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Preparation of cyclic carbonate via cycloaddition of CO_2 on epoxide using amine-functionalized SAPO-34 as catalyst

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ABSTRACT

Amine-functionalized chabazite (CHA) type silicoaluminophosphate (SAPO-34) materials were prepared under hydrothermal conditions by a direct co-condensation method. Different concentrations of an organo-amine (3-aminopropyltrimethoxysilane) were incorporated into the CHA-type framework under hydrothermal conditions. The crystalline structures of the organoamine modified SAPO-34 materials with different concentrations of amine functionalities were confirmed by powder XRD. The morphology of the materials was confirmed by SEM, FE-SEM, and TEM analysis. The successful incorporation of amine-functionalities into the wall of SAPO-34 framework was confirmed by ^{29}Si and ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The acidity and basicity of the materials was studied by NH_3 and CO_2 temperature programmed desorption (TPD). The resultant amine-functionalized SAPO-34 materials were utilized for the cyclo-addition of CO_2 to epoxide in liquid phase medium. The organoamine-modified SAPO-34 acted as a bi-functional (acidic and basic) catalyst. The incorporated amine sites played a crucial role in CO_2 activation on the surface, while the acidic sites of the SAPO-34 framework accelerated the epoxide ring opening. Thus, the amine-functionalized SAPO-34 prepared as described in this work can be an effective catalyst for the activation and utilization of CO_2 in cyclic carbonate synthesis from epoxides (98%) conversion of epichlorohydrin with 96% selectivity toward cyclic carbonate.

1. Introduction

Carbon dioxide (CO_2) is a major pollutant responsible for global warming and climate change. Hence, the transformation of CO_2 into useful products such as urea, salicylic acid, and organic and inorganic carbonates has become an important area of research in the past few decades [1–11]. Consequently, CO_2 is now an abundant and cheap source of carbon (C_1) that can be utilized for the synthesis of various organic products [12,13]. Because of the inertness of CO_2, the development of efficient catalysts for CO_2 utilization is a major challenge in the field of catalysis. Conventionally, CO_2 capture was achieved using basic solvents and porous sorbents [14,15]. In this regard zeolites and zeolite-like framework materials, metal organic frameworks, and amine-functionalized mesoporous materials showed excellent CO_2 adsorption ability [16]. In particular, phosgene-free synthesis of five-membered cyclic carbonates via cycloaddition of CO_2 to epoxides, as well as synthesis of carbamate by using amines and alkyl halides with CO_2 as the starting material are the important organic transformations utilizing CO_2 [17,18]. Cyclic carbonates are useful organic intermediate used as aprotic polar solvents, electrolytes in lithium-ion batteries, and intermediates for polycarbonate synthesis [19,20]. Polyurethanes and polycarbonates are also important organic intermediates in the production of pharmaceuticals and fine chemicals [21,22]. For the synthesis of cyclic carbonates via cycloaddition of CO_2 to epoxides a variety of catalysts such as ionic liquids [23,24], quaternary ammonium salts [25], metal oxides [26,27] and metal complexes [28–30] have been previously reported. Zhang, et al. [31] attempted to use amine-functionalized silica as the catalyst for cyclic carbonate synthesis. Further attempts have been made to develop adenine-modified Ti-substituted SBA-15 material and to apply this material for the synthesis of cyclic carbonates from epoxides and CO_2 [32]. In the Ti-substituted SBA-15 material, Ti played crucial role in ring opening and the amine played a role in CO_2 activation on the surface of the catalyst. It would be interesting to synthesize amine-functionalized crystalline zeolite-type materials possessing surface organo-basic sites and framework acidic sites, without the incorporation of a metal. The former plays a crucial role in CO_2 activation, while the framework plays a role in epoxide ring opening. Thus, in the present work, we investigate the synthesis of

