Supporting Information for

Hierarchically porous Sn-β zeolites via an OSDA-free synthesis

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Detailed experimental procedures

OSDA-free synthesis of Sn-β

First, an aqueous mixture with the following chemical composition and molar ratio was prepared: Na_2O /SiO_2 /TiO_2 /Al_2O_3 /H_2O = 30:100:0.5:4:25. Then, 10 wt% β seeds (SiO_2/Al_2O_3=25) relative to the silica source in the above mixture were added. The final mixture was transferred into a sealed autoclave and treated at 120-140 °C under static conditions for 4–7 days to form crystals. The solid product was separated and dried to obtain Al-containing β(OSF). As-synthesized β(OSF) was then treated with aqueous NH_4NO_3 (2.0 mol/L) at 80 °C for 24 h, and the solid product was separated by filtration to obtain ion-exchanged β(OSF). Ion-exchanged β(OSF) was further treated with water steam in N_2 flow (50 kPa) at 400–600 °C for 90 min to afford steam-treated β(OSF). Subsequently, steam-treated β(OSF) was washed with HNO_3 solution (6.0 mol/L) at 80 °C for 2 h to obtain dealuminated sample of β(OSF)-DeAl. Dried β(OSF)-DeAl sample further mixed with certain amounts of tin(II) acetate solid in a mortar, and ground this solid mixture for 10-30 min. Then, the mixture was transferred into a crucible and calcined at 550 °C for 6 hours to obtain final product of Sn-β(OSF).

Synthesis of Sn-β(Nano)

The synthesis was mainly according to the method of reference (C. Hammond et al., Angew. Chem. Int. Ed., 2012, 51, 11736). Firstly, nano-sized β zeolites (Si/Al=13) were refluxed in 69% HNO3 solution at 110 °C for 24 h to remove the aluminum in the sample. Solid was separated, washed with distilled water and dried. Then the dried solid further mixed with certain amounts of $Sn(Ac)_2$ solid in a mortar, and ground this solid mixture for 15 min. Then, the mixture was transferred into a crucible and calcined at 550 °C for 6 hours to

obtain Sn-β(Nano), which was used as control sample.

Zeolite characterization

Powder X-ray diffraction (PXRD) measurements were performed on a Bruker Powder D8 Advance diffractometer at 40 kV and 40 mA using CuKα radiation (λ=1.5418 Angstrom). Diffuse reflectance UV/Vis (DRUV/Vis) spectra were recorded on a SHIMADZU UV-2450 spectrophotometer at 298 K using BaSO4 as a reference. Raman spectra were obtained using a Thermo SCIENTIFIC DXR Raman microscope with an excitation wavelength at 532 nm. Nitrogen adsorption-desorption isotherms were measured on Quantachrome Instruments Autosorb iQ2. Elemental analyses (Si, Sn and Al) were performed on an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer ICP Optima 2000DV). Field-emission SEM images were obtained on a JEOL JSM-7600F microscope operated at 5 kV. TEM observations were performed on a JEOL JEM-1400 TEM microscope, working at 100 kV.

Catalytic reactions

Oxidation reactions were performed in a 20 mL glass reactor immersed in a 90 ^{o}C oil bath in the presence of H_2O_2 (30 wt.% in water). In a typical run, the reactions were carried out with catalyst (Sn content = 0.8 mol %), cyclohexanone (2 mmol), H_2O_2 (3 mmol) in 1,4-dioxane (6 mL) with vigorous stirring for different times. After the reaction, the mixture was analyzed by gas chromatography. The amount of unconverted H_2O_2 was determined by titrating with $Ce(SO_4)_2$ aqueous solution (0.1 M). The conversion of dihydroxyacetone (DHA) into ethyl lactate was performed in in a 20 mL glass reactor immersed in a 60 ^{o}C oil bath. In a typical run, the reactions were carried out with catalyst (Sn content = 0.8 mol %) and 0.25 M DHA in methanol solution (5 mL) with vigorous stirring for different times. After the reaction, the mixture was analyzed by gas chromatography. The products were verified using authentic chemicals commercially available or determined by mass spectrometer.

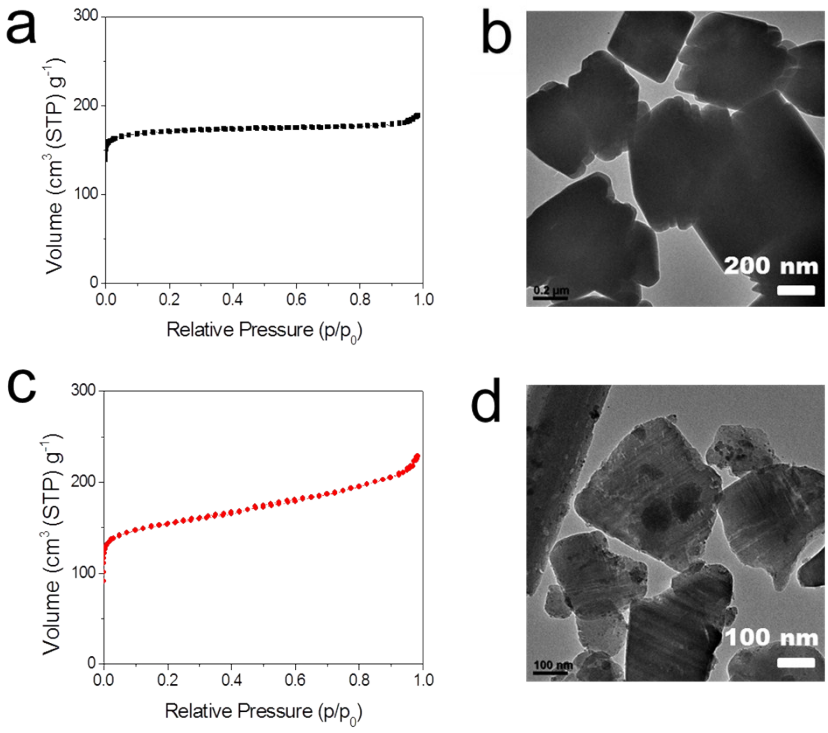

Fig. S1 Nitrogen adsorption-desorption isotherms and TEM images of (a, b) β(OSF) sample and (c, d) Sn-β(OSF) zeolite.

