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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

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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, $\left[M^{II}_{1-x}M^{III}_{x}(OH)_2\right]^{x+}.\left(X^{x-}_{x/q}\cdot nH_2O\right)$ 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

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

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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.

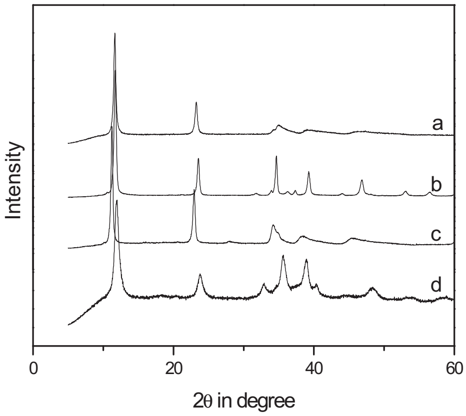


Fig. 1. XRD pattern of different LDHs. (a) Mg–Al (b) Zn–Al (c) Ni–Al (d) Cu–Al.

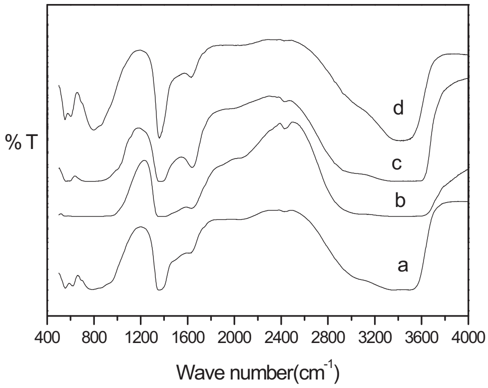


Fig. 2. FT-IR spectra of different LDHs (a) Zn–Al, (b) Mg–Al, (c) Ni–Al, (d) Cu–Al.

3. Results and discussion

3.1. XRD analysis

The different as-synthesized LDHs were analysed by X-ray diffraction with Shimadzu MAXima_X XRD-7000 X-ray diffractometer using Cu Kα radiation. Fig. 1 shows the XRD profiles of freshly prepared different LDH materials. It can be observed that, Zn–Al, Mg–Al, Ni–Al and Cu–Al LDHs showed all the classical reflections at 003, 006, 012 for 2θ values 11°, 24° and 37° respectively corresponding to well crystallized hydrotalcite like structure. This is confirmed from the literature [26–28].

3.2. FT-IR spectra

The FT-IR spectra of Zn–Al, Mg–Al, Ni–Al and Cu–Al LDHs are shown in Fig. 2. The broad peak around 3400 cm^{-1} is ascribed to the stretching frequency of OH groups attached to metal ions. The bending vibration of interlayer water is seen at 1650 cm^{-1}. The antisymmetric vibration of $CO_3{}^{2-}$ appears at 1360 cm^{-1}. The lower wave number bands at 400–700 cm^{-1} is due to LDH lattice vibrations M—O—H, where M is Mg, Al.

Table 1
BET surface area and basicity of LDH samples by benzoic acid titration method.

Catalysts	Surface area m^2/g	Basicity (μmol/g)
Mg–Al LDH	51	101.41
Cu–Al LDH	49	92.57
Ni–Al LDH	40	95.11
Zn–Al LDH	46	108.23

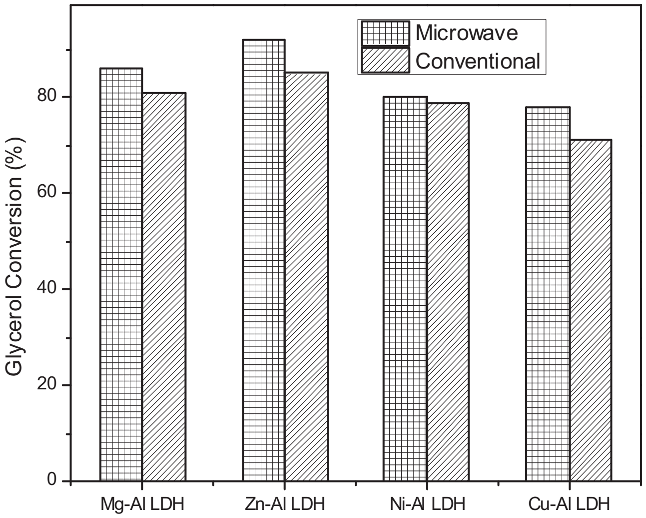


Fig. 3. Conversion of glycerol under microwave and conventional heating for different LDHs prepared.
Reaction conditions: catalyst amount, 0.5 g; mole ratio G:DMC, 1:3; temperature,120 °C, MW, 60 min and conventional, 8 h.

