

Short communication

Solid imidazolium halide catalysts for the solvent free synthesis of glycerol carbonate

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ABSTRACT

The synthesis of glycidol carbonate via the cycloaddition of carbon dioxide and glycidol had been studied using MCM-41-Imi/x (x = Cl, Br and I) catalysts under solvent free condition. Within the limit of experimental error, all three catalysts showed a yield > 97.2% at 90 °C, 20 bar CO₂ pressure and a reaction time of 4 h.

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1. Introduction

Glycerol carbonate (GC) is one of the new and interesting material used in industrial applications. This compound has found use in many areas of chemistry, such as in the production of surfactants, in the synthesis of polymers such as polyesters, polycarbonates, polyurethanes and polyamides; lubricating oils, coatings, paints, detergents, as solvent in lithium ion batteries and as de-emulsifier [1,2]. GC is also an important intermediate for the production of glycidol (GOH). Glycidol is known as a bifunctional organic compound that contains both epoxide and hydroxyl group. The compound is slightly viscous and unstable. It is used as a precursor for the synthesis of polymers [3].

GC can be obtained via the traditional method by reacting glycerol and phosgene. However, due to the high toxicity of phosgene [4], alternative routes such as direct carbonation of glycerol and ethylene carbonates using catalysts (zeolites) have been explored under supercritical carbon dioxide. However, the yield of GC was lower than 32% due to the poor reactivity of CO₂ [5]. GC can also be synthesized from carbonylation of glycerol by reacting glycerol with a mixture of carbon monoxide and oxygen [6]. However, the use of a large amount of toxic solvent such as nitrobenzene, long reaction time of about 20 h, and the inflammable nature of CO, renders the synthesis of GC unfavorable from this method.

Another possible method for the synthesis of GC is via glycerolysis of urea. The reaction is carried out under vacuum (40 mbar) to shift the equilibrium toward GC production by means of the continuous separation of ammonia from the gaseous phase [7]. Even though, it is a new and clean route, but it is an economically costly process for industrial exploitation. Alternatively, Aresta et al. [8] prepared GC directly by carboxylation of glycerol with CO₂ using Sn-complexes as catalysts. However, the yield of GC was very low.

Motokucho et al. [9] reported the synthesis of branched polycarbonates from the copolymerization of glycidol with CO₂ using CsCl as catalyst. However, to date there has been no report on the synthesis of glycerol carbonate from the cycloaddition of CO₂.

In a previous study, we reported the characterization and the catalytic performance of MCM-41-Imi/Br in the synthesis of styrene carbonate by the cycloaddition of carbon dioxide and styrene oxide [10]. In this work, we report the synthesis of GC in high yield and selectivity via cycloaddition of CO₂ with glycidol under moderate and solvent free conditions using MCM-41-Imi/Br, MCM-41-Imi/Cl and MCM-41-Imi/I. We believe that this reaction is attractive from both economic and environmental aspects.

2. Experimental

2.1. Materials

The rice husk (RH) was obtained from a rice mill in Penang. Other materials used were 1,2-dichloroethane (Fisher Scientific, 99.9%),

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1,2-dibromoethane (Merck, >99%), 1,2-diiodoethane (Aldrich, 99%), imidazole (Scharlau, 99.0%) and glycidol (Aldrich, 96%). The carbon dioxide was purchased from CAMBREX-HENKEL, Penang and used as received. All other reagents used were of analytical grade and used without further purification.

2.2. Synthesis of MCM-41-Imi/x (x = Cl, Br and I)

The MCM-41 was prepared using rice husk as a silica source according to reported method [11]. The low angle XRD pattern reveals four characteristic peaks corresponding to MCM-41. These phases (100, 110, 200 and 210) are clear evidence for the presence of highly ordered mesoporous straight-channels with long-range order which is a distinctive feature of MCM-41.

The MCM-41-Imi/Br was also prepared according to a previously reported method [10]. To prepare MCM-41-Imi/Cl, 2.0 g of MCM-41-Imi was added into 30 mL of dry toluene. Then, 1.3 mL of 1,2-dichloroethane was added slowly into the flask and the reaction mixture was stirred 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 24 h. MCM-41-Imi/I was synthesized in a similar way using 2.19 g of 1,2-diiodoethane. The yield of MCM-41-Imi/Cl and MCM-41-Imi/I were 2.1 g and 2.2 g, respectively. The possible structure of MCM-41-Imi/Cl and MCM-41-Imi/I are shown in Scheme 1, based on the characterization of MCM-41-Imi/Br [10].

2.3. Characterization

Transmission electron microscope (TEM), model Phillips CM12 was used to visualize the morphology of the catalysts. CHN analysis was carried out using Perkin Elmer Series II, 2400 to determine the percentage of carbon, hydrogen and nitrogen in the prepared catalysts. The percentage of nitrogen obtained was used to calculate the amount of organic amine immobilized on the catalyst.

