using 200 MHz ^{1}H-NMR (Varian, Gemini 200), FTIR, and GC-MS (Finnigan MAT, INCOS XL).

3. Results and discussion

3.1. Characterization

The XRD pattern of the HMOR sample represented the characteristic peaks of the zeolite MOR although there exists a large fraction of amorphous alumina (data not shown here). The bulk Si/Al ratio of the HMOR is analyzed to be 0.8.

MAS-NMR spectra of ^{29}Si and ^{27}Al are shown in figure 1 (a) and (b). At −112.2 and −107.5 ppm, the Q_4 resonances of $Si(OSi)_4$ and $Si(OSi)_3(OAl)$ were detected for HMOR (figure 1(a)). A shoulder at ca. –102 ppm is attributed to the Q_4 resonance of $Si(OSi)_2(OAl)_2$ as in the literature [13]. Figure 1(b) shows the ^{27}Al MAS-NMR spectrum for HMOR. Three peaks are observed at 7.7, 54.5, and 67.9 ppm, respectively. A peak at 7.7 ppm, which was found at −1 ppm for a mordenite sample with the Si/Al ratio of 11 [13], is assigned to octahedral Al ions. Considering the shift of resonances of about 9 ppm, the peak at 67.9 ppm is attributed to tetrahedrally coordinated Al^{3+} ions in the framework positions of the catalyst. At this moment the nature of the peak at 54.5 ppm is not clear. However, in analogy to the finding by Samoson and coworkers [14] of similar peaks at about 44–46 ppm for hydrothermally treated HY samples, we attribute this peak to tetrahedrally coordinated Al ions at nonframework positions. The alumina used as a binder is believed to be a source for these ions and octahedral ions. Assuming that the parent mordenite is highly crystalline, the ratio of zeolitic Al ions to non-zeolitic Al ions is calculated to be 2.0 based on the ^{27}Al MAS-NMR data. Consequently, the HMOR sample is composed of 48 wt% of mordenite and 52 wt% of amorphous alumina, which agrees well with the information supplied by the manufacturer (binder content: about 50%).



(a)

(b)

Figure 1. (a) ^{29}Si MAS-NMR and (b) ^{27}Al MAS-NMR spectra of HMOR.

Figure 2 shows the FTIR spectra of adsorbed pyridine against purge temperature. At room temperature, three peaks are observed at the wavenumbers of 1,545 (Brønsted acid sites), 1,490 (a combination of Brønsted and Lewis acid sites), and 1,445 cm^{-1} (Lewis acid sites), respectively [15]. As the purge temperature is raised, the peak at 1,545 cm^{-1} is shifted towards lower wavenumbers and the intensity decreases. However, the peak intensity did not change appreciably even after purging for more than an hour at 450 °C suggesting the catalyst has very strong Brønsted acid sites.

The NH_3-TPD spectra of the mordenite samples with and without binders are shown in figure 3. In the case of a binderless sample (trace (a)), two peak maxima are found at 285 and 565 °C. As discussed by us from the results of the NH_3-TPD and ^{27}Al MAS-NMR [10], the TH peak at 565 °C results from the ammonia desorbed from Brønsted acid sites. A peak at a temperature of 285 °C is attributed to the ammonia desorption from non-zeolitic sites [11,12,16]. Two peaks at similar temperatures are also detected for the HMOR extrudate sample. A rather intense peak at 290–295 °C is assigned to result from sites

