n-Butene Skeletal Isomerization to Isobutylene on Shape Selective Catalysts: Ferrierite/ ZSM-35

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Ferrierite/ZSM-35 is a shape selective zeolite catalyst for *n*-butene skeletal isomerization to isobutylene. Hydrothermal methods were used to synthesize well-crystallized ferrierite/ZSM-35 materials of different silicon to aluminum ratios and crystallinities in the presence of an organic template, pyrrolidine. Non-templatesynthesized ferrierite was also studied. XRD, FTIR, SEM-EDX, NMR, ammonia TPD, pyridine chemisorption, and BET/pore size distribution methods were used to characterize these ferrierite materials. Ferrierite materials of high crystallinity contain more hydroxyl groups responsible for Brønsted acid sites and fewer Al species responsible for Lewis acid sites. Well-crystallized materials also have more perfect micropores. It is revealed that ferrierite materials of higher crystallinity are more shape selective for reaction of *n*-butene skeletal isomerization to isobutylene. Ferrierite materials of poorer crystallinity require more coke deposition to poison, block, and modify non-shape selective acid sites (external acid sites) in order to suppress side reactions such as butene dimerization followed by cracking. The presence of sodium ions in the zeolite is detrimental to isomerization reactions since they block the channels which have been partially blocked by the deposited coke. The preferential formation of *cis*-but-2-ene is observed and explained by a strong steric interaction between pore walls of small pore zeolites and methyl groups of the secondary butyl carbenium ions.

I. Introduction

Isobutylene is an important raw material for production of methyl *tert*-butyl ether (MTBE), which is currently used as a major booster of the octane number of gasoline.¹ However, the present market demand for MTBE is not met by the major supply of isobutylene from the catalytic cracking of petroleum. Therefore, finding a new source for isobutylene via skeletal isomerization of *n*-butene is of great practical significance.

Medium pore zeolite ZSM-5 (5.3×5.6 , 5.1×5.5 Å) has been widely used in industries as a shape selective catalyst for isomerization of ortho- and meso-xylenes to para-xylene, conversion of methanol to gasoline, and conversion of methanol to olefins. However, such a medium pore zeolite becomes nonshape selective for isomerization of *n*-butene (small molecule) to isobutylene. It is an active catalyst for interconversion of olefins due to both its pore size and acidity.² Our efforts have been devoted to weakening the acidity of ZSM-5 and ZSM-11 zeolites by substitution of aluminum with boron.³⁻⁸ Weakening of acidity leads to suppression of dimerization reactions and improvements of the yield and selectivity to isobutylene. However, pore sizes of zeolites ZSM-5 and ZSM-11 are large enough to allow butene molecules to dimerize inside the channels of the zeolites. Therefore, dimerization reactions which accompany *n*-butene skeletal isomerization cannot be effectively suppressed on these medium pore zeolites.

Small pore zeolites may have shape selectivities for reactions involved in small molecules. Our research has shown that ferrierite/ZSM-35,⁹⁻¹¹ ZSM-23,¹² and theta-1/ZSM-22¹³ are

shape selective catalysts for skeletal isomerization of *n*-butene to isobutylene. Zeolite ZSM-23 can catalyze *n*-butene skeletal isomerization at extremely high space velocities (170-340 WHSV (weight hour space velocity)) with excellent stability in catalytic activity.¹² Excellent selectivities to isobutylene (85%-95%) were obtained even though there was a sacrifice in the yield of isobutylene (only about 20%-30%), as compared to ferrierite/ZSM-35 catalysts (36%). Dimerization of butene molecules is a primary side reaction in *n*-butene skeletal isomerization. As the but-1-ene space velocity increases (the contact time decreases), secondary side reactions (cracking of octenes) and tertiary side reactions (dimerization of propylene and codimerization of butene and propylene molecules) are suppressed. The activation energy for dimerization reactions is found to be less than that for skeletal isomerization.

Ferrierite/ZSM-35 has an orthorhombic framework¹⁴ containing one-dimensional channels of 10-membered rings (4.2×5.4 Å) and one-dimensional channels of eight-membered rings (3.5×4.8 Å). These two kinds of channels are perpendicularly intersected. The eight-membered-ring channels contain spherical cavities with a size of about 6–7 Å.

Our previous work⁹ has shown that ferrierite/ZSM-35 with such a unique pore structure is a shape selective catalyst for *n*-butene skeletal isomerization to isobutylene. As high as 36% yield and near 90% selectivity to isobutylene have been achieved at a butene partial pressure of 0.5 atm. Our results (adsorption studies of different critical diameter molecules such as ammonia, 1-butene, and isobutylene, kinetic studies of coke formation, pore size distributions, and structural modeling) also suggested that side reactions for *n*-butene isomerization are mainly controlled by two factors, i.e., acidity and limitations of pore size.⁹ Poisoning of strong acid sites by coke deposition leads to suppression of dimerization reactions. Coke deposition also blocks channels and modifies the space around acid sites so

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that acid sites do not have enough room for dimerization reactions. Such coke formation is limited by the micropore volume of ferrierite/ZSM-35. However, ferrierite/ZSM-35 catalysts still have several disadvantages such as long initiation times and slight deactivation.

In this study, ferrierite/ZSM-35 materials with different ratios of silicon to aluminum were prepared by hydrothermal methods using pyrrolidine as a structure-directing template. Different autoclave times led to formation of ferrierite/ZSM-35 materials with different crystallinity. In addition, a ferrierite/ZSM-35 prepared without using organic templates was also used. *n*-Butene skeletal isomerization to isobutylene was also studied on these ferrierite catalysts. These ferrierite materials were characterized by XRD, FTIR, NMR, SEM-EDX, TPD, pyridine chemisorption, and BET/pore size distributions. Effects of crystallinity of ferrierite/ZSM-35 on n-butene skeletal isomerization have been elucidated. Preferential formation of *cis*-2butene was also observed and explained by a strong steric interaction between the pore walls of small pore zeolites and methyl groups of secondary carbenium ions.

