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Skeletal isomerization of 1-butene over surface modified ferrierite catalysts

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H-ferrierite was treated with oxalic acid to selectively remove external acid sites. The treatment led to the reduction of tetrahedrally coordinated aluminum ions and the increase of octahedrally coordinated aluminum species and micropore surface area. It was also found that the catalyst treated with oxalic acid is resistant to coking. Over modified H-FER, very high selectivity to isobutene is obtained at lower conversions suggesting the skeletal isomerization of 1-butene is occurring through a mono-molecular reaction mechanism.

Keywords: skeletal isomerization, surface modification, reaction mechanism, ferrierite, oxalic acid

1. Introduction

Skeletal isomerization of 1-butene to isobutene has recently been studied by many academic and industrial scientists mainly due to the high demand for methyl tertiary butyl ether in reformulated gasolines. There are a couple of review articles [1,2] which shed some lights on the active sites, reaction mechanisms and deactivation of various types of catalysts.

Among the catalysts employed for this reaction, ferrierite/ZSM-35 (FER) has been found to be most efficient [3–8]. It is generally agreed that small cavities in this zeolite resulting from intersecting 10-MR and 8-MR and mild cracking activity of FER play a decisive role to maintain the yield at high levels [3,4]. However, there have been a lot of controversies on the reaction mechanism by which isobutene is obtained more or less predominantly over FER. Based on the isotope-labeling studies, Meriaudeau and coworkers [7] proposed a mono-molecular reaction mechanism. Mooiweer et al. [3], on the other hand, suggested a mechanism consisting of butene dimerization, skeletal isomerization, and subsequent mild cracking to form isobutene. This bimolecular mechanism appeared to be valid on modified ZSM-35 catalysts at very early stages of the reaction under which, in addition to butenes, equimolar amounts of propene and pentenes are formed by a dimerization–cracking mechanism [8]. In this case, however, bulky dimerized intermediates might have been formed on the non-selective external catalytic sites as well as internal active sites of FER, which often misleads the interpretation of the reaction mechanism. As a natural consequence, it is necessary to study the isomerization over acidic zeolites having only selective internal active sites. This goal can be achieved by either poisoning or dealumination of external active sites. Depending on the applications, there are numerous methods to modify the surface acidity of the zeolites, e.g., surface silation [9,10], selective neutralization [11], acid treatment [12,13] and so on, which sometimes restrict pore mouth openings rather than either selective neutralization or removal of unwanted acid sites.

In this paper, we report the characteristics of H-FER catalysts modified by oxalic acid treatment, which is known to selectively remove surface acid sites of medium pore zeolites [12,13], and results of the skeletal isomerization of 1-butene over modified H-ZSM-35/FER catalysts in an attempt to unravel the reaction mechanism.

2. Experimental

NaK-FER with a Si/Al ratio of 8.4 received from Tosoh Corporation ($Na_{0.96}K_{2.23}[Al_{3.19}Si_{26.81}O_{72}]$) was ion-exchanged two times with 1.0 M aqueous solution of ammonium hydroxide at room temperature for 12 h. After drying at 110 °C overnight, NH_4-FER was calcined at 500 °C for 2 h under a flowing oxygen atmosphere to obtain H-FER.

H-FER was treated with 0.1–1.5 M aqueous solution of oxalic acid (Junsei) in order to remove the external acid sites following the procedure of Mobil researchers [12,13]. The catalysts treated with oxalic acid will be referred to as H-FER($x.yz$), e.g., H-FER(0.5), where $x.yz$ stands for the concentration of oxalic acid.

Reaction tests were carried out at 425 °C as described elsewhere [8].

^{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

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7 mm CP/MAS probe). ^{27}Al and ^{29}Si spectra were acquired at the resonance frequencies of 130.3 and 99.4 MHz, respectively. 10° pulses with a 1 s recycle delay were used for ^{27}Al, and 30° pulses with a 8 s recycle delay for ^{29}Si. ^{27}Al and ^{29}Si spectra were obtained with references to $KAl(SO_4)_2$ and tetramethylsilane, respectively. All the samples were further characterized with XRD (MAC M03XHF, Cu Kα at 40 kV and 40 mA), XRF (Philips, Type 9430), SEM (Philips SEM 515), NH_3-TPD (Altamira AMI-1), and nitrogen adsorption/desorption (Micromeritics ASAP 2010).

