Electronic Supplementary Data

Solvent-free facile synthesis of di-octyl phthalate over heterogeneous sulfated zirconia acid catalyst

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Catalyst characterization

Structural properties

The prepared SZr catalyst was characterized by powder X-ray diffractometer (Philips X'pert, The Netherlands) using CuKα radiation (λ = 1.5406 Å) by scanning the sample in 2θ range of 10–80°. The crystallite size was determined from the characteristic peak of tetragonal phase of zirconia [°2θ = 30.37 for (111) reflection] using Scherrer formula as below: Crystallite size = Kλ/ W cosθ, where K is the Scherrer constant (0.9), λ = 1.5406 Å, W = Wb −Ws; Wb is the broadened profile width of experimental sample and Ws is the standard profile width of reference silicon sample and θ is the angle of diffraction. The FT-IR spectrum was recorded on a spectrophotometer (Perkin Elmer GX, USA) in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} as KBr pellets. The bulk sulfur (wt%) in the catalyst after sulfation and retained after calcination at 600°C was analyzed by elemental analyzer (Perkin Elmer 2400, USA). Thermogravimetric analysis (TGA) was performed using a thermal gravimetric analyser (NETZSCH STA 449 F1 Jupiter®, USA) coupled with mass spectrometer (NETZSCH QMS 403 Aeolos®) by heating the sample in the temperature range of 30-900°C with a heating rate of 10°C min^{-1} under N_2 flow. The data analysis was carried out with the NETZSCH Proteus® software.

Textural properties

BET specific surface area, pore volume and pore diameter were calculated from N_2 sorption isotherms at −196°C by surface area and porosity analyzer (ASAP 2010, Micromeritics, USA) after pre-activation of the sample under vacuum (1×10^{-3} mmHg) at 120°C for 4 h. Surface area and pore size distribution were determined by BET (Brunauer-Emmett-Teller) equation and BJH (Barrett-Joyner-Halenda) methods, respectively.

Acidic properties

The total surface acidity, i.e., strength and number of acid sites present in the catalyst was measured by NH_3-TPD (Micromeritics AutoChem II, USA). In a typical procedure, a mixture of 10% NH_3 and He gas was passed for 30 min at 40°C over the sample (in-situ activated at 120°C for 2 h). The excess physisorbed NH_3 was flushed out for 10 min with pure He gas flow. The sample was then heated at a rate of 10°C min^{-1}, up to 900°C and volume of desorbed NH_3 was measured.

Diffuse reflectance FT-IR spectroscopy (DRIFT) measurements, a technique used to differentiate between Brönsted (B) and Lewis (L) acid sites of pyridine adsorbed SZr sample, were recorded on a FT-IR spectrophotometer (Perkin Elmer, GX, USA) equipped with Diffuse Reflectance FT-IR (DRIFT) accessory (Graseby Specac, P/N 19900) and an automatic temperature controller (Graseby Specac, P/N 20130).[22]The sample was exposed to pyridine vapor under vacuum for 1 h followed by evacuation of excess physisorbed pyridine for 10 min.The spectra were recorded at room temperature (~27 °C) to 450 °C after holding at each temperature for 10 min, thus allowing sufficient time for pyridine desorption. The quantification of B and L acid sites concentration and B/L ratio were calculated using molar extinction coefficient method (using ε_B=1.67 cm/μmol and ε_L = 2.22 cm/μmol).[23]

Morphology

The microscopic study was done byTEM micrographs that were obtained using a transmission electron microscope (Jeol JEM 2100, USA).The catalyst sample was dispersed in ethanol by sonication and deposited on a Cu grid coated with carbon film.

Table S1 – Structural, elemental, textural and acidic properties of SZr catalyst	
Crystallite size (nm)	11
Sulfur (wt%)	2.3
BET surface area (m^2/g)	99
Average pore volume (cm^3/g)	0.12
BJH desorption pore diameter (Å)	37
Total acid sites(mmol/g)	1.19
Bronsted acid sites (mmol/g)	0.056 (150°C)
Lewis acid sites (mmol/g)	0.04 (150°C)
B/L ratio	1.4 (150°C)
	1.7 (250°C)
	2.0 (350°C)
	2.0 (450°C)

Table S2 – Strength and amount of acid sites of fresh and used (after five cycles) SZr catalyst

