The role of carbonaceous deposits in the skeletal isomerization of 1-butene over ferrierite zeolites

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The inner pores of ferrierite (FER) with a Si/Al ratio of 21 have been modified by plasma-polymerized propylene loading and subsequent thermal treatment under a flow of He at 550°C in order to identify the exact role of carbonaceous deposits (coke) in the skeletal isomerization of 1-butene. It was found that even a small weight loading (0.8 wt%) of carbonaceous deposits within the inner pores of FER zeolite was sufficient to modify the pore structure of the zeolite, leading to a noticeable enhancement of the selectivity to isobutene. This may be attributed to the increased spatial constraints inside the pores which restrict undesired side reactions, such as 1-butene dimerization followed by cracking to light hydrocarbons.

Keywords: 1-butene skeletal isomerization; ferrierite; catalyst modification; carbonaceous deposits

1. Introduction

Isobutene is an important raw material for the production of methyl tert-butyl ether (MTBE), which is widely used as a major octane-enhancer in reformulated gasoline. However, the current supply of isobutene from the catalytic cracking of petroleum is not sufficient to meet the increasing demand for MTBE. Therefore, considerable interest has been devoted to finding a new isobutene source via skeletal isomerization of *n*-butene [1]. Numerous papers and patents describe the use of zeolites with 10-ring pores for this reaction, because their pore sizes are suitable to achieve high activity and selectivity [1–10]. Among the zeolites tested so far, ferrierite (FER topology) is known to show the highest selectivity to isobutene.

Unlike other zeolite-catalyzed reactions, the skeletal isomerization of *n*-butene over FER zeolite is not significantly influenced by variations in zeolite acidity [10]. Therefore, it is speculated that the exceptional selectivity of skeletal isomerization of *n*-butene over FER zeolite is mainly due to its unique pore system. However, FER exhibits not enough selectivity to isobutene at the beginning of the reaction in its form. Xu et al. [6,7] reported that the high isomerization selectivity was achievable only after partial deactivation by carbonaceous deposits, i.e., coke. They also suggested that the enhanced selectivity of FER zeolite was attributed either to coke poisoning of strong acid sites or to increased spatial constraints limiting *n*-butene dimerization. It has repeatedly been shown that the inner pores of properly used FER zeolites giving the high isobutene selectivity were almost blocked by coke. The level of the coke formed was usually 8–10 wt%.

The purpose of this study is to identify the exact role of coke deposited on FER zeolite in the skeletal isomerization of 1-butene. In this study, plasma polymerization of propylene on FER zeolite and subsequent thermal treatment under a flow of He at 550°C has been used in order to modify the zeolite pore structure without causing serious pore blocking. Plasma polymerization of hydrocarbons has widely been used for coating of ultrathin layers on many solid surfaces [11,12]. Changes in the physicochemical properties of FER zeolite resulting from coke deposition were characterized by thermal analyses, ^{129}Xe NMR and ESR spectroscopies, and temperature-programmed desorption (TPD) of ammonia. In addition, the effect of coke deposits on 1-butene isomerization activity and selectivity was explored.

2. Experimental

2.1. Catalyst modification and characterization

FER zeolite with a Si/Al ratio of 21 was synthesized using pyrrolidine as a structure-directing agent following the procedure of Plank et al. [13]. The X-ray diffraction pattern of ferrierite prepared here was consistent with that reported in the literature. As-synthesized FER zeolite was calcined in air at 500°C for 16 h to remove the occluded organic structure-directing agent. The proton form of FER zeolite was prepared by ion exchange of the calcined zeolite twice with 1.0 M NH_4NO_3 solution fol-

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lowed by calcination in air at 550°C for 16 h. The FER zeolite was transferred to a RF plasma reactor vacuum of 10^{-3} Torr. Plasma-polymerized propylene loading on FER zeolite was performed at room temperature for a given period of time, using a discharge power of 50 W and propylene pressure of 0.2 Torr. Three FER zeolites with different contents of polymerized propylene were prepared by varying deposition time in the plasma reactor. Finally, these FER zeolites were treated under the flow of He at 550°C for 2 h. FER zeolites after treatment by plasma polymerization and thermal treatment are denoted as P-FER and C-FER, respectively.

Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were performed in air in a DuPont 950 thermogravimetric analyzer and a Simatzu differential analyzer. Approximately 20 mg of sample were used at a heating rate of 5°C $\min^{-1}$. Nitrogen BET surface areas were measured on a house-built volumetric adsorption unit. Temperature-programmed desorption (TPD) of ammonia was done in a TPD apparatus described previously [10].

^{129}Xe NMR spectra were obtained at room temperature in a Bruker AM-300 FT-NMR spectrometer operating at a ^{129}Xe frequency of 83.0 MHz with a 0.5 s recycle delay. Prior to ^{129}Xe NMR experiments, the samples were placed in conventional NMR tubes of 10 mm outer diameter jointed with coaxial ground-glass vacuum stopcocks, and sample tubes were subsequently evacuated to 10^{-5} Torr at room temperature. Then, Xe gas (99.995%, Matheson) was equilibrated with the sample under a given pressure. The chemical shifts are referenced relative to the NMR signal of the xenon gas extrapolated to zero pressure.

The ESR spectra were recorded at room temperature on a Bruker ER-200D spectrometer operating at X-band ($\sim$ 9.45 GHz) with a 100 kHz modulation. Prior to ESR measurements, approximately 30 mg of sample was placed in a quartz tube of 3 mm inner diameter and the sample tube was evacuated to 10^{-4} Torr at room temperature for 2 h. The microwave frequency was monitored by an Anritsu MF76A microwave frequency counter to an accuracy of ± 0.1 kHz, and g values were determined through comparison of the resonant field with that of the 1,1-diphenyl-2-picryl-hydrazyl (DPPH) radical at $g = 2.0036$.

2.2. Reactor system

1-butene isomerization was carried out in a conventional continuous flow microreactor loaded with 0.2 g of ferrierite catalyst at atmospheric pressure. The reactor was heated to reaction temperature under Ar flow. In order to examine the effect of partial pressure of 1-butene on the conversion of 1-butene and the selectivity to isobutene, reactant streams with Ar/1-butene molar ratios of 1.3 to 8.9 were passed over the catalyst. The reaction products were analyzed by an on-line gas chromatograph equipped with a sebaconnitrile column and a thermal conductivity detector. The connecting lines from reactor to GC were wrapped with ribbon heater and kept at 100°C. Conversion was calculated in terms of mole percent of 1-butene consumed and selectivity to isobutene was calculated by dividing the yield of isobutene by the conversion of 1-butene. Here 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. All catalytic results are reported after 1 h on stream.

3. Results and discussion

3.1. Characterization of the deposited coke

It is well-established that the catalytic properties of zeolites are significantly changed when their pore structures are modified by deposition of catalytically inert materials such as silicon or phosphorus. Plasma polymerization of hydrocarbons is referred to as a deposition process which is applicable to almost all organic molecules [11,12]. The FER structure is composed of 10-ring channels with a free cross-section of 4.2 × 5.4 Å intersected by 8-ring channels with a cross-section of 3.5 × 4.8 Å. Thus, it is expected that lower olefins such as propylene may be small enough to enter the inner pores of FER zeolite, where they can be plasma-polymerized and deposited. The FER zeolites with plasma-polymerized propylene are white like fresh FER zeolite. When these zeolites were heated under the flow of He at 550°C for 2 h, however, their color changed from white to dark gray. This may be attributed to the formation of coke, which originated from the decomposition of polymerized propylene species in the zeolite.