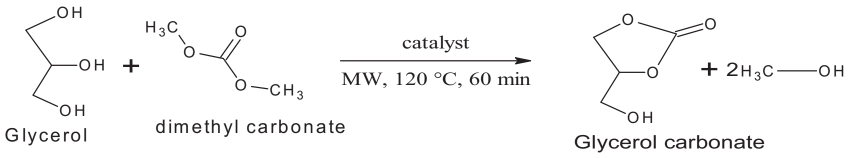
3.3. BET surface area

Measured surface areas of the samples are shown in Table 1. The as-synthesized Mg–Al, Cu–Al, Ni–Al, Zn–Al LDHs were found to possess surface areas in a narrow range from 40 m^2/g to 51 m^2/g. In the present study, the variation in activity arising due to change in surface area, apparently, is insignificant.

3.4. Comparison of catalytic activity of different LDHs

Effect of different modes of heating on reaction time was studied for transesterification of glycerol with DMC at 120 °C with 0.5 g of catalyst and G:DMC mole ratio of 1:3. Reaction was carried out at 60 min for MW heating and 8 h for conventional heating. Conversion of glycerol as a function of reaction time under microwave and conventional modes of heating are shown in Fig 3.

Difference in conversion was observed between two modes of heating. Under conventional mode of heating, reaction proceeds very slowly and takes 8 h for maximum conversion. On the other hand, under microwave mode of heating, conversion of glycerol was in the range of 80–92% with 100% selectivity for glycerol carbonate in 60 min. To compare the intrinsic activity of the catalysts, the reaction was studied at lower conversion (around 30%) at the same microwave irradiation time. Similar trend in glycerol conversion was observed for all the LDH samples. Among these, Zn–Al



Scheme 1. Transesterfication of glycerol with DMC.

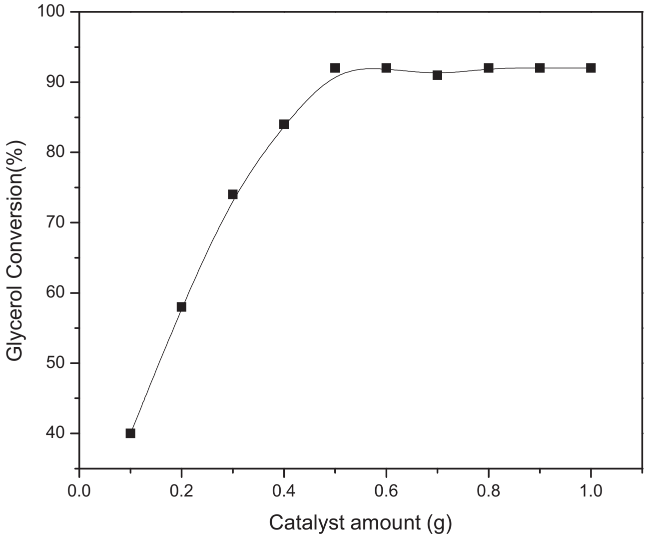


Fig. 4. Effect of catalyst (Zn–Al, LDH) amount on glycerol conversion.
Reaction condition: mole ratio G (glycerol): DMC, 1:3; reaction time, 60 min; temperature, 120 °C (MW).

LDH showed maximum activity and hence Zn–Al LDH was selected for optimization and further investigation. Higher activity of Zn–Al LDH was attributed to its high basicity as determined by benzoic acid titration method (Table 1).

Various parameters like effect of reaction time, reaction temperature, catalyst amount and mole ratio of the reactants for transesterification of glycerol with DMC with Zn–Al LDH catalyst were studied under microwave mode of heating.

3.5. Transesterification under MW heating using Zn–Al LDH as catalyst

3.5.1. Effect of catalyst amount

No reaction was observed between glycerol and DMC in the absence of Zn–Al LDHcatalyst. Under specified conditions, increase in the amount of glycerol conversion was observed with increase in catalyst amount from 0.1 to 1 g. Fig. 4 shows that the conversion of glycerol improved with the increase in catalyst amount and reached a maximum at 0.5 g and thereafter it became constant.

