

Supporting information

Fabrication of mesoporous zeolite microspheres by an one-pot dual-functional templating approach

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Experimental Section

I. Chemicals

Tetrapropylammonium hydroxide (TPAOH, 25% in water), tetraethyl orthosilicate (TEOS), aluminium isopropoxide [Al(^tPro)₃], methyl methacrylate (MMA, 99%), potassium peroxydisulfate (KPS, +99%), sodium dodecyl sulfate (SDS, 98.5%), NaOH, and ethanol (99.9%) were purchased from Aldrich.

II. Direct synthesis of the mesoporous zeolite microspheres

(1) A homogeneously mixed solution was first prepared from tetrapropylammonium hydroxide (TPAOH), tetraethyl orthosilicate (TEOS), aluminium isopropoxide [Al(^tPro)₃], NaOH, ethanol and H₂O with a molar ratio of 3Na₂O/ 600SiO₂/10Al₂O₃/130TPAOH/3EtOH/8100H₂O; (2) The above precursor was introduced into the PMMA suspension under stirring¹, and the self-assembly between aluminosilicate sources, TPAOH and PMMA took place, leading to white precipitates, then the mixture was stirred at room temperature for 6 h. (3) The mixture was transferred into an autoclave and then hydrothermally treated at 180 °C for 2 days for crystallization. The product was collected by filtration, dried in air, and calcined at 550 °C for 10 h to remove the template. Finally, the obtained sample was converted

into the H-form by ion exchanges with 1 M NH_4NO_3 solution at 90 °C for three times and subsequent calcination in air at 550 °C for 5h. The resulting sample was zeolite microspheres (MZMs) with hierarchical mesoporous channels. For comparison, conventional ZSM-5 and mesoporous amorphous aluminosilicate (AAS) phase were prepared in this study following the literature reports.^{2,3}

III. Characterization

Powder XRD patterns were recorded on a Rigaku D/Max 2200PC diffractometer using Cu $K\alpha$ radiation (40 kV and 40 mA) with the scanning rate of $0.4^\circ \text{ min}^{-1}$ for small angle tests and 4° min^{-1} for wide angle tests, respectively. The N_2 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. ^{27}Al and ^{29}Si 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 N_2 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).

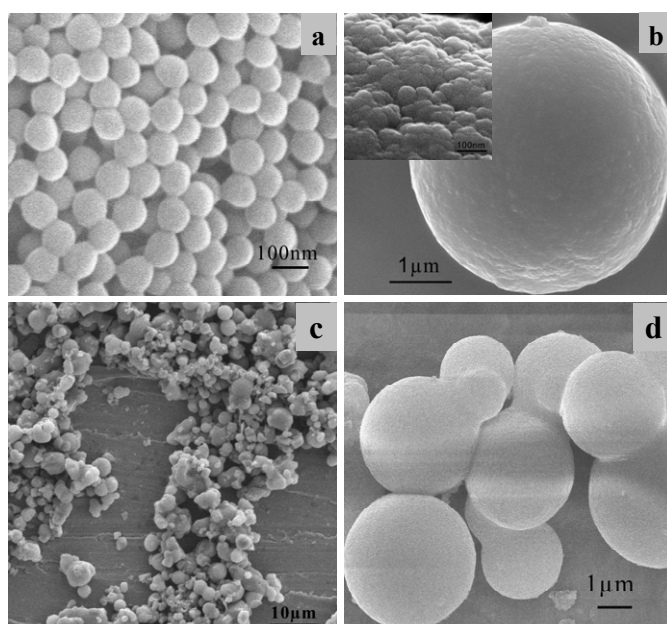


Figure S1. SEM images of (a) PMMA nanospheres, (b) self-assembled aggregate spheres containing aluminosilicate sources, PMMA nanoparticles and TPAOH molecules, (c, d) mesoporous ZSM-5 microspheres after crystallization and removal of PMMA templates.

