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Selective skeletal isomerization of 1-butene over FER-type zeolites derived from PLS-3 lamellar precursors



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ABSTRACT

Layered aluminosilicates of PLS-3 were hydrothermally synthesized and employed as the catalysts for the skeletal isomerization of 1-butene. PLS-3 lamellar precursors were successfully prepared at different Si/Al ratios ($40-\infty$) using layered silicate H-kanemite as silica source and tetramethylammonium hydroxide as structure directing agent. A direct calcination caused an interlayer dehydration condensation, converting the precursors into 3-dimensional FER structure with an intersecting micropore system of 8×10 -membered rings. The physicochemical properties of the Al-PLS-3 materials thus prepared were characterized by various techniques. Their catalytic properties in the skeletal isomerization of 1-butene has been investigated and compared with conventional ferrierite. Al-PLS-3 synthesized at Si/Al = 50 exhibited the same catalytic reactivity as commercial ferrierite. However, possessing smaller crystal size, Al-PLS-3 possessed a much longer catalytic duration against coke formation.

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1. Introduction

Skeletal isomerization of 1-butene into isobutene has long been of industrial and academic research interests as isobutene is widely used in the reaction with methanol to produce methyl *tert*-butyl ether (MTBE), which is an important additive of reformulated gasoline for enhancing the octane number [1–3]. Many researches have been carried out to investigate the catalytic performance of 1-butene isomerization over medium pore zeolites with shape-selective properties [4–12]. It seems that the proton form ferrierite zeolite with the FER topology, which contains a twodimensional pore system consisting of 10-membered ring (MR) channels intersected by 8-MR channels, is much more effective than other zeolites in terms of selective formation of isobutene. It is capable of giving an isobutene yield close to thermodynamic equilibrium value.

Many researches have dealt with the reason for the outstanding catalytic performance of FER in 1-butene isomerization. Although the intersected channels of 10-MR \leftrightarrow 8-MR endow the FER zeolite with unique abilities for skeletal isomerization, the isobutene selectivity and catalytic stability are not always guaranteed good unless the carbonaceous deposits are formed [13–15]. To explore the catalytic processes with enhanced selectivity, the acidic properties of less selective materials were modified, e.g. reducing the acid site

density by increasing the Si/Al ratio [9,12,15–18]. By decreasing the Al content, undesirable reactions like dimerization and cracking are suppressed effectively under lower acid site density and comparable weak acid conditions, and then better initial selectivity and longer catalyst lifetime are achieved. Furthermore, there is also report giving the viewpoint that smaller crystals are benefit for isobutene selectivity, for they can afford more 10-MR entrance mouths per unit weight [19]. Thus, direct synthesis of high silica FER zeolites simultaneously with nanosized particles if possible is of practical significance in terms of exploring more effective processes for 1-butene isomerization.

The FER zeolites are usually prepared in an inorganic system with the coexistence of alkali cation such as sodium and potassium [20]. This conventional synthesis generally requires relatively high crystallization temperatures. Meanwhile, it is difficult to exchange the potassium ions in the zeolites synthesized from this system, which directly restricts their applications as solid-acid catalysts and selective adsorbents. Recently, by using seeding technique, Xiao et al. have succeeded in the organotemplate-free synthesis of FER using CDO-structure zeolite building units that are obtained from the calcined layered silicate RUB-36 [21]. On the other hand, the hydrothermal synthesis of FER zeolites using organic compounds as the structure-directing agents (SDAs) has a long history dating back to 1977. Up to date, the organic SDAs employed for the synthesis of FER are over 30 kinds, most of which are nitrogen-containing ammoniums or amines [22–24].

Apart from the traditional ferrierite zeolites that already possess the 3-dimensional (3D) FER topology, the FER lamellar

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precursors have also been synthesized. Marler et al. reported that a PREFER aluminosilicate of 2D layered structure could be synthesized in fluoride media in the presence of 4-amino-2,2,6,6tetramethylpiperidine as SDA [25]. This precursor is composed of the layered stacking of the FER sheets that are intercalated by the SDA species. Upon calcination, interlayer dehydroxylation and condensation occur to cause a structural transformation to 3D FER topology. In the process, the layer structure-related [200] and [400] diffractions are shifted to higher angles because of a decrease in interlayer spacing. PREFER possesses a plate-like morphology with a relatively large crystal size of ca. 20 µm. Lately, a dual templating strategy using two SDAs with different molecular dimensions has also been developed to synthesize the FER-type layered materials which have similar structure to PREFER but a different interlayer distance [26-28]. Nevertheless, these lamellar precursors have a relatively large crystal size that is unsuitable for 1-butene isomerization.

