Electronic supplementary information

Break-through mesopore creation in BEA and its enhanced catalytic performance in solvent-free liquid phase *tert*-butylation of phenol

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1. Experimental details

1.1. Catalyst preparation

In a typical method, the mesoporous BEA zeolite material is obtained by sequential alkali and ammonium treatments, where 100 ml of 0.5 M NaOH solution was added to 5.0g BEA zeolite powder (SAR 25) placed in a round bottom flask and the resultant mixture is allowed to reflux at 100^0C for 2h under atmospheric pressure and vigorously stirred condition. At the end of the treatment, the zeolite suspension was cooled down in an ice-water bath followed by its slow filtration. The solid collected in the funnel was thoroughly washed with distilled water until the pH of filtrate is neutral. The wet cake obtained after filtration was allowed to dry at room temperature followed by heating at 100ºC for 6h. The dry powder (4.8g) obtained was used for treatment with ammonium nitrate (without any high temperature calcinations), where the powder is refluxed with 100 ml solution of 1M ammonium nitrate at 100^0C for 4h, followed by repeated steps of cooling, filtration and drying. Finally the sample was calcined in static air flow at 500^0C for 4h and the resultant sample was denoted as DSB.

1.2. Catalyst characterization

The Scanning Electron Microscope (SEM) images were recorded for obtaining particle morphology on Quanta 200f instrument, Netherland. Transmission Electron Microscopy (TEM) images were recorded on Tecnai-12 model, FEI, Netherland. X-ray powder diffraction (XRD) patterns were measured on D8 advance, Bruker, Germany equipped with rotating anode and CuKα radiations. The measurements were conducted in continuous θ/2θ scan refraction mode. The anode was operated at 30 KV and 15 mA the 2θ angles were measured 5^0–60^0 at the rate of 2^0/min. Low angle XRD patterns also measured at low angle ($2\text{-}5^0\theta$). The Fourier transform infrared spectroscopy (FTIR) spectra of the zeolite samples were recorded on Thermonicolate 8700 instrument, Thermo scientific Corporation, USA. The BET surface area, pore size and pore volume measurements of all the zeolite based catalysts were carried out using a standard adsorption equipment (ASAP 2010, Micromeritics Instruments Inc., Norcross, GA, USA) using N_2 gas (99.995% pure). For measuring above characteristics, 0.2g of the sample is taken in a specially designed sample tube and degassed at 573 K under vacuum of 1.3 $\times10^{-6}$ bar for 4h A frit is attached to the mouth of the sample tube, so that when the sample tube is removed from the preparation mode, it does not allow the sample to expose in atmosphere. The sample is cooled to room temperature under vacuum and the sample tube is removed from the preparation port and attached to the analysis port of the instrument. For all the samples, N_2 adsorption desorption isotherms were obtained at 77K and the temperature was maintained constant by using liquid nitrogen, whereas helium gas was used for measuring the dead space. The surface area, pore volume and pore size distribution were obtained by measuring the volume adsorbed at different P/P0 values and by applying different methods. Total pore volume was estimated by measuring the volume of gas adsorbed at P/P0 of 0.99 whereas, t-plot method was used to calculate the micro pore surface area (0-20 Å) using the Harkins–Jura equation. The total micro pore volume (0-20 Å) and the micro pore size distribution were obtained by applying the Horvath–Kawazoe method (H-K). The acidity of the catalyst was measured by temperature programmed desorption of NH_3 (NH_3-TPD) using a Micromeritics chemisorbs 2750 pulse chemisorbs 2750 pulse chemisorption system. 0.1 g sample was used for each TPD experiment. It was carried out after of the catalyst sample was dehydrated at 500^{0}C in helium gas (30 cm^3 min^{-1}) for 1 h. The temperature was decreased to 100^{0}C and NH_3 was adsorbed by exposing sample treated in this manner to a stream containing 10% NH_3 in helium for 1h at 100^{0}C. It was then flushed with helium for another 1h to remove physicosorbed NH_3. The desorption of NH_3 was carried out in helium gas flow (30 cm^3 min^{-1}) by increasing the temperature upto 950^{0}C at 10^{0}C min^{-1} heating rate, measuring NH_3 desorption using TCD detector.

