Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Microwave rehydrated Mg-Al-LDH as base catalyst for the acetalization of glycerol

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

Chemistry Research Centre, Bangalore Institute of Technology, KR Road,

Bangalore 560 004, India

*Corresponding author: E-mail-bhatys@yahoo.com,

Tel.: +91 80 26615865; fax: +91 80 26426796

Abstract:

Acetalization of glycerol with aldehydes to form cyclic acetals is an industrially important reaction and is generally carried out using acid catalysts. Base catalysts such as LDH can bring about microwave assisted acetalization of glycerol and aldehydes to form 5-membered and 6-membered cyclic acetals. Among the different LDHs used, Mg-Al-LDH was found to exhibit maximum conversion of glycerol into 5-membered cyclic acetal. Modification of Mg-Al LDH involving calcination at 450^{o}C and subsequent microwave assisted rehydration showed improved glycerol conversion rate under similar reaction conditions. Rehydration of calcined Mg-Al-LDH by microwave irradiation was found to result in LDH regaining its layer structure with higher basicity possibly exposing more hydroxyl ions responsible for basicity. Multiple use of methanol washed spent catalyst showed good repeatability for conversion up to three cycles which subsequently showed a marginal decrease in the conversion. Further dehydration followed by rehydration of the spent LDH catalyst under microwave irradiation was found to rejuvenate the catalytic activity to its initial level.

Keywords: Mg-Al-LDH, glycerol, acetalization, rehydration, microwave irradiation

1. Introduction:

Glycerol (Gly) is a major by-product of biodiesel synthesis leading to large accumulation of crude glycerol. This necessitates the conversion of crude glycerol into valuable products. Some potential uses of glycerol include, synthesis of acrolein, ethanol, epichlorhydrin, production of citric and lactic acids, as components in anti-freezing agents and soaps, additives in fuels, composite materials and as cosmetic bonding agents. The different reaction procedures for conversion of glycerol to value-added chemicals reported in literature include oxidation, transesterification, dehydration, hydrogenolysis, pyrolysis, etherification, esterification, steam reforming, acetalization, and polymerization by catalytic processes [1]. Among these, the acetalization of glycerol is recognized as the most important process for the synthesis of green and commercially important chemicals from glycerol.

Glycerol reacts with aldehydes and ketones giving 1,3-dioxalane (5-membered) and 1,3-dioxane (6-membered) cyclic acetals which find industrial applications [2-6]. These cyclic acetals are used as precursors for the production of green platform compounds 1,3-propanediol and 1,3-dihydroxyacetone [7].

Acetalization of glycerol has been studied with various acid catalytic systems like H_2SO_4, $AlCl_3$, $FeCl_3$, $ZnCl_2$, p-TSA and HCl [8-11] in homogenous medium. Anchored silicontungstates on MCM-41, K10, supported metal oxides, heteropolyacids, zeolites, momtmorillonite, Amberlyst-15, mesoporous MoO_3/SiO_2, SBA-15, sulfated zirconia, Zr-SBA-16, ion exchange resins, nanocrystalline SnO_2-based solid acids, aluminium triflate grafted MCM-41, organo iridium derivatives, Hf-TUD-1, Zr-TUD-1, Sn-MCM-41, USY-2 , Mo and W-promoted SnO_2, mesoporous cellular foams (MCFs) modified by niobium or tantalum, acidic ionic liquids, TiO_2–SiO_2 mixed oxides and Ni–Zr supported on mesoporous activated carbon have been used as heterogeneous catalysts [12-32].

Layered double hydroxides (LDHs) are layered minerals and are also called anionic clays. These constitute a class of compounds with positively charged layers and to maintain the electrical neutrality possess interlayer anions. They are represented by general formula, $\left[M^{II}_{1-x}M^{III}_{x}(OH)_2\right]^{x+}.\left(X^{x-}_{x/q}\right)$, M representing layer cations and X interlayer anion. M^{II} and M^{III} represent divalent and trivalent metal ions such as Mg, Cu, Ni, Co, Zn and Al, Zr, Fe, Cr, Ga respectively, $\left(X^{x-}_{x/q}\right)$ represents interlayer anion of charge q such as CO_3^{2-}, Cl^-, NO_3^-, and SO_4^{2-}. A wide range of composition of LDH can be prepared by co-precipitation method. LDHs have potential applications such as adsorption materials, carriers for drugs, electrode modifiers and catalysts. LDH itself can be used as catalyst or can be calcined to get decomposed LDH containing mixture of mixed oxides. The decomposed LDH (mixed oxides) is known to regain its original layered structure through a structural memory effect upon rehydration.

