CO_2 activation and synthesis of cyclic carbonates and quinazoline-2,4(1H,3H)-dione over amine and ionic liquids functionalized basic Nano-ZSM-5 catalysts

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Chemicals and materials

AR grade chemicals were purchased and used without any purification. Tetraethyl orthosilicate (TEOS, 98%), tetrapropyl ammonium hydroxide (TPAOH, 40% aqueous solution), sodium aluminates (53 % Al_2O_3, 43% Na_2O), *n*-propyltriethoxy silane, organic substrates used in the synthesis and catalytic reactions were procurred from Sigma-Aldrich, India. Ammonia (28-30%) and solvents were obtained from Merck India Pvt. Ltd.

Catalysts characterization

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–80° 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. The material was de-gassed at 423 K in the degas port of the adsorption apparatus. The specific surface area of the material was calculated from the desorption data points obtained at P/P_0 between 0.05–0.3 using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using Barrett-Joyner-Halenda (BJH) and NLDFT methods. Scanning electron microscopy (SEM) measurements were carried out on a JEOL JSM-6610LV to investigate the morphology of the zeolites. The nanostructure was investigated using high-resolution transmission electron microscope (TECHNAI, FEI-G2) at an accelerating voltage of 300 kV at RSIC Centre, IIT Bombay. The sample was dispersed in ethanol using an ultrasonic bath, and dispersed sample was mounted on a carbon-coated Cu grid, dried, and used for TEM measurement. Thermogravimetric analysis (TGA) was performed on a TGA/DSC 1 STAR^e SYSTEM from Mettler Toledo instrument with temperature increments of 10 K/min in air stream from ambient temperature (300 K) to 1273 K. Catalysts were also characterized by Fourier transform infrared (FT-IR) spectroscopy on Bruker FT-IR instrument. Solid-state NMR was carried out with ^{29}Si and ^{13}C frequencies of 79.4 and 100.5 MHz, respectively, on a 4 mm MAS probe using 400 MHz ECX JEOL NMR spectrometer. ^{29}Si cross-polarization magic-angle spinning (CPMAS)

spectrum was measured at room temperature with the following condition: magic-angle spinning at 8 kHZ; contact time of 5 ms and a repetition delay of 4.05s; 16454 scans (18 h) which was referenced to tetramethylsilane. ^{13}C CPMAS spectrum was measured with a contact time of 1ms with recycle delay of 4s, 10000 scans (11 h). Finally, temperature-programmed desorption (TPD) experiments were conducted on a Quantachrome ChemBET^{TM} TPR/TPD instrument. For CO_2-TPD, initially, the sample was pre-treated in He (50 mL/min) at 873 K for 1 h. After cooling to 323 K, carbon dioxide (partial pressure 100 Torr) was passed through the samples for 1 h. Then, the sample was subsequently flushed by He stream (50 mL/min) at 323 K for 1 h to remove physically adsorbed CO_2. TPD experiments were carried out in the range of 323-573 K at a heating rate of 10 K/min.