The modification conditions for FER zeolite used in this study are given in table 1. The weight losses associated with the combustion of polymerized propylene or coke in the modified FER zeolites are also listed in table 1. These data were obtained from TGA analyses, where specific weight losses were assigned from DTA analyses. The color of the modified FER zeolites after heating to 800°C in the TGA chamber was white. This indicates that each weight loss value listed in table 1 can be used as a measure of the polymerized propylene or coke loading in modified FER zeolites. The weight loading of polymerized propylene in FER zeolite was found to increase with increasing the deposition time of the plasma generator. For example, the content (4.9 wt%) of polymerized propylene in P-FER(III) is approximately four times as large as that (1.2 wt%) in P-FER(I). Table 1 also shows that the content of the coke deposited is considerably small (1.7 wt% or less) as compared to that of the polymerized propylene adsorbed on the zeolite before thermal treatment under the flow of He at 550°C.

Table 1
Physical data of modified FER zeolites

Sample	Modification method used		Weight loss from organic[a] (wt%)	BET surface area[b] (m^2/g)
	plasma-polymerized propylene loading (min)	thermal treatment at 550°C for 2 h		
H-FER	0	no	0.0	250
P-FER(I)	50	no	1.2	210
P-FER(II)	100	no	2.8	190
P-FER(III)	200	no	4.9	172
C-FER(I)	50	yes	0.8	231
C-FER(II)	100	yes	1.2	220
C-FER(III)	200	yes	1.7	214

[a] Calculated from TGA/DTA data.
[b] BET surface areas calculated from nitrogen adsorption data.

This is not unexpected because the polymerized propylene could be partially removed or converted to coke with the consequent weight loss. The BET surface areas of modified FER zeolites were calculated from nitrogen adsorption data and are also listed in table 1. Before nitrogen adsorption experiments, FER zeolites with different contents of plasma-polymerized propylene were evacuated at 200°C for 2 h. Therefore, their BET surface areas are approximate since a portion of polymerized propylene can be removed by evacuation under the conditions stated above. However, these data reveal that the BET surface area decreases in the order P-FER(I) > P-FER(II) > P-FER(III). This indicates that most, if not all, polymerized propylene species are located inside the pores of FER zeolite. On the other hand, no significant differences are observed among the BET surface area of C-FER(I), C-FER(II) and C-FER(III) zeolites. Also, their BET surface areas are similar to the BET surface area obtained from H-FER. Therefore, it appears that the blocking of their inner pores caused by coke deposition is not significant.

To more accurately identify the location of plasma-polymerized propylene or coke in FER zeolite, selected samples have been analyzed by ^{129}Xe NMR spectroscopy. Fig. 1 shows ^{129}Xe NMR spectra of xenon adsorbed on H-FER, P-FER(III) and C-FER(III). All the spectra in fig. 1 consist of two broad xenon NMR peaks, which correspond to differences in the location of xenon atoms occluded inside the zeolite pores. The ^{129}Xe NMR spectrum of H-FER in fig. 1a shows two peaks at 105 and 170 ppm. These values are in agreement with those reported by Ito et al. [14]. The high-field NMR peak is assigned to xenon atoms in the 10-ring channels of FER zeolite, while the low-field peak is due to xenon in the 8-ring channels. This suggests that changes in the relative intensity ratio of high- to low-field peak, caused by the deposition of polymerized propylene or coke into FER zeolites, can provide valuable information on the intrazeolitic distribution of deposited materials. Fig. 1b was obtained from P-FER(III). Interestingly, the relative intensity ratio (0.73) of high- to low-field peak in fig. 1b is considerably lower than that (1.67) in fig. 1a. This indicates that the polymerized propylene species are mainly located inside the 10-ring channels rather than inside the 8-ring channels. On the other hand, the spectrum of C-FER(III) in fig. 1c shows a higher relative intensity ratio (1.86) than H-FER. This can be explained by the site preference of coke for 8-ring channels versus 10-ring channels. Further study is necessary to determine the underlying mechanism of the coke formation in FER zeolite.