Fresh SZr		Re-used SZr	
Temp. (^oC)	Quantity (mmol/g)	Temp. (^oC)	Quantity (mmol/g)
110	0.720	88	0.66
404	0.013	598	0.13
579	0.462	799*	0.51*
834*	0.59*		
Total	1.19	Total	0.79

* Not included in calculating surface acidity (as explained in main text)

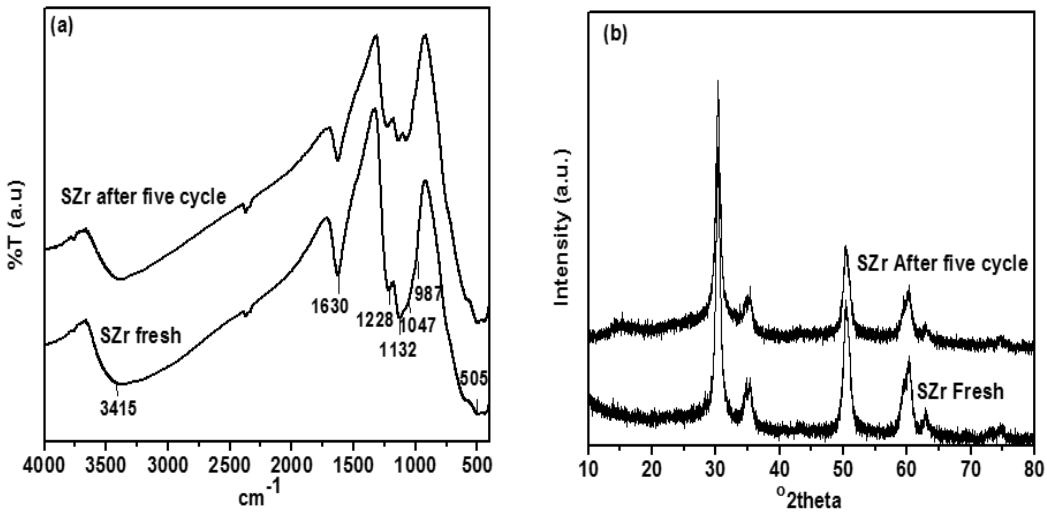

Fig.S1 – (a) FT-IR spectra and (b) PXRD patterns of fresh and used (after five cycles) SZr catalyst.

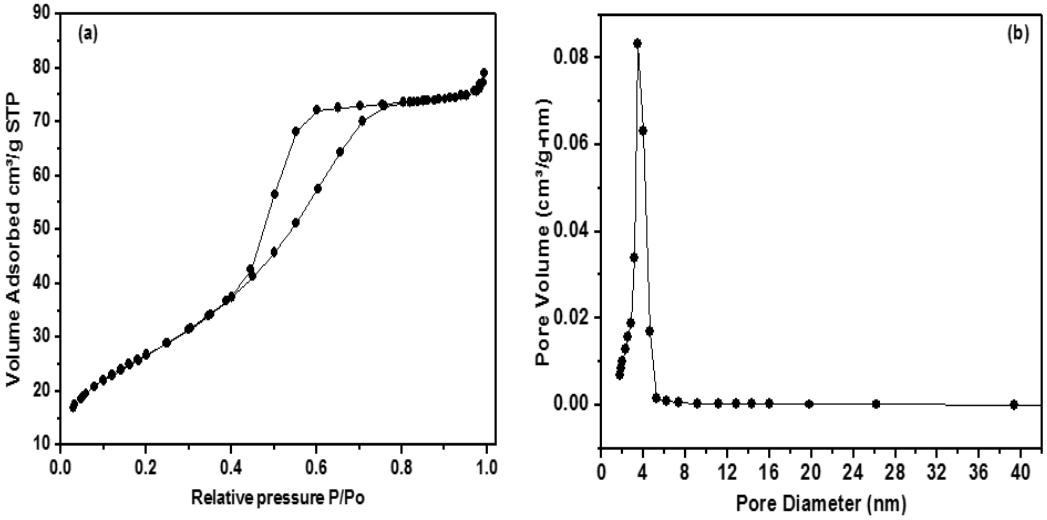

Fig. S2 – (a) N_2-sorption isotherm and (b) pore size distribution of SZr catalyst.