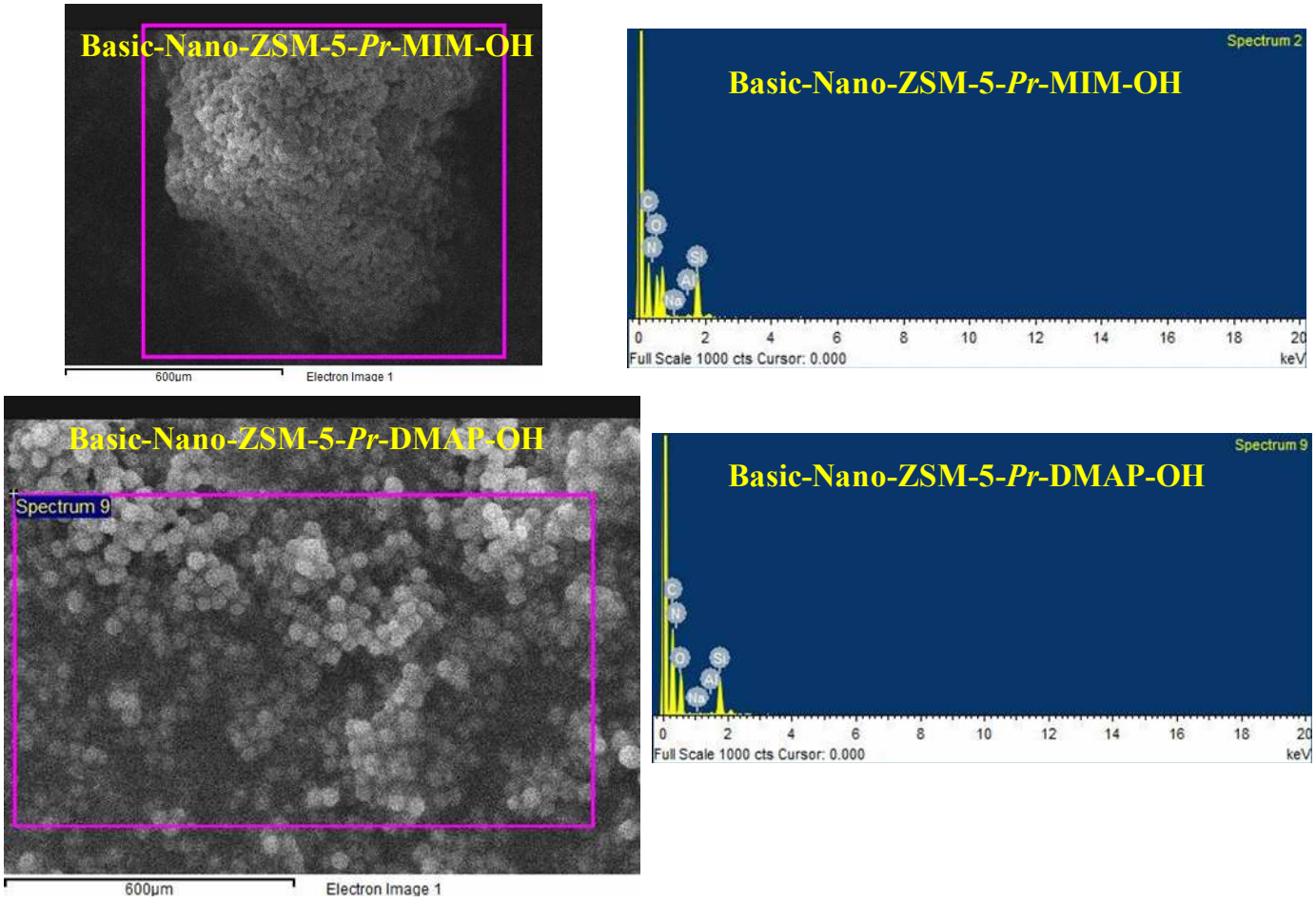


Figure S1. EDAX spectra of Basic-Nano-ZSM-5-*Pr*-DMAP-OH and Basic-Nano-ZSM-5-*Pr*-MIM-OH.

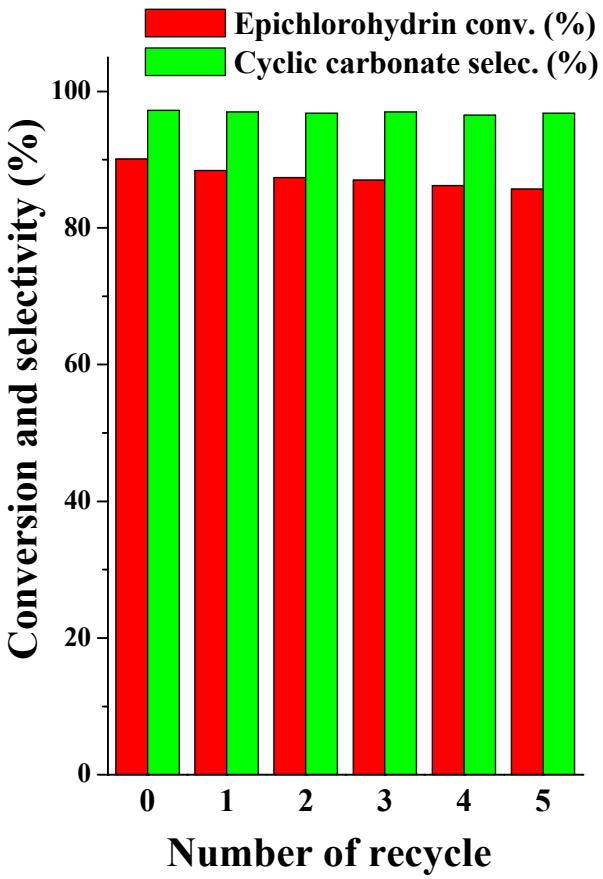


Figure S2. Recycling data obtained by the reaction between CO_2 and epichlorohydrin using Basic-Nano-ZSM-5-*Pr*-MIM-OH.