Fig. 2 shows the EPR spectra of H-FER and C-FER(III). H-FER shows a weak ESR line at $g = 2.0035$. This line can be attributed to the residual carbonaceous materials produced during the calcination step for the elimination of the organic structure-directing agent in as-synthesized FER zeolite. C-FER(III), like H-FER, shows an ESR line at $g = 2.0035$. However, the ESR line

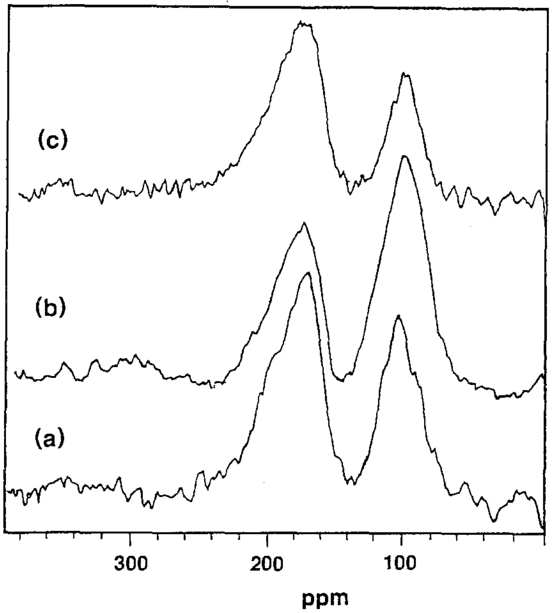

Fig. 1. ^{129}Xe NMR spectra obtained at 400 Torr and room temperature of xenon gas adsorbed on (a) H-FER, (b) P-FER(III) and (c) C-FER(III).

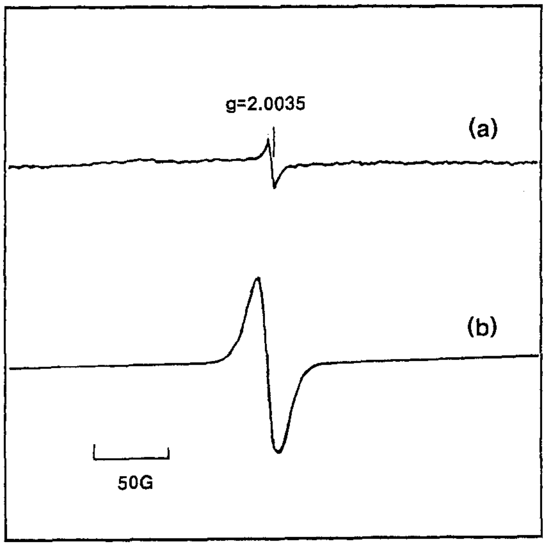

Fig. 2. ESR spectra at room temperature of (a) H-FER and (b) C-FER(III).

from C-FER(III) is approximately two orders of magnitude stronger than that from H-FER. This result clearly demonstrates that the plasma-polymerized propylene loading to FER zeolite followed by thermal treatment under the flow of He at 550°C gives rise to the formation of coke.

Fig. 3 shows the TPD profiles of ammonia from H-FER, C-FER(I), C-FER(II) and C-FER(III). All the TPD profiles in fig. 3 are characterized by two desorption peaks which appear in the temperature regions of 190–200°C and 440–450°C. These low and high temperature desorption peaks correspond to weak and strong acid sites, respectively. Notice that the low temperature desorption peak from C-FER(I), C-FER(II) or C-FER(III) is slightly smaller than that of H-FER, while no significant differences in the area of the high-temperature peak are observed. In addition, the total areas of ammonia desorption from C-FER(I), C-FER(II) and C-FER(III) are quite similar. This indicates that the poisoning of weak and strong acid sites in FER zeolite is not significant.