Recently, a new lamellar precursor with the structure similar to PREFER, i.e. PLS-3, has been reported [29]. It is worth mentioning that the crystal size of PLS-3 is of nanometer scale (50–150 nm). Al-containing material, Al-PLS-3, was also patented [30], but the detailed synthesis conditions for the crystallization at different Si/Al ratio still need further investigation, and its catalytic properties are not yet mentioned.

In this study, we have optimized the synthesis conditions for Al-PLS-3 in particular the crystallization process depending on the Si/Al ratio. The physicochemical properties of the products were well characterized with various techniques. Their catalytic performances were further investigated in the skeletal isomerization of 1-butene by comparing to commercial ferrierite. Characteristics of small crystal size and high Si/Al ratio, Al-PLS-3 proved to be a more stable isomerization catalyst with a prolonged lifetime.

2. Experimental

2.1. Material synthesis

The lamellar precursors of aluminosilicate Al-PLS-3 were synthesized through a solid-state conversion of protonated kanemite using tetraethylammonium hydroxide as the SDA according to literature procedures [29,30]. In a typical synthesis, H-kanemite, Al(NO₃)₃·18H₂O, NaOH and distilled water were dissolved in TEAOH (25 wt.% aqueous solution) under magnetic stirring. The molar composition of the starting mixture was $1.0 \text{ SiO}_2:1/x$ $Al_2O_3:0.2$ TEA⁺: *y* NaOH:6.5 H₂O, where *x* and *y* were varied in the range of $20-\infty$ and 0-0.36, respectively. The synthetic gel was charged into a stainless autoclave equipped with a Teflon liner and heated at 443 K for 4–24 h under static conditions. The solid product was collected by filtration, washed with distilled water, and dried overnight in an oven at 353 K. The material with the PLS-3 lamellar structure was calcined in air at 823K for 10h to remove the organic species occluded, giving rise to 3D FER structure. The calcined Al-PLS-3 samples were then converted into ammonium form by stirring in 1 M NH₄Cl solution at a solid-to-liquid ratio of 1:50 for 2 h. The ion-exchange was repeated for three times. The samples were converted into proton form by calcination at 773 K for 5 h.

For control experiment, a commercial FER sample (Si/Al=8.4; Na, K form) was provided by Tosoh, and Al-Beta was synthesized in the above-mentioned system at a higher Na/Si ratio of 0.24. They were similarly converted into proton form by ammonium ion-exchange and calcination.

2.2. Characterization methods

The X-ray powder diffraction (XRD) patterns were measured on a Rigaku Ultima IV X-ray diffractometer using Cu-K α radiation $(\lambda = 1.5405 \text{ Å})$. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 microscope. Al content was determined by inductively coupled plasma emission spectrometry (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. The IR spectra were collected on Nicolet Nexus 670 FT-IR spectrometer in absorbance mode at a spectral resolution of 4 cm⁻¹. The sample was pressed into a self-supported wafer with 4.8 mg cm⁻² thickness, which was set in a quartz cell sealed with CaF₂ windows and connected to a vacuum system. After evacuated at 723 K for 2 h, pyridine adsorption was carried out by exposing the pretreated wafer to a pyridine vapor at 298 K for 0.5 h. The adsorbed pyridine was evacuated successively at different temperatures (423-723 K) for 1 h. The spectra were collected at room temperature. ²⁷Al solidstate MAS NMR spectra were recorded on a VARIAN VNMRS-400WB spectrometer under one pulse condition. The spectra were recorded at a frequency of 104.18 MHz, a spinning rate of 10.0 kHz, and a recycling delay of 4 s. KAl(SO₄)₂·12H₂O was used as the reference for chemical shift. Nitrogen gas adsorption measurements were carried out at 77 K on a BEL-MAX gas/vapor adsorption instrument. The samples were evacuated at 573 K for at least 6 h before adsorption.