3. Results and discussion

3.1. Characteristics of modified H-FER

The shape of the particles of H-FER looked like an elliptical ball with the particle size ranging between 5 and 50 microns. Modification with oxalic acid did not change the external shape and size appreciably. The XRF analysis results, e.g., the Si/Al ratio, agree well with the information provided by the manufacturer. The samples, even after ion exchange and acid treatment, still possess large amounts of K^+ ions, but do not contain Na^+ ions within the detection limit. By acid treatment, some aluminum ions are removed together with K^+ ions.

MAS-NMR spectra of and ^{29}Si and ^{27}Al give more direct evidence for dealumination (figures 1 and 2). At -110 and -115 ppm, Q_4 resonances of $Si(OSi)_4$ were detected for the untreated H-FER (figure 1(a)). The resonance of Q_4 $Si(OSi)_3(OAl)$ was also detected for H-FER at -105 ppm. Upon treating with oxalic acid, the intensity of the resonance at -105 ppm was reduced implying the dealumination of the framework Al species (figure 1 (b) and (c)). The treatment of H-FER with highly concentrated oxalic acid (>0.5 M) did not change the intensity significantly. Figure 2 shows ^{27}Al MAS-NMR spectra for H-FER, H-FER(0.25), and H-FER(0.5). At 54 ppm, tetrahedrally coordinated Al^{3+} ions are observed for all samples. Also at -2 ppm are observed octahedral Al ions located at the extra-framework sites for unmodified and modified samples. However, as the sample is dealuminated, this peak becomes higher and broader (figure 2 (b) and (c)). The approximate ratio of the intensity of the peak at 54 ppm to that at -2 ppm for H-FER is 15 : 1. In the cases of H-FER(0.25) and H-FER(0.5), it was impossible to calculate this ratio because the peaks were too broad to integrate. Thus, it can be concluded that the oxalic acid treatment not only removes the external acid sites [12,13], but also brings

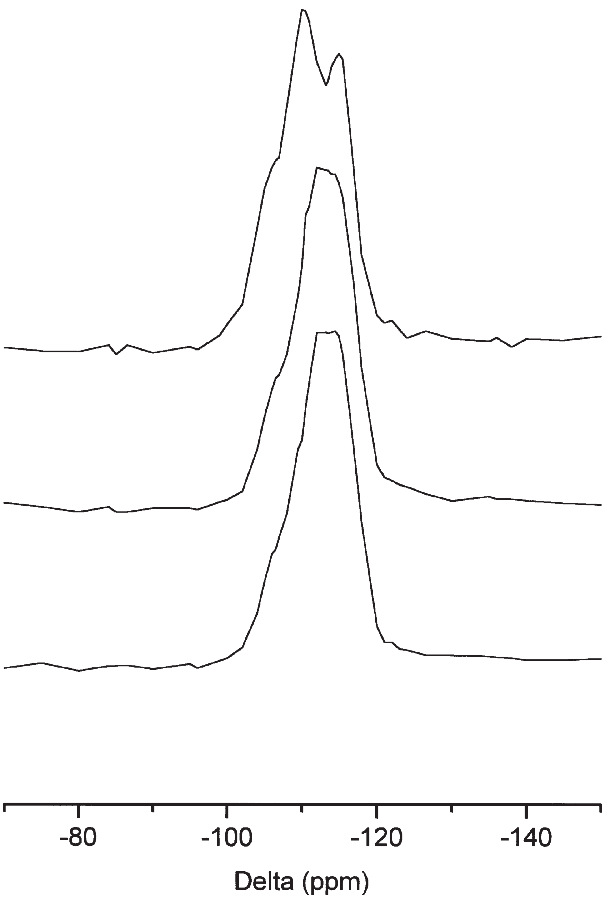

Figure 1. ^{29}Si MAS-NMR spectra for unmodified and modified samples: (a) H-FER, (b) H-FER(0.25), (c) H-FER(0.5).

