Supplementary Information

Transformation synthesis of aluminosilicate SSZ-39 zeolite from ZSM-5 and Beta zeolite

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Experimental

Computational Method

The number of organic structural directing agents (OSDAs) in per unit cell was obtained by Mote Claro calculation. Subsequently, the stabilization energy was defined as the difference in energy between OSDAs occluded per unit cell of zeolites and the energy of isolated OSDAs and the empty zeolite framework according Deem's method.¹ Based on this method, these structures were firstly optimized, and the energy values were taken as the average energy calculated from the last 5 ps of a 30 ps molecular dynamics calculation at 25 °C. During the optimization and molecular dynamics program GULP to calculate these energies.³ In the process of calculation, lower stability energy of the OSDA with the zeolite framework means more stable zeolite structure.

Materials

ZSM-5 zeolite (Si/Al=15.0, H-form), Beta zeolite (Si/Al=12.5, H-form), and USY zeolite (Si/Al=10.8, H-form) were provided by BASF. Sodium hydroxide (NaOH, AR, 96%, Sinopharm Chemical Reagent Co., Ltd.), *cis*-2,6-dimethylpiperidine (97%, Sigma-Aldrich Reagent Co., Ltd.), iodoethane (99%, Aladdin Chemical Co., Ltd.), methanol (AR, 99.5%, Sinopharm Chemical Reagent Co., Ltd.), anion-exchange resin (Amberlite IRN-78, OH-form, Thermofisher Chemical Reagent Co., Ltd.),

 $Cu(NO_3)_2 \cdot H_2O$ (AR, 99%, Sinopharm Chemical Reagent Co., Ltd.), and ammonium nitrate (NH₄NO₃, AR, 99%, Beijing Chemical Reagent Co., Ltd.) were used without further purification. The deionized water was home-made.

Synthesis

Synthesis of OSDA

N,N-diethyl-*cis*-2,6-dimethylpiperidine iodide was synthesized by reacting cis-2,6dimethylpiperidine, iodoethane, and an excess of KHCO₃ in the presence of methanol solvent, followed by refluxing at 70 °C for 4 days. The KHCO₃ was filtered and then the solvent and the excess iodoethane was removed by rotary evaporation. The product was washed with ether. The molecular structure was verified using ¹H and ¹³C nuclear magnetic resonance (NMR). The product was converted from the iodide form to the hydroxide form using an anion exchange resin.

Synthesis of conventional SSZ-39 zeolite

A synthetic mixture with a molar composition of $1.0 \text{ SiO}_2 : 0.046 \text{ Al}_2\text{O}_3 : 0.17 \text{ Na}_2\text{O} : 0.14 \text{ DMP} : 30 \text{ H}_2\text{O}$ was obtained by mixing Y zeolite (Si/Al=10.8, XRD pattern and SEM image shown in Figure S2), DMP, sodium hydroxide, and deionized water. Then, the synthetic mixture was transferred into a Teflon-lined autoclave oven and crystallized at 140 °C for 3 days under rotation conditions (50 rpm). After filtering, washing, drying, and calcining at 550 °C for 4 h, the product was finally obtained, which was designated as Y-SSZ-39 (Yield: 75%). The H-form of the sample (H-Y-SSZ-39) was prepared by ion-exchange with 1 M NH₄NO₃ solution and calcination at 550 °C for 4 h. This ion-exchange procedure was repeated once. The Cu-form of the sample (Cu-Y-SSZ-39) was prepared by ion-exchange the H-Y-SSZ-39 zeolite with 0.1 M Cu(NO₃)₂ solution and calcination at 550 °C for 4 h.