2.4. General procedure for coupling reaction of GOH and CO₂

In a typical reaction, glycidol (2.0 mL; 30 mmol) with 300 mg of MCM-41-Imi/Br were charged into a high pressure laboratory autoclave (Amar equipment, India), equipped with a magnetic stirrer and a heating mantle system. The reactor was carefully flushed once with CO₂ and re-pressurized with CO₂ (20 bar). The temperature was then raised to 80 °C. The reaction was allowed to go on for 4 h at a stirring speed of 400 rpm. After the reaction was complete, the autoclave was allowed to cool down to room temperature, and the excess CO₂ was released by opening the outlet valve. To a 0.5 mL of the reaction product, 20 μL of cyclohexanol was added as internal standard. The resulting mixture was analyzed with a gas chromatograph (Clarus 500 Perkin Elmer) equipped with Elite 1 capillary column (Perkin Elmer) and a flame ionization detector (FID); with nitrogen as carrier gas. The temperature program used for the analysis were: initial oven temperature 100 °C; initial hold time 2 min; ramp 1: at 25 °C min⁻¹ for 2.8 min then hold for 4 min followed by ramp 2: at 25 °C min⁻¹

for 2.4 min; injector port temperature: 240 °C; detector temperature: 240 °C. The reaction mixture was also analyzed by GC–MS (Clarus 600 Perkin Elmer) with a mass selective detector and helium as the carrier gas to identify the products formed. The GC–MS results are presented in the supplementary data.

3. Results and discussion

3.1. Characterization of catalyst

The TEM of the prepared catalysts are shown in Fig. 1. The results clearly reveal the presence of hexagonal ordered mesoporous arrays with uniform pore size and wall thickness. Thus, we can conclude that, the post grafting method did not damage the regular structured ordering of the mesoporous material. A similar result was obtained for MCM-41-Imi/Br [10].

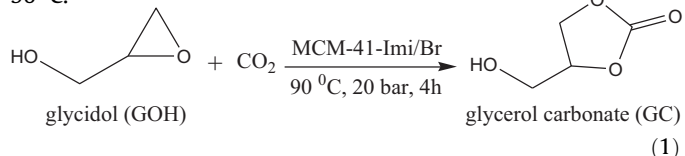
The results of elemental analysis from CHN and N₂ physical adsorption are listed in Table 1. The highest percentage of carbon and nitrogen was found in MCM-41-Imi/Br followed by MCM-41-Imi/Cl and MCM-41-Imi/I. Nevertheless, in all the cases, the content of C, H and N was higher than Cl-MCM-41 [10]. Since C and N content increased in all the catalysts compared to MCM-41 and Cl-MCM-41, it can be concluded that the imidazole and 1,2-dihaloethanes were indeed immobilized on the silica matrix. It was found that the amount of organic amine in MCM-41-Imi/Cl, MCM-41-Imi/Br and MCM-41-Imi/I are 0.90, 1.03 and 0.66 mmol/g, respectively. Furthermore, the immobilization of imidazolium halides caused a drastic reduction in specific surface area and pore volume of the support; MCM-41 (S_{BET} = 1115 m²/g, pore volume = 0.92 cm³/g). The loading amount of organic amine in MCM-41-Imi/Cl, MCM-41-Imi/Br and MCM-41-Imi/I are 2.62 × 10⁻³, 7.92 × 10⁻³, and 10.48 × 10⁻³ mmol/m², respectively.

3.2. Catalytic activity

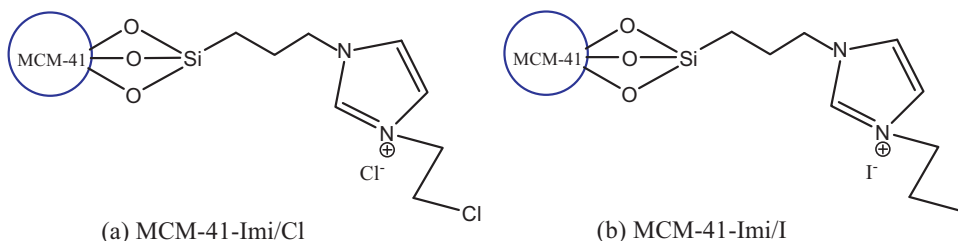
3.2.1. Effect of temperature

The effect of temperature on the conversion and selectivity was studied in the range of 80–100 °C and the results are shown in Fig. 2.

The major product obtained was glycerol carbonate (GC) which is shown in Eq. (1). However, small amounts of glycerol were observed as a byproduct. When the temperature increased from 80 °C to 100 °C the conversion of glycidol increased. The selectivity of GC was observed to be 90.8% at 80 °C and increased to 98.3% at 90 °C.



A slight decrease was noted on the selectivity when the temperature was increased to 100 °C (94.3%). This shows that to obtain a higher yield of the expected product, an optimal



Scheme 1. The postulated structures of (a) MCM-41-Imi/Cl and (b) MCM-41-Imi/I, showing the bonding connections of the organic ligands.

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