Supporting Information:

A facile approach for preparation of tunable acid nano-catalyst with hierarchically mesoporous structure

Youngbo Choi[‡], Yang Sik Yun[‡], Hongseok Park, Dae Sung Park, Danim Yun, and Jongheop

Yi*

World Class University Program of Chemical Convergence for Energy & Environment, Institute of Chemical Processes School of Chemical and Biological Engineering Seoul National University, Seoul 151-742, Republic of Korea

[‡]These authors contributed equally.

*To whom correspondence should be addressed: jyi@snu.ac.kr

Tel: +82 2-880-7438

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Experimental details

1. Preparation of ASN samples

Tetraethyl orthosilicate (99%, Sigma-aldrich) and aluminium sulphate octadecahydrate $(Al_2(SO_4)_3 \cdot 18H_2O)$ (98%, Sigma-aldrich) were used as silica and aluminium precursors, respectively. Cetylprydinium bromide hydrate (98%, Sigma-aldrich), cyclohexane (99%, Sigma-aldrich) and 1-pentanol (99%, Samchun) were utilized as the surfactant, oil phase and co-solvent, respectively, in the microemulsions. Urea and HCl were purchased from Sigma-aldrich. All chemicals were used as received.

In a typical synthesis, cetylpyridinium bromide hydrate (1 g; 2.6 mmol) and urea (0.6 g; 10 mmol) of were dissolved in deionized water (30 mL). A stirred solution containing tetraethyl orthosilicate (2.5 g; 12 mmol), cyclohexane (30 mL), and 1-pentanol (1.5 mL) was then added, and the solution was stirred for additional 30 min at room temperature. The resulting solution was loaded into a glass-lined autoclave and hydrothermally treated with continuous stirring at 120 °C for 2.5 h. After cooling to room temperature, the pH of the mother liquor (initial pH = ca. 9~10) was adjusted to pH 5 by adding a 2 mol L⁻¹ HCl solution. Then, Al₂(SO₄)₃·18H₂O solution was varied from 0.051 to 0.204 mol L⁻¹ to give Si/Al molar ratios of 15, 25, 40 and 60. Subsequently, the obtained mixture was hydrothermally treated again at 120 °C for another 4 h. The resulting acidic nanospheres were collected by centrifugation, washed with a solution of acetone and water, and then dried at room temperature for 24 h. The dried material was calcined in air at 550 °C for 6 h.

2. Preparation of ASPN samples

ASN samples were prepared by procedures identical to those for ASPN samples, except that the pH of the mother liquor was adjusted using a 2 mol L^{-1} H₃PO₄ (Sigma-aldrich) solution instead of a 2 mol L^{-1} HCl solution.

3. Preparation of reference AIMCM-41 and HZSM-5 samples

Mesostructured AlMCM-41 (Si/Al ratio = 40) was obtained from Sigma-aldrich (product No. = 643653). HZSM-5 was prepared through the calcination of commercial zeolite NH₄ZSM-5 (Si/Al ratio = 40, Zeolyst, product No. = CBV 8014) at 550 °C for 6 h in air atmosphere.

4. Characterization

Transmission electron microscopy (TEM) observations were carried out on a JEOL JEM-3010 microscope operating at 300 kV. The scanning electron microscope (SEM) images were obtained on a Carl Zeiss SUPRA 55VP field-emission scanning electron microscope. The elemental mapping images were obtained using of a FEI Tecnai F20 instrument equipped with an X-ray energy dispersive spectrometer. The elemental compositions of solid products were investigated by electron probe microanalysis (EPMA) using a JEOL JXA-8900R spectrometer.

 N_2 adsorption-desorption isotherms were measured at -196 °C using a Micrometrics ASAP-2010 system. Pore size distribution curves were obtained from the adsorption branches of the isotherms by using Barrett–Joyner–Halenda (BJH) method. The ²⁷Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) investigations were performed on a Bruker Avance II spectrometer with a 4 mm MAS probe. The spectra were recorded at a resonance frequency of 130.3 MHz with a sample spinning rate of 11 kHz. The X-ray diffraction (XRD) patterns were obtained using a Rigaku D-MAX2500-PC powder X-ray diffractometer with Cu K α radiation (1.5406 Å) at a scanning rate of 10.0 deg min⁻¹.

