

Supporting information

Direct Fabrication of Mesoporous Zeolite with A Hollow Capsular Structure

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Experimental Section

I. Chemicals

Tetrapropylammonium hydroxide (TPAOH, 25% in water), tetraethyl orthosilicate (TEOS), aluminium isopropoxide [Al(ⁱPro)₃], cetyltrimethylammonium bromide (CTAB), NaOH, and ethanol (99.9%) were purchased from Aldrich.

II. Direct synthesis of the hollow zeolite capsule

Zeolite precursor was prepared by adding tetrapropylammonium hydroxide (TPAOH) and NaOH to a mixed aqueous solution of aluminium isopropoxide [Al(ⁱPro)₃] and tetraethyl orthosilicate (TEOS) with stirring. To control the hydrolysis process of TEOS, the temperature was kept under 15 °C. The resulting solution was aged for 20h at the same temperature and then dropped into an aqueous solution of cetyltrimethylammonium bromide (CTAB) under vigorous stirring. Stirring was continued for another 2h and then the mixture was aged at room temperature for 4h. The mole composition of the gel was 100SiO₂/1Al₂O₃/18TPAOH/16600H₂O/44NaOH/5.6CTAB. The resulting gel was sealed in Teflon-lined autoclaves and heated at 150 °C for 16-48h. The solid product was recovered by filtration and dried

in an oven at 100 °C overnight. The as-synthesized material was then calcined in air at 550 °C for 10h to remove the templates. Finally, the obtained sample was converted into the H-form by ion exchanges with 1 M NH₄NO₃ solution at 90 °C for three times and subsequent calcination in air at 550 °C for 5h. For comparison, conventional ZSM-5 (H-ZSM-5) and mesoporous amorphous aluminosilicate (AAS) phase were prepared in this study following the literature reports.^{1,2} All samples were prepared with the same Si/Al molar ratio of 30.

III. Characterization

Powder XRD patterns were recorded on a Rigaku D/Max 2200PC diffractometer using Cu K α radiation (40 kV and 40 mA) with the scanning rate of 0.4° min⁻¹ for small angle tests and 4° min⁻¹ for wide angle tests, respectively. The N₂ sorption measurements were performed using Micromeritics Tristar 3000 and Micromeritics ASAP 2020 porosimeters at 77 K for mesoporosity and microposity, respectively, and the mesoporous specific surface area and the pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The micropore size distribution and pore volume were calculated by the Horvath-Kawazoe method. FE-SEM (Field Emission Scanning Electron Microscopy) analysis was performed on a JEOL JSM6700F electron microscope. Transmission electron microscopy (TEM) images were obtained on a JEOL-2010F electron microscope operated at 200 kV. Temperature-programmed desorption of ammonia (NH₃–TPD) was performed on a homemade apparatus PX200A (Tianjin Golden Eagle Technology CO. LTD). The NH₃ desorbed was collected in a liquid N₂ trap and analyzed by gas chromatography. ²⁷Al and ²⁹Si MAR NMR measurements were performed on a Bruker DMX500 spectrometer and a Bruker DSX300 spectrometer, respectively.

Catalytic Reaction: The catalytic reactions were carried out in a three-necked flask equipped a reflux condenser under N₂ atmosphere. The molar ratios of benzaldehyde with glycol and n-butyl alcohol were 1:2 and 1:4, respectively. In a typical reaction, benzaldehyde (5.3 g, 0.05mol), glycol (6.2 g, 0.1mol) or n-butyl alcohol (14.8 g, 0.2mol) and catalyst (0.2 g) were mixed under continuous stirring. The mixture was

stirred for a few minutes at ambient temperature (ca. 20 °C) and then the reaction temperature was kept at 78 °C. In the aldol condensation of benzaldehyde with glycol or n-butyl alcohol, reactions were continued until the equilibrium, or in other words, till that the composition of the products became unchanged. The samples were analyzed by a GC-MS (Agilent, 6890/5973N).