There are many reports in the literature for the acetalization of glycerol with carbonyl compounds carried out by using various solid acid catalysts. To the best of our knowledge, use of base catalysts in the glycerol acetalization reaction has not received much attention in the literature. The main objective of the present investigation is to carry out acetalization of glycerol with different as synthesized, calcined and rehydrated LDH samples as catalysts with different aldehydes to produce cyclic acetals. The reactions have been conducted in presence of microwave irradiation with an intention to know the efficiency of acetalization and rehydration of the LDHs in presence of microwaves.

Heterogeneously catalyzed liquid phase organic reactions are usually carried out by conductive heating with an external heat source like heating in a hot air oven or oil bath. In this method, transfer of heat from source to reaction mixture depends on thermal conductivity of various materials which must be penetrated. This is a comparatively slow and inefficient method for transferring energy from the source into the reaction mixture. And also, reaction mixture is not uniformly heated, resulting in the temperature of the reaction vessel being higher than that of the reaction mixture. In contrast, in microwave irradiation, heat is directly transferred from the source to the reaction mixture by direct coupling of microwave energy with the molecules (solvents, reagents, catalysts) that are present in the reaction mixture. This produces more rapid, efficient, uniform internal heating of reaction mixture. The advantageous effects of microwave irradiation compared to conventional heating are mainly because of this in-core volumetric heating (Kappe et al.) [33].

2. Experimental section

2.1. Catalysts and chemicals

Glycerol AR grade, cinnamaldehyde, benzaldehyde, anisaldehyde, chlorobenzaldehyde, nitrobenzaldehyde, 1-pentanol, $Mg(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, $Cu(NO_3)_2.3H_2O$, $Co(NO_3)_2.6H_2O$, NaOH and Na_2CO_3 were procured from SD fine chemicals, and CDH chemicals India and used without purification.

2.2 Catalyst preparation

All the LDHs were prepared by co-precipitation method [34-38]. An aqueous solution of

Mg $(NO_3)_2.6H_2O$ (0.3 mole) and Al $(NO_3)_3.9H_2O$ (0.1 mole) were prepared and the above mixture was added drop wise into an alkaline solution mixture of Na_2CO_3 (0.23 mole) and NaOH (0.875 mole) at room temperature for 3 h with constant stirring. It was then allowed to age for 30 minutes at 80°C under microwave heating in a microwave reactor described below. The solid material obtained was centrifuged and washed thoroughly with hot water until the pH of the washing becomes 7.0. The washed material was dried at 120 °C for 12h. Similarly, LDHs of Zn-Al, Co-Al, Cu-Al were synthesized under microwave irradiation.

Synthesized Mg-Al LDH was calcined in air at 450 °C for 3 h. Calcination results in mixed metal oxide formation as shown by XRD patterns. Rehydration of decomposed catalyst samples were carried out under microwave irradiation. 5 g calcined samples were mixed with 100 ml of water, the mixture was subjected to microwave irradiation at 100 °C with continuous stirring for 2h in presence of nitrogen atmosphere. The irradiated mixture was cooled, centrifuged, the solid was separated and dried in hot air oven at 120°C. The rehydrated LDH was designated as RH-Mg-Al LDH.

2.3 Characterization

All the prepared catalyst samples, including the calcined and rehydrated ones, were characterized using different techniques viz. XRD, FTIR, and total basicity by benzoic acid titration and TPD-CO_2. The structural integrity of the catalysts was analysed by Powder X-ray diffraction patterns. The data were recorded with PAN analytical X'Pert PRO MPD X-ray diffractometer using graphite monochromatized Cu Kα radiation (λ= 1.5406 Ǻ) with step scanning at 0.020° per second and in the 2θ range of 4° to 80°.

The total basicity of LDH samples was estimated by benzoic acid titration method [39]. 0.5 g of LDH sample was dispersed in 5ml of toluene as solvent and stirred for 30 minutes. To the suspension, 5 drops of dilute phenolphthalein indicator solution were added and the suspension was titrated against 0.01M benzoic acid in toluene till the pink color of the indicator on the catalyst sample sharply disappears. The amount of benzoic acid consumed was used for the calculation of total basicity.

Temperature programmed desorption of (TPD-CO_2) was also done for the measurement of basicity of the catalyst. Pre-treatment of the catalyst samples was carried out in He flow at 300°C for 1h, and then cooled to 50°C prior to the adsorption of CO_2 at this temperature. The sample was flushed with He for 1h at 100°C to remove the physisorbed CO_2 from the catalyst surface. The desorption of CO_2 was measured by heating the sample from 100°C to 850°C at a heating rate of 10°C min^{-1} and the desorbed CO_2 was measured with a TCD detector [40].