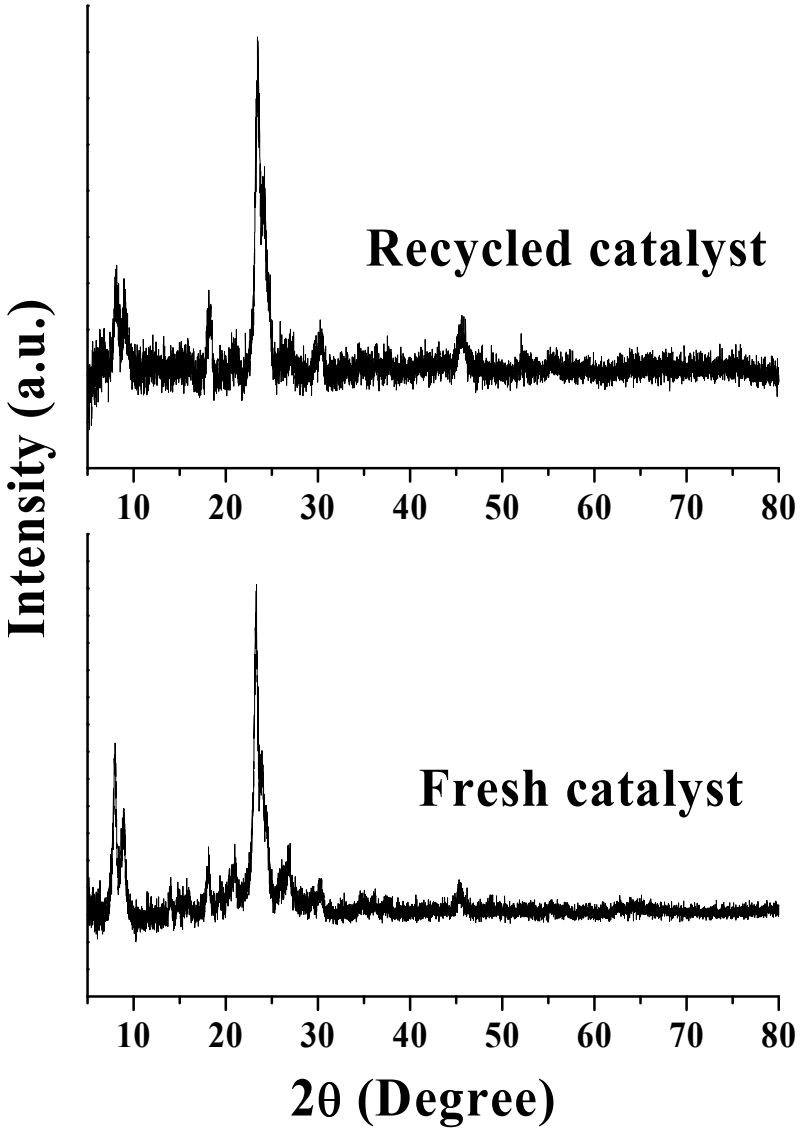


Figure S3. XRD pattern of fresh and recycled Basic-Nano-ZSM-5-*Pr*-MIM-OH obtained after 5^{th} recycle.