3.5.2. Effect of temperature

Effect of temperature was studied under the same reaction conditions by varying temperature from 50 to 120 °C. Higher temperature beyond 120 °C could not be conducted with the available MW reactor facility. The results are shown in Fig. 5. Temperature showed a marked effect on the conversion of glycerol which enhanced with increase in temperature indicating endothermic nature of the reaction.

3.5.3. Effect of mole ratio

Effect of mole ratio of reactants on glycerol conversion was studied by varying the mole ratio of G: DMC from 1:3 to 3:1, other conditions being similar. Results are tabulated in Table 2. The results show an increase in conversion (93%) of glycerol at 1:3 ratio. The highest conversion occurs in the mole ratio of G: DMC at 1:3. As the availability of DMC molecule increases, the glycerol conversion also increases because the probability for alkoxy group (see Scheme 2) to find carbonate groups is high. Increase in glycerol content in the reaction mixture showed a decrease in the conversion to glycerol carbonate.

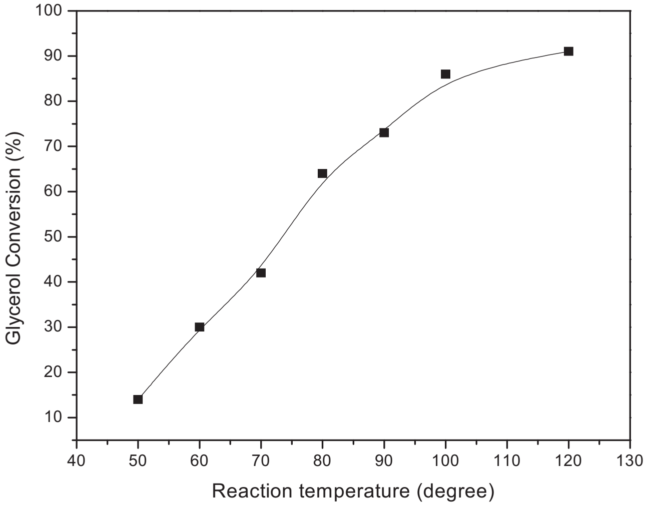


Fig. 5. Effect of temperature on glycerol conversion.
Reaction conditions: catalyst Zn–Al_LDH; amount of catalyst, 0.5 g; mole ratio G:DMC (1:3); reaction time, 60 min (MW).

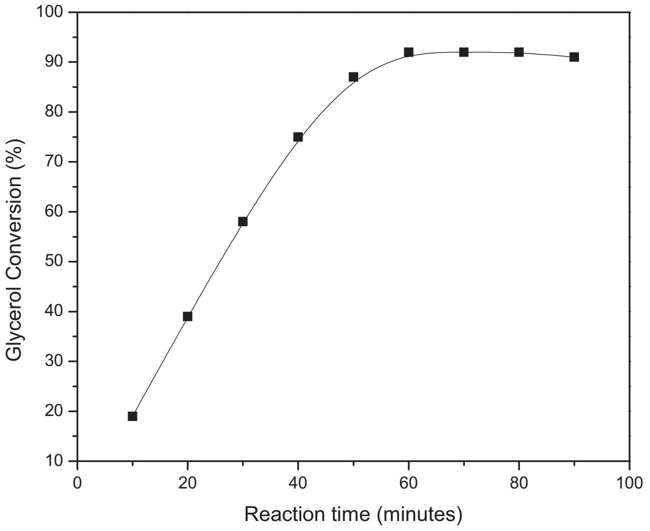


Fig. 6. Effect of time on glycerol conversion using Zn–Al–LDH as catalyst.
Reaction conditions: mole ratio G: DMC, 1:3; catalyst amount 0.5 g; reaction temperature, 120 °C, (MW).

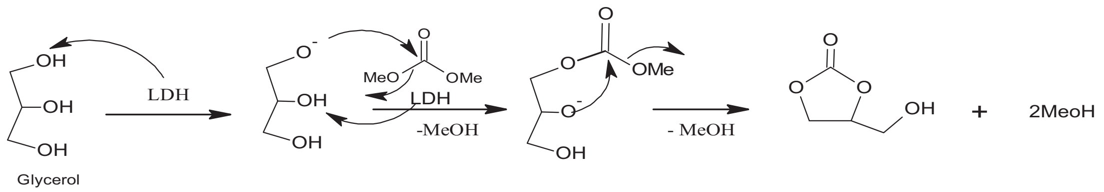
3.5.4. Effect of reaction time

Conversion of glycerol as a function of reaction time under same reaction conditions is shown in Fig. 6. Initially, conversion of glycerol was observed to be less and as the time increased from 10 to 90 min, the conversion gradually increased to a maximum value of 92% with 100% selectivity for GC in 60 min. Thereafter it remained same.