The NH₃ temperature-programmed desorption (TPD) profiles were obtained using a conventional apparatus. 0.1 g of a sample loaded in a quartz reactor was preheated at 200 °C for 2 h under a He flow (20 mL min⁻¹). After cooling to room temperature, 20 mL of NH₃ injected every minute into the reactor under a He flow (5 mL min⁻¹). The injection was

repeated until the sample was saturated with NH₃. The NH₃ that was physisorbed to the sample was eliminated by evacuation at 50 °C for 1 h. The TPD procedures were performed from room temperature to 800 °C with a heating rate of 10 °C min⁻¹ under a He flow (10 mL min⁻¹). The desorbed NH₃ (m/z = 16)^{S1} was quantitatively detected by a GC-MS detector (Agilent, 5975MSD-6890N GC).

The *in situ* FTIR spectra of NH_3 adsorption were measured using a Midac 2100 spectrometer. A self-supported pellet containing a sample (40 mg) was placed in an *in situ* FTIR cell, designed by Moon et al.^{S2} The pellet was pre-treated at 200 °C under a He flow for 1 h. After cooling to room temperature, the pellet was exposed to NH_3 gas at 5 kPa for 3 min. The desorption of NH_3 was carried by evacuation at room temperature and then the spectrum was recorded.

Thermogravimetric (TG) analysis was performed in a TA instruments SDT Q600 analyzer. The experiment was carried out from room temperature to 800 °C with a heating rate of 10 °C min⁻¹ under air.

5. Cracking of 1,3,5-triisopropylbenzene

The catalytic cracking of 1,3,5-triisopropylbenzen (1,3,5-TIPB) was carried out at atmospheric pressure at 300 °C. A 50 mg sample of catalyst was loaded to a quartz reactor (8 mm inner diameter), the reactor was then placed in an electric furnace. The temperature of the catalyst bed was monitored by a thermocouple and controlled through a PID controller. Before the reaction, the catalyst was preheated to the reaction temperature under a N₂ flow (30 mL min⁻¹) for 1 h. 1,3,5-TIPB (Sigma-aldrich) was injected into a vaporizer at a rate of 0.01 mL min⁻¹ by using a syringe pump. The 1,3,5-TIPB vapor was diluted with a N₂ flow (30 mL min⁻¹) in the vaporizer and then fed into the catalyst bed. The composition of the reaction products was determined on-line by a gas chromatograph (Younglin, ACME 6100) equipped with a FID detector and a HP-Innowax capillary column. In order to reveal the

deactivation kinetics, the 1,3,5-TIPB conversion vs. time data were fitted in first order deactivation model, which is described by the Equation (1).

$$X(t)/X(0) = \exp(-k_d t)$$
(1)

where X(t) represents the 1,3,5-TIPB conversion at a given time, X(0) is initial conversion, and k_d is first order deactivation rate constant. ^{S3,S4}

6. Hydrolysis of sucrose to glucose and fructose

The reaction was carried out using 0.1 g of a catalyst, 0.1 g (0.29 mmol) of sucrose (Sigma-aldrich) and 10 mL of deionized water at 80 °C for 8 h. The reaction products were analysed by a high performance liquid chromatograph (Younglin, YL9100) with a Varian Metacarb 67C Ana. column.

Supplementary Figures



Fig. S1 (a) TEM and (b) SEM images of the sample (Si/Al molar ratio = 15) prepared by the direct-synthetic approach, in which the Al precursor was included in the initial preparation solution. (c-e) SEM images of ASN-15 samples prepared for different time periods of the first hydrothermal treatment; (c) 1 h, (d) 2.5 h, and (e) 4 h. (f-j) SEM images of ASN-15 samples prepared at different pH values. The Al precursor solution was added into the first hydrothermal treated solution (f) without adjusting the pH value (pH = 9-10) and after adjusting the pH value to (g) 7, (h) 6, (i) 5 and (j) 4.



Fig. S2 (a) SEM and (b) TEM images of ASN and ASPN samples with different Si/Al molar ratios



Fig. S3 ²⁷Al MAS NMR spectra of (a) ASN and (b) ASPN samples with different Si/Al mola r ratios.



Fig. S4 Comparison of ASN-40 and AlMCM-41 samples with Si/Al molar ratio = 40: (a) N_2 adsorption-desorption isotherms, (b) ²⁷Al MAS NMR spectra, (c) NH₃-TPD curves, and (d) *in situ* FTIR spectra for adsorbed NH₃.



Fig. S5 X-ray diffraction (XRD) patterns of ASN samples with different Si/Al molar ratios and AlMCM-41.



Fig. S6 Amount of coke per reacted 1,3,5-TIPB for ASN-40, ASPN-40, AlMCM-41, and HZSM-5 samples.



