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Electronic Supplementary Information

Design and preparation of efficient hydroisomerization catalysts by the formation of stable SAPO-11 molecular sieve nanosheets with 10-20 nm thickness and partially blocked acidic sites

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Experimental section

Materials

Polyhexamethylene biguanidine hydrochloride (PHMB, 20.6 wt.% in water, MW at ~2500, pH=5.27) was supplied from Dasheng Technology Company in Shanxi (China), phosphoric acid (H₃PO₄, 85 wt.%) was supplied from Shanghai Chemical Reagent Company (China), Pt(NH₂)₄Cl₂ (98 wt.%), di-*n*-propylamine (DPA), fumed SiO₂ were supplied from Aladdin Shanghai (China), and pseudoboehmite with purity of 70 wt.% was supplied from Senchi Fine Chemicals Company in Shandong (China).

Characterization

X-ray powder diffraction (XRD) patterns were measured with a Rigaku Ultimate VI X-ray diffractometer (40 kV, 40 mA) using CuK α (λ =1.5406 Å) radiation. The simulation of powder XRD diagrams of SAPO-11 nanosheets was performed using DISCUS software.^[1] The N₂ sorption isotherms were measured at 393K using Micromeritics ASAP 2020M and Tristar system. The sample composition was determined by inductively coupled plasma (ICP) with a Perkin-Elmer 3300DV emission spectrometer. Scanning electron microscopy (SEM) experiments were performed on Hitachi SU-1510 electron microscopes. ²⁷Al, ²⁹Si, and ³¹P MAS NMR spectra were recorded on a Bruker AVANCEIII 500WB spectrometer. Chemical shifts were referenced to 2,2-dimethyl-2-silapen-tane-5-sulfonate sodium salt (DSS) for ²⁹Si, 1 mol/L of Al(H₂O)₆³⁺ for ²⁷Al, and 85% H₃PO₄ for ³¹P. The sample was spun at 4, 10, and 5.2 kHz for ²⁹Si, ²⁷Al, and ³¹P, respectively. TEM sample was prepared from N-SAPO-11 powder. Cross-sections of the nanosheets for TEM observation were made by ultramicrotomy. TEM studies were performed on a JEOL JEM2100F microscope operated at 200 kV. Through-focus series of HRTEM images were recorded, from which the structure projection was reconstructed using the software QFocus.^[2] Pyridine IR spectra were measured using BRUKER TENSOR 27 FT-IR system. Thermogravimetric analysis (TG) and differential scanning calorimete (DSC) were performed with a SDT Q600 V8.2 Build 100 instrument in air at a heating rate of 10 °C/min.

Computational method

In order to systematically evaluate the influence of thickness on the stability of nanosheet structures, a complete 10-membered ring channel with varying layers that extracted from the crystallographic structure of SAPO-11 zeolite were employed in the present work (see Figure 1A).^[3] It's noteworthy that the thicknesses of zeolite nanosheets used in the theoretical calculations were ranged from 0.8 to 10 nm with the cluster size extending from 1 to 12 layers. All the terminal oxygen atoms in the cluster models were saturated with hydrogen atoms. In order to preserve the integrity of the cluster model structures during the geometry optimizations, only the boundary -OH groups and the corresponding P and Al atoms of the cluster models were allowed to relax, while the rest of atoms of the zeolite frameworks were kept fixed at their crystallographic locations. It's noteworthy that, due to the calculations involved amounts of atoms (2784 atoms for the maximum 12 layers cluster, and 276 atoms for even the minimum 1 layer cluster), therefore, the semiempirical AM1 method was applied for all the geometry optimizations for a suitable computational cost. In the calculations, the formation energy of *n* layers cluster ($E_{formation(n)}$) was defined as the reaction energy between the 1 layer and the n-1 layers clusters during the formation of *n* layers zeolite ($n \ge 2$), i.e., $E_{formation(n)} = E_n + 16 E_{water} - (E_1 + E_{n-1})$, where E_n , E_{n-1} and E_{water} represent the energy of *n* layers cluster, n-1 layers cluster and H₂O in the free state, respectively.

