Synthesis of Mesoporous ZSM-5 Zeolite Crystals by Conventional Hydrothermal Treatment

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Supporting information:

Synthesis of mesoporous ZSM-5. All zeolite samples were prepared from clear synthesis solutions, similar to the ones described by Gevert et al.¹ The molar compositions of the synthesis mixtures used in the present work and sample codes are given in Table S1. The silica source was tetraethylorthosilicate (TEOS, 98%, Aldrich) and the alumina source was aluminium isopropoxide (Al(O-i-Pr)₃, Aldrich). Sodium was added in the form of a 1M sodium hydroxide solution prepared from sodium hydroxide pellets (NaOH, \geq 98%, Aldrich) and template molecules were added in the form of tetrapropylammonium hydroxide (TPAOH, 40 wt% aqueous solution, AppliChem). Deionized and then distilled water were used both for the zeolite synthesis and during purification.

The sample preparation procedure consisted of six steps as outlined below.

(i) Preparation of silicate solution: All the required TEOS, about half of the TPAOH and half of the water were added to a polypropylene bottle, which was placed on shaker for 24 h to hydrolyze TEOS at room temperature and obtain a clear solution.

(ii) Preparation of aluminate solution: After about 22 h of hydrolysis of TEOS in step (i), all Al(O-i-Pr)₃, NaOH and the remaining water and TPAOH were added to a glass beaker and stirred for about 2 h until a clear aluminate solution formed.

(iii) Preparation of synthesis mixture: The clear silicate solution was added to the clear aluminate solution in the glass beaker under strong stirring. The stirring of the resulting clear solution was continued for about 10 minutes in total.

(iv) Hydrothermal treatment: An 100 ml Teflon lined autoclave equipped with magnetic stirring was filled to about 2/3 with synthesis mixture. The autoclave was sealed and placed in an oil bath kept at 150 °C. The stirred autoclave was kept in the oil bath for certain duration as specified in Table S1.

(v) Product purification: After cooling the autoclave to room temperature, it was opened and the synthesis mixture containing dispersed crystals was removed from the autoclave. The dispersed

crystals were purified by repeated centrifugation followed by re-dispersion in water for four times in total. The purified crystals were freeze dried. For synthesis containing aluminium, crystals also formed on the walls of the autoclave.

(vi) Calcination: The freeze dried crystals were finally calcined at 500 °C (the heating rate was 5 °C/min) in air for 16 h to remove the template molecules.

Characterizations. X-ray powder diffraction (XRD) patterns were recorded using a Siemens D 5000 diffractometer operating in Bragg-Brentano geometry. Nitrogen adsorption/desorption isotherms were recorded using a Micromeritics ASAP 2010 instrument at -196 °C, and the surface area, mesopore size distribution and external surface area were calculated according to Brunauer-Emmett-Teller (BET) equation, Barrett-Joyner-Halenda (BJH) method and the t-plot methods, respectively. The morphology of the zeolites crystals was observed using a FEI Magellan[™] 400L high resolution Scanning Electron Microscopy (SEM) instrument. The average crystal length was determined by measuring the length of 50 crystals for each sample. Elemental analyses (ICP-AES) were carried out using a Perkin-Elmer Emission spectroscopy Model Plasma 1000 instrument.

Sample*	Crystallization Time (h)	SiO ₂ /Al ₂ O ₃ Ratios in synthesis mixture	Molar Compositon of synthesis mixture			
ZSM-100	1.5-72	100	3 TPAOH: 0.5 Na ₂ O: 0.25 Al ₂ O ₃ : 25 SiO ₂ : 1500 H ₂ O: 100 EtOH: 1.5 PrOH			
ZSM-50	24	50	3 TPAOH: 0.5 Na ₂ O: 0.5Al ₂ O ₃ : 25 SiO ₂ : 1500 H ₂ O: 100 EtOH: 3PrOH			
Silicalite-1	24	∞	3 TPAOH: 0.5 Na ₂ O: 25 SiO ₂ : 1500 H ₂ O: 100 EtOH			

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 * ZSM-X: X is SiO_/Al_2O_3 ratio in synthesis mixture.

Table S2. Properties of the products

Sample [*]	SiO ₂ /Al ₂ O ₃ Ratios ^a	length c-axis ^b	length <i>a</i> -axis ^b	Aspect ratio <i>c-/a-</i> axis	S _{BET}	S _{meso}	V _{total} (cm ³ g ⁻¹) ^e	$V_{micro} \ (cm^3g^{-1})^f$	V _{meso} (cm ³ g ⁻¹) ^g
_		(µm)	(µm)		$(\mathbf{m}^2 \mathbf{g}^{-1})^c$	$(m^2g^{-1})^d$			
ZSM-100-1.5	628	1.5	1.1	1.4	338	106	0.18	0.11	0.07
ZSM-100-3	114	1.8	1.7	1.1	354	116	0.21	0.11	0.10
ZSM-100-6	94	2.0	2.2	0.91	384	133	0.25	0.12	0.13
ZSM-100-12	91	1.8	2.1	0.86	383	136	0.25	0.12	0.13
ZSM-100-18	94	1.9	2.2	0.86	399	134	0.25	0.12	0.13
ZSM-100-24	106	2.0	2.1	0.95	388	148	0.23	0.11	0.12
ZSM-100-48	93	1.7	2.0	0.85	396	167	0.28	0.11	0.17
ZSM-100-72	83	1.7	2.4	0.71	397	149	0.26	0.12	0.14
ZSM-50-24	50	1.8	2.4	0.75	395	214	0.46	0.08	0.38
Silicalite-1	∞	2.8	2.0	1.4	364	94	0.19	0.13	0.06

* ZSM-X-Y: X is SiO₂/Al₂O₃ ratio in synthesis mixture; Y is hydrothermal treatment time (h).

^a Determined by ICP-AES.

^bEstimated from SEM.

°Surface areas were obtained by the BET method using adsorption data in p/p_0 range from 0.05 to 0.25.

^dMeasured by *t*-plot method.

 $^{e}\mbox{Total}$ pore volumes were estimated from the adsorbed amount at $p/p_{0}\mbox{=}0.995.$

^fMeasured by *t*-plot method.

 ${}^{g}V_{meso} = V_{ads,p/p0=99} - V_{micro}.$



Figure S1. FT-IR spectrum of mesoporous ZSM-5 crystals with SiO_2/Al_2O_3 ratio of 50, which were grown at 150 °C under constant stirring for 24 h (ZSM-50-24) and 72 h (ZSM-50-72). In the *v*(OH) region, two bands at 3744 and 3600 cm⁻¹ were observed, they originate from silanol groups and bridging-OH (or acidic-OH) groups,^{2,3} respectively.

Reference

- (1) B. Gevert, L. Eriksson, A. Torncrona, J. Porous Mat. 2011, 18, 723-728.
- (2) J. Datka, E. Tuznik, Zeolites 1985, 5, 230-232.
- (3) F. Wakabayashi, J. N. Kondo, K. Domen, C. Hirose, J. Phys. Chem. 1996, 100, 4154-4159.