1.3. Reaction studies

The alkylation of phenol with tert-butyl alcohol was carried out in a 25ml PARR reactor 4848 equipped with four bladed pitched turbine impeller. The temperature was maintained at ±1^{0}C of the desired value with the help of an in-built PID controller while the cold water was circulated through the coil. In a typical reaction; 0.5g of the catalyst, 3.8g of phenol (Merck India Limited) and 7.6g of tertiary butyl alcohol (Merck India Limited) was taken in autoclave and the reactor was heated @ 2^{0}C/min. The reaction temperature was maintained at 150^{0}C and reaction mixture stirred at 550 RPM for 7h under 2.0bar nitrogen gas pressure. At the end of the reaction, the mixture was cooled upto room temperature (25^{0}C). The reaction product and catalyst was separated by filtration and catalyst was washed with ethanol, dried at 120^{0}C and reused for four times. The reaction product was analyzed by using GC equipped with the DB-Wax column (30m x 0.53 mm x 1.0 μm) and FID detector. Since the concentration of tertiary butyl alcohol was taken in excess in the reaction mixture, conversion was calculated based on the phenol.

Supporting Tables

Table : S1 Performance comparison of the present catalyst with those reported for tertiary butylation of phenol

Catalyst	Phenol Conversion (wt%)	Product Yield (wt%)		
		4TBP	2,4 di TBP	Others
DSB (present study)	***90.2***	***36.1***	***48.7***	***5.4***
[1]Normal H –BEA	54.2	43.5	0.8	9.9
[2]Steamed HBEA	96.6	72.4	22.1	2.1
[3]Hierarchical ZSM-5	32.2	3.0	26.9	2.3
[4]Hierarchical ZSM-5	81.2	42.4	32.9	5.9
[5]Hierarchical ZSM-5	83.8	34.7	44.2	4.9
[6]Sulfonated carbon silica	50.0	15.0	9.0	26.0
[7]H-AlMCM-41	31.0	26.1	0.4	4.5
[8]FeAlMCM-41	70.1	52.7	9.9	7.5
[9]H-AlMCM-48	98.9	69.5	27.7	1.7
[10]MCM-22	94.0	63.0	28.8	2.2
[11]Fe-Montmorillonite	100.0	66.8	2.7	30.5
[12]Steamed HY	48.6	38.3	2.9	7.4
[13]Ionic Liquid	88.0	13.2	59.8	15.0
[14]Ionic Liquid	81.4	12.1	46.0	23.3

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Table : S2 Effect of TBA : Phenol molar ratio on product composition over DSB catalyst

TBA : Phenol (Molar ratio)	Conversion of Phenol (wt%)	Product Selectivity (%)			
		2TBP	4TBP	2,4 di TBP	2,4,6 tri TBP
1.25 : 1	83.3	3.4	76.6	17.9	2.1
2.5 : 1	90.2	2.6	40.0	54.0	3.4
5 : 1	77.0	7.8	63.5	27.3	1.4

Reaction Condition : Catalyst = 0.5g; T=150^{0}C; Reaction time = 7h; Pressure = 2bar (N_2);

Table : S3 Catalytic activity and product distribution with reaction cycles on DSB catalyst

Reusability (Cycle)	Reaction time (h)	Conversion of Phenol (wt%)	Product Selectivity (%)			
			2TBP	4TBP	2,4 di TBP	2,4,6 tri TBP
1	7	90.2	2.6	40.0	54.0	3.4
2	7	89.6	2.4	39.4	53.8	3.2
3	7	87.8	2.2	38.6	53.0	2.6
4	7	86.1	2.0	37.2	52.1	2.0

Reaction Condition : Catalyst = 0.5g; T=150^{0}C; Reaction time = 7h; Pressure = 2bar (N_2); TBA : Phenol = 2.5:1 (Molar ratio)