Table 2
Effect of mole ratio on Glycerol conversion.

G:DMC	Conversion of glycerol (%)
1:1	68
1:2	91
1:3	93
2:1	57
3:1	46

Reaction condition: catalyst amount (Zn–Al–LDH), 0.5 g; reaction time, 60 min; reaction temperature, 120 °C (MW).



Scheme 2. Possible reaction mechanism of LDH catalysed transesterification reaction.

Table 3
Reusability of Zn–Al LDH.

Cycles	Glycerol conversion (%)
First cycle	91
Second cycle	91
Third cycle	85
Fourth cycle	69

Reaction conditions: catalyst amount, 0.5 g; mole ratio G: DMC, 1:3; temperature, 120 °C, MW, 60 min.

3.6. *Catalyst deactivation*

After carrying out the transesterification reaction, the catalyst was separated by filtration, washed with methanol (5 ml) and dried at 110 °C for 2 h and was reused for second, third and fourth time under mentioned reaction conditions. The results are shown in the Table 3. Conversion of glycerol decreased slightly in the third cycle and a drastic decrease was observed in the fourth cycle. Further, the catalyst reused after the fourth cycle showed almost complete loss of its activity. Thermograms of the Zn–Al LDH samples before and after the reaction (4th cycle) showed a significant weight loss in the case of the used sample (Fig. 7). The loss of activity is attributed to the species adsorbed on the surface of the used catalyst which apparently blocked access to the active sites. To regain back its original activity, the used catalyst was subjected to thermal treatment at 430 °C for 3 h and rehydrated with water using different techniques.

3.7. *Thermal treatment and rehydration*

After thermal treatment of LDH, the layered structure was found to collapse and the thermally treated sample showed typical features of Zn(Al)Ox mixed oxide. The XRD reflections characteristic of the mixed oxide appeared at $2\theta = 31°$, $34°$ and $36°$ (JCPDS 74-1136) as shown in Fig. 8. The thermally treated material was rehydrated by different modes such as mechanical stirring (MS), microwave (MW), ultrasonication (US) and vapor phase (VP) method to regain the LDH structure. Mechanical stirring was carried out for 24 h, ultrasonication for 2 h, vapour phase rehydration for 7 h and MW irradiation for 1 h. The XRD patterns of the samples RH-MS RH-US, RH-VP and RH-MW are shown in Fig. 8. The patterns exclusively show the diffraction lines of pure Zn–Al LDH due to well known LDH memory effect [30,31]. It can be clearly seen from Fig. 8 that the intensity of all reflections in the case of microwave rehydrated (RH-MW) sample was similar to that of as-synthesized sample. Other modes of rehydration such as US, VP and MS were not so effective in regenerating the layered structure within the treatment time for rehydration as shown by their XRD pattern. This indicates that rehydration with just 1 h-MW irradiation is enough to facilitate almost complete regaining of the layered structure. Even though microwave rehydration is effective in not completely regenerating the layer structure, the regained structure possesses more active basic sites for the transesterification. MW radiations thus, are much faster, superior and more effective in regaining of the LDH structure.

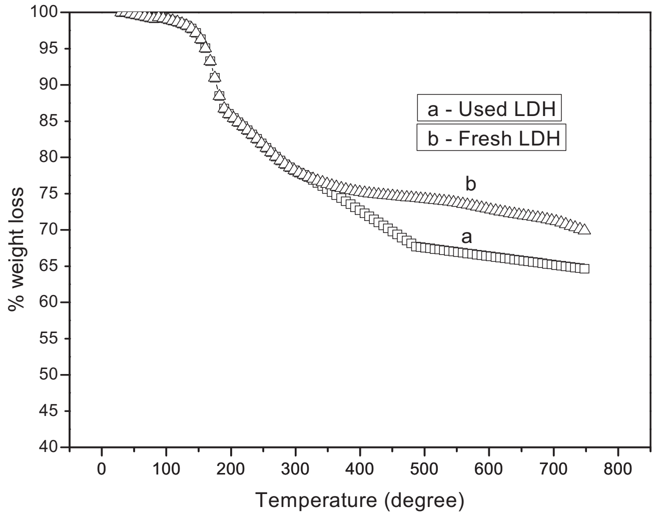


Fig. 7. TGA of Zn–Al LDH a) used, b) fresh Zn–Al LDH.