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amine-functionalized chabazite (CHA)-type silicoaluminophosphate (SAPO-34) materials via an *in-situ* approach under hydrothermal conditions. For the first time, a CHA-type SAPO-34 material has been functionalized with different concentrations of 3-aminopropyltrimethoxysilane, ranging from 0.16 to 0.64 M under hydrothermal conditions via *in-situ* synthesis. SAPO-34 possessing a CHA-type framework is an excellent catalyst for the synthesis of various petrochemicals and fine chemicals [33]. Importantly, it is the best known catalyst for methanol to olefin conversion, giving the highest reported production of C_2 and C_3 components [34]. Amine-grafted SAPO-34 was also used for CO_2 capture and separation of CH_4 and CO_2 [35,36]. The seed precursors of CHA-type SAPO-34 were used in order to retain the structure of the material at high concentrations of organoamine. The functionalized materials were utilized as catalysts for the cycloaddition of CO_2 on various epoxides (viz. epichlorohydrin, propylene oxide, styrene oxide and 1, 2-epoxyoctane). The materials showed promising results, with up to 98% conversion of epichlorohydrin and 96% selectivity of carbonate at 85 °C.

2. Experimental sections

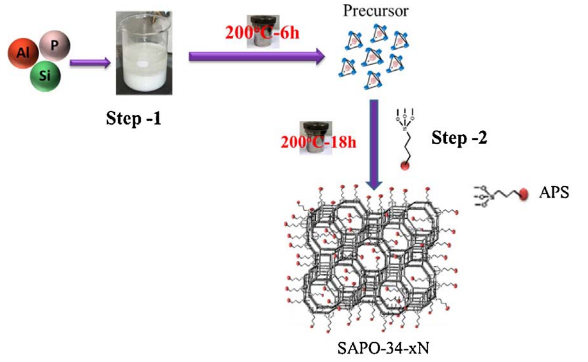
2.1. Chemicals

Pseudoboehmite (76% Al_2O_3; ACE, India), fumed silica (Aerosil-200 from Aldrich), (3-amoninopropyl)trimethoxysilane (Aldrich), *ortho*-phosphoricacid (H_3PO_4; 85%) from Merck, morpholin (99%, Thomas Baker), Propylene oxide (99% from Spectrochem), epichlorohydrin (99%, SRL), 1,2-epoxyoctane (96%), and styrene oxide (97%) from Aldrich. All chemicals were used as received form.

2.2. Synthesis of amine functionalize CHA type SAPO-34

Microporous SAPO-34 material having amine functionality with various concentrations on its surface was prepared via *in-situ* synthesis under hydrothermal conditions by using morpholin as template. The synthetic methodology involved in two steps, in first step microporous seed precursor were prepared by using molar gel composition of 1.0 Al_2O_3: 1.06 P_2O_5: 1-x SiO_2: 2.09 R: 66H_2O. 1.0 Al_2O_3 (x = 0.16, 0.24, 0.32, 0.40, and 0.64 and R stand for morpholin) by crystallizing the gel at 200 °C for 6 h under hydrothermal condition by the modified procedure described elsewhere [37,38]. In the typical procedure solution A of *ortho*-phosphoric acid (5.71 ml; 85%) and pseudoboehmite (5.24 g; 77.6%) in distilled water was allowed to stir for 8 h in order to get uniform mixture. Another solution B was obtained by mixing fumed silica (with different concentrations i.e. 1-x $SiO_{2,}$ where x = 0.16, 0.24, 0.32, 0.40, and 0.64) and morpholin (7.28 ml) in distilled water under constant stirring conditions for 8 h. Subsequently the solution B was added drop wise into the solution A and mixture was allowed to stirrer overnight. The resultant final gel was crystallized at 200 °C for 6 h under hydrothermal condition in Teflon lined autoclave in order to get seed precursor of SAPO-34 material as shown in Scheme 1.

