



A facile and efficient synthesis of styrene carbonate via cycloaddition of CO₂ to styrene oxide over ordered mesoporous MCM-41-Imi/Br catalyst



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ARTICLE INFO

Article history:

Received 22 April 2012

Received in revised form 4 January 2013

Accepted 29 January 2013

Available online 7 February 2013

Keywords:

Cycloaddition

Styrene oxide

Styrene carbonate

Carbon dioxide

Imidazole

ABSTRACT

MCM-41 was successfully immobilized with imidazole using 3-chloropropyltriethoxysilane (CPTES) as the anchoring agent followed by alkylation with 1,2-dibromoethane at 110 °C. The resulting catalyst was designated as MCM-41-Imi/Br. TEM showed the catalyst had ordered mesoporous straight-channels with average wall thickness of 2.14 nm and average pore size of 1.56 nm. The ²⁹Si MAS NMR analysis confirmed the presence of T², T³, Q³ and Q⁴ silicon centers. The ¹³C MAS NMR showed that MCM-41-Imi/Br had three chemical shifts corresponding to the three carbon atoms of the propyl group. The aromatic imidazole peaks were detected at 110–140 ppm. The catalyst was used in the solvent-less synthesis of styrene carbonate (SC) from CO₂ and styrene oxide (SO) under ambient conditions. It was demonstrated that the synergistic effect due to the stronger nucleophilicity of Br⁻ and amine in the catalyst could lead to a maximum selectivity of 99.1%. Based on the results, a plausible reaction mechanism was proposed for the catalytic reaction. The catalyst could be recovered and reused several times without significant loss in the catalytic activity.

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1. Introduction

Naturally, the presence of carbon dioxide (CO₂) in the atmosphere is to help in the photosynthesis of plants for their food. Even though this gas has a pivotal role for all the living things in the world, it is also the main constituent among the greenhouse gases [1]. About 32% of CO₂ is produced due to hydrocarbon combustion and gasification and are being released into the atmosphere. The use of fossil fuel in transportation releases ~30% of the total CO₂. The natural phenomena such as volcanic eruption and decay of plants and animals also release CO₂ into the atmosphere. As a consequence, the CO₂ concentration increased in the atmosphere and has resulted in severe climatic change due to the greenhouse effect [2]. In recent years, various utilization of this naturally abundant CO₂ has gained considerable momentum in an effort to reduce the concentration of CO₂ in the atmosphere.

Carbon dioxide is a linear molecule with double bonds between the carbon and oxygen atoms (O=C=O). It is a colourless and odourless gas. It is recognized as a non-flammable, non-toxic, inexpensive reagent and environmentally benign molecule [3]. It is a safe, renewable carbon source [4] and thermodynamically stable

compound [5]. It is a kinetically inert molecule and is used as C1 building block in organic synthesis [6]. More importantly it is a substitute for the poisonous and toxic phosgene, carbon monoxide and isocyanates [1] in chemical reactions. Carbon dioxide plays a versatile role in the process of various chemical transformations such as in the production of formic acid, dialkyl carbonate, dimethyl formamide, methanol, urea, salicylic acid, cyclic carbonates, and polycarbonates. Apart from this, the cycloaddition of CO₂ with epoxide has attracted much attention lately [7].

Since 1967, the production of cyclic carbonate from the cycloaddition reaction is well established [8]. These cyclic carbonate compounds are colourless, odourless and biodegradable [9]. They are widely used as aprotic polar solvents, additives and also monomers for polymer synthesis [7]. Besides, it has been used in electrolytic materials such as secondary batteries (lithium batteries), resins, cleaning, cosmetics and personal care products [10]. Furthermore, cyclic carbonates are used as intermediates for pharmaceutical and biomedical fine chemical synthesis [4]. In the agricultural industry, cyclic carbonates are used in the synthesis of herbicides and disinfectants [11]. In addition, cyclic carbonates also play an important role as an intermediate for the synthesis of fuel additives [12].

Recently, a wide range of homogeneous and heterogeneous catalysts have been developed to catalyze the reaction for the generation of cyclic carbonates. Both homogeneous and heterogeneous catalysts have their own advantages and disadvantages. Usually,

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homogeneous catalyst give higher catalytic activity compared to heterogeneous catalysts. Heterogeneous catalysts have the inherent problem of lower activity and need the use of co-solvent [9]. However, homogeneous catalysts are undesirable in industry due to the catalyst-product separation problem [13] which may require more energy and may result in the decomposition of the catalysts [4]. Therefore, heterogeneous catalysts are more suitable for the continuous flow operation and it is more appropriate than batch wise process for large scale industrial synthesis [5]. Besides, it can also be easily separated from the reaction products [2] and be subjected for regeneration for subsequent reuse. However, due to the lower activity, it is important to design and synthesize more efficient heterogeneous catalysts. The production of cyclic carbonates like all other chemical synthesis, not only depends on the type of catalyst, but also other reaction conditions such as reaction time, temperature, pressure and the type of solvent.

Rice is a primary source of food for billions of people and its cultivation covers 1% of the earth's surface. In Malaysia, approximately 163000 MT (1.24%) of rice has been produced and about 0.575 MT of rice husk was generated in 2011 [14]. Rice husk is an agricultural residue (biomass), produced from the processing of rice and is either burnt or dumped as waste. The ash is composed of 92–95% silica (SiO₂). It is highly porous and lightweight, with a very high external surface area [15]. Such attributes of materials can be taken advantage of to synthesize value added materials from this biomass.

