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NOTE

Skeletal Isomerization of 1-Butene on 10-Member Ring Zeolite Catalysts

Effects of zeolite pore structure on skeletal isomerization of 1-butenes are investigated. Three 10-member ring zeolites, ferrierite, ZSM-23, and ZSM-5, are studied and compared. Results show that ferrierite, with intersecting 10-MR and 8-MR channels, has better isomerization activity than ZSM-23, with monodirectional 10-MR channels, ZSM-5 with two intersecting 10-MR channels is not a selective isomerization catalyst.

Skeletal isomerization of *n*-butenes has emerged as an attractive route to provide isobutylene for the manufacture of methyl *tert*-butyl ether, an important oxygenate used in reformulated gasoline. Several papers and patents have discussed such reaction on amorphous and zeolite catalysts (1–5). Because of their unique pore structures, zeolite catalysts have proven superior to amorphous catalysts in suppressing the side reactions, e.g., oligomerization, cracking, H-transfer, and coking. Acidity and pore size are the two important parameters for consideration when choosing a selective zeolite catalyst. It has been shown that the isomerization activity of ZSM-5 (MFI) could be improved by substituting aluminum with boron to reduce its acidity (4). However, the improvement is limited because the pore size of MFI is too big. Here we report the effects of pore size on the skeletal isomerization of 1-butene; three 10-member ring zeolites, ferrierite (FER), ZSM-23(MTT), and MFI, are studied and compared.

A sample, HSZ-720KOA, of FER in the Na/K form was obtained from TOSOH USA, Inc. The zeolite contained 1.5% of Na_2O and 5.6% of K_2O. A sample, CBV 1502, of MFI in the H form (0.024% content of Na_2O) was obtained from The PQ Corporation. A sample of MTT in the Na form was prepared according to patent procedures (6). The samples of FER and MTT were ion exchanged twice with ammonium nitrate and then calcined in air at 600°C for 4 h. The calcined H–FER contained 0.12% of K and <0.05% of Na, the calcined H–MTT contained <0.05% of Na, and both samples have been characterized extensively by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and temperature-programmed desorption (TPD) techniques (7, 8). The sample of H–MFI was also calcined under the same conditions. The calcined samples were compressed to form granules and sized to 20–40 mesh fraction for catalytic testing. About 1 g sample was loaded to a 0.5″ (1.27 cm) ID S.S. tube reactor. The catalyst was heated to reaction temperature in flowing nitrogen and then a 1/1 (mole ratio) mixture of 1-butene (99.5%) and nitrogen was passed over the catalyst. Table 1 is a list of zeolites and run conditions. During the reaction the product stream was analyzed by an on-line GC system every hour.

Figure 1 shows catalytic results by plotting isobutylene yield vs conversion. The double-bond isomerization of 1-butene to 2-butenes rapidly reaches equilibrium under reaction conditions; the conversion is calculated by grouping three *n*-butenes together. The initial conversions of FER, MTT, and MFI are all very high: 71.9, 66.0, and 73.3%, respectively. The thermodynamic equilibrium of isobutylene at 420°C is calculated to be 48% and it decreases at higher temperatures. Side reactions will become dominant if the conversion is higher than 48%. At the end of run the conversion decreases to 41.8, 52.3, and 68.7%, respectively. However, the isobutylene yield of FER increases rapidly from 25.3% to a maximum of 39.0% after 13 h, then decreases very slowly to 38.1% at the end. The major by-products are propylene and pentenes, which are produced by the dimerization of butenes to octenes followed by cracking. Small amounts of hydrogen transfer products, propane and butanes (total selectivity less than 15%), are also observed in the first few hours when the conversion is very high (>60%). The high initial selectivity to side reactions is due to the strong acid sites that have enough space around them for these reactions. The exterior acid sites, which are not governed by shape selectivity, also could be contributing to these by-products. As the run time increases, some of these acid sites are poisoned or blocked by coke formation, so the activity of side reactions decreases and/or the isomerization activity increases (7).

For the MTT catalyst, the isobutylene yield varies from 27.8 to 29.9% during the run. The MTT catalyst has a high initial selectivity to side reactions which does not decrease as quickly as that of the FER catalyst. At the end of the run, the total selectivity to by-products is still high, 43%, compared with the isomerization selectivity, 57%. Although the Si/Al ratios of MTT and FER catalysts

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TABLE 1

List of Zeolites, Pore Structures, and Run Conditions

Zeolite	8-MR (Å)	10-MR (Å)	Si/Al	Run conditions T (°C)	P (kN/m^2)	WHSV (h^{-1})	Run time (h)
FER	3.5 × 4.8	4.2 × 5.4	8.8	420	101.3	8	18
MTT		4.5 × 5.2	65	420	101.3	8	18
MFI		5.4 × 5.6 (straight) 5.1 × 5.5 (zigzag)	87	500	101.3	100	18

