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Skeletal isomerization of 1-butene over ferrierite and ZSM-5 zeolites: influence of zeolite acidity

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Three ferrierite (FER) and five ZSM-5 (MFI) zeolites with SiO_2/Al_2O_3 ratio ranging from 27 to 2000 are tested as catalysts for the skeletal isomerization of 1-butene at 350–450°C and atmospheric total pressure in order to study the influence of acidity and pore structure of zeolite on conversion and selectivity. The catalytic and NH_3 temperature-programmed desorption results from FER and MFI catalysts with the same SiO_2/Al_2O_3 ratio reveal that the pore structure of FER zeolite rather than its acidity may play an important role in achieving high selectivity for the skeletal isomerization of 1-butene to isobutene.

Keywords: skeletal isomerization of 1-butene; ferrierite; ZSM-5 zeolite; SiO_2/Al_2O_3 ratio; acidity

1. Introduction

It has recently been recognized that skeletal isomerization of *n*-butene to isobutene is an attractive route for the production of raw materials for methyl tert-butyl ether (MTBE), an environmentally approved oxygenate used in reformulated gasoline. From a point of industrial applications, the matter of primary concern is the improvement of the selectivity to isobutene. Thus, many catalysts including halogen-modified metal oxide and zeolites have been employed [1,2]. The medium-pore zeolite ferrierite (FER topology) is of current interest since it shows exceptional selectivity for the skeletal isomerization of 1-butene [3,4]. The FER structure contains a two-dimensional pore system consisting of ten-membered rings (4.2 × 5.4 Å) intersected by eight-membered rings (3.5 × 4.8 Å) and this pore structure is considered to play an important role in achieving high selectivity to the skeletal isomerization.

It has been repeatedly shown that the conversions and product distributions in many zeolite-catalyzed reactions are greatly influenced by the acidity of zeolites, as well as their pore structures. ZSM-5 (MFI topology) is one of the most widely studied and industrially important zeolites. The selectivity to isobutene in 1-butene isomerization on this zeolite is reported to be very low as compared to that from FER [3]. This has been attributed to the strong acidity of MFI zeolite which can increase the activity of side reactions such as 1-butene dimerization, hydrogen transfer or cracking to light hydrocarbons. Mooiweer et al. [3] suggest that the high isomerization selectivity of the FER catalyst is due to the mild cracking activity of the zeolite together with its product shape selectivity. However, the exact role of the catalyst acidity in 1-butene skeletal isomerization of FER zeolite is not yet identified. The concentration and strength of acid sites in zeolites usually differ according to the amount and nature of the framework Al atoms, respectively. Therefore, it is of fundamental importance to investigate the catalytic activity of FER zeolites with different SiO_2/Al_2O_3 ratios, in order to elucidate the influence of zeolite acidity on the skeletal isomerization of 1-butene. In particular, it is of interest to compare the isomerization activities of zeolites with different framework structures but the same or quite similar SiO_2/Al_2O_3 ratio. Here we report the catalytic and NH_3 temperature-programmed desorption SiO_2/Al_2O_3 results obtained from three FER and five MFI zeolites with SiO_2/Al_2O_3 ratio ranging from 27 to 2000.

2. Experimental

Three FER samples with different SiO_2/Al_2O_3 ratios were synthesized using pyrrolidine as a structure-directing agent following the procedure of Plank et al. [5]. The SiO_2/Al_2O_3 ratio in the final product was varied by adjusting the amount of Al source added in the synthesis mixture. Five MFI zeolite samples were used for comparison. Two MFI zeolites with SiO_2/Al_2O_3 ratios of 27 and 55 were obtained from ALSI-PENTA Zeolithe GmbH. The other three MFI samples with higher SiO_2/Al_2O_3 ratios were prepared according to the procedures described elsewhere [6]. As-synthesized FER and MFI

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samples prepared in this work were calcined in air at 500°C for 16 h to remove the occluded structure-directing agents. The calcined samples were then refluxed twice in 1.0 M NH_4NO_3 solution for 6 h followed by calcination at 550°C for 16 h in order to ensure that the samples were in their complete proton form.