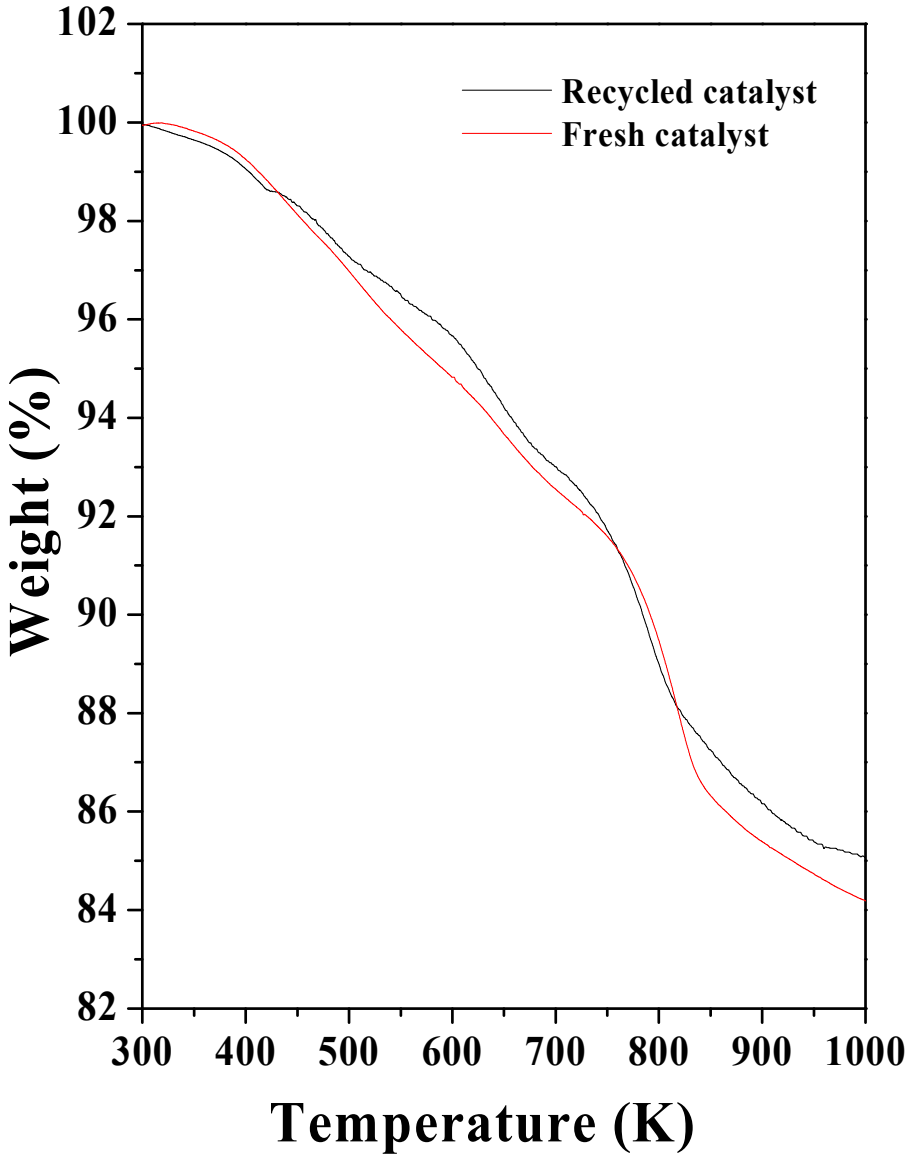


Figure S4. Thermograms of fresh and recycled Basic-Nano-ZSM-5-*Pr*-MIM-OH obtained after 5th recycle.