Table S1. Conversions (%) of benzaldehyde in aldol condensations with glycol or n-butyl alcohol in 8 h on conventional ZSM-5, amorphous aluminosilicate (AAS) and mesoporous ZSM-5 microspheres (MZMs) as catalysts.

	H-ZSM-5	AAS	MZMs
Benzaldehyde + glycol	58.4	52	74.6
Benzaldehyde + n-butyl alcohol	34.5	31.3	79.2

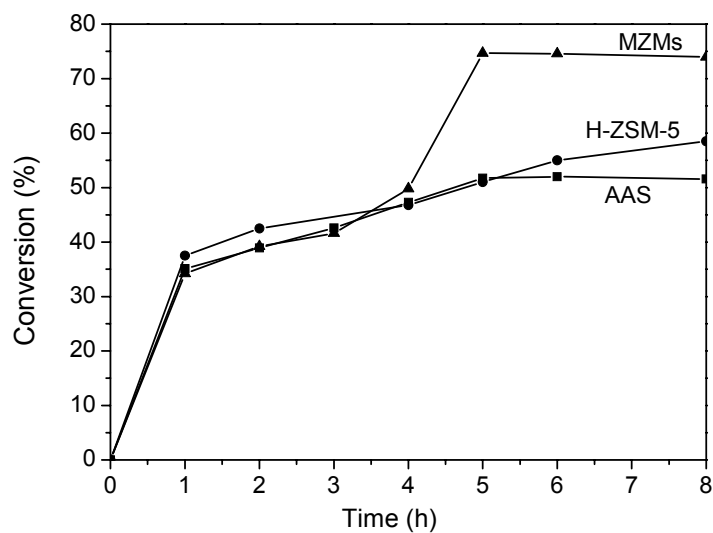


Figure S2 Conversions (%) of benzaldehyde in aldol condensations with glycol on Conventional ZSM-5, amorphous aluminosilicate (AAS) and mesoporous ZSM-5 microspheres (MZMs) as catalysts.

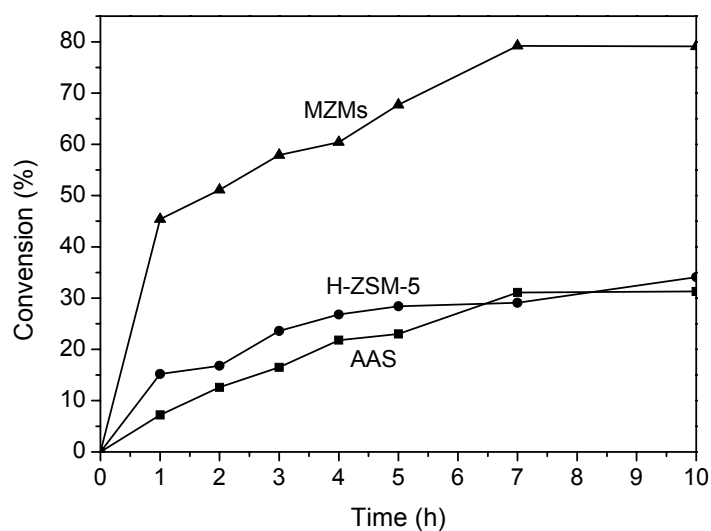


Figure S3 Conversions (%) of benzaldehyde in aldol condensations with n-butyl alcohol glycol on Conventional ZSM-5, amorphous aluminosilicate (AAS) and mesoporous ZSM-5 microspheres (MZMs) as catalysts.

- (1). T. W. Wang, O. Sel, I. Djerdj and B. Smarsly, *Colloid Polym. Sci.*, 2006, **285**, 1-9
- (2). S. Lee, C. S. Carr, and D. F. Shantz, *Langmuir* 2005, **21**, 12031.
- (3) D. T. On, and S. Kaliaguine, *Angew. Chem.-Int. Edit.* 2002, **41**, 1036.