Synthesis

Conventional SAPO-11 zeolite was synthesized according to the references. As a typical run, 1.96 mL H₃PO₄ (85%) was dissolved in 14 g distilled H₂O under stirring, followed by addition of 2.0 g pseudoboehmite. After stirring for 2 h, 2.4 mL DPA was slowly added. After stirring for additional 2 h, 0.168 g fumed SiO₂ was added. The reaction mixture was further stirred for 2 h, leading to the formation of a gel (molar ratio at $0.2SiO_2/Al_2O_3/P_2O_5/1.25DPA/59H_2O$). Then, the gel was transferred into an autoclave for crystallization at 200 °C for 48 h. After filtrating, washing with distilled water, drying in air, and calcination at 600 °C for 6 h to remove the organic template, the product of SAPO-11 was finally obtained, which was designated as C-SAPO-11.

SAPO-11 nanosheets were synthesized in the presence of PHMB under hydrothermal conditions. In a typical run, 1.94 mL H₃PO₄ (85%) were dissolved in 14 g distilled H₂O under stirring, followed by addition of 2.0 g pseudoboehmite. After stirring for another 2 h, 2.4 mL DPA, 4.0 g PHMB, and 0.168 g fumed SiO₂ were gradually added. The reaction mixture was further stirred for 2 h, giving a gel with molar ratio of $0.2SiO_2/Al_2O_3/1.1P_2O_5/1.28DPA/0.024PHMB/69H_2O$, which was transferred into an autoclave for crystallization at 200 °C for 48 h. After filtrating, washing with distilled water, drying in air, and calcination at 600 °C for 6 h to remove the organic template, the product of SAPO-11 nanosheets was finally obtained, designated as N-SAPO-11.

Catalyst preparation and catalytic tests

Pt (0.5 wt.%) was loaded on both calcined C-SAPO-11 and N-SAPO-11 by wet impregnation using Pt(NH₃)₄Cl₂ as a Pt source, followed by drying at 120 °C overnight, and finally calcined at 450 °C for 3 h. The obtained samples were pressed into tablets with a diameter of 12.7 mm, using a hand-operated press for 10 min. Then, the as-prepared tablets were crushed into particles with 20-40 mesh sizes, denoted Pt/C-SAPO-11 and Pt/N-SAPO-11, respectively.

Prior to the hydroisomerization of *n*-dodecane, the catalysts (*ca.* 10 mL, 20-40 mesh) were reduced in flowing hydrogen (*ca.* 120 ml/min) at 450 °C for 2 h. Hydroisomerization of *n*-dodecane (*n*-C₁₂) was carried out in a fixed-bed continuous reactor at 8.0 MPa pressure. The reaction conditions were H_2/n -C₁₂ (mol/mol) at 13, weight hourly space velocity (WHSV) at 1.0 h⁻¹, and reaction temperature ranged from 250 to 350 °C. The reactant and the products were analyzed on-line by a gas chromatograph (Agilent 7890A), equipped with a flame ionization detector and an HP-5 (60 m × 0.32 mm) capillary column.

Model	Formation	Energy (kcal/mol)
S1	$H_{56}O_{156}Al_{32}P_{32}$	
S2	$H_{80}O_{296}Al_{64}P_{64}$	-157.8
S3	H ₁₀₄ O ₄₃₆ Al ₉₆ P ₉₆	-239.1
S4	$H_{128}O_{576}Al_{128}P_{128}$	-285.7
S5	$H_{152}O_{716}Al_{160}P_{160}$	-309.8
S6	$H_{176}O_{856}Al_{192}P_{192}$	-323.6
S7	$H_{200}O_{996}Al_{224}P_{224}$	-332.3
S8	$H_{224}O_{1136}Al_{256}P_{256}$	-337.2
S9	$H_{248}O_{1276}Al_{288}P_{288}$	-342.5
S10	$H_{272}O_{1416}Al_{320}P_{320}$	-344.8
S11	$H_{296}O_{1556}Al_{352}P_{352}$	-346.8
S12	$H_{320}O_{1696}Al_{384}P_{384}$	-346.1