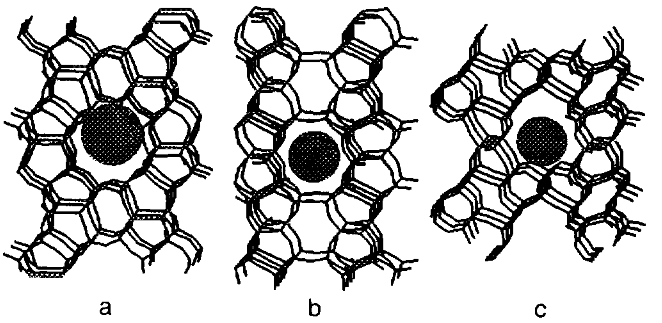

FIG. 2. Molecular modeling of (a) MFI, (b) FER, and (c) MTT showing free sphere diameters around the intersections and channels.

are quite different, the results suggest that at the same levels of conversion the FER catalyst is more selective than the MTT catalyst (9). When the same conditions of FER and MTT were used for MFI, oligomerization was dominant and liquid products were produced. In order to have a reasonable isomerization activity, a higher temperature (500°C) and a higher weight hour space velocity (100 h^{-1}) were used. The conversion is always high, between 68.7 and 73.2%; the isobutylene yield is low, varying from 13.2 to 14.9%. Propylene and pentenes are the major products. Certain amounts of methane, ethylene, propane, and butanes are also observed. MFI is known for the catalytic conversion of light olefins to gasoline and diesel (10).

TPD of ammonia on FER and MTT has been studied (7, 8). For the fresh H–FER, there are two desorption peaks of ammonia at 204 and 477°C. The total amount of desorbed ammonia is 2.35 mmol/g. The ratio of the amount desorbed at 477°C to that at 204°C is about 1.2. For the fresh H–MTT, two desorption peaks are observed at 175 and 390°C, and the total desorption ammonia is 0.316 mmol/g. The ratio of the higher temperature peak to the lower temperature peak is about 0.82. The H–FER has stronger acidic sites and a higher acid density than the H–MTT. H–MFI has a desorption peak around 400°C according to the literature (11). However, no correlation between the acidity and the isomerization activity can be drawn based on the TPD results. Our results clearly show the impact of pore structure on the isomerization activity is significant. To be an efficient isomerization catalyst, the undesired reactions, oligomerization, cracking, H-transfer, and coking need to be suppressed. All these reactions involve multimolecular reactions that need a large space. However, isomerization is an unimolecular reaciton where a smaller space is required. The free diameter at the MFI and FER intersections and in the MTT channels are calculated to be 6.2, 5.2, and 4.8 Å, respectively, using molecular modeling techniques, see Fig. 2 (12). The intersection of two 10-MR channels in MFI creates a large void, which is large enough to accommodate two butenes and undergo dimerization, cracking, and H-transfer. MTT has only monodirectional 10-MR channels. The void volume at the MFI channel intersections is about 2.1 times that calculated for the MTT channels themselves. The activity of side reactions in the MTT channels is therefore lower than that in the MFI channels. Similar results have been observed for theta-1 (TON) zeolite, another monodirectional 10-MR zeolite (13). The free diameter at the FER intersection is 0.4 Å larger than that of MTT and 1.0 Å smaller than that of MFI. It is clear that FER with intersecting 10-MR and 8-MR channels is more selective than MFI. However, it is not clear why FER is more selective than MTT even though FER has slightly larger intersected channels. It is possible that the diffusion of butenes is more favorable in multidirectional channels than in monodirectional channels. Nevertheless, our results suggest that zeolites with constrained channel systems can decrease the activity of oligomerization, cracking, and H-transfer, and/or improve the isomerization activity attributed to transitional state selectivity.

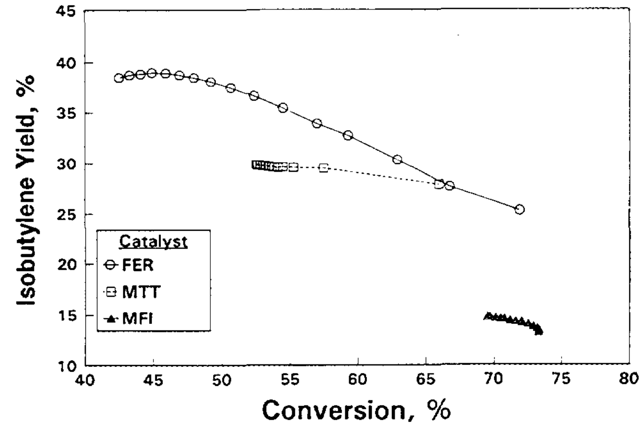

FIG. 1. Skeletal isomerization of 1-butene on 10-MR zeolites.

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