Supporting Information

Starch Coated Silica Nanospheres Parenting the Growth of Trimodal Porous Zeolites for Catalysis Involving Large Molecules

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Material Characterization

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–50° with a scan speed of 2°/min on a PANalytical X’Pert PRO diffractometer, using Cu Kα radiation (λ=0.1542 nm, 40 kV, 40 mA). Nitrogen adsorption measurements were performed at 77 K by Quantachrome Instruments, Autosorb-IQ volumetric adsorption analyzer. Sample was outgassed at 523 K for 3 h in the degas port of the adsorption apparatus. The specific surface area was calculated from the adsorption branch using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using non-local density functional theory (NLDFT) and Barret–Joyner–Halenda (BJH) method. Scanning electron microscopy measurements (SEM) were carried out on a JEOL JSM-6610LV to investigate the morphology and chemical composition of the MOF. The surface morphology was recorded by a field emission scanning electron microscope (FESEM, Quanta 200, Zeiss). Structural analysis of the as prepared samples were carried out by TEM using FEI, Tecnai G² F30 microscope operating at 300 kV at IIT Bombay. The sample was dispersed in hexane using ultrasonic bath, drop costed on a carbon coated Cu grid, dried, and then used for TEM measurements. Fourier transform infrared (FTIR) spectra were recorded on a Bruker spectrophotometer in the region 400–4000 cm⁻¹ (spectral resolution = 4 cm⁻¹; number of scans = 100). Thermo gravimetric analysis (TGA) was performed in the range of 298-873 K on a TGA/DSC 1 STAR² SYSTEM from Mettler Toledo, Switzerland, with temperature increments of 10 K /min in air atmosphere. NH₃-TPD was performed using CHEMBET™ TPR/TPD, Quntachrome, USA. In a typical TPD experiments, 100 mg of sample was placed in a U-shaped, flow through, quartz sample tube. The catalyst was pretreated in He (30 mL/min) at required temperature for 1 h. After cooling down to desired temp, ammonia (partial pressure 100 Torr) was adsorbed on the samples for 1 h. The sample was subsequently flushed by He stream (30 mL/min) at desired temperature for 1 h to remove physisorbed ammonia. The TPD experiments were carried out in the different range at a heating rate of 10 K/min. The ammonia concentration in the effluent was monitored by using a gold-plated, filament thermal conductivity detector. Solid-state NMR was carried using a 2.5 mm HXMAS rotor using 400 MHz JNM-ECX JEOL NMR spectrometer.
Details of Catalytic Investigation

**Ion-exchange of zeolite catalyst**

For catalytic applications, ion-exchange of zeolite material was carried out with NH$_4$NO$_3$. Calcined Na-form of material (2 g) was ion-exchanged (thrice) into the NH$_4$-form by using 1 M aqueous NH$_4$NO$_3$ solution (100 mL) at 353 K for 4 h then calcined at 823 K to obtain the H$^+$ form of the zeolites.

**Esterification of Benzyl Alcohol with Hexanoic Acid**

Carboxylic acid (5 mmol), benzyl alcohol (5 mmol), 2 mL of toluene and 50 mg of catalyst were added to Teflon-lined steel autoclave and the reaction was conducted at 403 K for 4 h. After the reaction, autoclave was cooled to ambient temperature and the catalyst was separated by centrifugation and the final products were analyzed by Gas-chromatograph (GC, Younglin YL6100) and products were identified by GC-MS (Shimadzu GCMS-QP 2010 Ultra; Rxi-5Sil MS; 30m × 0.25mm × 0.25μm). Recovered catalyst was washed with ethyl acetate, centrifuged and dried at 423 K for 2 h and then recycled.

**Synthesis of Vitamin E**

Trimethylhydroquinone (2.8 mmol), isophytol (2 mmol), 12 mL of hexane, and 100 mg catalyst were placed into the 50 mL round bottom flask equipped with refluxed condenser and the reaction was conducted at 343K for 10 h. After the reaction, the solid catalyst was filtered and the reaction mixture was analyzed by GC and products were identified by GC-MS.

**Condensation of 2-Hydroxyacetophenone with Benzaldehyde**

In a typical condensation reaction, benzaldehyde (7 mmol), 2-hydroxyacetophenone (3.5 mmol), and 50 mg of catalyst were placed into the 10 mL round bottom flask equipped with refluxed condenser and the reaction was conducted at 423 K for 8 h. After the reaction, the solid catalyst was centrifuged and the final products were analyzed by GC and products were identified by GC-MS.
Figure S1. TGA profiles of different silica sources prepared in this study. Where SS is silica nanosphere, SSS was obtained by the reaction of 5 g of Cl-functionalized SS and 2 g of starch. 2SSS was obtained by the reaction of 5 g of Cl-functionalized SS and 4 g of starch. 0.5SSS was obtained by the reaction of 5 g of Cl-functionalized SS and 1 g of starch. CSS was obtained by the reaction of 5 g of Cl-functionalized SS and 2 g of cellulose.
Figure S2. FT-IR spectra of starch, SS and SSS prepared in this study.
**Figure S3.** XRD patterns of SS and SS-ZSM-5 materials obtained at different crystallization time.
Figure S4. TEM micrographs of SSS-ZSM-5 and Nano-SSS-ZSM-5 prepared in this study.
Figure S5. SEM images of different ZSM-5 materials prepared by using SS and SSS.
**Figure S6.** FE-SEM images of different ZSM-5 materials prepared in this study by using SS and SSS.
Figure S7. SEM images of Nano-SSS-ZSM-5 recorded for the samples withdrawn at different crystallization time.
Figure S8. XRD patterns of nanocrystalline ZSM-5 materials prepared by using CSS, 2SSS and 0.5SSS prepared in this study.
Figure S9. N$_2$-adsorption isotherms of nanocrystalline ZSM-5 samples prepared by using 2SSS and 0.5SSS. Inset shows the pore size distribution determined from Barret–Joyner–Halenda (BJH).
Figure S10. SEM images of nanocrystalline ZSM-5 materials prepared using 2SSS and 0.5SSS prepared in this study.
Figure S11. N$_2$-adsorption isotherms of nanocrystalline ZSM-5 samples prepared by using CSS and SS. Inset shows the Barret–Joyner–Halenda (BJH).
Figure S12. (a) SEM and, (b) FE-SEM images of Nano-CSS-ZSM-5.
Figure S13. Reusability of ZSM-5 (Comm.) and Nano-SSS-ZSM-5 in the condensation of (a) hexanoic acid, and (b) oleic acid, respectively.