3.8. *Catalytic activity of Rehydrated LDH*

Catalytic activity of as-synthesized and rehydrated samples viz., RH-MW, RH-VP, RH-US, and RH-MS LDH samples was investigated. The results are shown in Fig. 9. Among these, RH-MW catalyst showed pronounced activity compared to other rehydrated catalysts. Rehydration by microwave irradiation as a heating source

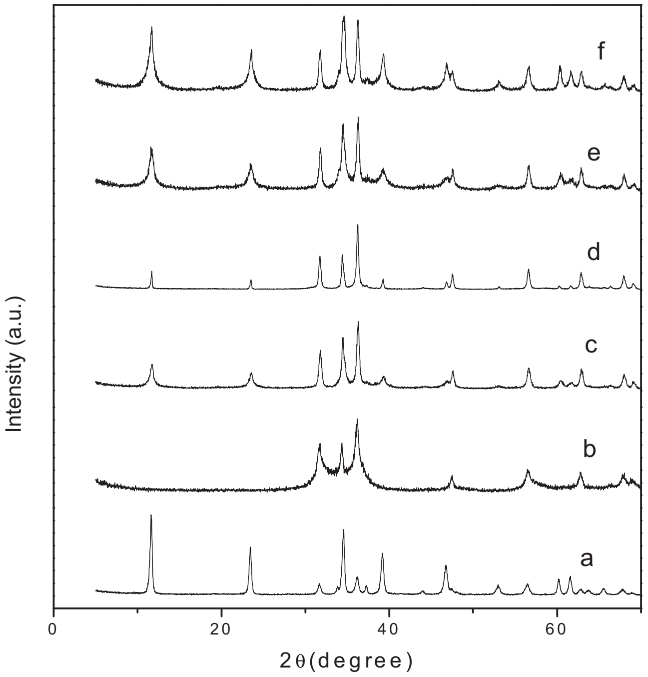


Fig. 8. Comparison of XRD patterns of Zn–Al LDH sample; (a) as synthesized; (b) thermally treated; (c) RH-US, (d) RH-VP, (e) RH-MS and (f) RH-MW.

Table 4
Strength of basic sites, total basicity and surface area of as-synthesized and rehydrated Zn–Al LDH samples.

Catalyst	Strength of basic sites (μmol/g)			Total basicity (μmol/g)	Surface area m^2/g	TON
	Weak	Medium	Strong			
Zn–Al LDH	153	128	113	394	46	148
RH-MW	142	150	204	496	51	104
RH-US	133	154	181	468	57	122
RH-MS	125	142	167	434	47	127
RH-VP	114	146	118	378	58	139

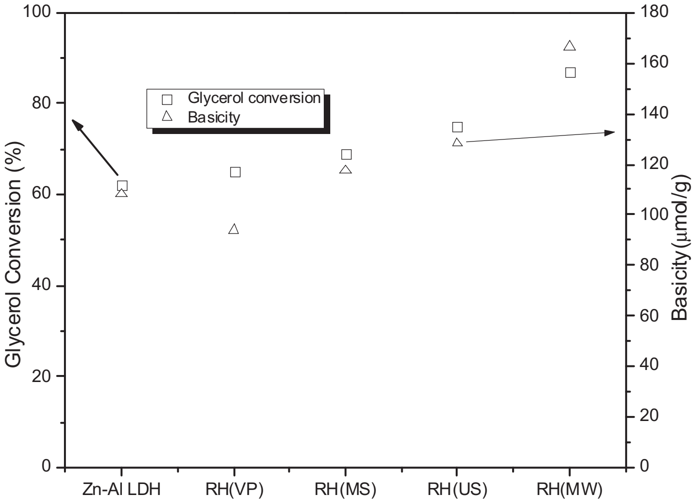


Fig. 9. Comparison rehydrated catalyst for glycerol conversion in transesterification reaction.
Reaction condition: catalyst amount, 0.5 g; mole ratio G: DMC, 1:3; temperature, 120 °C, MW 30 min

facilitates enhanced rate of reconstruction of LDH. The most striking feature of the rehydrated material was the increased intensity of the characteristic peaks as observed in the XRD pattern (Fig 8). Rehydration by MW shows the increased catalytic activity owing to the recovery of almost all of its original layered structure resulting in significant increase in the OH^- sites on the surface of the catalyst.

