



Editor's choice paper

Functionalized SBA-15 material with grafted $-\text{CO}_2\text{H}$ group as an efficient heterogeneous acid catalyst for the fixation of CO_2 on epoxides under atmospheric pressure

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ARTICLE INFO

Article history:

Received 19 October 2016

Received in revised form 8 January 2017

Accepted 11 January 2017

Keywords:

Acid functionalised SBA-15

AFS-1

Mesoporosity

Heterogeneous catalysis

Cyclic carbonate derivatives

ABSTRACT

Carboxylic acid functionalized SBA-15 material AFS-1 has been synthesized through post synthetic route and the mesophase of the material has been characterized by powder X-ray diffraction, transmission electron microscopy and N_2 adsorption/desorption studies. Post-synthesis functionalization resulted high loading of carboxylic acid groups at the surface of highly ordered mesoporous silica. The material showed excellent catalytic activity for the production of cyclic carbonates from a wide range of epoxides in the presence of carbon dioxide (CO_2) at atmospheric pressure and room temperature. The catalyst can be reused five times without significant loss of its catalytic activity.

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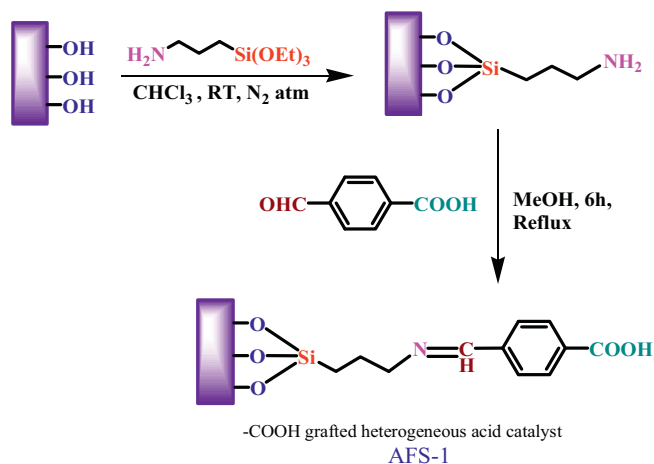
Introduction

CO_2 is a green-house gas, which originates from activities of human and thus its accumulation is a serious threat to the environment. Fossil fuels are considered as the principal source of energy, which upon burning leads to carbon dioxide, which due to its high heat storage capacity is responsible for global warming and related atmospheric changes [1]. The reaction between CO_2 and epoxides can lead to either polycarbonates or cyclic carbonates; both having considerable market value. CO_2 is an attractive C1 feedstock because it is renewable, cheap and can substitute usually used poisonous C1 building blocks (phosgene). Since CO_2 is a non-hazardous carbon source and abundant in nature and played key role in global warming, a great deal of attention has been paid in the recent years for its direct chemical fixation [1]. Several synthetic pathways have been invented to convert carbon dioxide into valuable organic compounds [2]. Among which a promising methodology is the production of cyclic five-membered carbonates from epoxide and CO_2 , which is very attractive in the context of economy and resource utilization [3]. Thus, CO_2 fixation reaction is considered as one of the

major environmentally hazardless chemical transformations [4]. Cyclic five-membered organic carbonates produced via the combination of epoxides and CO_2 are the precursors material of polymeric compounds, electrolytes in polar aprotic solvents, rechargeable batteries, fine chemicals and intermediates in organic synthesis etc. [5]. Various heterogeneous and homogenous catalytic systems such as titanosilicates [6], ionic liquids [7], smectite [8], alkali metal salts alone [9], halostannanes [10], organic bases [11], mixed oxides [12], quaternary ammonium salt or phosphonium salt [13], zeolite [14], crown ether [15], metal complexes [16] have been explored for this conversion. Soluble different alkali metal halides [17] are reported as a catalyst to synthesize cyclic five-membered carbonates. Homogeneous catalysts including metal complexes [18], alkali metal salts [19], bromine [20], alkali metal halides [21], ionic liquids [22], quaternary ammonium and phosphonium salts [23], etc. are also utilized for this reaction. But there are some disadvantages in these homogeneous catalysts such as they may simply be destroyed during the reaction time and cannot be reused. Although some heterogeneous catalysts are employed for this reaction, there are some drawbacks, such as addition of harmful organic solvent, requirements of high-pressure, drastic conditions of reaction and low activity of the catalyst [24,25]. From these points of view, it is highly desirable to utilize a reusable halogen-free highly reactive catalyst. Often, silica supported liquid phase catalysts (SLPC) are employed for this reactions where the halides of alkali metal

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Scheme 1. Schematic diagram for the formation of acid functionalized SBA-15.

are efficiently anchored on the surface of high surface area silica materials.