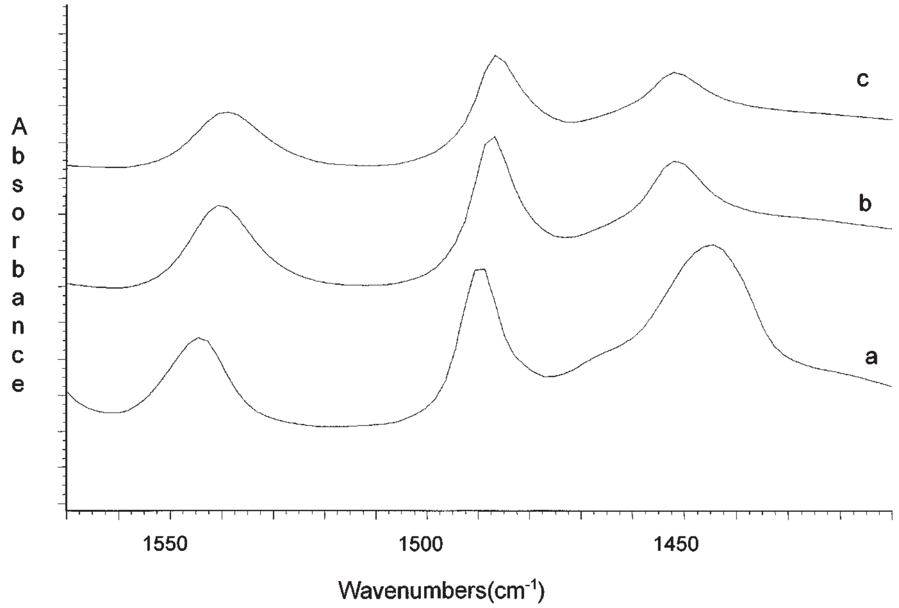


Figure 2. FTIR spectra of pyridine adsorbed on HMOR. The sample was purged at (a) room temperature, (b) 350 °C, and (c) 450 °C after pyridine adsorption at room temperature.

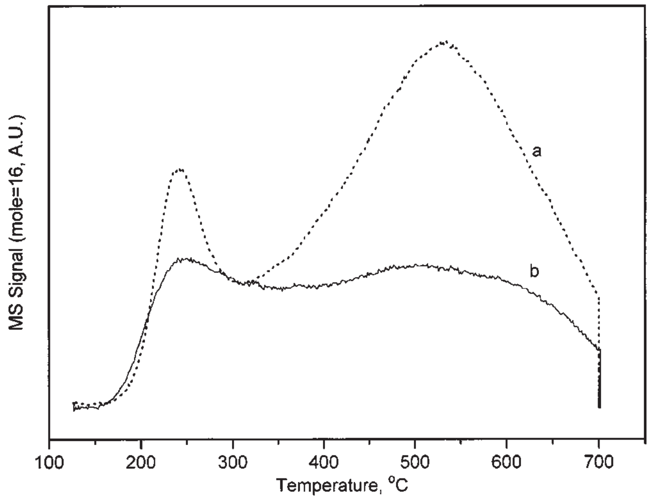


Figure 3. NH_3-TPD spectra of (a) HMOR (Si/Al = 45, binderless) and (b) HMOR (extrudate).

of the alumina which was used as a binder and another very broad peak at 560–570 °C to the presence of Brønsted acid sites. It is noteworthy that in the case of the HMOR extrudates the intensity ratio of the second peak to the first peak has been decreased considerably compared with that of the binderless sample. From the position of the peak maximum, the acid strength of the two HMOR samples is much stronger than that of HZSM-35 [10], which is in accordance with the FTIR results. The nitrogen adsorption/desorption results indicate that the BET surface area of the HMOR (extrudate, 387 m^2/g) is in between those of common alumina and mordenite samples. Of the total surface area, the contribution from non-zeolitic mesopores is estimated to be 41% from the t-plot analysis [17]. The pore volume of the sample (0.460 cm^3/g) is also larger than that of an ordinary binderless mordenite sample.