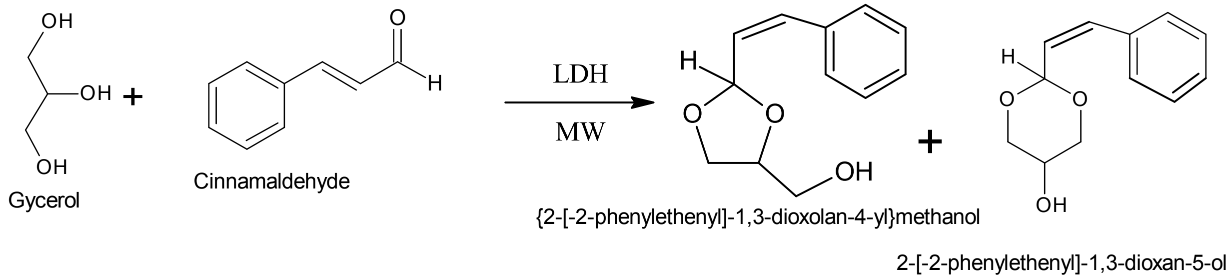
FTIR spectra of the catalyst samples were recorded on Shimadzu IR Affinity-1 spectrophotometer, in the range of 400-4000 cm^{-1} using the KBr pellet method.

2.4 Catalytic tests:

Microwave heating: Ten mmol of glycerol (Gly) and thirty mmol of cinnamaldehyde (CA) were mixed with 1g catalyst in a microwave reactor vessel with magnetic stirring. Reactor vessel was kept in microwave lab station 'START-S'. Variable power up to 1200W was applied by microprocessor-controlled single-magnetron system. Initial power of 900 W was applied for 1 minute to attain the reaction temperature of 140°C. The reaction temperature was then maintained for 59 minutes to achieve maximum conversion. The reaction mixture (scheme 1) was then cooled, followed by addition of 5ml of pentanol, stirred for about 20 minutes to extract adsorbed reactants and products. The used catalyst was separated by centrifugation and the filtrate was analysed in Chemito GC-1000 gas chromatograph with TR-WAX capillary column (30 m length, 0.32 mm thickness and 0.5μm internal diameter) attached with flame ionization detector. The products were analyzed and confirmed by GC-MS [41].

Conventional heating:

Same amount of catalyst and reactants were taken as in microwave heating in a 50ml autoclave placed in a hot air oven at 140°C for 2,4,8,14,24 hours. After the completion of the reaction, analysis was done as in microwave heating.



Scheme.1: Acetalization reaction of glycerol with cinnamaldehyde.

3. Results and discussion:

Figure 1 shows the powder X-ray diffraction patterns of Zn-Al, Mg-Al, Cu-Al and Co-Al as synthesized. Catalyst samples showed sharp and symmetric peaks at 2θ values 11°, 24° and 37° corresponding to the typical LDH reflections (003), (006) and (012) planes respectively.

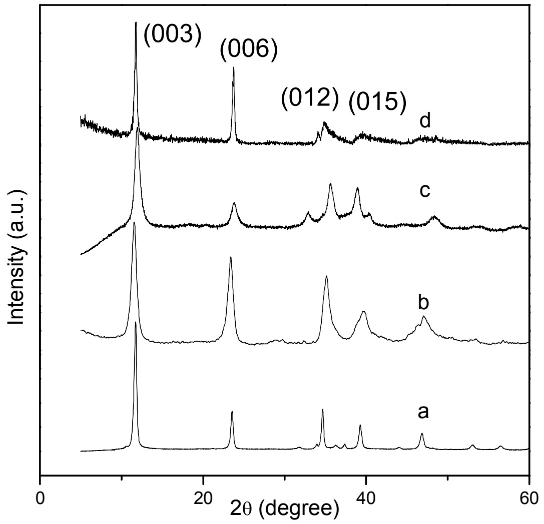


Fig.1 XRD pattern of different LDHs. (a) Zn-Al (b) Mg-Al (c) Cu–Al (d) Co-Al

The FTIR spectra of LDH samples (Fig.2) showed a broad, asymmetric peak around 3400 cm^{-1} generally ascribed to the OH groups attached to the metal ions in the brucite-like layer. The bending mode of interlayer water molecule was observed at 1640 cm^{-1} and the antisymmetric band at 1365 cm^{-1} corresponded to interlayer carbonate anion.