2.3. Skeletal isomerization of 1-butene

The isomerization of 1-butene was carried out on a continuous flow microreactor under atmosphere pressure. In a typical run, 0.2 g catalyst in proton form was put into a quartz tube with inner diameter of 11 mm, where it was activated at 673 K for 1 h in nitrogen flow. Then, the mixed gas of 1-butene (99.9%) and nitrogen were fed into the reactor to start the isomerization at 673 K. The partial pressures of 1-butene and nitrogen were controlled with mass flowmeter to be 0.1 and 0.9 bar, respectively. The weight hourly space velocity (WHSV) was $5.2 \,h^{-1}$ with respect to 1-butene. Reaction products were analyzed on-line by a gas chromatograph equipped with an Al_2O_3/S column (50 m × 0.53 mm × 0.25 µm). Since there is a thermodynamic equilibrium for the butene isomers at isomerization temperature even in the absence of any catalyst, the linear butenes were thus considered as the reactant when calculating the conversion and product distribution.

3. Results and discussion

3.1. Hydrothermal synthesis of PLS-3 precursors

Fig. 1 shows the XRD patterns of the samples that were synthesized from the kanemite/TEA⁺ system at a fixed Si/Al ratio of 50 while changing the Na/Si ratio. According to the literature [29], the PLS-3 phase is easily crystallized for a pure silica system. However, the addition of heteroatom Al into the gels made the nucleation and crystallization complicated. The results indicated that the sodium ion content was an important parameter determining the phase purity. The product phase emerged depended greatly on the gel Na/Si ratio. Increasing the Na/Si ratio from 0 to 0.36, amorphous silica, Al-PLS-3, Beta and MOR phases were obtained, respectively (Fig. 1a-d). This implied that this synthetic system was less stable and controllable in terms of phase discrimination. This outcome differed slightly from the patent that claimed the pure Al-PLS-3 materials were crystallized readily not strictly related to the Na/Si ratio [30]. Different from rigid 3D zeolite structure, Al-PLS-3 possessed a modifiable and changeable layered structure. The layered structure-related [200] diffraction shifted from 7.5° to 9.4° after the calcination at 823 K for 6 h (Fig. 1b and b'). This is simply a result of removal of occluded organic species accompanied by condensation of hydroxyl groups between the layers, inducing a topotactic transformation from precursor to 3D FER topology as shown in



Fig. 1. XRD patterns of the samples as-synthesized at Na/Si ratio of (a) 0; (b) 0.04; (c) 0.24; and (d) 0.36 as well as corresponding calcined ones (b'-d'). Other crystallization conditions: gel molar composition, $1.0SiO_2$: $0.01Al_2O_3$: $0.2TEA^+$: $6.5H_2O$; temperature, 443 K; time, 5 h.

Fig. 2. The crystallization rate in this synthetic system was relatively rapid. Generally, highly crystalline materials were obtained within 5 h.

Fig. S1 shows the XRD patterns of the samples synthesized at different Si/Al ratios (20– ∞) at 443 K for 5 h before and after calcination. The Na/Si ratio was fixed at 0.04, an appropriate value for crystallizing a pure Al-PLS-3 phase as indicated above. The product obtained at Si/Al ratio of 20 exhibited the reflections due to pure phase Beta topology (Fig. S1a). Increasing the Si/Al ratio to 40, the reflections due to the FER phase emerged together with the Beta topology (Fig. S1b and c). While the Si/Al ratio was increased over 50, pure FER zeolites were crystallized free of Beta phase (Fig. S1d-g). Based upon a systematical investigation into the synthesis parameters, a schematic diagram for the crystalline products from the H-kanemite/TEAOH system was achieved (Fig. S2). Since TEAOH is a typical SDA for synthesizing Beta zeolites [31], it is reasonable that the crystallization conditions should be carefully optimized in order to obtain pure FER zeolites. We found that this purpose could be realized by adjusting the gel Si/Al ratio over 50.

To further explore the synthesis process for Al-PLS-3, we investigated the time course of crystallization at fixed Si/Al ratio of 50. At initial stage, only amorphous products were obtained, whereas the FER phase appeared at 3.5 h (Fig. S3). Fig. S4 shows the change of relative crystallinity of Beta to FER with the crystallization time. Fully crystallized Al-PLS-3-50-6h with a pure FER phase was assumed to be of 100% crystallinity. The relative crystallinity of the samples synthesized for a different period time was then calculated by comparing their sum intensity of XRD diffractions of the FER or Beta phase to that of Al-PLS-3-50-6h. After crystallization for 5 h, the