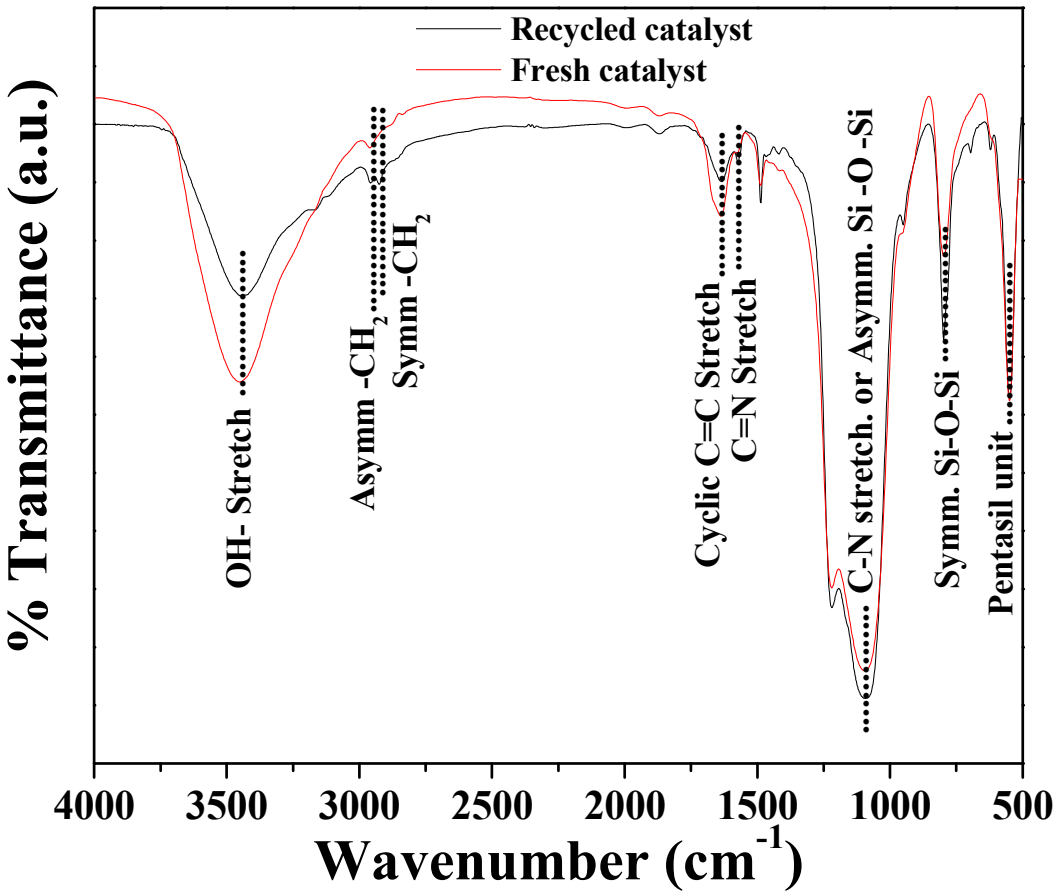


Figure S5. FT-IR spectra of fresh and recycled Basic-Nano-ZSM-5-*Pr*-MIM-OH obtained after 5th recycle.

