Journal of Molecular Catalysis A: Chemical 408 (2015) 214–220

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Microwave assisted synthesis of glycerol carbonate over LDH catalyst: Activity restoration through rehydration and reconstruction

H.R. Prakruthi, B.S. Jai Prakash, Y.S. Bhat*

Chemistry Research Centre, Bangalore Institute of Technology, KR Road, Bangalore 560 004, India

ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form 30 July 2015
Accepted 31 July 2015
Available online 3 August 2015

Keywords:
LDH
Glycerol carbonate
Microwave
Rehydration
Structure reconstruction

ABSTRACT

Zn–Al layer double hydroxide (LDH), as synthesized, was found to be an effective base catalyst for microwave (MW) assisted conversion of glycerol to glycerol carbonate. The used catalyst deactivated after three successive usages in the reaction necessitating regeneration for further usage. Regeneration of the catalyst by thermal treatment at 430 °C for 3 h resulted in the collapse of layer structure forming Zn/Al mixed oxide, the latter being less efficient as base catalyst for glycerol conversion. Reconstruction of the thermally treated catalyst to regain the layered structure was done through rehydration. Among the four methods used for rehydration, microwave approach was found to be faster and superior than other techniques. One hour irradiation with microwave completely regenerated the structure and restored the catalytic activity for glycerol conversion comparable to original LDH sample. Other procedures of rehydration for several hours such as mechanical stirring, vapour phase and ultrasonication were found to be less effective.

1. Introduction

Glycerol is being produced in large quantities as a major byproduct in biodiesel synthesis. Efforts are being made to convert glycerol into value added derivatives. Among glycerol derivatives, glycerol carbonate (GC) (4-hydroxymethyl-1,3-dioxalan-2-one) is at the center of attraction because of it is multifunctional character and its use as chemical intermediate for the synthesis of variety of new chemicals including monomers for new functional polymers. GC is nonflammable, nonvolatile, biodegradable and non-toxic. It is employed as solvent in many applications [1,2]. With increase in interest towards GC, several studies are being made towards its synthesis. Synthesis of GC by direct reaction of glycerol with carbonating agents such as urea [3], CO_2 [4], diethyl carbonate [1,5], alkaline carbonates and bicarbonates [6] and dimethyl carbonate (DMC) [7–9] have been reported in the literature. GC has also been synthesized using glycerol derivatives like 3-chloro-1, 2-propanediol as starting material with CO_2 [10]. DMC is non-toxic, biodegradable, and its transesterification with glycerol is thermodynamically favoured. A yield of 86% of GC was reported by Yoo and Mouloungui using $ZnSO_4$ as catalyst with a glycerol/urea molar ratio of 1 at 140 °C and 30 mbar [11]. In glycerol carbonate synthesis, close to 100% conversion and yield were obtained when K_2CO_3 was used as catalyst [12]. When CaO was used as catalyst in transesterification of glycerol with DMC, GC yield of 90% has been reported [13]. Other catalysts like MgO, ZnO, mixed oxides of Al/Ca, HTc-Mg, HTc-Zn and HTc-Li showed glycerol conversion in the range of 73–92% with selectivity in the range 5–88 % for glycerol carbonate [14]. Malyaadri et al., found Mg/Al/Zr mixed oxides to be efficient catalysts for the synthesis of glycerol carbonate by the transesterification of glycerol with dimethyl carbonate [15]. This has been investigated using various ionic liquids as catalysts [16]. Also, the lipase and Novozyme 435 catalyzed the transesterification reaction, yielding glycerol carbonate, with almost quantitative yield [17]. In these processes, conversions ranging from 65 to 92% with selectivities of 80–99% for GC have been reported.