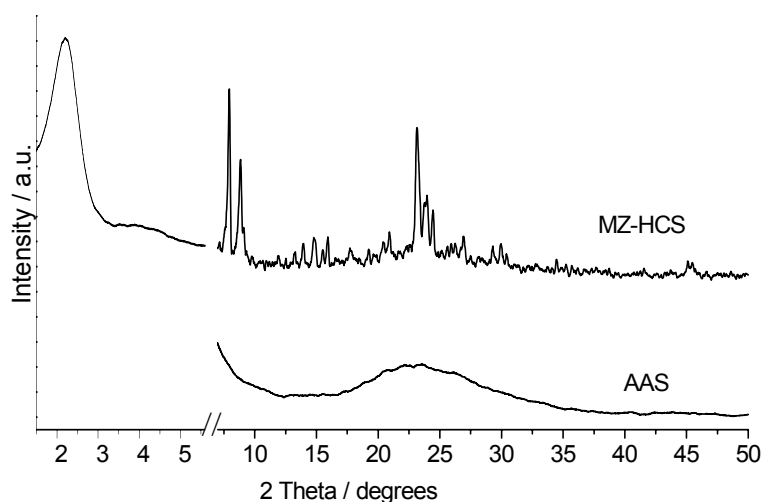


Figure S1. XRD patterns of MZ-HCS and AAS

Table S1. Pore structural properties of the prepared different aluminosilicate materials.

Sample	$S_{\text{BET}}^{[\text{a}]}$ / $\text{m}^2 \text{g}^{-1}$	$V_{\text{micro}}^{[\text{b}]}$ / mL g^{-1}	$V_{\text{meso}}^{[\text{b}]}$ / mL g^{-1}
H-ZSM	370	0.18	/
MZ-HCS	717	0.31	0.66
Meso-AAS	1149	/	0.92

[a] S_{BET} is BET surface area. [b] V_{micro} is micropore volume calculated from Saito-Foley analysis.

V_{meso} is mesopore volume (total pore volume - V_{micro}).

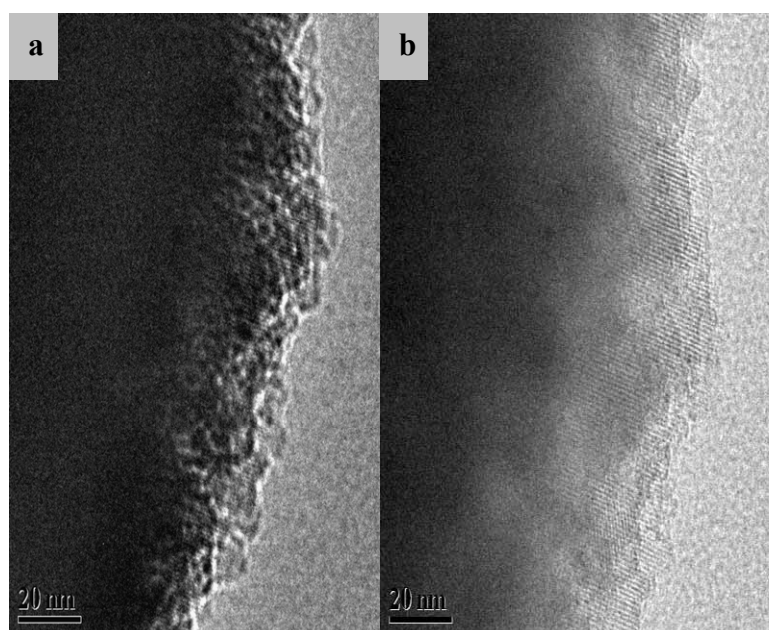


Figure S2. TEM image (a) of MZ-HCS showing the coexistence of mesoporous structure and the zeolite lattice structure by compromising the focusing lengths of the two structures; HR-TEM image(b) for the zeolite crystalline lattice at the identical area of Figure S2a