II. Experimental Section

A. Synthesis of Ferrierite/ZSM-35. Ferrierite/ZSM-35 samples were prepared by hydrothermal methods using pyrrolidine as a structure-directing template. Sodium aluminate and Ludox HS-30 were used as aluminum and silicon sources, respectively. Sodium hydroxide was used for pH adjustment. Sodium chloride was used to control the ratio of aluminum to sodium. Two recipes for preparing ferrierite/ZSM-35 of the sodium form are as follows: (i) 10 SiO₂/Al₂O₃/1.6 Na₂O/12 pyrrolidine/431 H₂O and (ii) 20 SiO₂/Al₂O₃/1.6 Na₂O/12 pyrrolidine/400 H_2O . The gels of the zeolite precursors were formed by mixing NaAlO₂, NaCl, 1 M NaOH, H₂O, and pyrrolidine followed by addition of LUDOX HS-30 while stirring. Each gel was divided into five stainless steel autoclaves with Teflon liners of 110 mL volume. These autoclaves were then put into an oven in which temperature was controlled at 448 K. Hydrothermal reactions were terminated by taking these five autoclaves out of the oven after 20, 40, 60, 80, and 100 h, respectively. Resultant solid powders were then filtered, washed with DDW, and dried at 403 K overnight to obtain ferrierite/ ZSM-35 of the sodium form.

In addition, another ferrierite/ZSM-35 sample of the sodium/ potassium form was prepared without using any organic templates. This sample, having a silicon to aluminum ratio of 8.8, was received from Texaco, Inc.

Ferrierite/ZSM-35 materials were all calcined at 823 K for 4 h in nitrogen and another 4 h in air. The objectives of twostep calcination processes were to thermally decompose organic templates in an inert atmosphere (nitrogen) and then to burn the decomposition residues off by oxygen (air). This prevented occurrence of a steam atmosphere during zeolite calcination since direct introduction of air into the system would combust organic template to form a significant amount of steam. Ferrierite/ZSM-35 materials of an ammonium form were obtained by ion-exchanging their alkali forms two times with a 1 M aqueous solution of ammonium nitrate at 353 K. The information about different ferrierite/ZSM-35 samples is tabulated in Table 1.

B. Characterization. X-ray diffraction (XRD) experiments were done on a Scintag Model XDS 2000 diffractometer with a monochromatic X-ray beam and scintillator. Samples were mounted on a glass plate that remained horizontal during all experiments. A beam voltage of 45 kV and a current of 40 mA were used with Cu K α radiation.

 TABLE 1: Information about Different Ferrierite/ZSM-35

 Materials

	FER00	FER15	FER23	FER25
template	none	pyrrolidine	pyrrolidine	pyrrolidine
Si/Al in gel	N/A ^a	5.0	10.0	10.0
autoclave time (h)	N/A ^a	100	60	100
Si/Al in zeolite	8.8	5.7	9.2	9.2

^a N/A: not determined.

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses were done on an Amray Model 1810 D microscope with an Amray PV 9800 energy dispersive X-ray analyzer. This energy dispersive X-ray analyzer was equipped with a windowless detector for observation of elements with atomic numbers smaller than Na and greater than Be.

Fourier transform infrared (FTIR) experiments were done on a Nicolet 750 spectrometer at a resolution of 4 cm⁻¹ by using either KBr pellets or self-supporting wafers. Pyridine chemisorption experiments were done on self-supported wafers in an *in situ* IR cell. The sample was dehydrated at 773 K for 5 h under a vacuum of 10^{-5} Torr followed by adsorption of purified pyridine vapor at room temperature for 15 min. The system was then evacuated at 423 K overnight to remove physisorbed pyridine as much as possible. Note that a pyridine molecule chemisorbed on a weak site located at the center of a ferrierite crystal would not be able to escape the crystal if all its neighbors were strongly adsorbed. An infrared spectrum was then recorded.

Magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy data were acquired on a Varian Unity-300 spectrometer. ¹H and ²⁹Si spectra were obtained at resonance frequencies of 300 and 59.9 MHz, respectively, using a Doty Scientific 7 mm CP/MAS probe. The ²⁷Al spectra were acquired with a Chemmagnetics 7 mm CP/MAS probe at a resonance of 78.8 MHz. A 10° tip angle in conjunction with a 1 s recycle delay was employed to obtain both the ¹H and ²⁷Al spectra, while a 30° tip angle and 8 s recycle delay were used to obtain the ²⁹Si spectra. The ¹H and ²⁹Si spectra are referenced to tetramethylsilane (TMS), and the ²⁷Al spectra are referenced to crystalline KAl(SO₄)₂.

Pore size distributions were determined by nitrogen adsorption and desorption data acquired on an Omicron Omnisorp 100CX adsorptive and desorptive apparatus. The Kelvin theory was used to determine the distributions of meso- and macropores. The Horvath-Kawazoe method¹⁵ was used to determine the distribution of micropores.

Temperature-programmed desorption (TPD) experiments were done on a TPD apparatus described previously.^{3,16} The sample was first heated from room temperature to 823 K at a ramping rate of 15 K/min and then soaked at 823 K for 1 h under a flow of 30 mL/min ultrapure helium. The system was then cooled to 373 K over 100 min. Ammonia was then flowed over the sample for 30 min. The sample was then purged with helium for 40 min in order to eliminate physisorbed species. The temperature was ramped at 15 K/min from 373 to 883 K, and TPD data were acquired.

C. Catalysis. Butene isomerization reactions were carried out in a microreactor loaded with 140 mg of zeolite catalysts. The reactor was heated from room temperature to 823 K at a ramping rate of 15 K/min in a flow of nitrogen of 60 mL/min. The temperature of the reactor was maintained at 823 K for 30 min in order to obtain zeolite catalysts of the hydrogen form from an ammonium form. Then the reactor was cooled to 693 K for 20 min. The reactor was then maintained at 693 K, and the nitrogen flow was switched to a mixture of but-1-ene and



Figure 1. pH of Mother liquors with autoclave times for different gel precursors. Ratios of silicon to aluminum are equal to 5 (open circles) and 10 (solid circles).

nitrogen (1:1 molar ratio). Flow rates of both but-1-ene and nitrogen were controlled at 5 mL/min. Reaction products were analyzed every hour after 10 min time on stream with a Hewlett-Packard 5890 Series II GC. This GC was equipped with a GS-Alumina capillary column (J&W Scientific) and a thermal conductivity detector (TCD). Literature values for TCD response coefficients were used for calibration.^{17,18}

III. Results

A. pH of Mother Liquors. Figure 1 illustrates that the pH changes with autoclave time during synthesis of ferrierite/ZSM-35 by using pyrrolidine as a structure-directing template. There is a minimum pH at an autoclave time of 20 h for both gel precursors of Si/Al = 5 (open circle) and 10 (solid circle). No ferrierite crystals were observed in SEM and XRD studies when the autoclave time is 20 h. The pH of the mother liquor is then increased back to about 12.6 when the autoclave time is increased beyond 20 h (such as 40, 60, 80, and 100 h). In addition, the minimum pH for the gel precursor of silicon to aluminum of 5 is smaller than that for the gel precursor of silicon to aluminum of 10.