Interzeolite transformation from ZSM-5 zeolite to SSZ-39 zeolite

A synthetic mixture with a molar composition of 1.0 SiO_2 : $0.033 \text{ Al}_2\text{O}_3$: $0.17 \text{ Na}_2\text{O}$:

0.14 DMP : 30 H₂O : 0.02 seeds was obtained by mixing ZSM-5 zeolite (XRD pattern and SEM image in Figure S3), DMP, sodium hydroxide, deionized water and SSZ-39 zeolite seeds. In a typical run, 1 g of ZSM-5 zeolite was mixed with 10 g of DMP solution (0.23 M in water), stirring at room temperature for 2 h. Then, 0.24 g of NaOH was added. After stirring for 2 h, 0.02 g of SSZ-39 zeolite seeds was added. After stirring for 10 min, the mixture was transferred into a Teflon-lined autoclave oven and crystallized at 140 °C for 3 days under rotation conditions (50 rpm). After filtering, washing, drying, and calcining at 550 °C for 4 h, the product was finally obtained, which was designated as Z-SSZ-39 (Yield: 63%). The H-form of the sample (H-Z-SSZ-39) was prepared by ion-exchange with 1 M NH₄NO₃ solution and calcination at 550 °C for 4 h. This ion-exchange procedure was repeated once. The Cu-form of the sample (Cu-Z-SSZ-39) was prepared by ion-exchange the H-Z-SSZ-39 zeolite with 0.1 M Cu(NO₃)₂ solution and calcination at 550 °C for 4 h.

Interzeolite transformation from Beta zeolite to SSZ-39 zeolite

A synthetic mixture with a molar composition of $1.0 \text{ SiO}_2 : 0.04 \text{ Al}_2\text{O}_3 : 0.17 \text{ Na}_2\text{O} : 0.14 \text{ DMP} : 30 \text{ H}_2\text{O}$ was obtained by mixing Beta zeolite (XRD patterns and SEM image in Figure S4), DMP, sodium hydroxide, and deionized water. Then, the synthetic mixture was transferred into a Teflon-lined autoclave oven and crystallized at 140 °C for 3 days under rotation conditions (50 rpm). After filtering, washing, drying, and calcining at 550 °C for 4 h, the product was finally obtained, which was designated as B-SSZ-39 (Yield: 68%). The H-form of the sample (H-B-SSZ-39) was prepared by ion-exchange with 1 M NH₄NO₃ solution and calcination at 550 °C for 4 h. This ion-exchange procedure was repeated once. The Cu-form of the sample (Cu-B-SSZ-39) was prepared by ion-exchange the H-B-SSZ-39 zeolite with 0.1 M Cu(NO₃)₂ solution and calcination at 550 °C for 4 h.

Characterizations

X-ray powder diffraction (XRD) patterns were measured with a Rigaku Ultimate VI X-ray diffractometer (40 kV, 40 mA) using $Cu_{K\alpha}$ (λ =1.5406 Å) radiation. Scanning electron microscopy (SEM) experiments were performed on Hitachi SU-1510 and SU-8010 electron microscopes. The N₂ sorption isotherms at the temperature of liquid nitrogen were measured using Micromeritics ASAP 2020M and Tristar system. The thermogravimetrydifferential thermal analysis (TG-DTA) experiments were carried out on a Perkin-Elmer TGA 7 unit in air at heating rate of 10 °C/min in the temperature range from room temperature to 800 °C. The sample composition was determined by inductively coupled plasma (ICP) with a Perkin-Elmer 3300DV emission spectrometer. ²⁹Si and ²⁷Al MAS NMR spectra were recorded on a Varian Infinity Plus 400 spectrometer. UV-Raman spectra were measured with a Jobin-YvonT64000 triple-stage spectrometer with spectral resolution of 2 cm⁻ ¹. The laser line at 325 nm of a He/Cd laser was used as an exciting source with an output of 50 mW. The power of the laser at the sample was about 3.0 mW. The acidity of the catalysts was measured by the temperature-programmeddesorption of ammonia (NH₃-TPD). The catalyst was prepared at 450 °C in a He flow for 60 min, followed by the adsorption of NH₃ at 100 °C for 1 h. After saturation, the catalyst was purged by He flow for 3 h to remove the physically adsorbed ammonia on the sample. Then, desorption of NH₃ was carried out from 100 to 600 °C with a heating rate of 5 °C/min. The amount of NH₃ desorbed from the sample was detected by a thermal conductivity detector.

Catalytic tests

Catalytic activities in selective catalytic reduction of ammonia (NH₃-SCR) were measured in a fixed-bed quartz reactor in a gaseous mixture containing 500 ppm of NO, 500 ppm of NH₃, 10% of O₂, and N₂ as a balance gas. The gas hourly space velocity (GHSV) was 400 000 h⁻¹. Zeolite samples were prepared *via* ion-exchanged method with the Cu(NO₃)₂ aqueous solution, and the copper

loading of all of the samples was about 2.4 wt%, which was determined by ICP analysis.