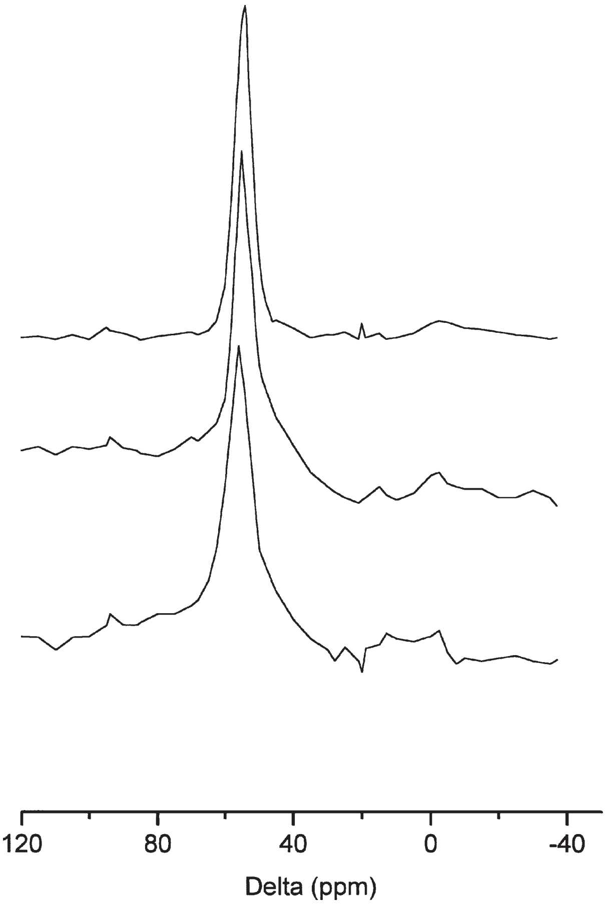

Figure 2. ^{27}Al MAS-NMR spectra for unmodified and modified samples: (a) H-FER, (b) H-FER(0.25), (c) H-FER(0.5).

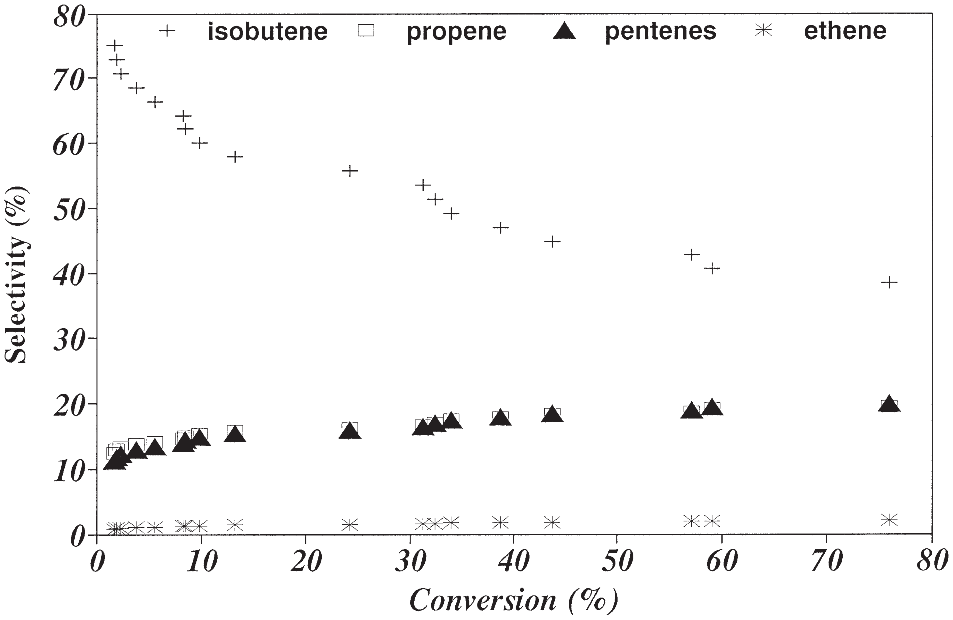

Figure 3. NH_3-TPD spectra for H-ferrierite samples. Temperature was raised from 110 to 710 °C at the rate of 8 °C/min and was kept at the final temperature for 30 min.

Table 1
NH_3-TPD results for H-FER and oxalic-acid-treated H-FER catalysts.[a]

	TH peak			OH peak		
	$T_{\max}$ (°C)	NH_3 uptake	Fraction	$T_{\max}$ (°C)	NH_3 uptake	Fraction
H-FER	447	7.56×10^{-4}	93.8	707	0.50×10^{-4}	6.2
H-FER(0.25)	414	2.28×10^{-4}	79.9	707	0.57×10^{-4}	20.1
H-FER(0.5)	364	1.13×10^{-4}	57.4	710	0.84×10^{-4}	42.6

[a] Spectra were deconvoluted using GRAMS software.

Table 2
Nitrogen adsorption–desorption results for H-FER samples.[a]

	Micropore area	External surface area	BET area
H-FER fresh	284.4	21.1	305.5
H-FER-20	101.3	21.4	122.7
H-FER-190	14.8	18.2	32.9
H-FER(0.25) fresh	311.5	32.0	343.5
H-FER(0.25)-20	115.7	23.1	138.8
H-FER(0.5) fresh	305.8	35.9	341.7
H-FER(0.5)-20	297.7	35.8	333.6
H-FER(0.5)-200	170.8	29.6	200.4

[a] The numbers after sample name denotes reaction time-on-stream (in minutes); area unit is m^2/g.

about a partial collapse of the local structure in the channels by dealumination. Similar observations were made by Xu et al. [14] for H-FER with the Si/Al ratio of 8.8 upon steam treatment at different temperatures and duration. SEM and XRD results (not shown here), on the contrary, did not indicate any noticeable change by acid treatment.