X-ray powder diffraction patterns of all samples were recorded on a Rigaku Geigerflex X-ray diffractometer. Chemical analysis was performed by a Jarrell-Ash Polyscan 61E inductively coupled plasma (ICP) spectrometer in combination with a Perkin-Elmer 5000 atomic absorption spectrophotometer. The nitrogen BET surface areas were measured on a house-built volumetric adsorption unit. Temperature-programmed desorption (TPD) of ammonia was recorded on a fixed bed, flow-type apparatus equipped with a thermal conductivity detector. Approximately 0.2 g of sample were activated in flowing He at 550°C for 3 h, then ammonia was passed over the sample at 80°C by pulse. The sample was subsequently purged with He at this temperature for 1 h in order to eliminate the physisorbed ammonia. The TPD profiles were obtained in flowing He (200 cm^3 min^{-1}) from 80 to 600°C with ramping rate of 10°C min^{-1}.

1-butene isomerization was carried out in a conventional continuous flow microreactor loaded with 0.5 g of zeolite catalyst at atmospheric pressure. The reactor was heated to reaction temperature in flowing Ar and then a reactant stream having a fixed Ar/1-butene molar ratio of 4.5 was flowing over the catalyst. The reaction products were analyzed by an on-line gas chromatograph with a sebaconnitrile column and a thermal conductivity detector. Conversion was calculated as the mole percent of 1-butene consumed and selectivity to isobutene was calculated by dividing the yield of isobutene by the conversion of 1-butene. 2-butenes were not considered as products, since the isomerization between 1-butene and 2-butenes is much faster than the skeletal isomerization and 2-butenes can also be converted to isobutene. Changes in the product distribution were small along with the time-on-stream and all catalytic results were thus reported after 1 h on stream.

3. Results and discussion

Table 1 lists the SiO_2/Al_2O_3 ratios and surface areas of FER and MFI zeolites used in this work. These data reveal that our zeolite samples span the SiO_2/Al_2O_3 ratio from 27 to 2000 and they are highly crystalline. Note that FER(II) and MFI(I) samples have the same SiO_2/Al_2O_3 ratio.

Table 1
FER and MFI zeolite catalysts used in this work

Catalyst	SiO_2/Al_2O_3 ratio	Surface area (m^2 g^{-1})
FER(I)	19	334
FER(II)	27	362
FER(III)	41	400
MFI(I)	27	383
MFI(II)	55	294
MFI(III)	100	279
MFI(IV)	300	380
MFI(V)	2000	402

X-ray powder diffraction patterns of the three FER samples with different SiO_2/Al_2O_3 ratio are given in fig. 1. The X-ray powder diffraction patterns of FER(I) and FER(II) samples are in good agreement with those reported in the literature [5]. No reflections of a dense phase or any other zeolitic phase are found. However, the FER(III) sample shows several small peaks other than those from the FER zeolite, as indicated by an asterisk in fig. 1c. The zeolites that can be synthesized with pyrrolidine include MFI, MTT, MTN, MAZ as well as FER [7]. The zeolites except MTT show no noticeable reflection lines in the 2θ region of 20–22° [8]. As seen in fig. 1c, the FER(III) sample gives two small peaks at $2\theta = 20.8$ and 21.7°. A highly crystalline pure form of MTT zeolite is reported to be obtained from the aluminosilicate gel with SiO_2/Al_2O_3 ratio from 55 to 70 and OH/SiO_2 ratio between 0.01 and 0.05, when pyrrolidine is used as a structure-directing agent together with