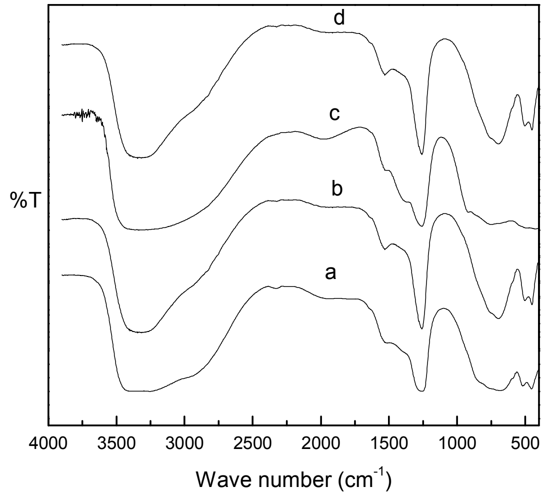
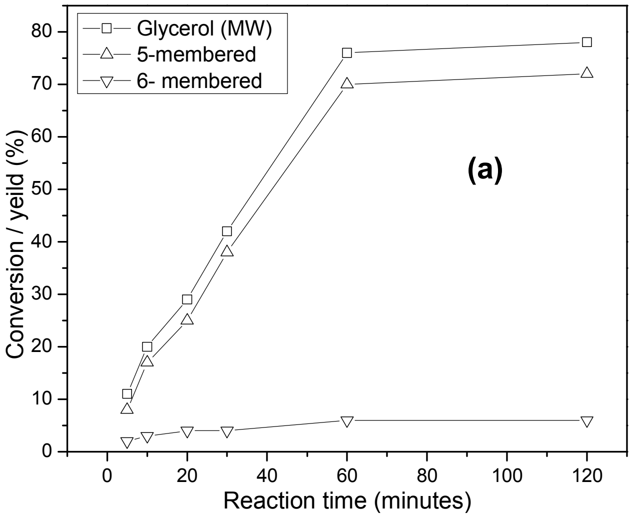


Fig.2. FT-IR Spectra of different LDHs (a) Zn-Al,(b) Mg-Al, (c) Cu-Al, (d) Co-Al

3.1 Comparison of Conventional and Microwave mode of heating:

The effects of variation of reaction conditions during conventional and microwave modes of heating on acetalization of glycerol with CA are compared in Fig.3 (a) and (b). Reaction time was varied from 5 to 120 min and 2 to 24 h under microwave and conventional heating respectively.



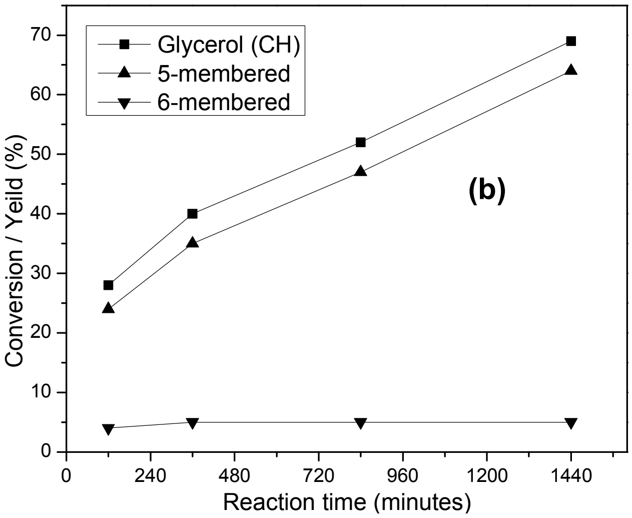


Fig.3 Acetalization of Gly with CA under (a) microwave and (b) conventional heating. Reaction condition: catalyst amount, 1 g; mole ratio Gly: CA, 1:3; temperature, 140^{0}C.

Under conventional heating, reaction proceeded very slowly and showed conversion of 68% in 24 h. On the other hand, under microwave heating, conversion of glycerol was 77% in 60 minutes. This is attributed to intensive, localized and uniform heating of reaction mixture by microwaves. Microwave irradiation processes are known to decrease reaction time from hours to minutes enhancing the rate of reaction [42]. In the present study, glycerol and cinnamaldehyde used as reactants for acetalization reaction gives higher rate of conversion under MW irradiation. The heating characteristics of a particular material (for example, a solvent) under microwave irradiation conditions are dependent on its dielectric properties. The ability of a specific substance to convert electromagnetic energy into heat at a given frequency and temperature is determined by the so-called loss factor tan d. This loss factor is expressed as the quotient tan d = e″/e′, where e″ is the dielectric loss, which is indicative of the efficiency with which electromagnetic radiation is converted into heat, and e′ is the dielectric constant describing the ability of molecules to be polarized by the electric field. A reaction medium with a high tan d value is required for efficient absorption and, consequently, for rapid heating [Kappe et al.]. In the present work, enhancement in the rate of product formation under microwave irradiation is attributed to relatively high tan d values of the reactants.