Supplementary Figure Captions

Figure S1. Positions of DMP molecules within the FAU zeolite framework.

Figure S2. (a) XRD pattern and (b) SEM image of Y zeolite.

Figure S3. (a) XRD pattern and (b) SEM image of ZSM-5 zeolite.

Figure S4. (a) XRD pattern and (b) SEM image of Beta zeolite.

Figure S5. XRD pattern of Y-SSZ-39 zeolite sample.

Figure S6. SEM image of Y-SSZ-39 zeolite sample.

Figure S7. N₂ sorption isotherms of H-Y-SSZ-39 zeolite sample.

Figure S8. Dependence of Z-SSZ-39 zeolite crystallinity on crystallization time.

Figure S9. ²⁷Al MAS NMR spectra of Z-SSZ-39 zeolite samples crystallized at (a) 0, (b) 6, (c) 14, (d) 16, (e) 24, (f) 36, and (g) 48 h, respectively.

Figure S10. NH₃-TPD curve of H-Z-SSZ-39 zeolite sample.

Figure S11. NH₃-TPD curve of H-Y-SSZ-39 zeolite sample.

Figure S12. XRD pattern of B-SSZ-39 zeolite sample.

Figure S13. SEM image of B-SSZ-39 zeolite sample.

Figure S14. N₂ sorption isotherms of B-SSZ-39 zeolite sample.

Figure S15. TG-DTA curves of B-SSZ-39 zeolite sample.

Figure S16. ²⁹Si MAS NMR spectrum of B-SSZ-39 zeolite sample.

Figure S17.²⁷Al MAS NMR spectrum of B-SSZ-39 zeolite sample.

Figure S18. XRD patterns of B-SSZ-39 zeolite samples crystallized at (a) 0, (b) 2, (c) 8, (d) 16, and (e) 24 h, respectively.

Figure S19. SEM images of B-SSZ-39 zeolite samples crystallized at (a) 0, (b) 8, (c) 16, and (d) 24 h, respectively.

Figure S20. Dependence of B-SSZ-39 zeolite crystallinity on crystallization time.

Figure S21. UV-Raman spectra of B-SSZ-39 zeolite samples crystallized at (a) 0, (b) 8, (c) 16, and (d) 24 h, respectively.

Figure S22. ²⁹Si MAS NMR spectra of B-SSZ-39 zeolite samples crystallized at (a) 0, (b) 2, (c) 8, (d) 16, and (e) 24 h, respectively.

Figure S23. ²⁷Al MAS NMR spectra of B-SSZ-39 zeolite samples crystallized at (a) 0, (b) 2, (c) 8, (d) 16, and (e) 24 h, respectively.

Figure S24. NH₃-TPD curve of H-B-SSZ-39 zeolite sample.

Table S1. BET surface area and micropore volume of H-SSZ-39 zeolite samples.

Table S2. Peak positions in ²⁹Si MAS NMR spectra of Z-SSZ-39 zeolite samples.

 Table S3. Peak intensities in ²⁹Si MAS NMR spectra of Z-SSZ-39 zeolite samples.

 Table S4. Peak positions in ²⁹Si MAS NMR spectra of B-SSZ-39 zeolite samples.

Table S5. Peak intensities in ²⁹Si MAS NMR spectra of B-SSZ-39 samples.



Figure S1. Positions of DMP molecules within the FAU zeolite framework.



Figure S2. (a) XRD pattern and (b) SEM image of Y zeolite.



Figure S3. (a) XRD pattern and (b) SEM image of ZSM-5 zeolite.



Figure S4. (a) XRD pattern and (b) SEM image of Beta zeolite.



Figure S5. XRD pattern of Y-SSZ-39 zeolite sample.



Figure S6. SEM image of Y-SSZ-39 zeolite sample.



Figure S7. N₂ sorption isotherms of H-Y-SSZ-39 zeolite sample.



Figure S8. Dependence of Z-SSZ-39 zeolite sample crystallinity on crystallization time.



