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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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