Fig. S7 TEM images of (A) AlMCM-41, and (B) ASN-40 samples (a) before and after hydrothermal treatment (b) in an autoclave at 180 °C for 24h and (c) with steam flow at 600 °C for 2 h.

Supplementary Tables

Sample	Si/Al molar ratio (precursor)	Si/Al molar ratio ^a (solid product)	Al/P molar ratio ^a (solid product)
ASN-15	15	16.1	-
ASN-25	25	24.6	-
ASN-40	40	42.5	-
ASN-60	60	57.7	-
ASPN-15	15	15.5	1.7
ASPN-25	25	23.9	1.9
ASPN-40	40	36.5	2.4
ASPN-60	60	57.2	2.1
AlMCM-41	-	43.9	-
HZSM-5	-	41.8	-

Table S1 Elemental compositions of the ASN, ASPN, AlMCM-41 and HZSM-5 samples.

Sample	$\frac{\mathrm{S}_{\mathrm{BET}}{}^a}{(\mathrm{m}^2\mathrm{g}^{\text{-1}})}$	$\frac{\mathrm{S}_{\mathrm{micro}}{}^{b}}{\mathrm{(m}^{2}\mathrm{g}^{\text{-1}})}$	$\frac{\mathrm{V}_{\mathrm{micro}}^{b}}{(\mathrm{cm}^{3}\mathrm{g}^{-1})}$	$\frac{\mathrm{V_{total}}^c}{(\mathrm{cm}^3\mathrm{g}^{-1})}$	D _{ave} ^d (nm)	Al(tet)/(Al(tet)+Al(oct)) ^e (%)
ASN-15	479	9	0.006	0.917	6.0	70.8
ASN-25	516	-	-	1.046	6.5	73.4
ASN-40	494	19	0.011	0.988	6.4	74.2
ASN-60	498	9	0.006	0.937	5.9	77.3
ASPN-15	488	22	0.011	1.006	6.4	50.6
ASPN-25	514	20	0.011	0.998	6.2	54.1
ASPN-40	475	10	0.007	0.899	6.0	51.4
ASPN-60	516	35	0.017	1.029	6.3	49.0
AlMCM-41	1087	266	0.134	0.889	2.6	50.8
HZSM-5	523	297	0.121	0.282	< 1.5	90.7

Table S2 Physicochemical properties of ASN, ASPN, AIMCM-41, and HZSM-5 samples.

^{*a*}The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was determined from the N₂ adsorption branch in the relative pressure range from 0.05 to 0.25. ^{*b*}Micropore area (S_{micro}) and micropore volume (V_{micro}) were obtained by the t-plot method. ^{*c*}Total pore volume (V_{total}) was evaluated at a relative pressure of 0.99. ^{*d*}Average pore diameter (D_{ave}) was calculated by the Barrett–Joyner–Halenda (BJH) method. ^{*e*}The proportion of tetrahedral Al (AlO₄ structural unit, Al(tet)) was estimated from the relative intensities of the tetrahedral Al peak (ca. 50 ppm) and the octahedral Al peak (ca. 0 ppm, AlO₆ structural unit, Al(oct)) in the ²⁷Al MAS NMR spectra.^{S5-S7}

Sample	Total amount of acid sites ^a (mmol g ⁻¹)	Ratio of . Brønsted/Lewis acid sites ^b	Distribution of acid strength ^c					
			Weak acidity		Medium acidity		Strong acidity	
			T _m (°C)	X (%)	T _m (°C)	X (%)	T _m (°C)	X (%)
ASN-15	0.609	5.5	242.2	16.1	326.2	34.8	504.1	49.1
ASN-25	0.438	3.5	220.5	17.9	302.1	37.8	464.8	44.2
ASN-40	0.329	1.5	218.4	18.6	295.1	33.5	462.0	47.9
ASN-60	0.132	0.6	201.2	25.8	252.8	24.5	376.8	49.7
ASPN-15	0.655	6.2	202.7	28.7	271.0	32.5	467.4	38.8
ASPN-25	0.547	4.3	189.5	24.7	240.1	31.3	411.0	44.0
ASPN-40	0.414	2.9	177.1	36.5	225.6	29.3	347.0	34.2
ASPN-60	0.167	2.0	157.9	37.5	202.0	29.3	339.0	33.2
AlMCM-41	0.186	0.9	213.8	15.0	286.2	32.7	442.8	52.3
HZSM-5	0.475	3.8	247.8	19.1	315.3	39.1	512.6	41.8

Table S3 Acidic properties of the ASN, ASPN, AIMCM-41 and HZSM-5 samples.