Fig. 3. IR spectra in the hydroxyl stretching vibration region of (a) Al-PLS-3-50-5h; (b) Al-PLS-3-50; (c) Al-PLS-3-50-12h; and (d) Al-Beta-50.

crystallinity of the FER phase reached 85%, giving rise to a sample denoted as Al-PLS-3-50-5h (Fig. S4). When the crystallization time was prolonged to 6 h, the FER phase was fully crystallized, reaching a maximum crystallinity. Meanwhile, a small amount of Beta phase interfused in the product as evidenced by the XRD reflection around 7.5°. The crystallinity of Beta increased and that of FER decreased with further prolonging the crystallization time to 10 h. It seems that the Beta zeolite was formed at consumption of a part of the FER zeolite. Nevertheless, this kind of crystal transformation occurred to a limited extension of ca. 20%, as the system became almost steady during the crystallization for 10–20 h. Usually, the phase transformation in hydrothermal synthesis takes place from a metastable zeolite to a stable phase completely. However, the present system was capable of giving a final product dominated by FER topology at a relatively high Si/Al ratio of 50 (Figs. S3 and S4).

After optimizing the crystallization conditions, we synthesized the FER samples with different Al contents, Si/Al ratio of 40–100 (Fig. S5). To increase phase purity and crystallinity, they were crystallized by changing the heating time in the range of 5–24 h. It turned out that well crystallized FER zeolites were obtained at Si/Al ratio of 50–100, whereas a fraction of Beta phase co-existed at lower Si/Al ratios. Taking Al-PLS-3-40 as an example, it became more inclined to form the Beta phase, resulting in a FER zeolite with lower crystallinity (Fig. S5a). At Si/Al ratio of 100, the product was of pure FER phase even after the crystallization was carried out for a long time of 24 h. This result indicated again that a low Al content was suitable for synthesizing pure Al-PLS-3.

3.2. Physicochemical properties of Al-PLS-3 zeolites

IR and ²⁷Al NMR spectroscopies were applied to study the insertion procedure of Al ions into the framework. Fig. 3 shows the



Fig. 2. Schemiatic illustration for topotactic transformation of Al-PLS-3 lamellar precursor to 3D FER-type zeolite through calcination.

No.	Sample	Si/Alc	$S_{\text{BET}}^{a} (m^2 g^{-1})$	V_{total}^{b} (cm ³ g ⁻¹)	Conv. ^d (%)	Sel. ^d (%)					
						$C_2^=$	C ₃	C ₃ ⁼	n-C ₄	$i-C_4^=$	C ₅₊
1	Si-PLS-3	∞	379	0.27	_	-	-	-	-	-	-
2	Al-PLS-3-100	97	476	0.28	19.8	0.5	0.03	3.1	1.7	87.0	5.2
3	Al-PLS-3-80	74	477	0.29	22.2	0.4	0.0	2.0	1.8	88.6	5.6
4	Al-PLS-3-50	47	441	0.29	40.1	0.5	0.0	2.6	1.6	91.3	2.6
5	Al-PLS-3-40	39	306	0.23	23.0	0.3	0.02	3.5	1.8	90.4	3.0
6	Al-PLS-3-50-5h	45	354	0.30	20.6	0.4	0.02	3.0	2.0	89.8	2.7
7	FER-Tosoh	8.3	401	0.29	8.9	0.7	0.02	9.8	1.5	77.8	9.0

Physicochemical properties and catalytic performances in 1-butene isomerization of various FER zeolites

 $^{a}\,$ Specific surface area given by N_{2} adsorption at 77 K.

^b Calculated from the adsorption capacity at $P/P_0 = 0.9$.

^c Determined by ICP.

^d 1-Butene isomerization: WHSV, 5.2 h⁻¹; temperature, 673 K; TOS, 360 min.