B. Morphology: SEM. Figure 2 shows scanning electron microscopy results of different ferrierite/ZSM-35 samples. The FER00 sample was hydrothermally synthesized without using organic compounds as structure-directing templates. It has a ratio of silicon to aluminum of 8.8 and an egg-shape morphology, Figure 2a. The ratio of the length to the width of these egg-shape particles is about 2:1. However, an uneven distribution of particle sizes is characteristic of sample FER00. Some particles are as large as 100 μ m, while some particles are as small as several microns. The FER15 sample is a ferrierite/ ZSM-35 which was hydrothermally synthesized using pyrrolidine as a structure-directing template. It has a ratio of silicon to aluminum of 5.7 and a rectangle-shaped sheetlike morphology, Figure 2b. These kinds of rectangles are 16 μ m in length and 12 μ m in width. Hexagonal morphologies of sample FER25 are shown in the SEM results in Figure 2c. The particle size of FER25 is about 22 μ m in length, 12 μ m in width, and 12 μ m in height. Sample FER23 also has hexagonal morphologies which are similar to those for sample FER25.

SEM-EDX analysis was also conducted especially for sample FER15. It was revealed that there were significant amounts of sodium ions left inside the zeolite even after two ion-exchanges of the zeolite with a 1 M aqueous solution of ammonium nitrate. The ratio of aluminum to sodium was found to be about 2.44.

No sodium and potassium were detected for NH_4^+ -exchanged samples FER00, FER23, and FER25 by SEM-EDX analyses. However, ICP results showed less than 0.05 wt % of sodium in these FER00, FER23, and FER25 samples (FER00 also contains about 0.12 wt % of potassium).

C. Structure: XRD. The crystal structure of the prepared or as-received ferrierite/ZSM-35 materials was analyzed by XRD experiments, as shown in Figure 3. Szostak¹⁹ suggested that XRD peak heights can be successfully used in measuring X-ray crystallinity provided that the crystals being examined are larger than 0.3 μ m. Crystal sizes for ferrierite/ZSM-35 in this study are much larger than 0.3 μ m, as shown in Figure 2. The intensities of X-ray diffraction lines for FER25 (Figure 3a) are stronger than those for FER23 (Figure 3b). This indicates that longer autoclave time for synthesis of ferrierite/ZSM-35 leads to materials of higher crystallinity. The overall intensities of XRD lines for FER15 is weaker than FER23 and FER25. The XRD patterns of FER00 (Figure 3d) are very similar to those of FER23 and FER25. However, the XRD intensities of FER00 are weaker than those for FER23 and FER25. This indicates that, for ferrierite/ZSM-35 materials having similar ratios of silicon to aluminum, synthesis with an organic template yields ferrierite materials of higher crystallinity (FER23 and FER25) than the method of nontemplate synthesis (FER00).

D. Acidity: FTIR. Figure 4a presents a typical FTIR spectrum for FER25. IR radiation of about 1100, 800, and below 600 cm⁻¹ was completely absorbed since the spectrum was acquired on a self-supported wafer (about 10 mg). However, use of a self-supported wafer allowed observation of relatively weak IR bands such as 3742, 3601, 1985, 1873, 1628, and 682 cm⁻¹. The IR bands at 3742 and 3601 cm⁻¹ correspond to hydroxyl groups of terminal silanol and hydroxyl groups which are associated with framework silicon and aluminum ions, respectively. Ratios of peak areas at 3601 cm⁻¹ to those at 3742 cm⁻¹ are 38.3, 35.6, 24.6, and 29.2 for FER25, FER23, FER15, and FER00, respectively.

Figure 4b illustrates a typical FTIR spectrum of pyridinechemisorbed FER25. Infrared bands at 1540 and 1460 cm⁻¹ correspond to characteristics of pyridine molecules chemisorbed on Brønsted and Lewis acid sites, respectively. Peak areas of these two IR bands are listed in Table 2 for different ferrierite/ ZSM-35 materials. Sample FER15 has the smallest peak area at 1540 cm⁻¹ and largest peak area at 1460 cm⁻¹ among these four samples. For the other three ferrierite samples, the peak area at 1540 cm⁻¹ follows the order FER00 < FER23 < FER25. On the other hand, the peak area at 1460 cm⁻¹ follows a reverse order, i.e., FER00 > FER23 > FER25.

E. Acidity: TPD. The acidity of these ferrierite/ZSM-35 materials was also studied by ammonia TPD methods, Figure 5. Two peaks of ammonia desorption are observed at temperatures of 471 and 732 K, respectively. The amount of desorbed ammonia at high temperature is 1.17 times greater than that at low temperature. FER00 contains more framework aluminum ions (3.67 Al/uc) than FER23 and FER25 (3.53 Al/uc). Therefore, FER00 has more ammonia uptake (4.42 NH₃/uc, Figure 5a) than FER25 (4.08 NH₃/uc, Figure 5b) and FER23 (4.16 NH₃/uc, Figure 5c). However, FER15 has the least ammonia uptake (4.05 NH₃/uc) among these four ferrierite samples, even though it contains the most framework aluminum ions (5.37 Al/uc). Since NH₃/uc is consistently higher than Al/ uc by about 15%-20%, there may still be physisorbed ammonia after initial flushing which accounts for diffusional limitations.

F. ¹**H**, ²⁹**Si, and** ²⁷**Al MAS NMR.** Figure 6 illustrates typical MAS NMR spectroscopic ¹H (Figure 7a), ²⁹Si (Figure 7b), and ²⁷Al (Figure 7c) data for ferrierite materials. In Figure 7a, Si-



a



Figure 2. Scanning electron microscopy results of different ferrierite/ZSM-35 samples: (a) FER00; (b) FER15; (c) FER25.

OH (terminal silanol) resonances were found in the region of 1-2 ppm, centered at about 1.5 ppm. Resonances at about 4.0 ppm were also observed for Brønsted acid sites, Si-OH-Al (hydroxyl groups which are associated by framework silicon and aluminum ions). No extraframework Al-OH groups were detected in the region of 2.5-3.0 ppm.