LDHs are hydrotalcite like compounds with general formula, $\left[M^{II}_{1-x}M^{III}_{x}(OH)_2\right]^{x+}\cdot\left(X^{x-}_{x/q}\cdot nH_2O\right)$ representing layer cation and interlayer anion compositions respectively. M^{II} and M^{III} represent divalent and trivalent metal ions and q is the charge on X. LDHs can be prepared in a wide range of compositions by co-precipitation of metal salts in alkaline medium at constant pH followed by a hydrothermal ageing of the precipitate. The resulting materials can be used as such as catalysts. Further, thermal treatment of LDHs gives rise to the respective mixed oxides. LDHs exhibit unique structural memory effect, i.e., their layered structure which is lost on thermal treatment could be recovered after rehydration [18,19]. This property is used in fine tuning the basic properties of LDHs

---

* Corresponding author: Fax: +91 80 26426796.
E-mail address: bhatys@yahoo.com (Y.S. Bhat).

http://dx.doi.org/10.1016/j.molcata.2015.07.036

and hence, LDHs can behave as potential solid heterogeneous base catalysts for organic synthesis [1,20].

Microwave irradiation has been used for the synthesis of many organic compounds [21,22]. Advantages of microwave heating include more uniform and rapid heating resulting in reduced reaction time for synthesis of chemicals. To the best of our knowledge, use of microwave heating in synthesis and modification of LDHs, such as, in the rehydration of LDHs has not received much attention in the literature [23,24]. Moreover, glycerol is a very good absorber of microwave radiations and hence, microwave could play a greater role in the synthesis of GC. There are very few reports of LDHs as catalysts for the synthesis of GC [1,14,15,25]. The main objective of the present study is to investigate the effect of microwave heating in the synthesis and rehydration of LDHs followed by evaluation of the catalytic activity of the resulting LDHs in the transesterification of glycerol with DMC.

2. Experimental

2.1. Catalysts and chemicals

Analytical reagent grade glycerol, dimethyl carbonate, *N*,*N*-dimethyl formamide, Mg $(NO_3)_2{\cdot}3H_2O$, Zn $(NO_3)_2{\cdot}6H_2O$, Al $(NO_3)_3{\cdot}9H_2O$, Cu $(NO_3)_2{\cdot}3H_2O$, Ni $(NO_3)_2{\cdot}6H_2O$, NaOH and Na_2CO_3 were procured from SD fine chemicals, India and used without purification.

2.2. Catalyst preparation

Zn–Al layered double hydroxides were prepared by the co-precipitation method following the procedure described elsewhere [26–28]. Zn $(NO_3)_2{\cdot}6H_2O$ and Al $(NO_3)_3{\cdot}9H_2O$ were dissolved in distilled water with a Zn:Al molar ratio of 2:1(solution A). Solution A was mixed with a mixture of Na_2CO_3:NaOH molar ratio 3:7 (solution B) under vigorous stirring at ambient temperature with controlled pH between 10 and 11. The resultant mixture was allowed to age at 80 °C for 30 min under microwave heating. The mixture was centrifuged and repeatedly washed with hot water until the centrifugate was neutral. The solid separated was dried at 120 °C for 12 h. Sample was designated as Zn–Al LDH. Similarly, LDHs of Mg–Al, Ni–Al, Cu–Al were synthesized under microwave irradiation.

Synthesized Zn–Al LDH sample was thermally treated in air at 430 °C for 3 h. This resulted in mixed oxide formation with the loss of the layered structure. Rehydration of thermally treated catalysts was carried out in different modes. One of the methods of rehydration of thermally treated Zn–Al LDH catalyst sample involved microwave irradiation. Five grams of thermally treated sample were mixed with 200 ml (40 ml/g) of water and the mixture was subjected to microwave irradiation at 100 °C with continuous stirring for 1 h in presence of nitrogen atmosphere. The irradiated mixture was cooled, centrifuged, the obtained solid was separated and dried in hot air oven at 120 °C. In the procedure adopted using mechanical stirring, five grams of thermally treated LDH sample were mixed with 200 ml water in a beaker and stirred at room temperature for 24 h. In the sonication process of rehydration, thermally treated LDH (5 g) was rehydrated in water under sonication for 2 h at 60 Hz. Vapour phase rehydration of thermally treated catalyst sample was carried out in a quartz fixed bed reactor. Catalyst was packed at the center of the reactor between two plugs of quartz wool. Water vapour carried by nitrogen gas at 130 °C was passed over the sample for 7 h for rehydration to occur. The rehydrated solid was cooled, taken out and dried in hot air oven. These were designated as RH-MW, RH-MS, RH-US and RH-VP LDHs respectively.