In this current study, imidazole (Imi) was immobilized on MCM-41 using a 3-step process to give MCM-41-Imi/Br. This catalyst was successfully used for the synthesis of styrene carbonate (SC). The influence of various experimental factors such as temperature, CO₂ pressure, catalyst amount, reaction time and effect of reaction medium forms the basis of discussion reported in this communication. To the best of our knowledge this is the first report on the utilization of rice husk ash (RHA) as a support for the cycloaddition of CO₂ to styrene oxide (SO).

2. Experimental

2.1. Raw materials

The rice husk (RH) was obtained from a rice mill in Penang. Other materials used were silica gel (70–230 mesh, Merck), nitric acid (Qrec, 65%), sodium hydroxide pellets (R&M Chemicals, 99%), acetone (Qrec, 99.5%), cetyltrimethylammonium bromide (CTAB) (Riedel-de Haen, 98%), 3-chloropropyltriethoxysilane (CPTES) (Sigma-Aldrich, 95%), toluene (Qrec, 99.5%), acetonitrile (Qrec, 99.5%), *N,N*-dimethylformamide (Qrec, 99.8%), 1,2-dichloroethane (Fisher Scientific, 99.9%), styrene oxide (SAFC, >97%), 1,2-dibromoethane (Merck, >99%) and imidazole (Scharlau, 99%). The carbon dioxide was purchased from CAMBEX-HENKEL, Pinang and used as received. Other reagents used were of analytical grade and used without further purification.

2.2. Catalyst preparation

2.2.1. Preparation of MCM-41

MCM-41 was prepared according to the method of Appaturi et al. [16], using RHA as a silica source and CTAB as template. The resulting gel was aged at 80 °C for 48 h. The gel was separated by centrifugation and vacuum filtration and then washed with distilled water followed by acetone. The solid obtained was dried at 100 °C for 24 h, ground in a mortar and calcined in a muffle furnace at 600 °C for 6 h.

2.2.2. Preparation of Cl-MCM-41

To prepare Cl-MCM-41, 4.0 mL (16.6 mmol) of CPTES was added slowly into a mixture of 2.0 g of MCM-41 and 30 mL of dry toluene.

The reaction mixture was refluxed at 110 °C in a temperature controlled oil bath. After 24 h of refluxing, the flask was cooled to room temperature. The solid phase was filtered and washed twice with dry toluene, once with ethanol and distilled water to remove the un-reacted CPTES. The solid sample was then dried at 100 °C for 24 h and ground with a mortar and pestle to afford the Cl-MCM-41.

2.2.3. Synthesis of MCM-41-Imi

Imidazole (1.13 g, 16.6 mmol) was added to a suspension containing Cl-MCM-41 (2.0 g), dry toluene (30 mL) and triethylamine (Et₃N) (2.3 mL, 16.6 mmol). The mixture was refluxed at 110 °C for 24 h. The solid sample was separated by filtration and washed twice with dry toluene and thrice with ethanol to remove the excess amount of imidazole. After drying at 100 °C for 24 h, the sample was ground to fine powder and labeled as MCM-41-Imi.

2.2.4. Synthesis of MCM-41-Imi/Br

To prepare MCM-41-Imi/Br, 2.0 g of MCM-41-Imi was added into 30 mL of dry toluene. 1,2-dibromoethane (1.4 mL, 16.6 mmol) was added slowly and the mixture was refluxed at 110 °C for 24 h. The excess alkyl halide was removed by filtration, followed by repeated washing with dichloromethane. The resulting solid was then dried in an oven at 100 °C for one day. The reaction sequence and the possible structure of MCM-41-Imi/Br is shown in Scheme 1.

2.3. Catalyst characterization

The powder X-ray diffraction patterns of the catalyst were recorded on a Siemens X-ray powder diffractometer (D5000, Kristalloflex) equipped with Cu K α radiation ($\lambda = 0.15406$ nm). The Bruner-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) parameters were obtained from N₂-sorption analysis using a porosimeter (model NOVA Quantachrome porosimeter 2000e) at –196 °C. The surface morphology and topography images were obtained with a transmission electron microscope (TEM), model Phillips CM12, and scanning electron microscope (SEM), model Leica Cambridge S360 respectively. The elemental analysis was carried out using energy-dispersive X-ray spectroscopy (EDX Falcon System) and CHN analyses were carried out using PerkinElmer Series II, 2400. The FT-IR spectra were obtained using PerkinElmer System 2000. The ²⁹Si and ¹³C Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) was recorded using solid-state NMR instrument (400 MHz Bruker AVANCE III). Thermogravimetric analysis (TGA) was performed using (TGA SDTA851^e) Mettler Toledo equipment.

To study the active sites for CO₂ activation, the MCM-41-Imi/Br (300 mg) was heated to 140 °C and exposed to CO₂ for 2 h. The FT-IR spectra of the samples were recorded before and after exposure to CO₂ using PerkinElmer System 2000.

In order to confirm the exact amount of bromide in the catalyst, ion chromatography (IC) analyses was carried out. A 100 mg of MCM-41-Imi/Br was dissolved in 25 mL of 1 mol/L sodium hydroxide. The solution was stirred for 24 h. A clear solution was obtained after filtration with 0.45 μ m Nylon Millipore filter. About 2 mL of the solution was transferred into 100 mL volumetric flask and made up with deionized water. The analysis was conducted on IC equipment (Model: Metrohm 792 Basic IC), with anion column, METROSEP ASUPP 5–150, (size: 150 mm \times 4.0, particle size: 5.0 μ m), conductivity detector and ICNet 2.3 computer software for data handling to determine the presence of bromide. The mobile phases were 1.0 mmol L⁻¹ sodium carbonate with 3.2 mmol L⁻¹ sodium bicarbonate as first eluent and 100 mmol L⁻¹ of sulphuric acid as second eluent. The flow rate was 0.70 mL min⁻¹, and the injection volume was 1 mL.

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