Basicities of the rehydrated LDH samples as determined by the benzoic acid titration method are also shown in Fig. 9. There exists a proportional variation between the catalytic activity and basicity of the rehydrated catalyst samples. Rehydration is a process of hydrolysis of the oxide surface by water molecules. Thermal treatment brings about dehydration of the catalyst surface by the removal of water molecules formed by the combination of two adjacent hydroxyl groups generating O^{2-} ions and exposed Zn or Al atom with low coordination number on the surface. Rehydration results in the regeneration of the OH groups on the surface. Water molecules being polar interact with the MW radiations assisting the process of rehydration thus accelerating the surface reconstruction. Consequently, the catalyst surface regains the hydroxyl groups faster in the presence of MW radiations as shown by the appearance of XRD peaks within an hour of MW treatment. Besides, the surface being polar also assists the rehydration. Other processes of rehydration are slower as shown by the delay in the appearance of the XRD peaks. Even after several hours of treatment, full intensities of the peaks, compared to as-synthesized sample, do not develop. Consequently, RH-MS, RH-VP and RH-US samples show reduced basicities and accordingly, show low conversions.

TPD-CO_2 was used to determine the basicity and the basic strength distribution of the catalyst samples. By knowing the amount of CO_2 desorbed from the catalyst surface the basicity of the catalyst can be calculated. The basic strength of as-synthesised and rehydrated samples can be estimated based on the temperatures at which peak appear in TPD-CO_2 (Temperature programmed desorption) profiles. Obtained results of TPD-CO_2 analysis are given in Table 4. TPD profile showed three peaks such as weak (430 K), medium (600 K) and strong (780 K). In as-synthesised Zn–Al LDH sample, desorption of CO_2 at lower temperatures is high compared to others. This is attributed to weak basic strength. However, the rehydrated samples (MW, MS, US, VP) exhibited more CO_2 desorption at medium and high temperature which are ascribed to medium and strong basic strength. After rehydration under microwave irradiation, higher amounts of CO_2 desorption at medium and high temperature is attributed to the partial conversion of weak basic sites into medium and strong basic sites. This could be due to the restructuring and redistribution of OH groups during the rehydration process. Surface area values of as-synthesized and rehydrated samples are almost in the same range. It is clear from Table 4 that there exists a good correlation between the activity and basicity, there is no such correlation with surface area.

Table 5
Catalyst (RH-MW) reusability on transesterification.

Cycles	Glycerol Conversion (%)
First cycle	86
Second cycle	86
Third cycle	84
Forth cycle	71

3.9. *Recycling of RH-MW spent catalyst*

In heterogenous catalysis, it is important to evaluate the recovery and reuse of the catalyst. RH-MW Zn–Al catalyst was reused, up to four cycles, under mentioned conditions. The results of reused catalysts are given in Table 5. It could be seen that the conversion of glycerol decreased in the fourth cycle. From the results it is clear that the deactivated catalyst can be rejuvenated by calcination followed by rehydration under microwave irradiation. Rejuvenated catalyst can be used in several more cycles.

3.10. *Reaction mechanism*

Based on the above studies a plausible reaction mechanism is proposed in Scheme 2. LDH (OH groups) act as base catalyst. Deprotonation of hydroxyl groups of glycerol leads to generation of alkoxy group as shown in the reaction mechanism. It readily attacks the electrophilic carbonyl group of DMC with the elimination of two methanol molecules.

4. Conclusion

The well known memory effect of thermally treated LDHs for regaining their original structure upon rehydration is demonstrated. Out of the four methods followed for regeneration of thermally treated as-synthesized Zn–Al–LDH, rehydration with MW radiations for 1 h exhibited a quick regeneration of most of its structure. The regenerated LDH also showed complete recovery in the activity for MW assisted base catalyzed synthesis of glycerol carbonate from glycerol and dimethyl carbonate. The efficiency of MW radiations in rehydration and reconstruction of the collapsed LDH structure is attributed to the polar nature of the water molecules and the catalyst surface complementing each other in interacting with the MW radiations for building up the structure. The deactivated catalyst can be rejuvenated by calcination followed by rehydration under microwave irradiation and can be further used repeatedly for GC synthesis.

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