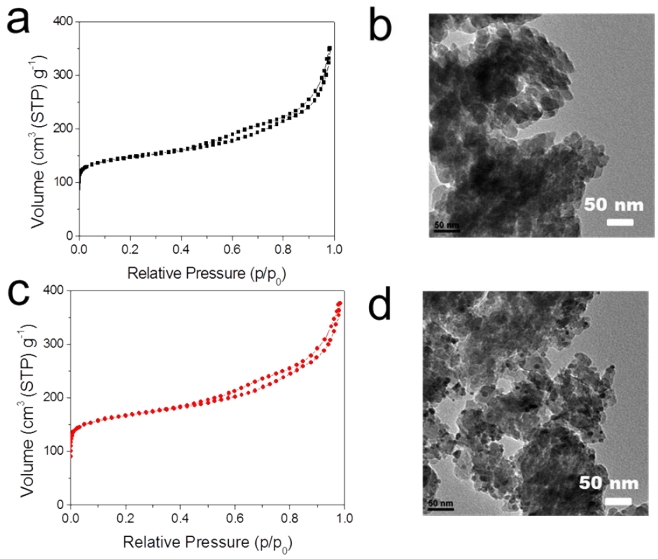

Fig. S2 Nitrogen adsorption-desorption isotherms and TEM images of control samples (a, b) β(Nano) and (c, d) Sn-β(Nano) zeolite.

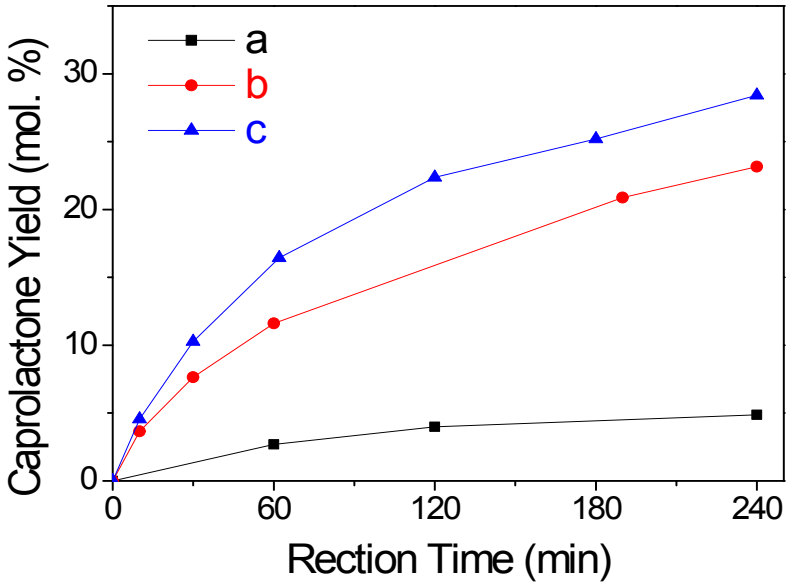

Fig. S3 Yield of caprolactone with the reaction time for the Baeyer–Villiger oxidation of cyclohexanone catalyzed by various catalysts of (a) Al-containing β(Nano), (b) Sn-containing Sn-β(Nano) and (c) Sn-containing Sn-β(OSF). Reaction conditions: catalyst (Sn content = 0.8 mol%,), 1,4-dioxane (6 mL), cyclohexanone (2 mmol), H_2O_2 (3 mmol), temperature 90 °C.

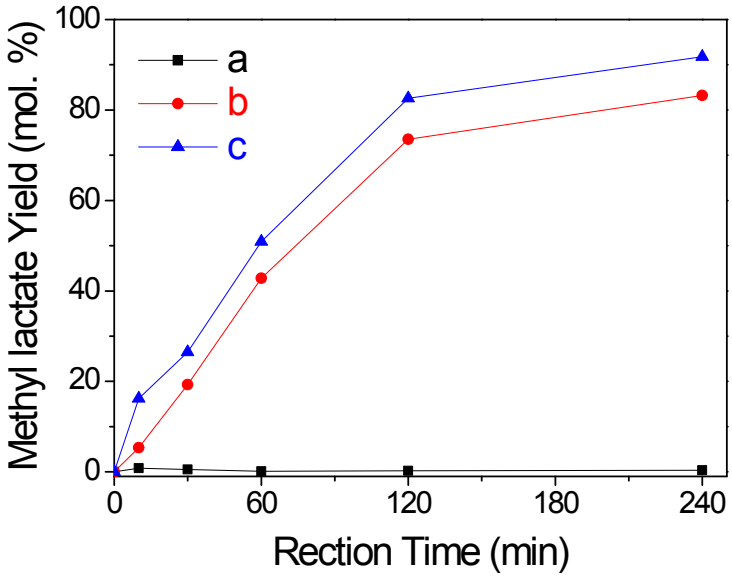

Fig. S4 Yield of methyl lactate with the reaction time for the oxidation of DHA catalyzed by various catalysts of (a) Al-containing β(Nano), (b) Sn-β(Nano) and (c) Sn-β(OSF). Reaction conditions: catalyst (Sn content = 0.8 mol. %), 0.25M DHA in MeOH (5 mL), temperature 60 °C.