For ²⁹Si MAS NMR spectra, samples FER00, FER23, and FER25 have very similar line shapes due to their similar ratios of silicon to aluminum. Q4 resonances of Si(OSi)4 for the sample FER25 (top) were clearly observed at -113 and -109 ppm, Figure 6b. The ²⁹Si MAS NMR spectrum for FER25 also shows a Q₄ Si(OSi)₃(OAl) resonance at -105 ppm. However, the resonance of Q_4 Si(OSi)₂(OAl)₂ at -100 ppm is not detectable due to the relatively high silicon to aluminum ratio for FER25 (9.2). Such a resonance becomes significant for sample FER15 (bottom) due to its lower silicon to aluminum ratio (5.7), as compared to that for sample FER25 (9.2). The resonance at -100 ppm for Q4 Si(OSi)3(OAI) is also significantly enhanced for sample FER15. In addition, there are very few differences in resonance line widths between these samples. Therefore, one cannot make any conclusions as to crystallinity based on the ²⁹Si MAS NMR line shapes.

Figure 6c shows an 27 Al MAS NMR spectrum of sample FER25. Framework tetrahedral aluminum ions have a resonance at 54 ppm, while extraframework aluminum ions show resonances at -2 ppm in an octahedral environment. The resonance

intensity for octahedral aluminum ions (-2 ppm) is relatively low, as compared to that for tetrahedral aluminum ions (54 ppm). In addition, similar MAS NMR line shapes were also observed for samples FER00, FER15, and FER23.

G. BET Surface Areas/Pore Size Distributions. Figure 7 presents the micropore size distributions (<10 Å) of ferrierite samples FER00, FER15 (FER23), and FER25. Non-templatesynthesized FER00 (Figure 7a) has the least micropore volume centered at an effective pore radius of 5.8 Å. Ferrierite samples (FER15, FER23, and FER25) which were synthesized by using templates contain more volume of micropores (Figure 7b,c), as compared to that for non-template-synthesized ferrierite sample, FER00 (Figure 7a). Both FER15 and FER23 samples show very similar micropore size distributions, and they are overlapped in Figure 7b. FER25, having a higher silicon to aluminum ratio (Figure 7c), as compared to sample FER15 (Figure 7b), is of higher crystallinity so it contains more volume of micropores centered at about 5.8 Å. Longer autoclave time also leads to sharper micropore distributions, as compared with Figure 7b for sample FER23 and Figure 7c for sample FER25.

Table 3 gives the results of pore size distributions and BET surface area measurements for the above four ferrierite samples. The ferrierite prepared without using any organic template (FER00) contains much more meso/macropores (589.0 μ L/g) as compared to template-synthesized ferrierites (FER15, FER23, and FER25) (about 365 μ L/g). However, this non-template-



Figure 3. X-Ray diffraction patterns of different ferrierite/ZSM-35 samples: (a) FER25; (b) FER23; (c) FER15; (d) FER00.



Figure 4. FTIR spectra of ferrierite/ZSM-35 samples: (a) fresh FER25; (b) pyridine-chemisorbed FER25.

TABLE 2: Brønsted (1540 cm⁻¹) and Lewis (1460 cm⁻¹) Acidities and Extinction Coefficients ($\epsilon_{I}/\epsilon_{B}$) for Different Ferrierites/ZSM-35 Determined by FTIR Studies of Pyridine Chemisorption

	Peak	Peak Areas		
sample	1540 cm ⁻¹	1460 cm ⁻¹	coefficients	
FER00	105.6	29.3	1.36	
FER15	88.3	39.6		
FER23	116.1	27.7	1.33	
FER25	120.5	23.7	1.26	

synthesized ferrierite sample (FER00) has the least volume of micropores. The total BET surface areas for these ferrierite samples range from 478.8 to 506.6 m^2/g .

H. Isomerization of *n*-Butene to Isobutylene on Ferrierite/ ZSM-35. 1. Ratio of Silicon to Aluminum. Ferrierite/ZSM-35 samples with different ratios of silicon to aluminum were



Figure 5. Temperature-programmed desorption data of ammonia for different ferrierite/ZSM-35 samples: (a) FER00; (b) FER25; (c) FER23; (d) FER15.



Figure 6. Nuclear magnetic resonance data for ferrierite materials. (a) ¹H MAS NMR spectrum of FER25; (b) ²⁹Si MAS NMR spectra of FER25 (top) and FER15 (bottom); (c) ²⁷Al MAS NMR spectrum of FER25.



Figure 7. Micropore distributions of different ferrierite/ZSM-35 samples: (a) FER00; (b) FER15 and FER23; (c) FER25.

prepared hydrothermally by controlling ratios of silicon to aluminum of precursor gels. Pyrrolidine was used for a structure-directing template. These ferrierite/ZSM-35 samples were tested for catalytic isomerization of *n*-butene to isobutylene



Time on Stream, mm.

Figure 8. Isomerization of *n*-butene to isobutylene at 693 K and at a but-1-ene space velocity of 5.34 WHSV on FER25 (open symbols) and FER15 (solid symbols) catalysts (reciprocal triangle; conversion; square; yield of isobutylene; and circle; selectivity to isobutylene).

 TABLE 3: Results of Pore Size Distributions and BET

 Surface Area Measurements for Different Ferrierite/ZSM-35

 Samples

	FER00	FER15	FER23	FER25
V _{meso+macro} , μL/g	589.0	372.0	361.0	366.0
$V_{\rm micro}, \mu L/g$	140.9	152.8	151.3	160.5
surface area, m ² /g	506.6	478.8	482.1	492.1

