Supporting Information

for

Monomolecular Skeletal Isomerization of 1-Butene over Selective Zeolite Catalysts

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Synthesis and Catalysis

An HPM-1 zeolite with an Si/Al ratio of 110 was synthesized by heating at 448 K for 19 days a gel of composition SiO$_2$:0.0046Al$_2$O$_3$:0.5ROH:0.49HF:4.0H$_2$O, where ROH stands for 2-ethyl-1,3,4-trimethylimidazolium hydroxide, and converted into its proton form by calcination in air at 823 K for 8 h. The Al source was aluminum hydroxide (Aldrich), and the rest of synthesis conditions were the same as those in our previous work.$^{51,52}$ A ferrierite with Si/Al = 85 was synthesized by a modification of the method of Pasquale et al.$^{53}$ The powder X-ray diffraction patterns of as-made HPM-1 and ferrierite show that they are highly crystalline and phase-pure (Figures S13). An H-FER zeolite with Si/Al = 8.9 and a ZSM-5 with Si/Al = 85 were obtained from Tosoh and converted to their proton form according to the procedures described elsewhere.$^{54}$

1-Butene skeletal isomerization was conducted under atmospheric pressure in a continuous-flow microreactor. Each catalyst was activated under flowing N$_2$ (50 mL min$^{-1}$) at 823 K for 2 h and kept at the desired temperature, allowing time for the reactant/carrier gas distribution to be stabilized. Then, 1-butene (99%, RIGAS) was fed into the microreactor containing 0.1 g of zeolite catalyst at 623 or 673 K and 7.5 or 24 h$^{-1}$ WHSV. The reaction products were analyzed online in a Varian CP-3800 gas chromatograph equipped with a CP-PoraPLOT Q capillary column (25 m × 0.25 mm) and a flame ionization detector, with the first analysis carried out after 5 min on stream.

$^{13}$C Scrambling Experiment

$^{13}$C scrambling experiments on fresh and aged zeolite catalysts were carried out using 1-[1-$^{13}$C]butene (99%, Aldrich) at 673 K and 7.5 h$^{-1}$ WHSV for 5 min under otherwise identical conditions as those given above. Aged catalysts were prepared by conducting 1-butene skeletal isomerization using normal 1-butene at 673 K and 7.5 h$^{-1}$ WHSV for 12 h followed by flowing under N$_2$ (50 mL min$^{-1}$) for 10 min to eliminate residues other than coke species. The reaction products were analyzed on-line in an Agilent 5975C series GC/MSD system (an Agilent 7890A gas chromatograph equipped with a Triple-Axis mass detector) using an HP-Al/KCl capillary column (50 m × 0.32 mm). The mass detector was set to only detect molecules with molecular weights > 50 for the safe instrumental run.

Analytical Methods

Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X’Pert diffractometer (Cu K$_\alpha$ radiation) with an X’Celerator detector. Elemental analyses for Al and Si were carried out by a Shimadzu ICPE-9000 inductively coupled plasma spectrometer. Thermogravimetric analyses (TGA) were performed on an SII EXSTAR 6000 thermal analyzer, where the weight losses related to the combustion of organic SDAs or coke deposits formed during 1-butene skeletal isomerization were further confirmed by differential analyses (DTA) using the same analyzer. Crystal morphology and average size were determined by a JEOL JSM-6510 scanning electron microscope (SEM). The N$_2$ sorption experiments were carried out on a Mirae SI nanoPorosity-XG analyzer.
$^{27}\text{Al}$ and $^{29}\text{Si}$ MAS NMR measurements were performed on a Varian Inova 300 spectrometer at a spinning rate of 6.0 kHz. The $^{27}\text{Al}$ MAS NMR spectra were measured at a $^{27}\text{Al}$ frequency of 78.16 MHz with a $\pi/8$ rad pulse length of 1.8 µs and a recycle delay of 0.5 s. The $^{29}\text{Si}$ MAS NMR spectra were recorded at a $^{29}\text{Si}$ frequency of 59.59 MHz with a $\pi/2$ rad pulse length of 5.0 µs and a recycle delay of 30 s. The $^{27}\text{Al}$ and $^{29}\text{Si}$ chemical shifts were referenced relative to $\text{Al(H}_2\text{O)}_6^{3+}$ solution and tetramethylsilane (TMS), respectively. The IR spectra in the OH region were measured on a Nicolet 6700 FT-IR spectrometer using self-supporting zeolite wafers of 1.3 cm diameter. Prior to IR measurements, the zeolite wafers were pretreated under vacuum at 773 K for 2 h inside a home-built IR cell with CaF$_2$ windows.

NH$_3$ temperature programmed-desorption (TPD) was carried out on a fixed bed, flow-type apparatus linked to a Hewlett-Packard 5890 series II gas chromatograph with a thermal conductivity detector. A sample of ca. 0.1 g was activated in flowing He (50 mL min$^{-1}$) at 823 K for 2 h. Then, 10 wt% NH$_3$ was passed over the sample at 423 K for 0.5 h. The treated sample was subsequently purged with He at the same temperature for 1 h to remove physisorbed NH$_3$. Finally, the TPD was performed in flowing He (30 mL min$^{-1}$) from 423 to 973 K at a temperature ramp of 10 K min$^{-1}$.

**Computational Details**

To investigate the equilibrium loading and positions of intrazeolitic 1-butene molecules, molecular mechanics and molecular dynamics simulations were carried out using the Sorption and Forcite modules in Materials Studio 7.0, respectively. The crystallographic data of STW and MFI structures were obtained from the literature data, and the CVFF forcefield and periodic boundary conditions were applied in all the calculations. The accessible solvent surface in Figure 4 was calculated at an initial solvent radius of 1.4 Å.