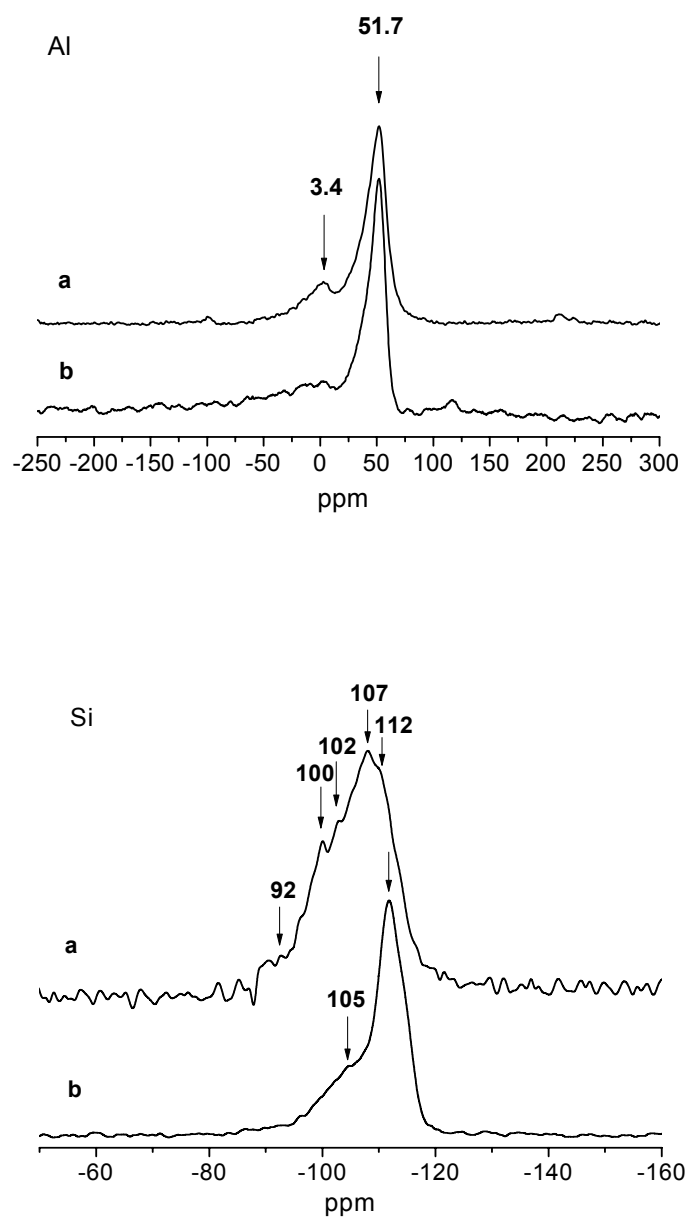


Figure S3. ^{27}Al and ^{29}Si MAS NMR spectra of (a) AAS and (b) MZ-HCS

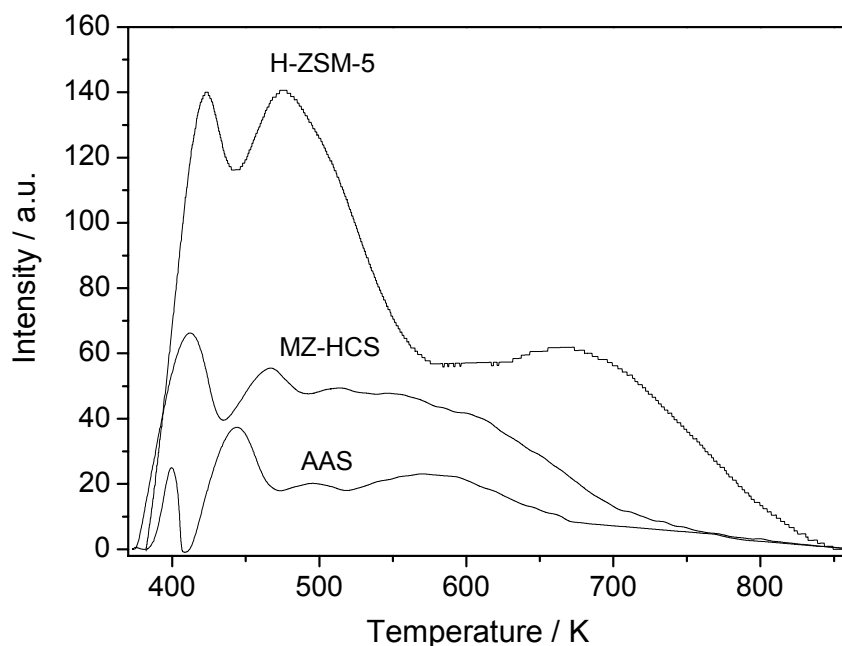


Figure S4 The amount of desorbed NH_3 from MZ-HCS, H-ZSM-5, and Meso-AAS as a function of temperature.

Table S2. Conversions (%) of benzaldehyde in aldol condensations with glycol or n-butyl alcohol on ZSM-5 (H-ZSM-5), amorphous AS and MZ-HCS as catalysts.

Reactions	ZSM-5(H-ZSM)	amorphous AS	MZ-HCS
Benzaldehyde + glycol	58.4	52	76.6
Benzaldehyde + n-butyl alcohol	37.2	31.3	90

(1). D. T. On, and S. Kaliaguine, *Angew. Chem.-Int. Edit.* 2002, 41, 1036.

(2). S. Lee, C. S. Carr, and D. F. Shantz, *Langmuir* 2005, 21, 12031.