TABLE 4: Selectivities to Side Products (%) as a Function of Time on Stream for *n*-Butene Skeletal Isomerization on FER25 at 693 K and a But-1-ene Space Velocity of 5.34 WHSV

t, min	C3=	<i>i</i> -C4 ⁻	<i>n</i> -C4 ⁻	C5=	C6=	C7=	C8=
10	15.1	0.4	4.3	19.1	4.1	3.2	2.1
70	7.0	0.2	2.0	7.5	1.0	0.8	3.7
130	4.9	0.1	1.5	5.1	0.7	0.4	2.5
250	2.9	0.1	1.5	2.6	0.2	0.4	2.2
370	2.3	0.0	1.3	1.9	0.2	0.4	1.6
490	2.0	0.0	1.3	1.6	0.1	0.4	1.5
670	1.7	0.0	1.2	1.2	0.2	0.0	1.7
910	1.4	0.0	1.1	1.0	0.0	0.0	1.5
1150	12	0.0	11	0.8	0.0	0.0	1.5

at 693 K and at a but-1-ene space velocity of 5.34 WHSV. The catalytic results for different ferrierites (Si/Al = 5.75 and 9.20) are shown in Figure 8. FER25 (Si/Al = 9.20) has very good stability in the yield of isobutylene (about 35%). For an initial 10 min time on stream, butene dimerization followed by cracking to light olefins is a very serious side reaction, as listed in Table 4. No hydrocarbons which have more than eight carbons were detected in this reaction system. As time on stream increases, these side reactions are suppressed to different degrees. Conversions of *n*-butene show a sharp decrease at an early time on stream. Then the decreasing trend for n-butene conversion becomes slower and slower as time on stream increases. Consequently, the selectivity to isobutylene increases from 48% to 78% from 10 to 70 min time on stream. Then the selectivity to isobutylene is gradually increased from 78% to 95% from 70 to 1150 min time on stream.

However, FER15 (Si/Al = 5.75) does not have stable activity for formation of isobutylene and side products. Yields of isobutylene decrease gradually from 17.1% to 1.0%, corresponding to 10 and 1150 min time on stream, respectively. Butene dimerization followed by cracking is a serious side reaction only at times on stream of 10 min. After 70 min time on stream, the products of these side reactions become less and less. Accordingly, selectivities to isobutylene then range from 91% to 97% after 70 min time on stream.





Figure 9. Isomerization of n-butene to isobutylene at 693 K and at a but-1-ene space velocity of 5.34 WHSV on FER25 (open symbols) and FER23 (solid symbols) catalysts (reciprocal triangle; yield of isobutylene; circle; selectivity to isobutylene).



Figure 10. Isomerization of *n*-butene to isobutylene at 693 K and at a but-1-ene space velocity of 5.34 WHSV on FER25 (open symbols) and FER00 (solid symbols) catalysts (reciprocal triangle; yield of isobutylene; circle; selectivity to isobutylene).

2. Crystallinity. FER23 and FER25 are ferrierite samples which were obtained by autoclave treatment of precursor gels for 60 and 100 h, respectively. Longer autoclave times lead to materials of higher crystallinity. Therefore, sample FER25 is of higher crystallinity than sample FER23 (see the Discussion section for details). The catalytic results for *n*-butene isomerization to isobutylene on these two catalysts are shown in Figure 9. As compared to FER25, FER23 has about a 3.6% higher *n*-butene conversion, from which there are about 2% higher yields of isobutylene and about 1.6% higher formation of side products. Therefore, selectivities to isobutylene for FER23 are about 3% lower than those for FER25. In addition, both FER23 and FER25 ferrierites show a very similar stability in activity for *n*-butene isomerization to isobutylene.

3. Synthetic Methods (Template and Nontemplate). FER00 has a ratio of silicon to aluminum (8.80) which is similar to that for sample FER25 (9.20). However, FER00 was prepared hydrothermally without using any structure-directing organic templates, while FER25 was prepared hydrothermally by using pyrrolidine as a structure-directing template. Figure 10 illustrates the results of *n*-butene skeletal isomerization to isobutylene on both FER00 and FER25 catalysts. FER00 has about 8%-10% higher *n*-butene conversion than FER25, as observed for 20 h time on stream. Selectivities to isobutylene for FER00 are 12%-20% lower than those for FER25. It takes more than 13 h for FER00 to achieve a selectivity to isobutylene

TABLE 5: Distributions of Three *n*-Butene Isomers at 1150min Time on Stream for *n*-Butene Isomerization toIsobutylene on Different Ferrierites at 693 K

sample	t-2-C ₄ =/1-C ₄ =	<i>c</i> -2-C ₄ =/1-C ₄ =
FER00	1.79	1.50
FER23	1.74	1.28
FER25	1.71	1.26
TD^a	1.72	1.06

^a TD: Thermodynamic data of three *n*-butene isomers at 693 K.

higher than 80%. Differences in the yields of isobutylene between FER00 and FER25 depend on time on stream. Formation of isobutylene for FER00 is less than that for FER25 when time on stream is shorter than 370 min. When time on stream goes beyond 370 min, the yield of isobutylene for FER00 is higher than that for FER25.

4. Distributions of Three n-Butene Isomers. Table 5 tabulates the data for distributions of three n-butene isomers at 1150 min time on stream over several ferrierite catalysts with but-1-ene as a feed. The ratio of *trans*-but-2-ene to but-1-ene for catalysts FER00, FER23, and FER25 is very close to its thermodynamic value (1.72). However, the ratio of *cis*-but-2-ene to but-1-ene for these catalysts is about 20%-40% greater than the thermodynamic value (1.06).

IV. Discussion

A. Synthesis and Characterization. Ferrierite/ZSM-35 materials have been synthesized by using organic compounds as structure-directing templates. These organic templates include alkene-polyamines,²³ 1,4-diaminocyclohexane,²⁴ cho-lin,²⁵ piperidine,²⁶ pyrrolidine,^{27,28} and cyclohexylamine.²⁹ Silicon to aluminum ratios for synthetic ferrierite/ZSM-35 materials have been reported to range from 5 to 30. It is also reported that aluminum-free ferrierite has been prepared from aqueous solutions containing boric acid by using ethylenediamine as a structure-directing template.³⁰ Without using any organic templates, successful synthesis of ferrierite/ZSM-35 requires precursor gels having a narrow range of silicon to aluminum ratio (about Si/Al = 9) and stirring conditions during autoclave treatment.³¹

In this study, pyrrolidine is used as a structure-directing template for synthesis of ferrierite/ZSM-35. The precursor gels are formed by mixing NaAlO₂, NaCl, 1 M NaOH, H₂O, and pyrrolidine followed by addition of LUDOX HS-30 while stirring. A minimum pH occurs when the autoclave time is equal to 20 h (Figure 1). The lower the ratio of silicon to aluminum in the precursor gel, the more the pH drops. SEM and XRD results have confirmed that there are no crystals of ferrierite formed at this autoclave time (20 h).

