Supporting Information

Hybrid porous Tin(IV) Phosphonate: an efficient catalyst for adipic acid synthesis and a very good adsorbent for CO₂ uptake

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Section S1: Experimental section

Material Synthesis: Commercially available tin(IV) chloride pentahydrate (SnCl₄·5H₂O; M_r =350.58) and N-cetyl-N,N,N-trimethylammonium bromide (CTAB; M_r =364.45) were purchased from Loba Chemie and pentaethylenehexamine-octakis-(methylphosphonic acid) hexadecasodium salt solution (PEHMP, 40% in water; M_r =1336.13) was obtained from Fluka. For catalytic study, cyclohexanone was purchased from Merck. All the reagents were used without further purification.

1.8 g CTAB (5.0 mmol) was dissolved in 15 g H₂O and stirred for 2 h. Then 1.67 g PEHMP (0.5 mmol) in 5 g H₂O was added to the CTAB solution and stirred for 12 hours. To this solution was added 1.75 g of SnCl₄·5H₂O (5.0 mmol) dissolved in 5 g H₂O. Soon after the addition of tin(IV) chloride a cream colored precipitate was observed. The whole mixture was stirred for another 4 h and finally transferred and sealed in a stainless steel autoclave for hydrothermal treatment at 393 K for 48 h. After the hydrothermal treatment the product was filtered and washed several times with distilled water. To remove the surfactant, 0.5 g of the as-synthesized material was extracted 3 times with 20 ml of acidified ethanol in each batch. Finally the extracted material was dried at room temperature.

Catalysis: In the typical catalytic procedure 0.5 g (0.0051mol) of cyclohexanone was suspended in 5 ml double distilled water and the whole solution was taken in a 10 ml two necked round bottom flask fitted with a water cooled condenser. The suspended solution was stirred vigorously. The flask was heated at 353 K and after preliminary heating of 15 min 0.025 g catalyst (HMSnP-1) was added to the solution and the heating was continued for 5 h. The flask was purged with a balloon filled with air in one neck and the temperature of the reaction vessel was maintained throughout 353 K. The mixture was filtered under hot condition to remove the catalyst (HMSnP-1) from the reaction mixture. The filtrate was concentrated in rotary evaporator and solid adipic acid was collected after washing with solvent and it gave 74% yield with respect to cyclohexanone. The product was characterized by (¹H and ¹³C) NMR (Figure S13 and S14) (chemical shifts are given below) and FT-IR spectroscopy (Figure S15). The separated catalyst was washed with water and dried at room temperature under high vacuum before conducting the recycling experiments.

¹H NMR (300MHz, DMSO-d₆): δ =1.50 (m, 4H), 2.18(m, 4H), 11.97(b, 2H)

¹³C NMR (300MHz, DMSO-d₆): δ =174.34, 33.39, 24.04



Scheme S1. Hexadecasodium pentaethylenehexamine-octakis-(methylphosphonate) (PEHMP) ligand used in the synthesis of HMSnP-1

Section S2: Characterization techniques

JEOL JEM 6700F field emission scanning electron microscope (SEM) was used for the determination of morphology of powder samples. The pore structure was explained by a JEOL JEM 2010 transmission electron microscope (TEM) operated at an accelerating voltage of 200 kV. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D-8 Advance diffractometer operated at 40 kV and 40 mA and calibrated with a standard silicon sample, using Ni-filtered Cu Ka (λ =0.15406 nm) radiation. Elemental analyses were carried out by using a Shimadzu AA-6300 atomic absorption spectrophotometer (AAS) fitted with a double beam monochromator and Perkin-Elmer 2400 Series-II CHN analyzer. Thermogravimetry (TG) and differential thermal analyses (DTA) of the samples were carried out between the temperature ranges 298 K to 1073 K in a TA Instruments thermal analyzer TA-SDT Q-600. Fourier transform infrared (FT IR) spectra of these materials were recorded using a Nicolet MAGNA-FT IR 750 Spectrometer Series II. Solid state MAS NMR studies have been performed by using Chemagnetics 300 MHz CMX 300 spectrometer. Nitrogen adsorption/desorption isotherms were obtained by using a Beckman Coulter SA 3100 Surface Area Analyzer at 77 K. CO₂ adsorption studies were carried out on a Bel Japan Inc. Belsorp-HP at 273 K. ¹H and ¹³C NMR experiments were carried out on Bruker DPX-300/500 NMR Spectrometer.