Table S1 Calculated crystal energies of SAPO-11 with different number of layers

Sample	$S_{\rm BET}$ (m ² /g)	$S_{\rm Ext}$ (m ² /g)	$V_{\rm meso}~({\rm cm^3/g})$	$V_{\rm micro}~({\rm cm}^3/{\rm g})$
C-SAPO-11	140	38	0.08	0.06
N-SAPO-11	83	51	0.29	0.01

 Table S2 Textural parameters for the C-SAPO-11 and N-SAPO-11 samples



Figure S1 Simulated XRD patterns of the AEL nanosheets with (a) 5, (b) 10, (c) 15, (d) 17, and (e) 20 nm thick along the channel as well as experimental XRD pattern of (f) the N-SAPO-11 sample.



Figure S2 XRD pattern of the as-synthesized C-SAPO-11 sample.



Figure S3 N₂ sorption isotherms of the calcined C-SAPO-11 sample.



Figure S4 TG-DSC curves of the C-SAPO-11 sample.



Figure S5 SEM images of the as-synthesized C-SAPO-11.



Figure S6 Reconstructed HRTEM image of the N-SAPO-11.



Figure S7 (A) ²⁹Si, (B) ³¹P and (C) ²⁷Al MAS NMR spectra of the calcined (a) C-SAPO-11 and (b) N-SAPO-11. In the ²⁹Si NMR spectra, both samples exhibit peaks ranged from -80 to -110 ppm associated with the silicon species in the framework. In the ³¹P NMR spectra, except for the peak at -29 ppm associated with the tetrahedral P sites with four AlO₄ neighbors, N-SAPO-11 gives a clear peak at -23 ppm, which could be assigned as tetrahedral P sites with three AlO₄ neighbors and one hydroxyl species. In the ²⁷Al NMR spectra, N-SAPO-11 has an additional peak at -10.2 ppm, which is related to 6-coordinative extraframework Al³⁺ species of amorphous alumina.



Figure S8 IR spectra of pyridine adsorbed on the calcined (a) C-SAPO-11 and (b) N-SAPO-11.



Figure S9 TEM images and Pt size distribution of (A) Pt/C-SAPO-11 and (B) Pt/N-SAPO-11. Both samples have similar Pt particle size distribution.

Sample	$S_{\rm BET}({ m m^2/g})$	$S_{\rm Ext}$ (m ² /g)	$V_{\rm meso}~({\rm cm^{3}/g})$	$V_{\rm micro}~({\rm cm}^3/{\rm g})$
Pt/C-SAPO-11	118	24	0.07	0.04
Pt/N-SAPO-11	92	46	0.30	0.01

Table S3 Textural parameters for the Pt/C-SAPO-11 and Pt/N-SAPO-11 samples



Figure S10 (A) N₂ sorption isotherms and (B) pyridine-IR spectra of the calcined (a) Pt/C-SAPO-11 and (b) Pt/N-SAPO-11 samples. Compared with C-SAPO-11 and N-SAPO-11, the Pt/C-SAPO-11 and Pt/N-SAPO-11 exhibit higher Lewis acidic density, which might be assigned to the interaction between pyridine with cationic Pt species.



Figure S11 XRD patterns of the N-SAPO-11 samples crystallized after (a) 0, (b) 1, (c) 2, (d) 4, (e) 8, (f) 12, (g) 18, (h) 24, and (i) 48 h, respectively.



Figure S12 SEM images of the N-SAPO-11 samples crystallized after (a) 0, (b) 1, (c) 2, (d) 4, (e) 8, (f) 12, (g) 18, and (h) 24 h, respectively. S21



Figure S13 ¹³C NMR spectra of (a) as-synthesized N-SAPO-11 and (b) aqueous PHMB liquid.



Figure S14 Proposed route for decomposition of PHMB.



Figure S15 (A) XRD pattern, (B) SEM image, and (C) N_2 sorption isotherm of the SAPO-11 sample synthesized in the presence of NH_4HCO_3 .

Supporting References:

- [1] Th. Proffen, R. B. Neder, J. Appl. Cryst. 1997, 30, 171-175.
- [2] W. Wan, S. Hovmöller, X. D. Zou, Ultramicroscopy, 2012, 115, 50-60.
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