IR spectra in the hydroxyl stretching vibration region for the Al-PLS-3-50-5h, Al-PLS-3-50 and Al-PLS-3-50-12h samples that were synthesized by the crystallization for 5 h, 6 h and 12 h along with Al-Beta-50. Sample Al-PLS-3-50-5h showed a main band at 3745 cm⁻¹ (Fig. 3a), which is attributed to terminal isolated silanols. However, it exhibited no obvious in the region of structural Si(OH)Al groups. On the other hand, Al-PLS-3-50, the sample crystallized for one hour longer than Al-PLS-3-50-5h, exhibited a new band at 3600 cm⁻¹ (Fig. 3b), assigned to the structural Si(OH)Al groups in the framework of FER zeolites [32]. This implies that more tetrahedrally coordinated framework Al ions were achieved by prolonging crystallization time. These two samples had very similar Si/Al ratios as evidenced by ICP analysis (Table 1, Nos. 4 and 6). It is deduced that the FER structure construction did not synchronize with the insertion of Al ions into the framework. The former took place more rapidly, whereas the latter had a delay during crystallization. The Al ions probably adhered to the crystallites first as extra framework species, and then they were gradually inserted into the framework.²⁷Al NMR spectra provided solid evidences to this postulation. The spectrum of Al-PLS-3-50-5h showed two resonances at 0 ppm and 54 ppm, representing the tetrahedral Al and octahedral extra framework Al, respectively [33]. In particular, the 54 ppm resonance was relatively broad, implying the Al species were of less symmetric (Fig. 4a). However, the Al-PLS-3-50 sample showed a single resonance at 54 ppm (Fig. 4b). This resonance was much sharper and more symmetric, suggesting the Al ions occupied the framework position to have a better coordination state.

One may suspect the occurrence of the 3600 cm^{-1} band is simply due to the Beta phase contaminated in the FER product. To rule out this possibility, we compared the spectra with that pure

Beta zeolite, Al-Beta-50, synthesized in this system but at a higher Na/Si ratio of 0.24. Al-Beta-50 showed the stretching vibration for the structural Si(OH)Al groups centered at 3610 cm⁻¹ (Fig. 3d). The position is fully in agreement with literature [34]. Thus, the structure difference leads to 10 cm⁻¹ difference in structural Si(OH)Al groups between BEA and FER. The 3600 cm⁻¹ band is considered to be contributed mainly by the tetrahedral Al in Al-PLS-3-50 but not by Beta phase. The spectrum of Al-PLS-3-50-12h was also given for comparison. As a result of longer crystallization, it contained more Beta phase than Al-PLS-3-50. It then showed peak at 3607 cm⁻¹ between 3600 cm⁻¹ and 3610 cm⁻¹ (Fig. 3c), indicating that structural Si(OH)Al groups of this material were generated from both the FER and Beta phases. As a result, it is necessary to control precisely the crystallization process of Al-PLS-3 in order to achieve the FER solid acid catalysts not only with a high crystallinity and purity but also containing the framework Al showing Brønsted acidity.

Fig. 5 shows the IR spectra in the hydroxyl stretching vibration region for the Al-PLS-3 samples synthesized at different Si/Al ratios. Silicalite Si-PLS-3 reasonably showed on the terminal silanol band at 3745 cm⁻¹ but no peak at 3600 cm⁻¹ (Fig. 5a). The 3600 cm⁻¹ band due to the framework Al increased in intensity with increasing Al content except for Al-PLS-3-40 with a lower crystallinity (Fig. 5b–e). The amount of Brønsted acid sites then would increase with increasing Al content. The ²⁷Al NMR spectra confirmed that these samples were almost free of the extra framework Al species, but contained predominately the tetrahedral ones independent of the Si/Al ratios (Fig. S6).

The catalytic properties of aluminosilicates are closely related to their Brønsted and Lewis acidity. Pyridine was then employed as a probe molecule to provide detailed information about the amount and strength of Brønsted and Lewis acid sites in Al-PLS-3



Fig. 4. ²⁷Al MAS NMR spectra of (a) Al-PLS-3-50-5h and (b) Al-PLS-3-50.



Fig. 5. IR spectra in the hydroxyl stretching vibration region of (a) Si-PLS-3; (b) Al-PLS-3-100; (c) Al-PLS-3-80; (d) Al-PLS-3-50; and (e) Al-PLS-3-40.

Table 1



Fig. 6. IR spectra of Al-PLS-3-50 after pyridine adsorption and desorption at (a) 423 K; (b) 523 K; (c) 623 K; and (d) 723 K.

samples. The IR spectra of adsorbed pyridine in the range of pyridine ring-stretching modes were measured after desorption at various temperatures. As shown in Fig. 6, the bands at 1599 and 1440 cm⁻¹ associated with hydrogen-bonded and physically adsorbed pyridine decreased in intensity with a rising desorption temperature [35–37]. On the other hand, the bands at 1540 cm⁻¹ corresponding to Brønsted acid sites and at 1455 cm⁻¹ corresponding to Brønsted acid sites and at 1455 cm⁻¹ corresponding to Lewis acid sites together with the bands at 1490 cm⁻¹ characteristic of both Brønsted and Lewis acid sites were more evacuation temperature resistant and remained even after desorption at 723 K. These bands are apparently correlated to the different vibration modes of the pyridine-rings adsorbed on the Al species and can be taken as the evidence for the presence of Brønsted and Lewis acid sites in Al-PLS-3-50.