XRD patterns (Figure 3) have confirmed that FER00, FER15, FER23, and FER25 materials are of the ferrierite structure. In addition, ²⁹Si MAS NMR spectra (Figure 6b) also show characteristic resonances for the zeolite framework silicon ions. The NMR resonance at 54 ppm in Figure 6c suggests that aluminum ions exist in the framework of the zeolite in a tetrahedral environment. The existence of extraframework octahedral aluminum ions is negligible due to a very weak NMR resonance at -2 ppm in Figure 6c.

The morphology of ferrierite/ZSM-35 depends on the synthesis method and silicon to aluminum ratio. Non-templatesynthesized ferrierite (FER00, Figure 2a) has an egglike morphology, and the particle sizes of FER00 range from a few microns up to 100 μ m. Template-synthesized ferrierite/ZSM-35 materials have morphologies different from non-templatesynthesized ferrierite/ZSM-35. Sample FER15 (Si/Al = 5.7) has a sheetlike morphology. The morphology of FER25 (Si/Al = 9.2) is hexagonal. These template-synthesized ferrierite samples have narrow distributions of particle sizes (about 22 \times 12 \times 12 μ m).

In addition to differences in morphologies and particle size distributions, template-synthesized ferrierite materials (FER23 and FER25) are of higher crystallinity than the non-template-synthesized ferrierite sample (FER00). This conclusion is supported by the results of XRD, FTIR, ¹H MAS NMR, and pore size distributions. Intensities of XRD patterns for FER00 (Figure 3d) are weaker than those for FER23 (Figure 3b) and FER25 (Figure 3a).

Ferrierite materials of high crystallinity contain fewer terminal silanol groups and more hydroxyl groups which are associated with framework silicon and aluminum ions. Experimental data of FTIR studies have shown that template-synthesized ferrierites have a greater ratio of peak area at 3601 cm⁻¹ to peak area at 3742 cm⁻¹ (38.3 for FER25 and 35.6 for FER23) than non-template-synthesized ferrierite (29.2). The infrared band at 3742 cm⁻¹ is characteristic of terminal silanol groups, while the infrared band at 3601 cm⁻¹ corresponds to hydroxyl groups which are responsible for Brønsted acid sites. Therefore, a greater ratio of peak area at 3601 cm⁻¹ to that at 3742 cm⁻¹ suggests higher crystallinity for the studied materials; that is, template-synthesized materials (FER23 and FER25) are of higher crystallinity than non-template-synthesized materials (FER00).

Ratios of hydroxyl groups associated with silicon and aluminum ions to hydroxyl groups of terminal silanol groups, obtained from ¹H MAS NMR analysis, are consistent with the results obtained from FTIR analysis. The NMR resonance at 4.0 ppm is assigned to the hydroxyl groups which are associated with Al^{3+} and Si^{4+} ions, while the NMR resonance at about 1.5 ppm is due to terminal silanol groups. Ratios of NMR resonance intensities at 4.0 ppm to those at 1.5 ppm for samples FER25, FER23, and FER00 are 9.77, 7.57, and 2.25, respectively. Therefore, ¹H MAS NMR results also suggest that template-synthesized materials (FER23 and FER25) are of higher crystallinity than non-template-synthesized materials (FER00).

Template-synthesized ferrierites have much sharper micropore distributions than non-template-synthesized ferrierite, Figure 7. On the other hand, non-template-synthesized ferrierites have more meso-/macropores than template-synthesized ferrierites, Table 3. These data are believed to be related to the degree of perfection of ferrierite crystals. Hence, template-synthesized ferrierites are of higher crystallinity than non-templatesynthesized ferrierite materials.

By using the same logic for discussing crystallinity of samples FER00 and FER23/FER25, a conclusion can also be drawn that sample FER25 is of higher crystallinity than sample FER23. The intensities of XRD patterns for FER25 (Figure 3a) are stronger than those for FER23 (Figure 3b). The ratio of the infrared peak area at 3601 cm⁻¹ to that at 3742 cm⁻¹ for FER25 (38.3) is greater than that for FER23 (35.6). The ratio of NMR resonance intensity at 4.0 ppm to that at 1.5 ppm for FER25 (9.77) is also greater than that for FER23 (7.57). Micropore distributions for FER25 (Figure 7c) are much sharper than those for FER23 (Figure 7b). The volume of micropores for FER25 (160.5 μ L/g) is greater than that for FER23 (151.3 μ L/g). All of these results suggest that crystallinity of ferrierite materials is increased with autoclave time during hydrothermal synthesis.

B. Acidity. Ferrierite materials of higher crystallinity contain more hydroxyl groups responsible for Brønsted acid sites and fewer terminal silanol groups than poorly crystalline samples,

as discussed in the last section. FTIR studies of pyridine chemisorption also provide information about the acidity of these ferrierite materials. The infrared band at 1540 cm⁻¹ is due to pyridine chemisorbed on Brønsted acid sites. The infrared band at 1450 cm⁻¹ is characteristic of pyridine adsorbed on Lewis acid sites. The peak areas at 1540 cm⁻¹ for different ferrierite samples follow the same order as their crystallinity, FER25 > FER23 > FER00, Table 2. However, the areas at 1450 cm⁻¹ for different ferrierites follow a reverse order, i.e., FER00 > FER23 > FER25. This suggests that ferrierite materials of lower crystallinity, such as FER00, contain greater amounts of Al species which are responsible for Lewis acidity. One reviewer also suggests that the band responsible for Lewis acidity partially reflects pyridine adsorption on Na or K sites, since FER00 contains about 1200 ppm K and 500 ppm Na.

The acidity of ferrierite materials can also be studied by temperature-programmed desorption of ammonia, Figure 5. Both strong and weak acid sites are present on these ferrierite materials. Ammonia molecules adsorbed on strong acid sites are desorbed at high temperature (732 K). Those adsorbed on weak acid sites are desorbed at low temperature (471 K). The amount of strong acid sites is 1.17 times greater than that of weak acid sites. The peak intensities for FER00 are stronger than samples FER23 and FER25, since FER00 contains more framework aluminum ions (Si/Al = 8.8) than FER23 and FER25 (Si/Al = 9.2). Sample FER15 has the least intense ammonia desorption peaks. This is not because FER15 contains the least amount of framework aluminum ions. Instead, FER15 contains the largest amount of framework aluminum ions among these four samples, i.e., Si/Al = 5.7. The reason for the weak ammonia TPD signal for FER15 is due to the fact that 40% of the sodium ions cannot be ion-exchanged by ammonium ions. Therefore, these unexchanged sodium ions reduce the amount of ammonia uptake.