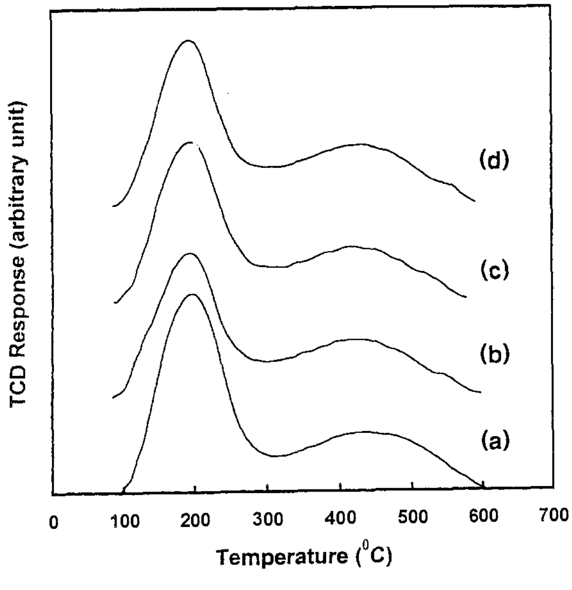

Fig. 3. Ammonia TPD profiles from (a) H-FER, (b) C-FER(I), (c) C-FER(II) and (d) C-FER(III).

3.2. Catalytic properties of modified FER zeolites

Table 2 lists the conversions and product distributions from the skeletal isomerization of 1-butene over H-FER, C-FER(I), C-FER(II) and C-FER(III) catalysts at different temperatures. As described earlier, the weight loading of coke increases in the order C-FER(I) < C-FER(II) < C-FER(III). However, these coke-loaded FER zeolites have nearly the same BET surface area and acidity. Therefore, comparison of the catalytic results from coke-loaded FER zeolites with those from H-FER will reveal differences that are related entirely to the modification of the zeolite pore structure by coke deposition. The data listed in table 2 clearly show that the coke-loaded FER zeolites convert 1-butene in a different manner than fresh FER (H-FER) zeolite, although the 1-butene conversions studied in this work increase significantly with the reaction temperature for all the FER zeolites. The coke-loaded FER zeolites show a continuous increase in the selectivity to isobutene over the temperature range of 350 to 450°C, while H-FER exhibits the highest isobutene selectivity at 400°C.

Table 2 lists the catalytic results from the three FER zeolites with different coke contents at 350°C. With increasing the weight loading of coke the 1-butene conversion decreases from 19.7 to 13.2%. However, the selectivity to isobutene increases from 57.9 to 66.5%. These trends exist at least over the temperature range studied here. Since the BET surface area and acidity are nearly the same for these three catalysts, the enhancement of selectivity to isobutene could be mainly due to the increased spatial constraints caused by coke deposition. The major by-products are propylene and pentenes, which are produced by the dimerization of 1-butene to octenes followed by cracking. Note that the selectivity to C_{5+} is much higher for C-FER(I) than for C-FER(II) and C-FER(III). Thus, it is most likely that the increased spatial constraints inside the channels restrict sterically bimolecular reactions. However, no significant differences in the selectivity to propylene over the three coke-modified FER zeolites are observed. The formation of propylene and pentenes may be due to the strong acid sites that have enough space around them. The exterior acid sites, which are not dominated by shape selectivity, could also produce these by-products.

Another important observation obtained from table 2 is that even a small weight loading (0.8 wt%) of

Table 2
Conversion and product distribution from 1-butene skeletal isomerization on modified FER zeolites at different temperatures [a]

Catalyst	Reaction temp. (°C)	Conversion (%)	Selectivity (%)					
			$C_2^=$	C_3	$C_3^=$	C_4	i-$C_4^=$	C_{5+}
H-FER	350	18.9	0.0	1.7	18.4	7.9	58.7	13.3
C-FER(I)	350	19.7	0.0	1.6	16.2	7.1	57.9	17.2
C-FER(II)	350	17.5	0.0	1.9	18.8	8.1	66.3	4.9
C-FER(III)	350	13.2	0.0	2.1	18.7	7.8	66.5	4.9
H-FER	400	33.2	0.6	1.2	10.7	3.3	74.2	10.0
C-FER(I	400	35.3	0.5	0.8	9.5	3.4	80.6	5.2
C-FER(II)	400	30.7	0.7	1.1	11.3	3.7	79.3	3.7
C-FER(III)	400	25.7	0.4	0.9	9.5	3.2	83.6	2.4
H-FER	450	38.0	0.9	0.4	8.9	10.7	71.4	7.7
C-FER(I)	450	37.2	0.5	0.0	7.2	1.5	87.0	3.8
C-FER(II)	450	32.4	1.0	0.4	9.1	1.8	87.7	0.0
C-FER(III)	450	28.4	0.7	0.0	7.3	1.2	88.8	2.0