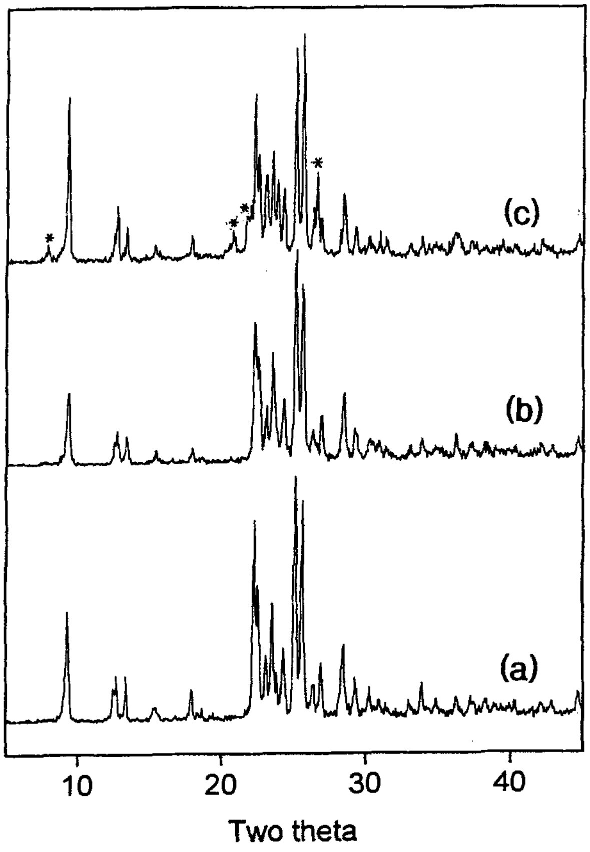

Fig 1. X-ray powder diffraction patterns of the FER zeolites prepared in this work: (a) FER(I), (b) FER(II), and (c) FER(III).

Na^+ ion [9]. This gel composition is similar to that used in the synthesis of the FER(III) sample. Therefore, it appears that the major impurity phase present in the FER(III) sample is MTT zeolite. Comparing the intensities of the two lines at $2\theta = 21.7$ and 22.3° observed in fig. 1c, the amount of MTT in the FER(III) sample can be approximately estimated to 10%. This result is important for the interpretation of the catalytic and NH_3 TPD results of the FER(III) sample (vide infra). X-ray powder diffraction patterns (not shown) of all five MFI zeolites used in this work show that they have the MFI structure; no reflections other than those from MFI zeolite are observed.

Fig. 2 illustrates the TPD profiles of ammonia obtained from three FER samples. Two desorption peaks are observed in the temperature regions of 190–200°C and 440–480°C. These low and high temperature peaks can be attributed to ammonia desorption from weak and strong acid sites, respectively [10]. Fig. 2 also shows that the total area of these two desorption peaks decreases with increasing SiO_2/Al_2O_3 ratio. This trend is more apparent in the TPD profiles of MFI zeolites with different SiO_2/Al_2O_3 ratios, which are given in fig. 3. For example, the total area of ammonia desorption from MFI(I) is approximately 150 times larger than that from MFI(V). This behavior is not unexpected because the acid site in zeolites is generally formed on the Si–O–Al linkage of the zeolite framework. When the TPD profiles in fig. 2 are compared with those in fig. 3, no noticeable differences in the temperature at peak maximum (T_M) of low and high desorption peaks from the FER and MFI zeolites studied in this work are observed. Therefore, it is most likely that no significant differences in the strength of both weak and strong acid sites exist between FER and MFI zeolites. In particular, the T_M values of low and high desorption peaks and their total area from the FER(II) sample are quite similar to those from MFI(I). This suggests that these two samples have similar acidity because of the same SiO_2/Al_2O_3 ratio (i.e., 27). On the other hand, the T_M values of two desorption peaks from FER and MFI zeolites shift continuously toward lower temperature region with increasing SiO_2/Al_2O_3 ratio, fig. 4a. This observation clearly shows that the desorption process of ammonia from one acid site can be hindered by the readsorption to another acid site [11,12]. However, a linear relationship between T_M value and SiO_2/Al_2O_3 ratio reveals that the effects of framework Al concentration on the T_M value of ammonia desorption are not significant. This may be because the FER and MFI zeolites studied in this work are high-silica zeolites. Another interesting result obtained from TPD measurements is that the extent of decrease in total area of ammonia desorption peaks is highly dependent on the structure type of the zeolites. Fig. 4b shows plots of the total area of two ammonia desorption peaks from FER and MFI zeolites versus SiO_2/Al_2O_3 ratio. Note that the decrease in concentration of acid sites with increasing SiO_2/Al_2O_3 ratio is much higher in MFI zeolites than in FER zeolites. This suggests that the acidic properties of FER zeolites are not exactly the same as those of MFI zeolites. Although the precise reason for this behavior remains unknown at this time, this can be attributed to the structural difference between FER and MFI zeolites.