C. Catalytic Isomerization of *n*-Butene to Isobutylene. n-Butene can be successfully isomerized to isobutylene over a well-crystallized ferrierite sample (FER25) at 693 K and at a 1-butene space velocity of 5.34 WHSV. The yield of isobutylene is very stable (about 35%) with respect to time on stream, Figure 8. At a time on stream of 10 min, selectivity to isobutylene is relatively low (48%). As time on stream increases, some strong acid sites are poisoned by deposited coke. Therefore, side reactions such as butene dimerization followed by cracking to light hydrocarbons on strong acid sites are greatly suppressed.⁹ It is also speculated that isomerization of n-butene to isobutylene may be achieved in a shape selective way since zeolite channels are modified by the deposited coke. The deposited coke may reduce the space in the interior of zeolite crystals and prohibit butene dimerization. Coke buildup may also confine the reaction zone for isomerization to a few nanometers of channels near the crystal surface. The total contact time is reduced because the product molecule is able to get out quickly and is less likely to further react. Consequently, selectivity to isobutylene is increased from 48% to 78% from 10 to 70 min time on stream. As time on stream increases further, selectivity to isobutylene is gradually increased from 78% (70 min time on stream) to 95% (1150 min time on stream).

As compared to FER25, crystallinity of ferrierite is reduced for FER23. FER23 contains less volume of micropores than FER25. More acid sites exist in meso-/macropores (nonzeolitic pores) for FER23, and these acid sites are called external acid sites. These external acid sites can cause dimerization followed by cracking side reactions so that they are non-shape selective acid sites. Therefore, achievement of a similar shape selectivity for FER23 requires longer time on stream than FER25. Longer time on stream allows more coke deposition to poison, block, and modify these external acid sites. This is the reason that selectivities to isobutylene for the catalyst of FER23 are lower than those for FER25, Figure 9. The main subject of our subsequent paper is that removal of non-shape selective acid sites (external acid sites) leads to significant improvements in shape selectivity for *n*-butene skeletal isomerization.¹⁰ On the other hand, diffusion of butene molecules becomes more difficult when the ferrierite catalyst is more shape selective for butene molecules due to its crystal perfection and coke deposition. Therefore, it is understandable that FER25 is less active than FER23 for isobutylene formation after time on stream exceeds 200 min, Figure 9.

Crystallinity for ferrierite is further reduced for FER00 as compared to FER23. More meso-/macropores and less micropores lead to a great decrease in the selectivity to isobutylene (about 12%-20% lower), Figure 10. FER00 needs more coke deposition to poison, block, and modify those non-shape selective acid sites in order to suppress side reactions such as butene dimerization. Therefore, a slow increase for selectivity to isobutylene is observed for FER00. At early times on stream (< 250 min), the yields of isobutylene are less than those for FER25 due to serious side reactions, Figure 10. After 310 min time on stream, the formation of isobutylene over FER00 is greater than that for FER25, Figure 10. This is simply due to the ease of butene diffusion inside shape selective zeolite channels. The enhanced shape selectivity of FER25 forces butene molecules to diffuse less readily so that FER25 is less active for isobutylene formation than FER00.

When the ratio of silicon to aluminum is decreased from 9.2 (FER25) to 5.7 (FER15), the morphology, crystallinity, and pore size distributions of ferrierites are very different. FER15 has a sheetlike morphology, while FER25 has a hexagonal morphology. FER25 is of higher crystallinity than FER15. FER25 also has sharper micropore size distributions. In addition, the greatest difference between FER15 and FER25 is that about 40% of sodium ions cannot be ion-exchanged out of FER15 with ammonium ions. Blocking of channels by the presence of these unexchanged sodium ions becomes fatal for the diffusion of butene molecules so that FER15 is less active than FER25 for *n*-butene isomerization. Yields of isobutylene also decrease with time on stream due to coke buildup. Improvement in shape selectivity for butene molecules by the presence of sodium ions is reflected by higher selectivities to isobutylene, as shown in Figure 8. Note that ferrierite of the sodium form, NaFER25, is inactive for *n*-butene isomerization to isobutylene.

Data shown in Table 5 suggest a preferential formation of *cis*-but-2-ene on a small pore zeolite, ferrierite, for double-bond migration of but-1-ene. The same kinds of phenomena have also been observed for another small pore zeolite, ZSM-23.¹² At low temperatures (below or around room temperature) and at early times on stream for but-1-ene double-bond migration, *cis*-but-2-ene is an exclusive product for small pore zeolite catalysts, such as ferrierite,³² NU-10,³³ and EU-12.³⁴

Leach and co-workers³²⁻³⁴ have proposed a mechanism to describe such preferential formation of *cis*-but-2-ene. Doublebond migration of but-1-ene over acid catalysts is generally considered to occur via secondary butyl carbenium ions. In small pore zeolites there are steric interactions between pore walls and the methyl group of the secondary butyl carbenium ions. Therefore, rotation of the $C_2^+-C_3$ bond in this carbenium ion is greatly restricted by such steric interactions between the methyl group and the pore wall. H⁺ abstraction from the C₃ atom of the secondary butyl carbenium can occur in two ways. One way for H⁺ abstraction requires a methyl group rotation for formation of *trans*-but-2-ene, while the other way leads to formation of *cis*-but-2-ene without rotating the methyl group. These mechanisms allow the formation of *cis*-but-2-ene to become preferential for double-bond migration of but-1-ene. For medium pore zeolites ZSM-5 and ZSM-11, the three *n*-butene isomers reach their thermodynamic equilibrium.³² Steric constraints between the pore walls of medium pore zeolites and the methyl groups of the secondary butyl carbenium ions are removed, as compared to small pore zeolites such as ferrierite and ZSM-23.

A reviewer has suggested that the *cis*-but-2-ene/but-1-ene ratio is an indication of shape selectivity, which may be so. Note that the data in Table 5 were obtained from kinetic data at the time on stream of 1150 min. Coke deposition may have certain effects on the ratios of *cis*-but-2-ene to but-1-ene.