In figure 3 and in table 1 are shown NH_3-TPD results for parent and modified samples. There are three peaks for H-FER at the temperatures of 225, 447 and 706 °C. As discussed by Bagnasco [15], the peaks at 447 (TH peak) and 706 °C (OH peak) are considered to represent the true acidic sites; the TH peak at 447 °C results from the ammonia desorbed from Brønsted acid sites, whereas the OH peak at 706 °C reflects the non-framework acidic sites. Based on the Si/Al ratio and K_2O content of 2.7 wt%, the total number of acid sites for H-FER is estimated to be 8.32×10^{-4} mol/g, which is in good agreement with the total ammonia uptake of 8.06×10^{-4} mol(NH_3)/g. The area of the OH peak for H-FER also agrees well with the ^{27}Al MAS-NMR results, indicating that the peak represents desorption of ammonia from octahedrally coordinated aluminum ions. When H-FER is treated with oxalic acid, the total number of acid sites decreases dramatically, as shown in table 1, in conformity to MAS-NMR results. As the severity of the treatment increases, the density of the extra-framework acid sites increases at the expense of the Brønsted acid sites.

In table 2 are shown nitrogen adsorption–desorption results. The acid treatment brings about the increase in the micropore areas of the samples as well as the increase in the external surface areas, calculated from the t-plot analysis [16], due to the leaching of the Al ions from framework. The main micropore diameter analyzed by the Horvath–Kawazoe method [17] was 5.5–5.7 Å in good agreement with the literature [18] and did not change appreciably with the acid treatment, suggesting the major pore size distribution is unaltered by the modification. The dealuminated samples are resistant to deactivation, as evidenced by high micropore areas after reaction.

3.2. Skeletal isomerization

Reaction studies were carried out for modified and unmodified H-FER/ZSM-35 samples using equimolar mixtures of argon and 1-butene; the feed rates and amounts of the catalysts were varied to get a wide range of conversion values, as shown in figure 4. Over all the samples, major products obtained are ethene, propene, butenes, and pentenes with small amounts of methane, ethane, propane, butane, and C_5^+ hydrocarbons, depending on the reaction conditions and catalysts employed. When the conversion is low and the surface of the catalyst is clean, propene, butenes, and pentenes are mainly observed (table 3). The dealumination of H-FER with oxalic acid reduces the activity, as the density of acidic sites is decreased, in accordance with MAS-NMR and NH_3-TPD results (figures 1, 2 and table 1). On the other hand, the selectivity to isobutene increases with the severity of the treatment. In the case of unmodified H-FER, the selectivity to isobutene extrapolated to zero conversion is 73.4%, while those to other products, i.e., ethene, propene, and pentenes, are maintained at relatively lower levels (figure 4, table 4). This high selectivity

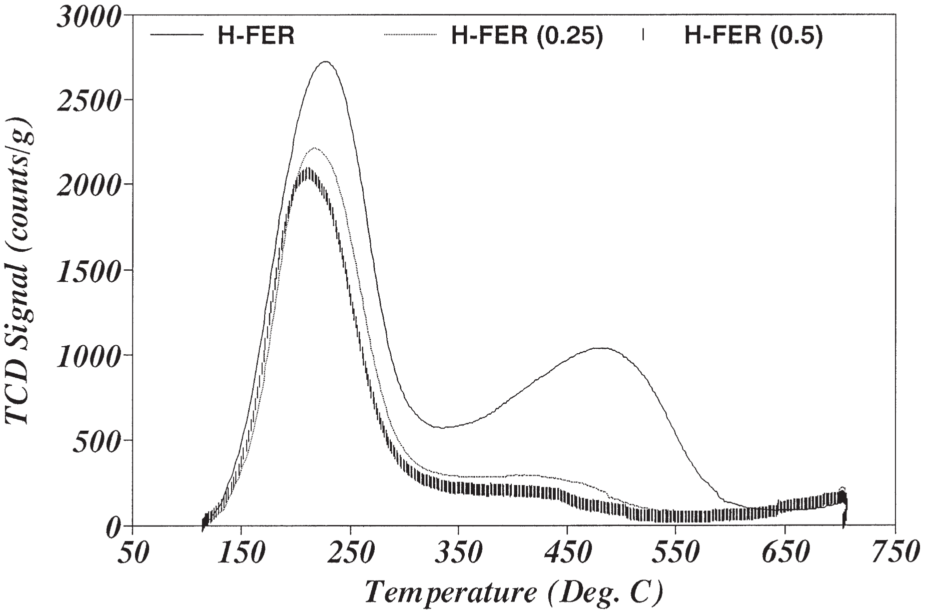

Figure 4. Selectivities for 1-butene skeletal isomerization over unmodified H-FER at 425 °C as a function of conversion.