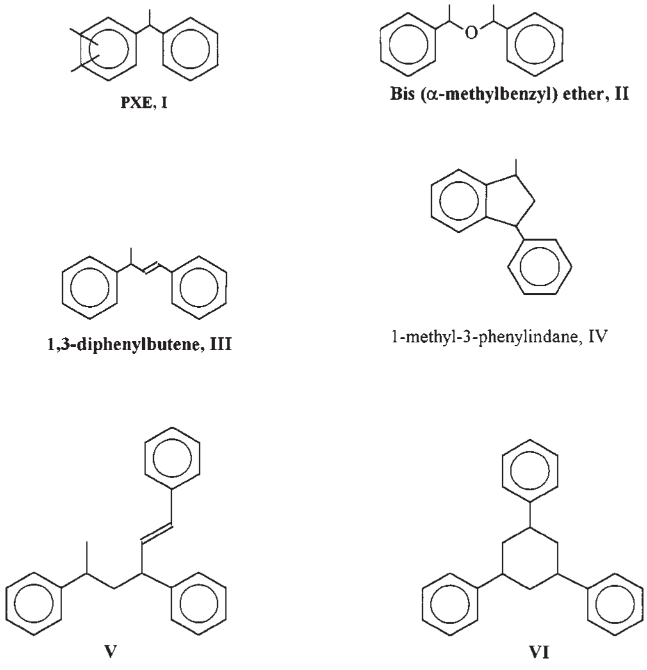
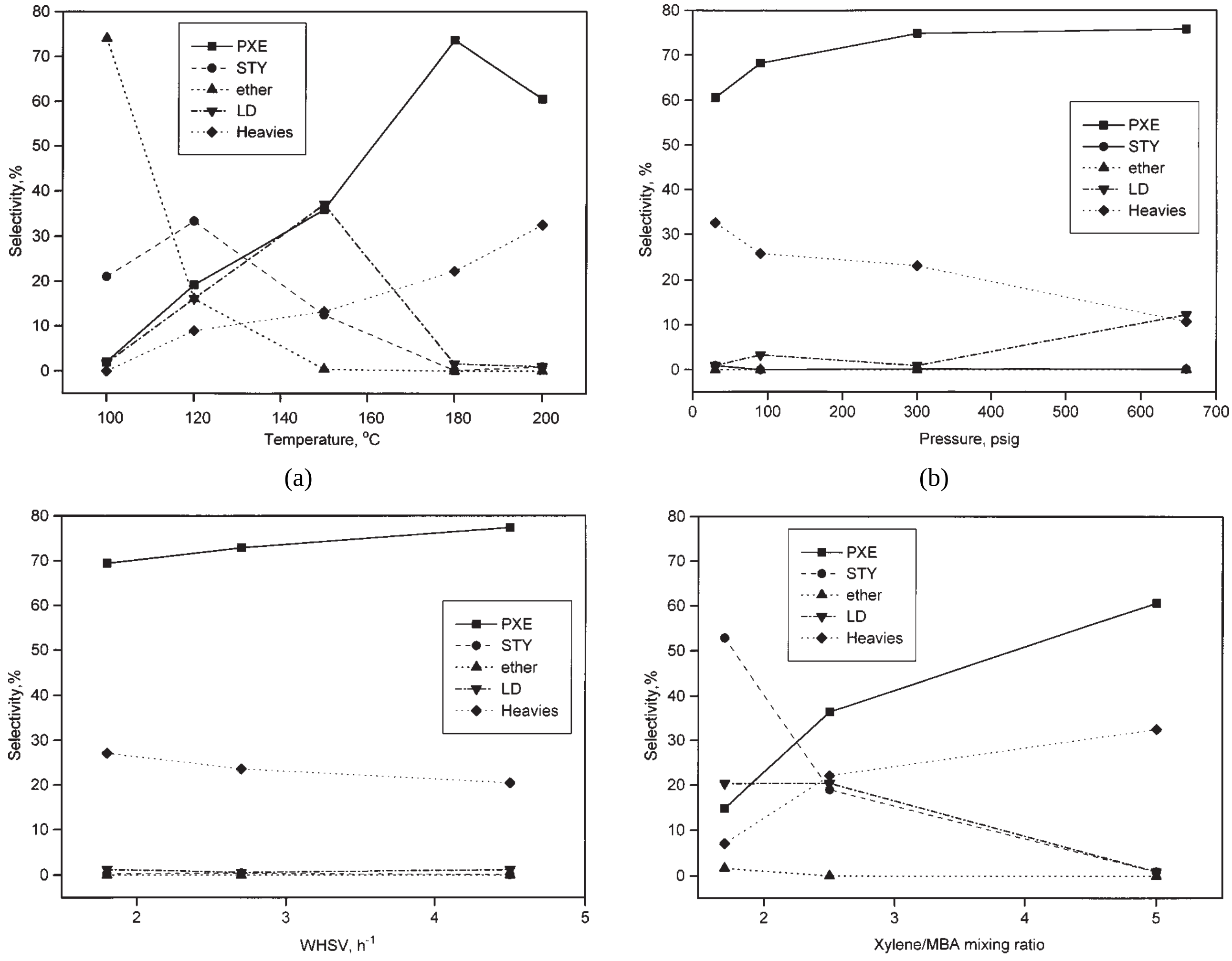


Figure 4. Structures of the products from the Friedel–Crafts alkylation of MBA and xylene.

3.2. Alkylation

When MBA was reacted with xylene over mordenite, major products were PXE (I), ether (bis(α-methylbenzyl) ether (II)), styrene, styrene dimers (III, IV)), and heavies (styrene trimers (V, VI) and heavier oligomers), as shown in figure 4; the relative compositions of these products change depending on the reaction conditions.

