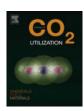


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# Preparation of cyclic carbonate via cycloaddition of CO<sub>2</sub> on epoxide using amine-functionalized SAPO-34 as catalyst



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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 <sup>29</sup>Si and <sup>13</sup>C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The acidity and basicity of the materials was studied by NH<sub>3</sub> and CO<sub>2</sub> temperature programmed desorption (TPD). The resultant amine-functionalized SAPO-34 materials were utilized for the cyclo-addition of CO<sub>2</sub> to epoxide in liquid phase medium. The organoamine-modified SAPO-34 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<sub>2</sub> in cyclic carbonate synthesis from epoxides (98%) conversion of epichlorohydrin with 96% selectivity toward cyclic carbonate.

### 1. Introduction

Carbon dioxide (CO2) is a major pollutant responsible for global warming and climate change. Hence, the transformation of CO2 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, CO2 is now an abundant and cheap source of carbon (C1) that can be utilized for the synthesis of various organic products [12,13]. Because of the inertness of CO<sub>2</sub>, the development of efficient catalysts for CO2 utilization is a major challenge in the field of catalysis. Conventionally, CO2 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 CO2 adsorption ability [16]. In particular, phosgene-free synthesis of fivemembered cyclic carbonates via cycloaddition of CO<sub>2</sub> to epoxides, as well as synthesis of carbamate by using amines and alkyl halides with CO<sub>2</sub> as the starting material are the important organic transformations utilizing CO<sub>2</sub> [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 CO2 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 CO2 [32]. In the Ti-substituted SBA-15 material, Ti played crucial role in ring opening and the amine played a role in CO2 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<sub>2</sub> 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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