Table 3
Conversion of 1-butene over H-FER catalysts.[a]

	Conv.	Selectivity							Coke
	(%)	$C_2^=$	C_3	$C_3^=$	C_4's	$iC_4^=$	$C_5^=$	$iC_4^{=}*$	(wt%)
H-FER	2.82	1.73	0.26	14.44	3.10	70.26	10.21	87.39	3.94
H-FER(0.25)	2.48	0.58	0	10.62	4.76	73.76	10.29	87.05	NA[b]
H-FER(0.5)	2.22	0.37	0	8.25	5.25	78.41	7.73	87.92	1.85

[a] All data based on weight were taken at 20 min on stream at the WHSV of 334 h^{-1}, except for the selectivity to isobutene (marked as $iC_4^{=}*$) which was taken at 200 min.

[a] No data available.

Table 4
Selectivities to major products over various molecular sieves.[a,b]

	Temp.	Selectivity			Ratio of	Conv.
	(°C)	$iC_4^=$	$C_3^=$	$C_5^= + C_5$	$C_3^=$ to C_5's	(%)
Cr silicate	400	39.13	21.93	36.45	0.60	4.61
H-ZSM-5	200	11.85	24.66	43.78	0.56	5.00
H-FER[b]	425	73.40	13.20	12.31	1.07	0
H-FER(0.5)[b]	425	95.23	1.57	2.91	0.54	0

[a] For Cr silicate and H-ZSM-5, reaction conditions were adjusted to get a similar conversion level.

[b] Data were obtained by extrapolation to zero conversion.

over H-FER is in good contrast with those obtained over other molecular sieves (table 4). For H-FER(0.5), the selectivity to isobutene is even higher at zero conversion (table 4) and does not change much with time, unlike H-FER and H-FER(0.25) samples (table 3), indicating that the active centers in H-FER(0.5) have already become selective by removing non-selective acidic sites by acid treatment [12,13] without the help of the cokes which impose increased spatial constraints in ferrierite leading to a high selectivity to isobutene [6,8]. As non-selective surface acid sites are removed, much less carbonaceous deposits requiring large cavities or channels are formed over H-FER samples modified by oxalic acid (table 3). Accordingly, the micropore areas of the modified samples are not much reduced after three hours on stream, as shown in table 2.

When only major products are considered, there are two reaction mechanisms for the skeletal isomerization of 1-butene:

$$2\ \text{1-butene} \longrightarrow \text{octene} \begin{array}{ll} \nearrow \text{2 isobutene} & \text{(1a)} \\ \searrow \text{propene} + \text{pentene} & \text{(1b)} \end{array}$$

$$\text{1-butene} \longrightarrow \text{isobutene} \qquad (2)$$

If the isomerization occurs following reaction (1a) according to a bimolecular reaction mechanism or dimerization–cracking mechanism, considerable amounts of propene and pentenes should be formed via reaction (1b) as well. This is the case for pentasil group molecular sieves, over which a quasi-stoichiometric weight ratio of propene to C_5's, i.e., ca. 0.6, through reaction (1b) is formed at relatively low conversions (table 4). Consequently, on chromosilicate and H-ZSM-5, there is no preferential formation of isobutene. A totally different situation, however, is found over H-FER samples. Mainly isobutene is formed with a propene to pentane weight ratio of 1.07 even over unmodified H-FER. This suggests that over H-FER prevailing reaction mechanism is not likely to be bimolecular in nature, because in such a case we should be able to observe much higher formation of propene and pentenes by a dimerization–cracking mechanism. However, we cannot rule out the possibility that some of propene and pentanes have been formed on non-selective external sites following the bimolecular reaction mechanism. Acid treatment results in much higher formation of isobutene through a mono-molecular reaction path (reaction (2)), as the selectivity to isobutene of about 95% cannot be achieved if the bimolecular reaction path is controlling.

Therefore, it is concluded that oxalic acid treatment is effective in removing surface acid sites of H-FER zeolite. During this process, it is inevitable that a part of the framework aluminum ions are either removed or moved to extra-framework positions. On H-FER having only internal active sites, the skeletal isomerization of 1-butene occurs through a mono-molecular reaction mechanism.

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