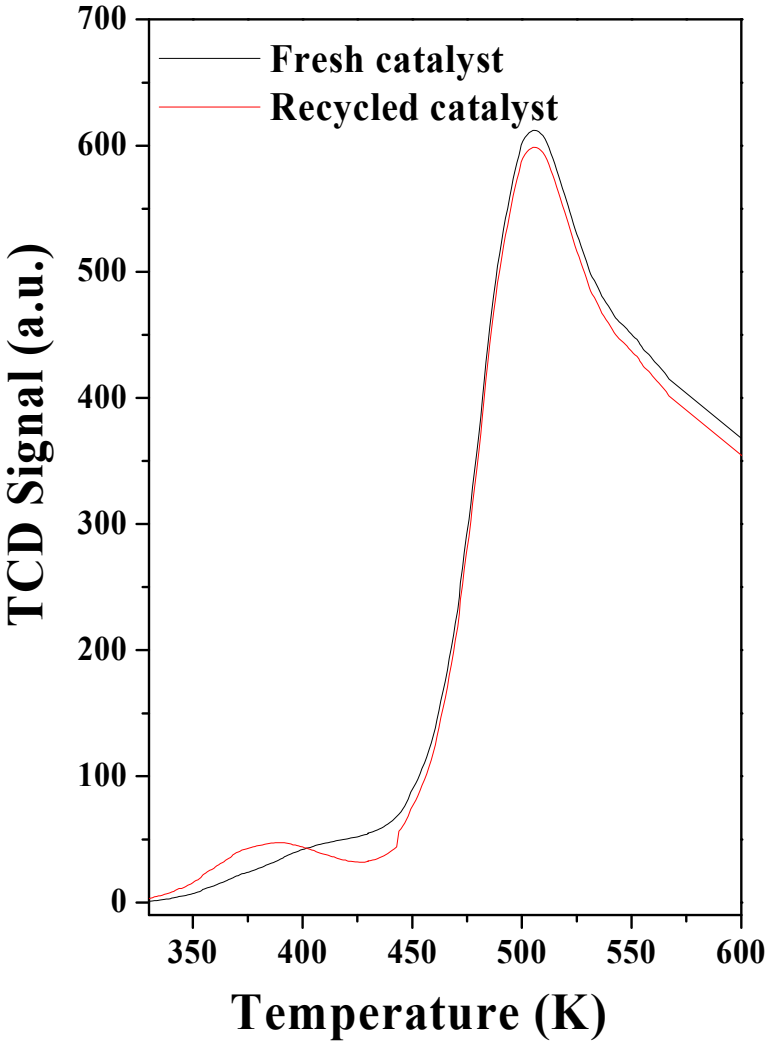
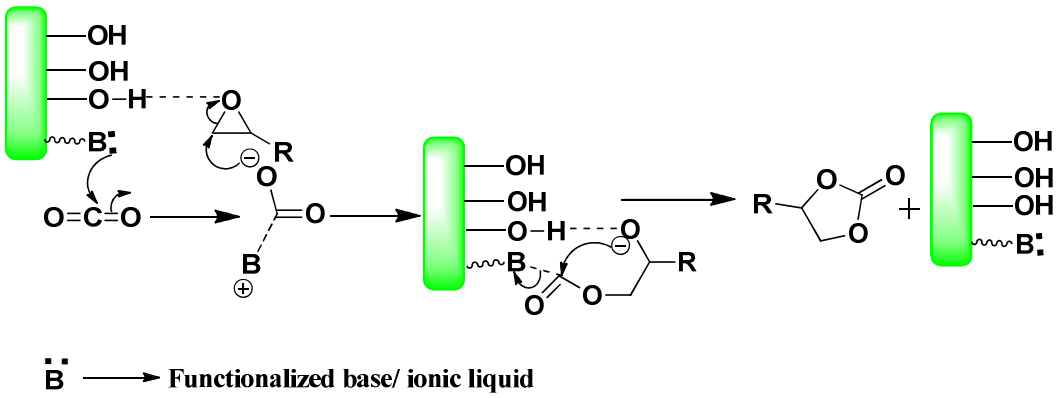
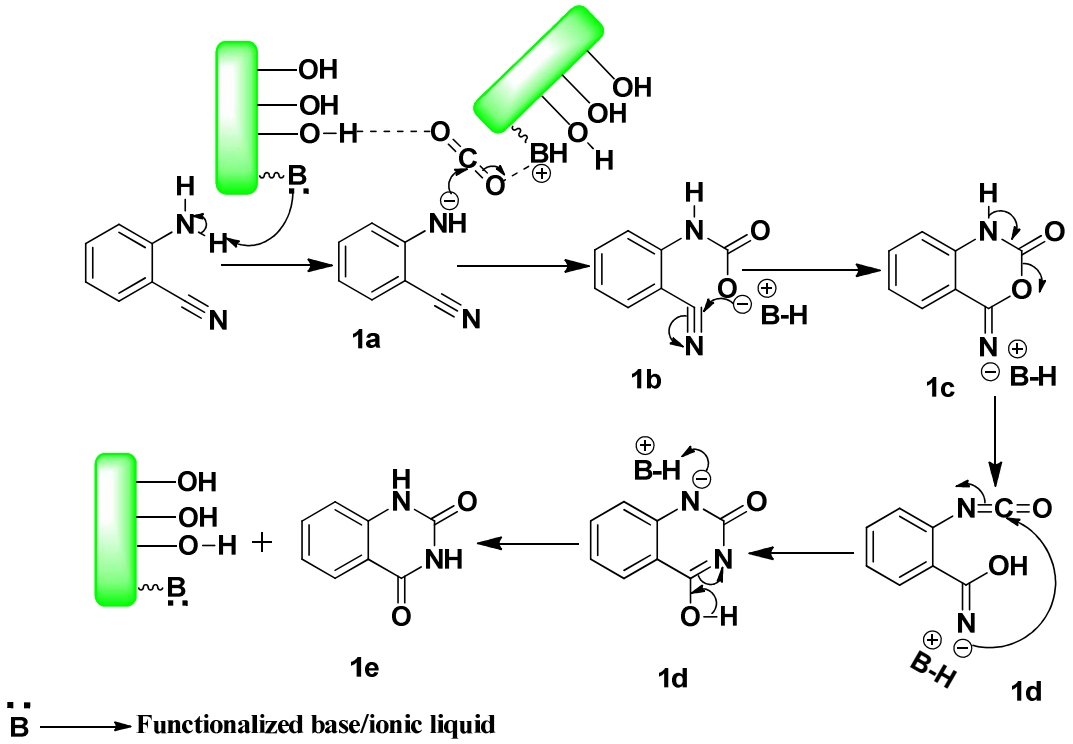


Figure S6. TPD profiles of fresh and recycled Basic-Nano-ZSM-5-*Pr*-MIM-OH obtained after 5th recycle.



Scheme S1. Proposed mechanism for the synthesis of cyclic carbonate by the cycloaddition reaction of CO_2 and epoxide over functionalized Basic-Nano-ZSM-5.



Scheme S2. Proposed mechanism for the synthesis of quinazoline-2,4(1H,3H)-dione by the cycloaddition reaction of CO_2 and 2-aminobenzonitrile over functionalized Basic-Nano-ZSM-5.