The pyridine adsorption was further carried out on the Al-PLS-3 samples with various Al contents. Fig. S7 compares the spectra of the samples after removing weakly adsorbed pyridine by evacuation at 423 K. The bands at 1540, 1490, and 1455 cm⁻¹ were absent for Si-PLS-3, but increased in intensity with increasing Al content except for Al-PLS-3-40 with a lower crystallinity. Thus indicated that with the introduction of tetrahedrally coordinated Al in Al-PLS-3 the amount of Brønsted and Lewis acid sites increased gradually.

Fig. 7 shows the representative scanning electron micrograph (SEM) of Al-PLS-3 using Al-PLS-3-50 as an example. The morphology of Al-PLS-3-50 was rod-like with a very small crystal length of 50–150 nm (Fig. 7a), which was similar to Si-PLS-3 reported in literature [29]. The image indicates that there was no amorphous phase or obvious Beta crystals, confirming that it was a highly crystalline material with high phase purity. Fig. 7b shows the SEM image of commercial FER-Tosoh. It showed a plate-like morphology and a larger crystal size of $0.5-1 \mu$ m, which was much different from Al-PLS-3-50. As shown in Fig. S10, the morphology of the Al-PLS-3

materials did not depend on the Si/Al ratios $(40-\infty)$ and the calcination or not. They were all rod-like materials with a similar crystal size.

The textural properties of Al-PLS-3 samples with different Si/Al ratios are given in Table 1 together with other physicochemical properties. The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method, whereas the total volume was obtained from the isotherms at $P/P_0 \le 0.9$ because a remarkable increase in the adsorbed volume was observed around $P/P_0 > 0.9$. This phenomenon suggested the presence of macropores due to interparticle condensation and adsorption of nitrogen for small crystal Al-PLS-3. This finding was similar to the adsorption properties of Si-PLS-3 reported previously [29]. The S_{BET} and V_{total} of Al-PLS-3-40 and Al-PLS-3-50-5h were smaller than other samples, which was mainly because of a lower crystallinity as evidenced by XRD and IR investigations. The bulk Si/Al ratios of Al-PLS-3 given by ICP were close to the gel compositions, indicating that the condensation of silicon source and aluminum source took place uniformly during crystallization. The adsorption data of FER-Tosoh were also measured for comparison (Table 1, No. 7). Its S_{BET} and V_{total} were at the same level as Al-PLS-3.

3.3. Catalytic properties Al-PLS-3 in 1-butene isomerization

The catalytic properties of these Al-PLS-3 samples were investigated in the 1-butene skeletal isomerization reaction. Catalytic tests of various Al-PLS-3 catalysts revealed a complex time on stream (TOS) diagram during the isomerization at atmospheric pressure, 673 K and a weight hourly space velocity (WHSV) of 5.2 h⁻¹ (Fig. S8). The catalytic activity and product distribution of Al-PLS-3 at TOS = 360 min are compared in Table 1, including the results obtained with FER-Tosoh. At the beginning of the reaction, TOS = 30 min, all the samples showed high conversions of ca. 70%, but very low selectivities for desirable product isobutene. The main products on this stage were propylene and pentene which occupied over 50% vield. This phenomenon was similar to the results reported before, which is assumed to be caused by the bimolecular mechanism on fresh FER zeolite [14,18,38-43]. At initial stage, the 1-butene molecules experienced dimerization and isomerization to form octenes, and then the cracking of octenes to the final products. A decrease in the activity and a significant increase in selectivity for isobutene can be observed with increasing time on stream. Many researches supported this view point that a tremendous increase of isobutene selectivity was caused by the monomolecular reaction occurred on isolated Brønsted acid sites of aged FER zeolites [40,41,44–46]. The coke deposition in the partially deactive FER restricted the steric space available for bulky intermediates around the acid sites and reduced the density of acid sites, afterwards suppressed the bimolecular processes then made the monomolecular mechanism to be the prevailing one [47]. The conversions decreased quickly in the first 2 h, and simultaneously the selectivity to isobutene rose from about 20% up to 85% for all these samples.