Supporting Figures

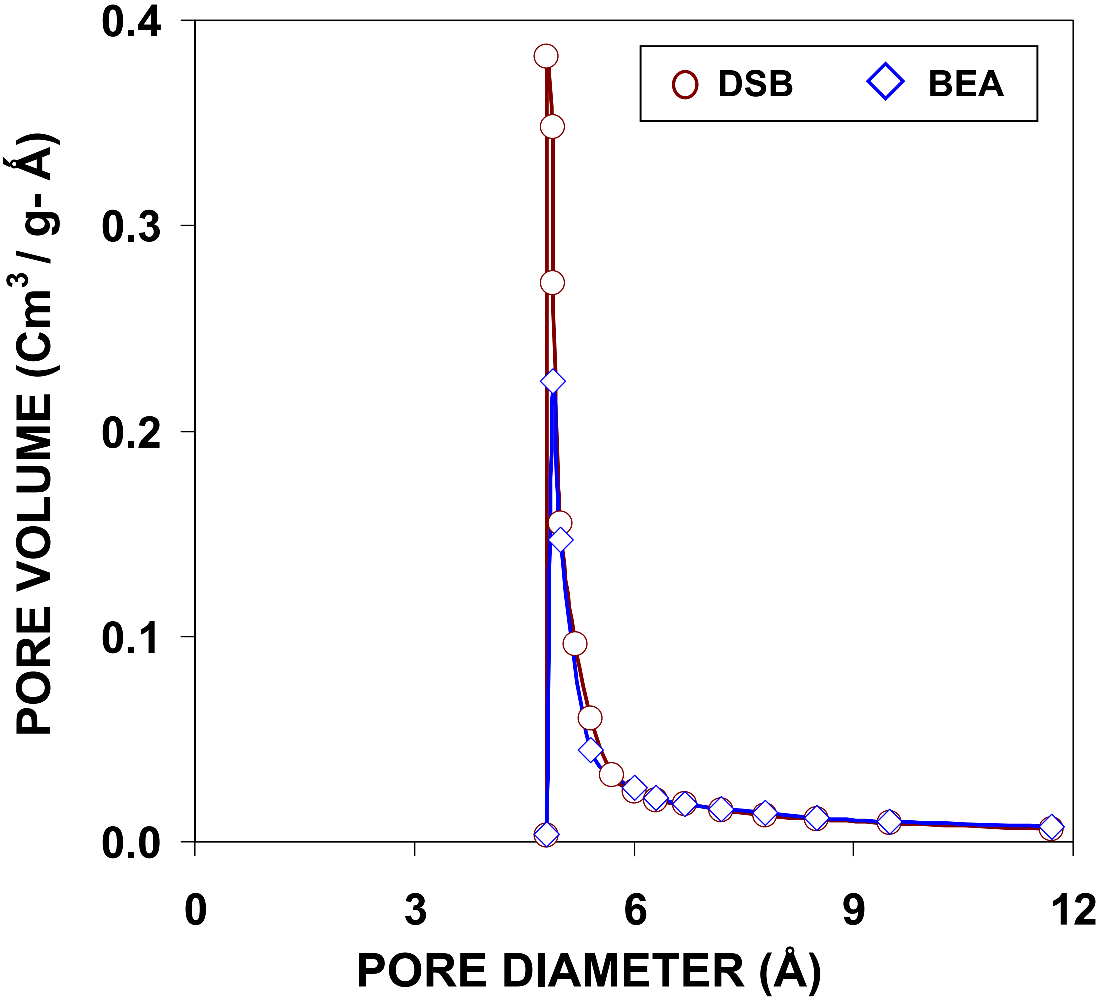

Fig. S1 Micropore size distribution patterns of BEA and DSB zeolite catalysts

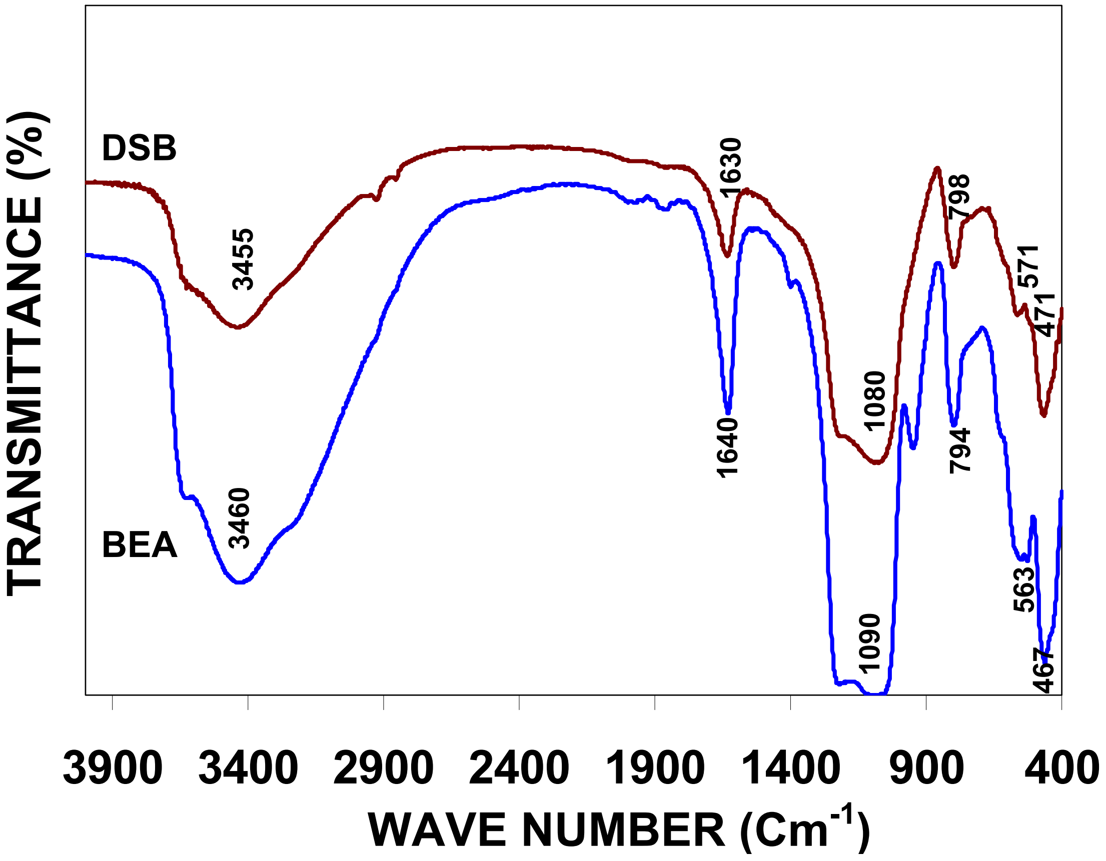