V. Conclusions

Ferrierite/ZSM-35 samples have been prepared by hydrothermal methods using pyrrolidine as a structure-directing template. Template-synthesized ferrierites have even distributions of particle sizes, while non-template-synthesized ferrierite has particle sizes that vary from several microns to about 100 μ m. More importantly, template-synthesized ferrierites are of higher crystallinity than non-template-synthesized ferrierite. Ferrierite materials of higher crystallinity have more hydroxyl groups responsible for Brønsted acid sites and fewer terminal silanol groups, i.e., fewer amounts of Al species responsible for Lewis acid sites. Ferrierite materials of higher crystallinity contain more perfect micropores and fewer meso-/macropores.

Reactions of *n*-butene isomerization to isobutylene require shape selective zeolite catalysts in order to suppress side reactions such as dimerization or oligomerization of butene. Ferrierite (small pore zeolite) is able to catalyze such reactions in a shape selective way. Ferrierite materials of higher crystallinity are more shape selective due to a larger volume of micropores. However, ferrierite materials of poorer crystallinity require more coke deposition (longer times on stream) to modify the less-developed micropores. More coke deposition is also necessary to poison or block non-shape selective acid sites located on meso-/macropores inside ferrierites of poorer crystallinity.

Blocking of zeolite channels by unexchanged sodium ions is fatal to skeletal isomerization of *n*-butene after some coke has accumulated inside the ferrierite catalyst. This catalyst is then deactivated to an almost inactive level for *n*-butene molecules.

Preferential formation of cis-but-2-ene is also observed for double-bond migration of but-1-ene. Such preferential formation of cis-but-2-ene may be due to a strong steric interaction between pore walls of small pore zeolites (ferrierite and ZSM-23) and methyl groups of secondary butyl carbenium ions.

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References and Notes

- Pecci, G.; Floris, T. Hydrocarbon Process 1977, 56, (12) 98-102.
 Harandi, M. N.; Owen, O.; Mead, B. US Patent 5,024,679, June
- 18, 1991.
 (3) Xu, W.-Q.; Suib, S. L.; O'Young, C.-L. J. Catal. 1993, 144, 285-
- (3) Xu, w.-Q.; Suib, S. L.; O Young, C.-L. J. Catal. 1993, 144, 285– 295.
- (4) Simon, M. W.; Nam, S. S.; Xu, W.-Q.; Suib, S. L.; Edwards, J. C.; O'Young, C.-L. J. Phys. Chem. 1992, 96, 6381-6388.
- (5) Simon, M. W.; Xu, W.-Q.; Suib, S. L.; O'Young, C.-L. Microporous Mater. 1994, 2, 477-486.

(6) Bianchi, D.; Simon, M. W.; Nam, S. S.; Xu, W.-Q.; Suib, S. L.; O'Young, C.-L. J. Catal. 1994, 145, 551-560.

- (7) US Patent 5,227,569, assigned to Texaco, Inc.
- (8) O'Young, C.-L.; Xu, W.-Q.; Simon, M. W.; Suib, S. L. In Zeolites and Related Microporous Materials: State of the Art 1994; Weitkamp, J., Karge, H. G., Pfeifer, H., Hölderich, W., Eds.; Studies in Surface Science and Catalysis, Vol. 84; Elsevier Science: New York, 1994; pp 1671– 1676.

(9) Xu, W.-Q.; Yin, Y.-G.; Suib, S. L.; O'Young, C.-L. J. Phys. Chem. 1995, 99, 758-765.

(10) Xu, W.-Q.; Yin, Y.-G.; Suib, S. L.; Edwards, J. C.; O'Young, C.-L. Manuscript in preparation.

(11) US Patent Pending, assigned to Texaco, Inc.

(12) Xu, W.-Q.; Yin, Y.-G.; Suib, S. L.; O'Young, C.-L. J. Catal. 1994, 150, 34-45.

- (13) Simon, M. W.; Suib, S. L.; O'Young, C.-L. J. Catal. 1994, 147, 484-493.
 - (14) Vaughan, P. A. Acta Crystallogr. 1966, 21, 983-990.

(15) Horvath, G.; Kawazoe, K. J. Chem. Eng. Jpn. 1983, 15, 470-475.

(16) Xu, W.-Q.; Suib, S. L. J. Catal. 1994, 145, 65-72.

(17) Messner, A. E.; Rosie, D. M.; Argabright, P. A. Anal. Chem. 1959, 31, 230-233.

(18) Rosie, D. M. Anal. Chem. 1957, 29, 1263-1264.

(19) Szostak, R. Molecular Sieves: Principles of Synthesis and Identification; Van Nostrand Reinhold: New York, 1989; p 290.

(20) Emeis, C. A. J. Catal. 1993, 141, 347-354.

(21) Datka, J. J. Chem. Soc., Faraday Trans. 1 1981, 77, 2877-2881.

(22) Datka, J.; Turek, A. M.; Jehng, J. M.; Wachs, I. E. J. Catal. 1992, 135, 186-199.

(23) Marosi, L.; Schwarzmann, M.; Stabenow, J. European Patent 49,386, April 14, 1982.

(24) Hellring, S. D.; Chang, C. D.; Luther, J. D. US Patent 5,190,736, March 2, 1993.

(25) Plank, C. J.; Rosinski, E. J.; Rubin, M. K. US Patent 4,046,859, Sept 6, 1977.

(26) Nanne, J. M.; Post, M. F. M.; Stork, W. H. J. European Patent 12,473, June 25, 1980.

(27) Suzuki, K.; Kiyozumi, Y.; Shin, S.; Fujisawa, K.; Watanabe, H.; Saito, K.; Noguchi, K. Zeolite **1986**, 6, 290-298.

(28) Dutta, P. K.; Rao, K. M.; Park, J. Y. Langmuir 1992, 8, 722-726.

(29) Whittam, T. V. European Patent 103,981, March 28, 1984.

(30) Gies, H.; Gunawardance, R. P. Zeolites 1987, 7, 442-445.

(31) Inaoka, W.; Kasahara, S.; Fukushima, T.; Igawa, K. In Synthesis and Characterization of Zeolites, Inui, T., Namba, S., Tatsumis, T., Eds., Studies in Surface Science Catalysis Vol. 60, 1991; p 37.

(32) Harrison, I. D.; Leach, H. F.; Whan, D. A. Zeolites 1987, 7, 21-27.

(33) Harrison, I. D.; Leach, H. F.; Whan, D. A. Zeolites 1987, 7, 28-34.

(34) Araya, A.; Blake, A. J.; Harrison, I. D.; Leach, H. F.; Lowe, B. M.; Whan, D. A. Zeolites **1992**, 12, 24-31.

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