Figure S9. ²⁷Al MAS NMR spectra of Z-SSZ-39 zeolite samples crystallized at (a) 0, (b) 6, (c) 14, (d) 16, (e) 24, (f) 36, and (g) 48 h, respectively.



Figure S10. NH₃-TPD curve of H-Z-SSZ-39 zeolite sample.



Figure S11. NH₃-TPD curve of H-Y-SSZ-39 zeolite sample.



Figure S12. XRD pattern of B-SSZ-39 zeolite sample.



Figure S13. SEM image of B-SSZ-39 zeolite sample.



Figure S14. N₂ sorption isotherms of B-SSZ-39 zeolite sample.



Figure S15. TG-DTA curves of B-SSZ-39 zeolite sample.



Figure S16. ²⁹Si MAS NMR spectrum of B-SSZ-39 zeolite sample.



Figure S17.²⁷Al MAS NMR spectrum of B-SSZ-39 zeolite sample.



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Figure S19. SEM images of B-SSZ-39 zeolite samples crystallized at (a) 0, (b) 8, (c) 16, and (d) 24 h, respectively.



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Figure S21. UV-Raman spectra of B-SSZ-39 zeolite samples crystallized at (a) 0, (b) 8, (c) 16, and (d) 24 h, respectively.



Figure S22. ²⁹Si MAS NMR spectra of B-SSZ-39 zeolite samples crystallized at (a) 0, (b) 2, (c) 8, (d) 16, and (e) 24 h, respectively.



Figure S23. ²⁷Al MAS NMR spectra of B-SSZ-39 zeolite samples crystallized at (a) 0, (b) 2, (c) 8, (d) 16, and (e) 24 h, respectively.



Figure S24. NH₃-TPD curve of H-B-SSZ-39 zeolite sample.

Samples	BET surface area (m ² /g)	Micropore volume (cm ³ /g)
H-Y-SSZ-39	602	0.26
H-Z-SSZ-39	587	0.26
H-B-SSZ-39	571	0.25

Table S1. BET surface area and micropore volume of H-SSZ-39 zeolite samples.

Crystallization	Si(4Si)	Si(4Si)	Si(3Si)	Si(2Si)
time (h)	(ppm)	(ppm)	(ppm)	(ppm)
0	-116.6	-113.9	-106.3	
6	-115.8	-112.7	-106.0	-99.3
14	-115.7	-112.4	-105.8	-98.9
16	-115.8	-111.9	-105.7	-99.5
24	-115.5	-111.7	-106.2	-99.7
36		-111.6	-106.0	-100.3
48		-111.5	-105.8	-98.9

 Table S2. ²⁹Si MAS NMR data of Z-SSZ-39 zeolite samples.

Crystallization	Si(4Si)/%	Si(4Si)/%	Si(3Si)/%	Si(2Si)/%
time /h				
0	16.0	73.7	10.3	0
6	9.2	67.3	22.0	1.5
14	8.7	66.5	23.0	1.8
16	8.4	66.1	23.2	2.3
24	4.3	63.8	29.1	2.8
36	0	62.1	33.5	4.4
48	0	60.7	34.8	4.5

Table S3. Structural information on Z-SSZ-39 samples from ²⁹Si NMR analysis.

Crystallization	Si(4Si)	Si(4Si)	Si(3Si)	Si(2Si)
time/h	(ppm)	(ppm)	(ppm)	(ppm)
0	-116.1	-112.5	-104.8	
2	-115.3	-112.3	-105.8	-99.6
8	-115.3	-111.9	-106.1	-100.5
16		-111.8	-106.3	-100.4
24		-111.9	-106.3	-100.3

 Table S4. ²⁹Si MAS NMR data of B-SSZ-39 zeolite samples.

Crystallization	Si(4Si)/%	Si(4Si)/%	Si(3Si)/%	Si(2Si)/%
time/h				
0	17.6	62.0	20.4	0
2	3.4	62.1	33.0	1.5
8	2.9	60.7	34.4	2.0
16	0	59.4	37.6	3.0
24	0	59.3	36.7	4.0

Table S5. Structural information on B-SSZ-39 samples from ²⁹Si NMR analysis.

Notes and references

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