^{*a*}The amount of acid sites was evaluated based on temperature-programmed desorption (TPD) of NH₃. ^{*b*}The ratio of Brønsted to Lewis acid sites (*BS/LS*) was estimated by the correlation equation.^{S8,S9} *BS/LS* = *ECR(IAB/IAL)*, where *ECR* = extinction coefficient ratio, *IAB* = integrated absorbance of Brønsted band centered at 1470 cm⁻¹ and *IAL* = integrated absorbance of Lewis band centered at 1640 cm⁻¹. The ECR was taken as 1/7.^{S10,S11} ^{*c*}The distribution of acid strength was determined by deconvoluting the NH₃-TPD profiles. The deconvolution was carried out using the Gaussian method, in which three peaks were used to indicate weak, medium and strong acidity, respectively.^{S12, S13} T_m and X indicate the peak maximum temperature and the fraction of each peak, respectively.

Sample	Sucrose Conversion (%)	1,3,5-TIPB	Selectivity (%)			
		Conversion ^{<i>a</i>} (%)	Benzene	Cumene	DIPBs ^b	
ASN-15	36.4	99.5	4.8	46.5	48.7	
ASN-25	32.6	99.4	3.5	46.6	49.9	
ASN-40	30.7	99.6	3.5	39.3	57.1	
ASN-60	28.2	91.2	0.4	15.4	84.2	
ASPN-15	70.2	99.8	1.7	27.5	70.7	
ASPN-25	62.2	99.2	0.5	16.2	83.3	
ASPN-40	57.7	99.8	0.3	14.3	85.3	
ASPN-60	52.6	94.3	0.4	14.2	85.5	
AlMCM-41	14.1	96.5	3.2	37.7	59.1	
HZSM-5	6.8	46.4	27.2	3.7	69.1	

Table S4 Catalytic activities for the cracking of 1,3,5-TIPB and hydrolysis of sucrose over ASN, ASPN, AIMCM-41, and HZSM-5 samples.

^{*a*}Data were obtained at 2 min after the initiation of the reaction. ^{*b*}DIPBs includes 1,3-DIPB and 1,4-DIPB.

Pathway of 1,3,5-TIPB cracking has been proposed as following steps: (a) dealkylation of 1,3,5-TIPB to 1,3-diisopropylbenzene (1,3-DIPB), (b) isomerization of 1,3-DIPB to 1,4-DIPB, (c) dealkylation of DIPB to cumene, (d) dealkylation of cumene to benzene.^{S14,S15} It is well known that selectivity of the products is closely related to strength of acid site. Acid strength required for dealkylation decreases in order: cumene > DIPB > 1,3,5-TIPB. ^{S16} In Table S4, different product distributions were obtained with different Si/Al ratios over the catalysts. Selectivities for benzene and cumene were increased with the decrease of Si/Al ratio in ASN catalysts, which is in agreement with acid strength order in TPD data. Over ASN-60 catalyst, DIPBs was major product, and relatively low conversion was obtained due to its weak acid strength and low acid amounts. Similar trend can be seen in case of ASPN catalysts. However, benzene was rarely observed, and large portion of products was occupied by DIPBs over the catalysts because they have weak acidity compared to ASN catalysts.

Catalyst	Treatment	1,3,5-TIPB Conversion ^c (%)
ASN-40	-	99.6
ASN-40	treated in an autoclave at 180 °C for 24 h ^a	95.8
ASN-40	treated with steam flow at 600 $^{\rm o}C$ for 2 h^b	67.4
AlMCM-41	-	96.5
AlMCM-41	treated in an autoclave at 180 °C for 24 h ^a	86.7
AlMCM-41	treated with steam flow at 600 $^{\rm o}C$ for 2 h^b	35.8

Table S5 Catalytic activities for the cracking of 1,3,5-TIPB of ASN-40 and AlMCM-41 samples before and after hydrothermal treatment.

^{*a*}0.15 g of catalyst and 30 mL of deionized water in a glass-lined stainless steel autoclave were heated at 180 °C for 24 h. ^{*b*}0.05 g of sample in a fixed-bed quartz reactor was exposed to a steam flow (90 vol. % H₂O in N₂) at 600 °C for 2 h. The flow rate of the steam was maintained at 50 mL min⁻¹ during the hydrothermal treatment. ^cData were obtained at 2 min after the initiation of the reaction.

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