In second step the organo-silane i.e., 3-aminopropyltrimethoxysilane in different molar concentrations was introduced into the prepared seed precursors. The final gel was allowed to crystallize for 18 h under same hydrothermal conditions in order to get amine functionalized SAPO-34 material which is represented as S-34-xN. The final crystallized amine functionalized material was filtered and dried after washing with ethanol. The samples with different concentrations of functionalities were represented as S-34-0.16N, S-34-0.24N, S-34-0.32N, S-34-40N and S-34-0.64N. The samples with different concentration of aminosilane were extracted in ethanol at 70 °C for 4 to 5 h and dried under reduced pressure at 80 °C in order to remove the extra framework organic template and functionalities. For the comparison, the amine functionalized silicoaluminophosphate with the different framework structure viz., AFI and FAU type SAPO-5 and SAPO-37 were also prepared with the 0.64 M concentration of aminosilane and are represented as S-5-0.64N and S-35-0.64N. The material with different silane functionalities viz. di aminosilane (NN) and aniline silane (AN) were also prepared using same methodology are represented as S-34-0.64NN and S-34-0.64AN.



$1.0\ Al_2O_3 : 1.06\ P_2O_5 : 1\text{-x}\ SiO_2 : \text{xAPS} : 2.09\ R : 66\ H_2O.$

x = 0.16, 0.24, 0.32, 0.40, and 0.64

Scheme 1. Schematic representation of preparation of functionalized CHA type SAPO-34 material.

2.3. Characterization methods

Powder X-Ray diffraction patterns of all the materials were collected on Brüker-D8 high resolution X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å), between 2θ range of 4–40°, with a scan speed and step size of 0.5°/min and 0.02° respectively. FT-IR spectra were measured on Brücker optic model tensor 27 FT-IR spectrometer in the range of 400–4000 cm^{-1} using KBr methods. Solid-state NMR experiments were carried out on a Bruker AVANCE 400 wide bore spectrometer equipped with a superconducting magnet with a field of 7.1 T using a 4 mm double resonance magic angle spinning (MAS) probe operating at resonating frequencies of 79.4, and 104.26 MHz for ^{29}Si, and ^{13}C respectively. The samples were packed in 4 mm zirconia rotors and subjected to a spinning speed of 10 kHz: single pulse experiment with pulse duration of 4.5 μs and a relaxation delay time of 6 s were used for recording all ^{29}Si, and ^{13}C MAS NMR patterns. All chemical shift values are expressed with respect to 2,2,-dimethyl-2-silapentane-5-sulfonate sodium salt (DSS) for the ^{29}Si and ^{13}C nucleus. The Temperature-programmed desorption (TPD) experiment was studied on a Micromeritics Auto Chem 2910 instrument. In first step helium was purge at 160 °C for 2 h, after that sample was brought to 40 °C and CO_2 was sent at the rate of 40 ml/min. The analysis was done in the range of 40 to 200 °C. In NH_3 TPD helium was purge at 160 °C for 2 h, after that sample was brought to 100 °C and mixture of NH_3 in He is then passed at the rate of 75 ml/min. The analysis was carried out in the range of 100 to 600 ^{0}C.

The morphology of the materials was studied using scanning electron microscopy (SEM, JEOL, JSM 6610 LV with gold sputter coater JEC 300) and transmission electron microscopy (TEM; Phillips Technai G2 30, operated at 300 kV). Field emission scanning electron microscopy (FE-SEM) images of the functionalized material were collected on a Tescan Mira 3 FE-SEM microscope. Nitrogen adsorption/desorption isotherms were recorded on Micromeritics ASAP 2020, USA. The samples were degassed at 150 °C for 12–14 h under 0.1333 Pa pressure and analysis was carried out at −196 °C prior to each analysis. The BET surface area was calculated in the relative pressure range (p/p_0) 0.05–0.3, over the adsorption branch of the isotherm. Thermo-gravimetry analysis (TGA) was carried out in a thermal analyzer (Perkin Elmer Pyris diamond TGA/DTA). About 5–10 mg of the sample was taken on a platinum pan and heated in nitrogen with the heating rate of 10 °C min^{-1} up to 900 °C.