Heterogeneous catalysts with active metal centers have been largely explored over last few decades for carrying out a wide range of chemical transformations [26]. Although metals in these catalysis are paramount to carry out these organic transformations but due to toxic nature of metals and their possibility of leaching these are not environmentally complete safe processes. So much attention has been paid for the development of catalysts devoid of metal and these materials are typically designated as organocatalysis [27]. Mesoporous silica based heterogeneous acid catalysts are very demanding in this context as their pores are in nanoscale range, they possess high BET surface area and outstanding host-guest combinations [28–30]. Such organically functionalized ordered mesoporous materials are largely explored in several frontline application areas, like catalysis [31], adsorption [32], ion-exchange [33], sensing [34] and so on. Rational grafting of the mesopore surface with reactive organic functionalities [35] can give rise to materials with enhanced catalytic properties. Herein, we have synthesized carboxylic acid grafted SBA-15 material AFS-1 employing post-synthetic functionalizations and the material has been utilized as a heterogeneous acid catalyst for the formation of cyclic carbonates using different kind of epoxides in the presence of carbon dioxide at atmospheric pressure and room temperature.

Experimental section

Synthesis of CO_2H functionalized SBA-15 (AFS-1)

Mesoporous SBA-15 has been synthesized through a previously reported procedure [36]. Then 0.3 g of SBA-15 material was stirred with 2.439 mmol (0.54 g) of 3-aminopropyltriethoxysilane (3-APTES) taken in 10 ml of chloroform for 12 h at room temperature under inert atmosphere. Then the solid product was filtered and washed with chloroform and dichloromethane successively. Resulting white solid product was dried in air. Then 4 mmol (0.45 g) 4-formyl benzoic acid was dispersed in 20 ml methyl alcohol and entire 3-aminopropyl functionalized SBA-15 was mixed with this solution. After that the mixture was refluxed at 333 K temperature for 6 h. Finally the product was separated by filtration. Remaining un-reacted carboxylic acid was removed from the solid product AFS-1 by repeated washing with hot methanol and ultimately dried under vacuum.

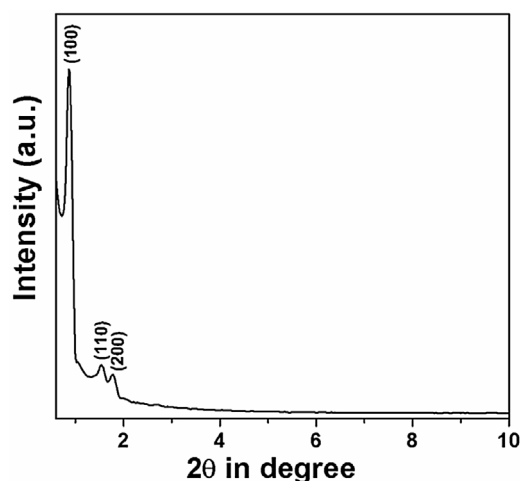


Fig. 1. Small angle XRD pattern of CO_2H grafted AFS-1.

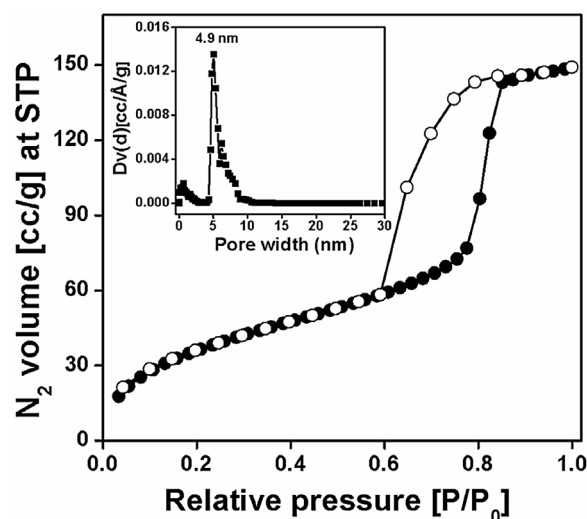


Fig. 2. Nitrogen adsorption-desorption isotherms of AFS-1 catalyst. Adsorption points are marked by filled circles and that of desorption by empty circles. Inset: pore size distribution analyzed using the BJH method.

Characterization of AFS-1 material

X-ray diffraction

The small-angle powder X-ray diffraction patterns of acid functionalised mesoporous silica AFS-1 is shown in Fig. 1. During functionalization of SBA-15 with organic moiety a steady reduction of the peak intensity is observed, however the periodicity of the 2D-hexagonal structure has been retained. Three diffraction peaks of high resolution can be obtained in the 2θ range 0.6–2.07 for this functionalized SBA-15 material. These reflections can be assigned to the (100), (110) and (200) diffractions for the two-dimensional hexagonal mesostructure [36].

Surface area measurement

The N_2 adsorption/desorption isotherm of AFS-1 is shown in Fig. 2. This isotherm can be classified to type IV according to the IUPAC nomenclature with a very high hysteresis loop of H2 type in the 0.5–0.9 P/P_0 range [37]. The step raise in the N_2 uptake is attributed to the filling of mesopores. Further, large hysteresis loop corresponding to large mesopores of SBA-15 material is observed. The surface area of AFS-1 is $240 \text{ m}^2 \text{ g}^{-1}$. Pore size distribution of the

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