Fig. S2 FTIR patterns of BEA and DSB zeolite catalysts

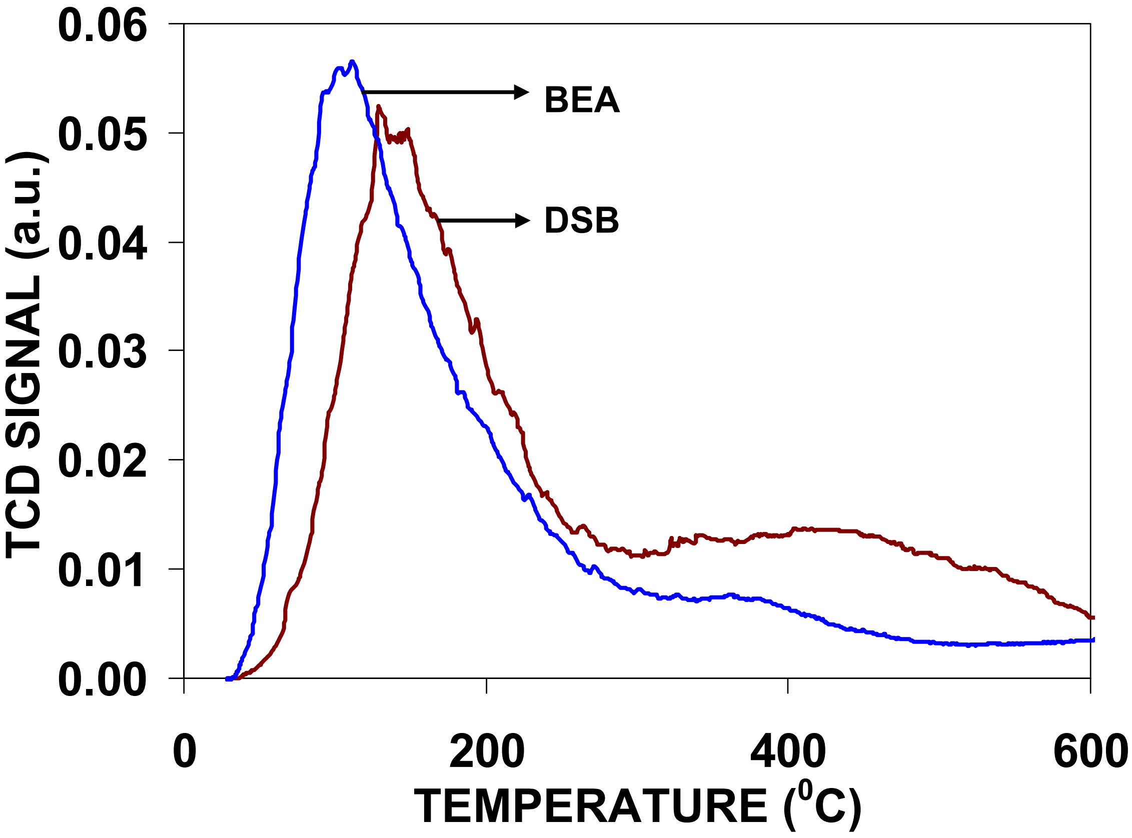

Fig. S3 TPD patterns of BEA and DSB zeolite catalysts