Figure 5(a) shows the effect of temperature on the product distribution. When the temperature and pressure are low, the ether is formed with the highest selectivity of



(a) (b)

(c) (d)

Figure 5. Effect of reaction variables on selectivities: (a) temperature (P: 30 psig, WHSV: 4.5 h^{-1}, xylene/MBA ratio: 5); (b) pressure (T: 200 °C, WHSV: 4.5 h^{-1}, xylene/MBA ratio: 5); (c) WHSV (T: 200 °C, P: 30 psig, xylene/MBA ratio: 5); (d) xylene/MBA ratio (T: 200 °C, P: 30 psig, WHSV: 4.5 h^{-1}).

ca. 75%. An ether having a similar structure was also formed in the case of alkylation of toluene with cinnamyl alcohol [9]. As the temperature is increased, the selectivity to ether decreases sharply while that to styrene goes through a maximum value at 120 °C suggesting the ether is a reaction intermediate. Upon elevating the temperature, the selectivity to PXE increases up to a temperature of 180 °C. The selectivity to linear dimer (LD, III) also shows a maximum value at 150 °C while that to heavies increases with temperature indicating that the linear dimer is a reaction intermediate to heavies. As a consequence, it can be concluded that on acidic sites the reaction proceeds in a parallel mode where either xylene or styrene reacts competitively with styrene or an intermediate (see figure 7) to form PXE or the linear dimer that further reacts with styrene to make heavies.

The effect of pressure on the product distribution is shown in figure 5(b). The selectivity to PXE increases with pressure while that to heavies decreases noticeably with pressure. Especially at 300 psig, the selectivity to PXE of about 75% is obtained. When the pressure is high, the formation of the ether is not observed. It should be noted that the selectivity to the linear dimer increases with pressure without leading to the increase in the selectivity to heavies. Particularly, the reaction is calculated to occur in the liquid phase when the pressure is 670 psig. In this case, it is interpreted that the liquid phase hinders the formation of heavier by-products [4].

The space velocity and xylene to MBA ratio also affect the selectivities to products (figure 5 (c) and (d)). As the space velocity is increased from 1.8 to 4.5 h^{-1}, the selectivity to PXE increases almost linearly whereas that to heavies decreases constantly. The selectivity to PXE also increases with the ratio of xylene to MBA as the collision probability between MBA and xylene gets higher with the ratio.

In figure 6 are plotted the conversion of MBA and the selectivities to products vs. time on stream. The HMOR catalyst maintains its activity for more than 40 h but gradually deactivates afterwards. PXE and heavies are the major

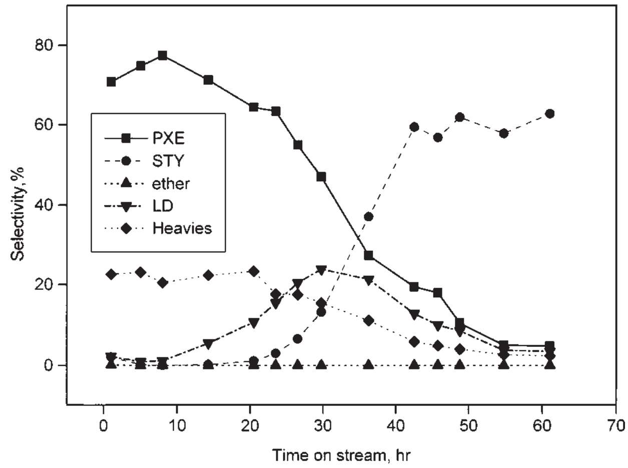


Figure 6. Plot of conversion and selectivities to products vs. time on stream (P: 100 psig, WHSV: 4.5 h^{-1}, xylene/MBA ratio: 5).