[a] Data are reported as the average values of 1 h time on stream at LHSV = 4.5^{-1}.

coke on FER zeolite is sufficient to lead to a noticeable enhancement of selectivity to isobutene. No noticeable differences in the 1-butene conversion between H-FER and C-FER(I) over the reaction temperature range from 350 to 450°C are observed. In addition, these two catalysts show nearly the same selectivity to isobutene at 350°C. However, the selectivity to isobutene was much higher over C-FER(I) than over H-FER when the reaction temperature was increased from 350 to 450°C. Such change led to a rapid increase in the isobutene selectivity over C-FER(I) from 57.9 to 87.0%, while the selectivity to isobutene over H-FER(I) increased from 58.7 to 71.4%.

Fig. 4 shows plots of the 1-butene conversion and isobutene selectivity over C-FER(III) versus partial pressure of 1-butene. As shown in fig. 4, the conversion increases with increase of the partial pressure of 1-butene. In contrast, the selectivity to isobutene first decreases from 0.10 to 0.2 bar. Then, it remains almost unchanged at higher partial pressures of 1-butene up to 0.43 bar. If the formation of isobutene over FER zeolite is mainly governed by the dimerization–cracking mechanism that involves two secondary carbenium ions, the observed selectivity to isobutene should become higher with increase of the partial pressure of 1-butene. As shown in fig. 4, however, the highest selectivity to isobutene over C-FER(III) was achieved at the lowest partial pressure of 1-butene in the pressure range studied here. This result suggests that the isomerization mechanism is monomolecular rather than bimolecular, since the possibility of 1-butene dimerization is reduced by lowering the concentration of the reactant. Very recently, Guisnet et al. [15] have proposed that after deactivation of the FER catalyst by coke, the skeletal isomerization of 1-butene into isobutene would occur through the pseudo-monomolecular mechanism involving as active sites tertiary carbenium ions blocked in the zeolite pores. Based on the overall results of this study, we cannot rule out the existence of tertiary-carbenium ions formed from the deposited coke. However, it is clear from our catalytic results that the increased spatial constraints inside the FER zeolite channels by coke deposition may play an important role in limiting undesired side reactions, such as 1-butene dimerization followed by cracking to light hydrocarbons.

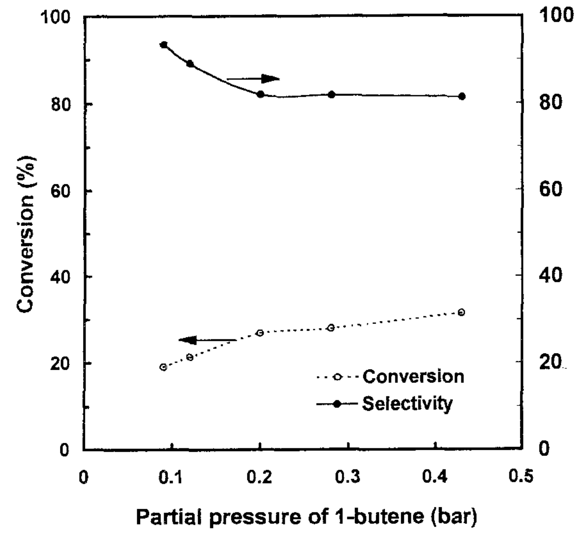

Fig. 4. 1-butene conversion and selectivity to isobutene as a function of partial pressure of 1-butene in the skeletal isomerization over C-FER(III) catalyst at 400°C and atmospheric total pressure.

In conclusion, the plasma-polymerized propylene loading on FER zeolite and the subsequent thermal treatment in inert atmosphere at high temperature is found to be effective for the modification of the inner zeolite pores without causing a serious pore blockage. The deposited coke suppresses the dimerization–cracking process and thus leads to the enhancement of the selectivity to isobutene.

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