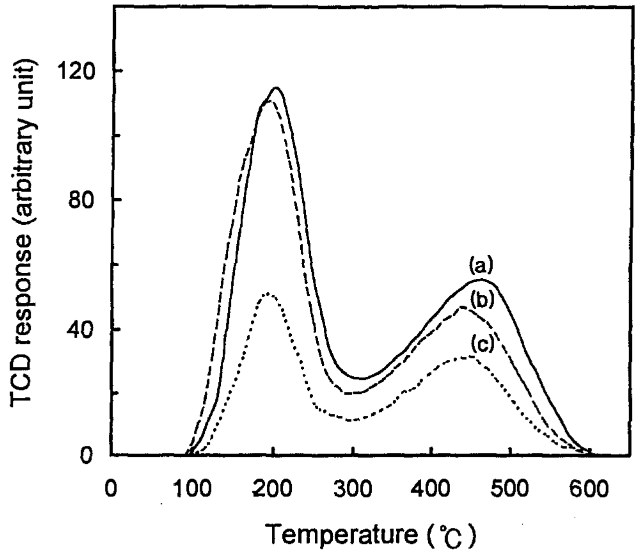

Fig 2. Ammonia TPD profiles from FER zeolites with SiO_2/Al_2O_3 ratios: (a) FER(I), (b) FER(II), and (c) FER(III).

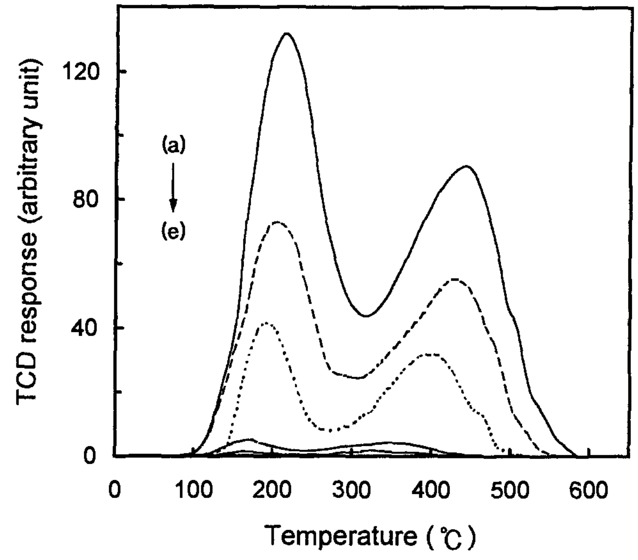

Fig 3. Ammonia TPD profiles from MFI zeolites with SiO_2/Al_2O_3 ratios: (a) MFI(I), (b) MFI(II), (c) MFI(III), (d) MFI(IV), and (e) MFI(V).

Fig. 5 shows the relationship between the conversion of 1-butene and the selectivity to isobutene formation, which was obtained from the reaction of 1-butene over the three FER and five MFI zeolite catalysts in the temperature region of 350–450°C. Notice that FER zeolites except FER(III) show 1-butene conversions (<40%)