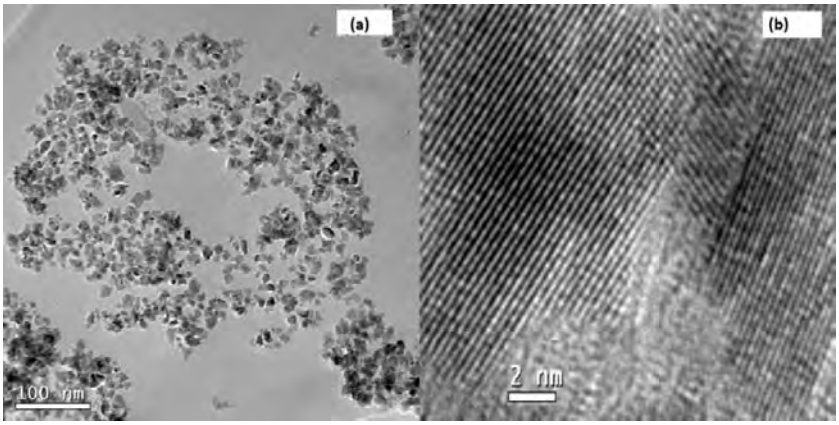

Fig. S3 – (a) TEM and (b) HR-TEM images of SZr catalyst.

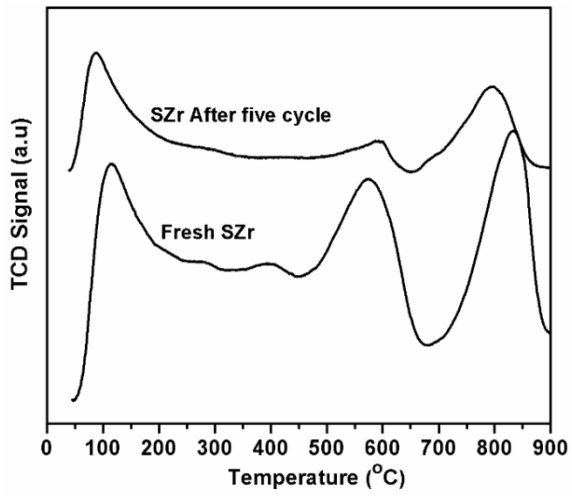

Fig. S4 – NH_3 TPD profile of fresh and used (after five cycles) SZr catalyst.

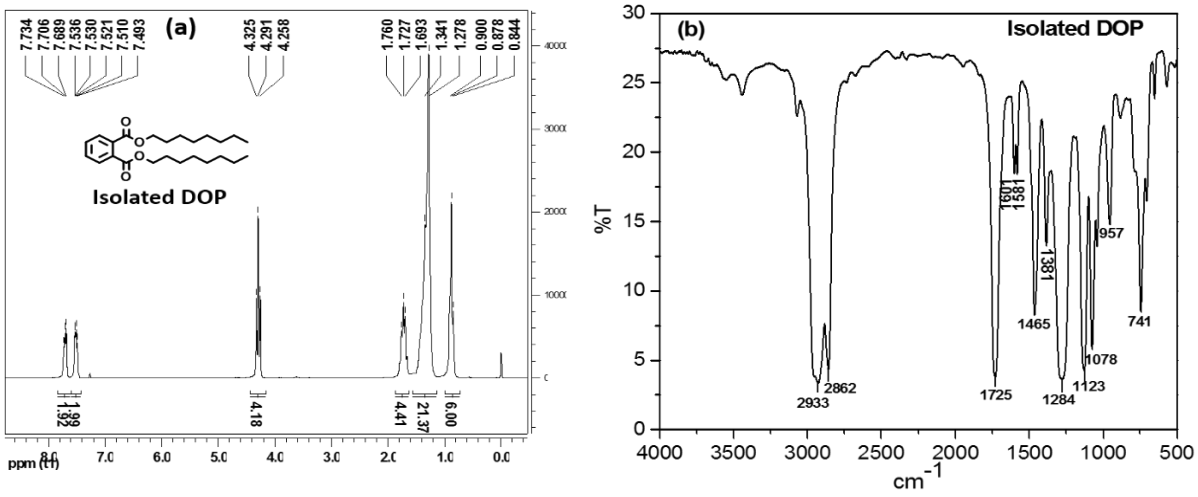

Fig. S5 – (a) ^{1}HNMR and (b) FT-IR spectrum of isolated pure DOP.