2.3. Characterization

The prepared samples were characterized using various techniques, such as BET, XRD, FTIR, TGA and total basicity by benzoic acid titration and temperature programmed desorption of CO2 (TPD- CO2). BET surface area measurements were carried out using Quantachrome Nova-1000 surface analyzer under liquid nitrogen temperature. X-ray diffraction (XRD) patterns were recorded by Shimadzu MAXima_X XRD-7000 X-ray diffractometer with step scanning at $2\theta = 0.02$ per step from 3° to 80° on graphite monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å). XRD patterns were also confirmed using files from the Joint Committee on Powder Diffraction Standards (JCPDS).

The total basicity of LDH samples were estimated by benzoic acid titration method [12,29]. Suspension of 0.5 g of sample in 2 ml toluene solvent was stirred for 30 m followed by addition of 2–5 drops of dilute phenolphthalein solution as indicator. The mixture was titrated against 0.01 M benzoic acid in toluene. The benzoic acid consumed was used for the calculation of total basicity. FTIR spectra of the samples were recorded by KBr pellet method using Shimadzu IR Affinity-1 spectrophotometer, in the range of 400–4000 cm^{-1} with 4 cm^{-1} resolution of 40 scans. The basicity of catalysts were determined by temperature programmed desorption of CO_2 (TPD-CO_2) in an indigenously built unit equipped with a furnace, quartz U tube and thermal conductivity detector using helium as a carrier gas. The catalyst sample was pre-treated in He flow at 100 °C for 1 h, and then cooled to room temperature prior to the adsorption of CO_2 at this temperature. After the adsorption of CO_2 for 30 min the sample was flushed with He for 1 h at 100 °C in order to remove physisorbed CO_2 from catalyst surface. The desorption profile was recorded at a heating rate of 10 °C min^{-1} from 100 to 900 °C and the evolved CO_2 was monitored with a thermal conductivity detector.

2.4. Catalytic tests

Catalytic tests were carried under microwave irradiation and conventional heating modes. Microwave irradiation reactions were carried out in a microwave lab station for synthesis 'START-S' model milestone, Italy, having software which enables on-line control of temperature of the reaction mixture with the aid of infrared sensor by regulation of microwave power output. All the reactions were carried out in a 50 ml glass vessel and the reaction mixture was stirred with the help of in-built automatic magnetic stirrer using teflon stirring bar. Reactor vessel was kept in such a way that the reaction mixture was exactly in line with infrared sensor which monitors the temperature. Variable power up to 1200 W was applied by microprocessor controlled single magnetron system.

Glycerol (10 mmol, 0.92 g) and DMC (30 mmol, 2.7 g) were mixed with the catalyst sample in a 50 ml reaction vessel. The reaction mixture was subjected to microwave irradiation by initially applying 1000 W power for 1 min to attain reaction temperature (120 °C) and then maintained for 59 min. After cooling, the product mixture was stirred with 5 ml of dimethyl formamide (DMF) solvent (used in the separation of catalyst after the reaction from the mixture) and then the used catalyst was filtered off. The reaction mixture (Scheme 1) was analysed in Chemito GC-1000 gas chromatograph with TR-WAX capillary column (30 m length, 0.5 μm internal diameter and column thickness 0.32 mm) and attached with flame ionization detector.

The catalytic activities of the rehydrated (RH) samples were also found out. The reactions were also carried in conventional heating and product formation was confirmed by procedure already given for comparison.