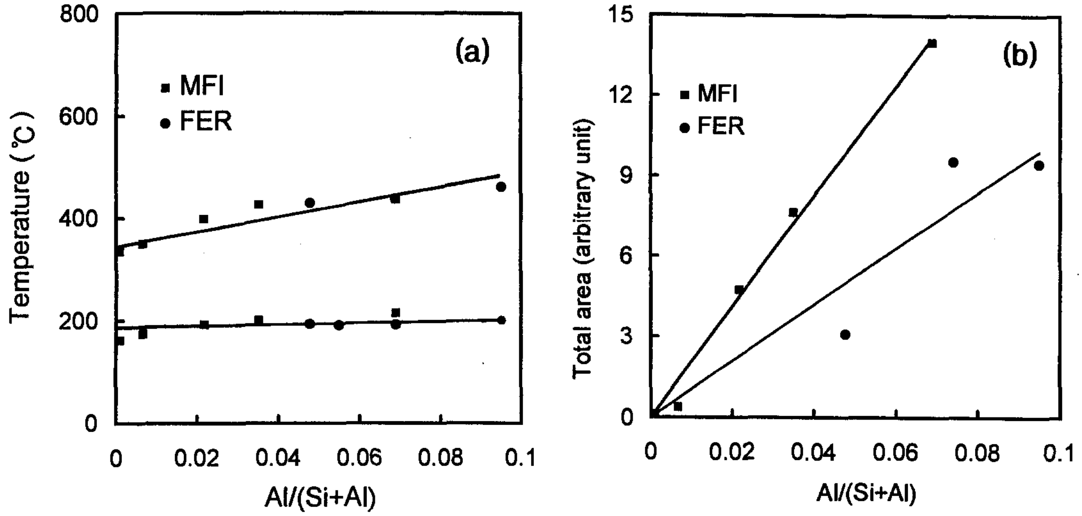

Fig 4. Plots of (a) temperatures at peak maximum (T_M) and (b) total area of low and high desorption peaks from FER and MFI zeolites versus SiO_2/Al_2O_3 ratio.

being much lower than those of MFI samples. However, their selectivities to isobutene, which have values up to 85%, are much higher than those obtained from MFI samples. The selectivities to isobutene on all five MFI zeolites increase with elevating reaction temperature, but they do not exceed about 40%, regardless of the big difference in SiO_2/Al_2O_3 ratio. In addition, their product distribution reveals that cracked hydrocarbons such as C_1–C_3 and C_5–C_6 are major products. These observations are in good agreement with those recently reported by O'Young et al. [13]. An important observation is that the FER(II) sample exhibits much higher selectivity to isobutene than the MFI(I) sample, although its acidity is quite similar to that of the MFI(I) sample. This clearly shows that the selectivity to isobutene on zeolite catalysts is strongly influenced by the type of structure of the zeolites rather than by their acidity. Further evidence to support this conclusion can be obtained from the catalytic results of the FER(III) sample. As seen in fig. 5, the FER(III) sample shows conversions much higher than those from FER(I) or FER(II), but its selectivities to isobutene are very low and are similar to those from MFI zeolites. The TPD data given in fig. 3 show that the concentration of both weak and strong acid sites in the FER(III) sample is approximately 30% of that from the FER(I) or FER(II) sample. Also, recall that the FER(III) sample contains a small but significant amount of MTT zeolite as an impurity. Unlike FER, the MTT structure contains a unidimensional channel system consisting of ten-membered rings (4.5 × 5.2 Å) [7].

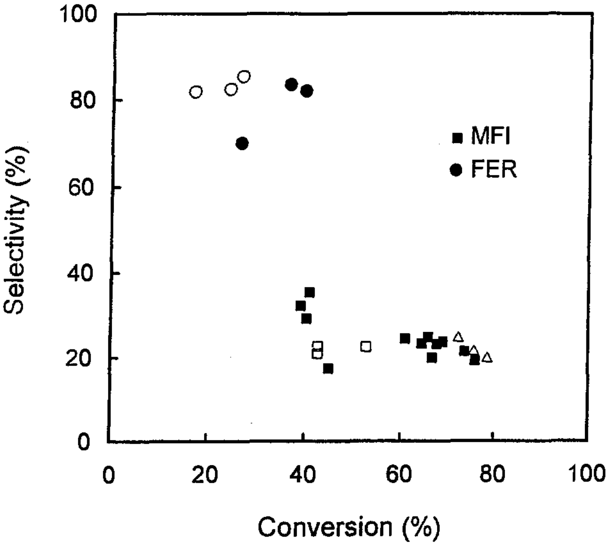

Fig. 5. Selectivity to isobutene as a function of 1-butene conversion in the temperature region of 350–450°C, Ar/1-butene = 4.5 and atmospheric pressure The open squares, circles and triangles represent the data points obtained from MFI(I), FER(II) and FER(III) samples, respectively.

In summary, the catalytic and NH_3 temperature-programmed desorption results of this study demonstrate that the high selectivity of FER zeolite for the skeletal isomerization of *n*-butene can be mainly due to the unique pore structure of the zeolite rather than its acidity.

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