Sorption simulations to acquire the intrazeolitic equilibrium loadings of 1-butene was performed using the Sorption module. Prior to the simulations, the molecular geometry of sorbate (i.e., 1-butene) was optimized in the gas state at the $\omega$b97xd/6-31g(d,p) level of theory, using Gaussian 09. Calculation details: sorbate, 1-butene (101.33 kPa fugacity); task, fixed pressure (equilibration steps, 100,000; production steps, 1000,000; temperature, 673 K); method, configurational-bias Monte Carlo (the torsional degree of freedom was imposed on the C$_2$-C$_3$ and C$_3$-C$_4$ bond in 1-butene); forcefield, CVFF; charges, QEq; electrostatic summation method, Ewald (accuracy, 1.0$^{-4}$ kcal mol$^{-1}$; buffer width, 0.5 Å); van der Waals summation method, atom based (truncation, cubic spline; cutoff distance, 15.5 Å; spline width, 1.0 Å; buffer width, 0.5 Å).

Simulated annealing calculations to determine the intrazeolitic equilibrium positions of 1-butene were carried out using the Forcite module. The initial structure for STW topology consists of the fixed STW unit cell (Si$_{60}$O$_{120}$) and four intrazeolitic 1-butene molecules optimized as above. Likewise, the initial structure for MFI topology includes the fixed MFI unit cell (Si$_{96}$O$_{192}$) and seven intrazeolitic 1-butene molecules. Calculation details: task,
anneal (annealing cycles, 5; initial temperature, 673 K; mid-cycle temperature, 873 K; heating ramps per cycle, 5; dynamics steps per ramp, 100; total number of steps, 5,000; Ensemble, NVE; initial velocities, random; time step, 1.0 fs); forcefield, CVFF; charges, QEq; electrostatic summation method, Ewald (accuracy, 1.0^85 kcal mol^-1; buffer width, 0.5 Å); van der Waals summation method, atom based (truncation, cubic spline; cutoff distance, 18.5 Å; spline width, 1.0 Å; buffer width, 0.5 Å).

References
(S3) Pasquale, G. M.; Murray, B. D. PCT WO/9640587, 1996.
(S5) Materials Studio 7.0, Accelrys Inc.: San Diego, CA, 2013.
Figure S1. (a) 1-Butene conversion and (b) selectivity to and (c) yield in isobutene at 623 K and 7.5 h⁻¹ WHSV in the 1-butene skeletal isomerization over different zeolites: H-HPM-1, ■; H-FER(85), ○; H-FER(8.9), ●.
Figure S2. \( \text{N}_2 \) adsorption (■) and desorption (□) isotherm on (a) H-HPM-1 and (b) H-FER(85).
Figure S3. $^{29}$Si MAS NMR spectrum of H-HPM-1 with Si/Al = 110 (top to bottom: experimental, simulated, and deconvoluted components).
Figure S4. $^{27}$Al MAS NMR spectrum of H-ITQ-12.
Figure S5. (a) NH$_3$ TPD curves and (b) IR spectra in the OH stretching region of (from bottom to top) H-ZSM-5 (Si/Al = 95), H-ITQ-12 (Si/Al = 96), and H-HPM-1 (Si/Al = 110).
Figure S6. SEM images of as-made (a) HPM-1 and (b) as-made ferrierite (Si/Al = 85). Scale bars, 1 µm.
Figure S7. Gas chromatograms and mass spectra of butenes produced after 1-butene skeletal isomerization using unlabeled 1-butene over (a) fresh H-HPM-1 and using 1-[1-\textsuperscript{13}C]butene over (b) fresh H-HPM-1, (c) aged H-HPM-1, (d) fresh H-FER(8.9), and (e) aged H-FER(8.9) at 673 K and 7.5 h\textsuperscript{−1} WHSV for 5 min.
Figure S8. Gas chromatograms and mass spectra of pentenes produced after 1-butene skeletal isomerization using unlabeled 1-butene over (a) fresh H-HPM-1 and using 1-[1-\textsuperscript{13}C]butene over (b) fresh H-HPM-1, (c) aged H-HPM-1, (d) fresh H-FER(8.9), and (e) aged H-FER(8.9) at 673 K and 7.5 h\textsuperscript{-1} WHSV for 5 min.
Figure S9. Gas chromatograms and mass spectra of butenes produced after 1-butene skeletal isomerization using unlabeled 1-butene over (a) fresh H-ZSM-5 and using 1-[1-13C]butene over (b) fresh H-ZSM-5, (c) fresh H-FER(85) at 673 K and 7.5 h⁻¹ WHSV for 5 min.
Figure S10. Gas chromatograms and mass spectra of pentenes produced after 1-butene skeletal isomerization using (a) unlabeled 1-butene and (b) 1-[1-13C]butene over fresh H-ZSM-5 at 673 K and 7.5 h⁻¹ WHSV for 5 min.
Figure S11. (a) 1-Butene conversion and (b) selectivity to and (c) yield in isobutene at 673 K and 7.5 h$^{-1}$ WHSV in the 1-butene skeletal isomerization over H-ZSM-5.
Figure S12. 1-Butene loading at 673 K in (a) STW and (b) MFI structures at a constant fugacity of 101.33 kPa obtained using the Sorption module in Materials Studio 7.0.
Figure S13. Powder XRD patterns of as-made (a) HPM-1 and (b) ferrierite (Si/Al = 85) samples.