Section S3: Electron microscopic images

Figure S1. Scanning electron microscopic (SEM) image (a), transmission electron microscopic (TEM) (b) and scanning transmission electron microscopic (STEM) images (c, d) of HMSnP-1 material.

Scanning electron microscopic (SEM) image in (a) shows almost uniform spherical morphology of the HMSnP-1 material. Transmission electron microscopic (TEM) image (b) and scanning transmission electron microscopic (STEM) images (c, d) clearly show the presence of randomly distributed mesopores in the material.

Section S4: Powder XRD



Figure S2. Small angle powder XRD pattern of HMSnP-1 material.



Figure S3. Wide angle powder X-ray diffraction pattern of HMSnP-1.

Section S5: Thermogravimetric analysis



Figure S4. TGA (a) and DTA (b) plots for HMSnP-1 material.

Section S6: Infrared scpectroscopy



Figure S5. FT IR spectra of HMSnP-1 before and after catalysis.

FT-IR spectrum of HMSnP-1 shows a strong band centered around 1050 cm⁻¹ and this can be assigned due to the formation of R-P-O-Sn framework bonding.¹ Two shoulder peaks around 1325 cm⁻¹ and 1425 cm⁻¹ can be attributed to C-N and P-C stretching vibrations and bending vibration for $-CH_2$ - groups appears at 1460 cm⁻¹.² The broad band centered at 3420 cm⁻¹ and the sharp band at 1634 cm⁻¹ correspond to the adsorbed water molecules at the surface of the material. The FTIR spectrum of HMSnP-1 after three repeated cycles of catalysis shows that there is no change in the framework bonding.



Section S7: Solid state MAS NMR spectroscopy

Figure S6. ³¹P solid state MAS NMR spectrum of HMSnP-1. Spinning side bands are marked



Figure S7. ¹³C solid state MAS NMR spectrum of HMSnP-1.

³¹P MAS-NMR spectrum of HMSnP-1 shows two resonances at 13.0 and -4.5 ppm. The resonance at 13.0 ppm could be attributed to phosphonate group having 001 type of connectivity (-CPO₃H-) where, only one oxygen atom is bonded to tin with some weak SnOP bonding. On the other hand the signal at -4.5 ppm could originate due to 111 connectivity, where all the three oxygen atoms are connected to metal.³ Both FT-IR and ³¹P MAS-NMR spectra indicate absence of free $-PO_3H_2$ group in the material. It may be due to high tin salt to ligand mole ratio (10:1) used during synthesis of the material. ¹³C MAS-NMR signal around 53.0 ppm corresponds to the carbon atoms of nitrilomethylene and ethylene diamine² indicating the incorporation of the organophosphorus ligand moiety PEHMP in the hybrid material HMSnP-1.



Figure S8. N₂ adsorption/desorption isotherm of HMSnP-1 at 77 K. Adsorption points are marked by filled symbols and desorption points by empty symbols.



Figure S9. Pore size distribution of HMSnP-1 employing NLDFT method.



Figure S10. N₂ adsorption/desorption isotherm of HMSnP-1 after three catalysis cycles. Adsorption points are marked by filled symbols and desorption points by empty symbols.



Figure S11. Pore size distribution (NLDFT) of HMSnP-1 after three catalysis cycles.

 N_2 sorption analysis of HMSnP-1 material after three catalysis cycles shows surface area of 709 m^2g^{-1} and pore structure of this material is also unchanged. From these results it can be concluded that the catalyst can be reused for repeated cycles maintaining its catalytic efficiency without any significant change in the framework.



Section S9: Scheme for templating and crosslinking mechanism

Figure S12. Interaction of CTAB micelles with the material (a) and cross linked connectivity of the ligand with tin centers (b).



Section S10: Recyclability test of CO₂ adsorption

Figure S13. CO₂ adsorption recycling efficiency of HMSnP-1.



Section S11: Catalytic recyclability test

Figure S14. Catalytic recycling efficiency of HMSnP-1 for the synthesis of adipic acid from cyclohexanone.



Section S12: ¹H and ¹³C NMR spectra of adipic acid

Figure S15. ¹H NMR spectrum of adipic acid.



Figure S16. ¹³C NMR spectrum of adipic acid.





Figure S17. FT IR spectrum of adipic acid.

References

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