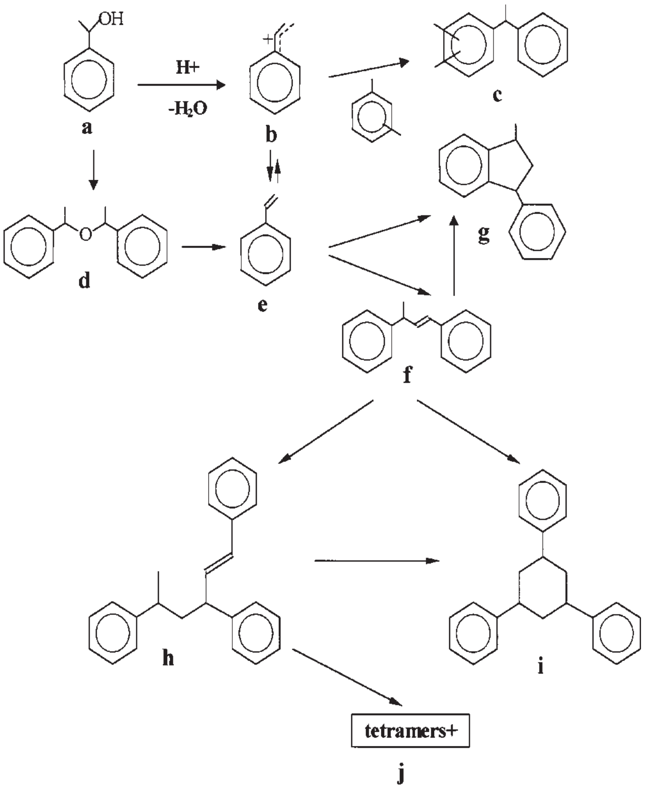


Figure 7. Reaction mechanism of Friedel–Crafts alkylation of xylene and MBA.

products at the start of the run and all other by-products are virtually negligible. Up to 20 h on stream, the selectivities to these two main products do not vary much with time on stream. As the activity of the catalyst decays, the selectivity to linear dimer begins to increase rapidly, passes through a maximum at 30 h on stream and then drops rather rapidly with time accompanied by the increase in the selectivity to styrene. Accordingly, it is concluded that the formation of PXE and heavies occurs on relatively strong acid sites. With the progress of the reaction, the heavy by-products formed block these sites, thereby leading to the decrease in the selectivities to PXE and rather bulky heavies. On the other hand, the selectivity to linear dimer is not at all affected for the time being indicating that the formation of linear dimer either requires relatively weak acid sites or occurs non-catalytically.

From the above results, a reaction mechanism is proposed, as shown in figure 7. MBA is first protonated and dehydrated to form the species **b** which then reacts with xylene to produce PXE on strong acid sites of the mordenite, not on the Al ions of the alumina used as the binder. This result is fully supported by our experimental results over various aluminas where the formation of PXE is almost negligible. In an experiment with a binderless sample (not shown here), more PXE and less dimers are formed, suggesting that the presence of the amorphous alumina binder contributes to a certain degree in the formation of the dimers. At lower temperatures, styrene is formed from the decomposition of the ether (figure 5(a)). As soon as styrene is formed, it either is protonated and reacts to form PXE on strong acid sites [1] or readily oligomerizes to form dimers (**f**, **g**) on mild acid sites or non-catalytically [18]. Among the dimers, 1,3-diphenylbutene (**f**) is predominant over HMOR unlike other literature data [19]. On the other hand, when sulfuric acid was used as a catalyst in our blank run with styrene at atmospheric pressure and 0 °C, the major product was 1-methyl-3-phenylindane (**g**) with the selectivity of almost 100%. It is also known that the dimer distribution is influenced by the polarity of the solvent depending on the catalyst [18]. As the HMOR catalyst possesses very strong acid sites (figures 2 and 3), the preferential formation of the linear dimer is attributed to the spatial constraints of the zeolite rather than the acid strength requirements. The dimers formed then further react with styrene and are converted to heavies on these strong acid sites. As the channels of the HMOR are composed of 12- and 8-membered rings having a maximum diameter of $\sim$7 Å, the bulky heavy oligomers are believed to form at the external surface of the HMOR, which has shown to possess many mesopores from the t-plot analysis.

In this study, we have shown that even under more severe reaction conditions, i.e., lower xylene to alkylating agent ratios and higher temperatures, than usually adopted in homogeneous reaction systems, high selectivity to PXE ($\sim$75%) can be obtained by using α-methylbenzyl alcohol instead of styrene in the Friedel–Crafts alkylation of xylene over a large pore zeolite. The presence of strong acid sites is a prerequisite for the formation of PXE. The formation of PXE is found to be favored by raising temperature, space velocity, pressure, and xylene/MBA ratio within the experimental ranges investigated. Also the channel structure of the HMOR prohibits the bulky styrene oligomers from forming in the channels thus enhancing the selectivity to PXE. This conclusion is supported by a series of experiments using binderless HMOR, HMFI, HBEA, and HY where toluene was used instead of xylene, which will be published elsewhere [20]. In this study, an HMOR catalyst showed the best performance among four zeolites. It is conjectured that the heavy oligomers, main by-products consisting of styrene trimers or heavier oligomers, are formed mainly on the external surface sites of the mordenite catalyst.

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