Fig. 7. SEM images of (a) Al-PLS-3-50 and (b) FER-Tosoh after calcination.



Fig. 8. The time course for the skeletal isomerization of 1-butene to isobutene over (a) Al-PLS-3-50 and (b) FER-Tosoh. Reaction conditions: WHSV, $5.2 h^{-1}$; temperature, 673 K; N₂/1-butene molar ratio, 9:1.

Afterwards, the decrease of conversion and increase of selectivity both slowed down. As shown in Table 1, the isobutene selectivity of all Al-PLS-3 samples reached about 90% at TOS = 360 min excepted for Al-PLS-3-40 with too less Brønsted acid sites. The TOS dependence of 1-butenes conversion, selectivity and yield of isobutene for Al-PLS-3-50 and FER-Tosoh are depicted in Fig. 8. On the first stage of the reaction, FER-Tosoh gave a higher conversion for 1butene than Al-PLS-3-50 since it had a higher Al content and more Al acid sites. Both catalysts were capable of giving an isobutene selectivity over 90% with prolonging time on stream. However, FER-Tosoh deactivated obviously more rapidly than Al-PLS-3-50. The FER zeolites originated from Al-PLS-3 lamellar served as more stabile catalysts for 1-butene isomerization.

Fig. 9 shows the dependence of isobutene yield on 1-butene conversion. Al-PLS-3-50 and FER-Tosoh both exhibited a correlation close to the indicated thermodynamic equilibrium. In terms of efficient production of isobutene, the former seemed to be more selective for isobutene. It is worth mentioning that the isobutene selectivity increased faster with TOS for Al-PLS-3-50 than for FER-Tosoh (Fig. 8). After the reaction run for TOS of 600 min, the coke formed on Al-PLS-3-50 accounted for 5.3 wt.%, but reached 9.8 wt.% on FER-Tosoh as given by TG analysis (Fig. S9). As mentioned above, the coke deposition play a crucial role in the isobutene selectivity increasing process, as it can reduce the density of acid sites and suppress the bimolecular reaction. Thus, a faster increase in selectivity for Al-PLS-3-50 can be understood easily as its acid site density was already low. And for the higher stability of Al-PLS-3-50 than FER-Tosoh, this may be contributed by less acid site change and micoropore volume loss in the former catalyst, because the carbonaceous deposition accumulated in its pore was lower.



Fig. 9. Isobutene yield as function of 1-butene conversion obtained for Al-PLS-3-50 and FER-Tosoh at 673 K.

Thus, the textural properties were measured for Al-PLS-3-50 and FER-Tosoh after being used in the 1-butene isomerization for 10 h (Table S1). In comparison to the fresh catalysts, the used ones both decreased greatly their surface area and pore volume. Nevertheless, Al-PLS-3-50 still possessed a surface area of $170 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.14 \text{ cm}^3 \text{ g}^{-1}$ after catalytic run, while the used FER-Tosoh showed a surface area of only $38 \text{ m}^2 \text{ g}^{-1}$. These results were in accordance with above-mentioned deduction. Furthermore, these catalytic behaviors were similar to the literature results on high Si/Al ratio FER reported by Martínez et al. [47], suggesting that a monomolecular mechanism was probably involved in the isomerization.

4. Conclusions

Lavered aluminosilicates Al-PLS-3 with different Al contents are prepared by hydrothermal synthesis at Si/Al ratios of 40-100. The calcination caused a structural transformation to 3D FER zeolites. The amount of sodium ions is confirmed to be an important factor to govern the crystallization of pure Al-PLS-3 phase. High sodium content in gels easily leads to the formation Beta and MOR zeolites. The insertion of Al ions into the framework of Al-PLS-3 does not take place in initial stage, but is achieved after the finishing up of the FER framework construction. The Al ions adhere to Al-PLS-3 in extra framework form firstly and then further crystallize into the framework. During this process a fraction of Beta mixed crystal will form, but it neither make contributions to the acidities of these materials nor influence their activities. All the Al-PLS-3 samples give excellent catalytic performance for 1-butene isomerization and among them Al-PLS-3-50 synthesized at Si/Al ratio of 50 is highly active and selective to isobutene (over 90%), giving an isobutene yield about 35%.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata. 2013.01.024.

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