Furthermore, catalyst surface also plays a major role. In the absence of catalyst, though the reactants are polar, microwave radiations fail to initiate the reaction. Microwave irradiation, however, has been found by many workers to be more effective in initiating and bringing the reaction to equilibrium at a faster rate than the thermal radiation[43-54].

In the present work, the initiation involves the active base sites (-OH and –O-) attached to the Mg and Al ions which accept a proton from the glycerol molecule. Apparently, proton accepting property is influenced by the vibrational (thermal) and rotational (microwave) motions of both the active sites on the catalyst surface and the proton donating property of glycerol molecule. It appears that rotational motions in some way facilitate the removal of protons from the polar glycerol molecule than the thermal vibrations [55].

3.2 Catalyst Screening:

The results of glycerol acetalization with cinnamaldehyde over different LDHs at Gly : CA mole ratio of 1:3 at 140°C for 60 minutes under microwave heating are shown in Fig. 4. It can be observed that, among the different LDHs, Mg-Al showed a maximum conversion of 56% which is attributed to its higher basicity as determined by benzoic acid titration method (Table 1). All the LDH samples showed higher selectivity towards 1,3 dioxalane (5-membered) than 1,3 dioxane (6-membered) product with Mg-Al LDH exhibiting a maximum selectivity of 96% for the 5-membered cyclic acetal. Further studies were carried out with Mg-Al LDH through modification to achieve higher conversion and product yield.

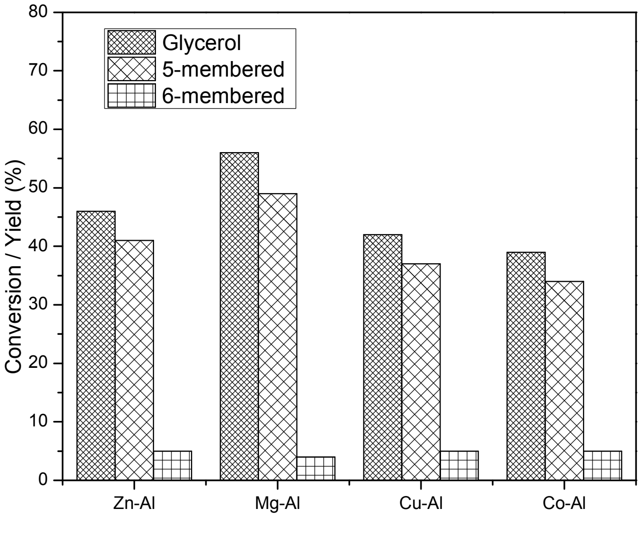


Fig.4 Acetalization of Glycerol with cinnamaldehyde (CA) with different LDH catalysts.
Reaction condition: reaction temperature, 140°C; mole ratio Gly:CA, 1:3; catalyst amount, 1g, reaction time, 60min; (MW)

Table.1 Basicity of as synthesized and modified LDH.

Catalyst	Basicity density (μmol/g)	% Conversion of of Gly
Zn-Al	112	46
Mg-Al	124	56
Cu-Al	105	42
Co-Al	98	39

3.3 Catalyst modification

LDHs are known to regain their structures upon calcination and rehydration. Rehydration of the calcined LDH samples is achieved by several methods. In the present study, rehydration by microwave irradiation and its effect on the catalytic activity of Mg-Al-LDH was studied. Mg-Al LDH catalyst was calcined at 450 ^{o}C for 3 h, and then rehydrated under microwave irradiation in N_2 atmosphere at 100 ^{o}C for 2h. Fig 5 shows the XRD patterns of the Mg-Al-LDH, calcined Mg-Al-LDH and the RH-Mg-Al-LDH. The XRD pattern of calcined sample (Fig 5b) showed the reflections which are ascribed to the oxides of Mg and Al and that of the rehydrated sample (Fig 5c) shows all the peaks corresponding to Mg-Al-LDH. Acetlization results are graphically represented in Fig. 6 for the as synthesized, calcined and the rehydrated samples. The catalytic activity of RH-Mg-Al-LDH for acetalization of glycerol showed increased conversion of 77 % with 96% selectivity towards 5-membered cyclic acetal.

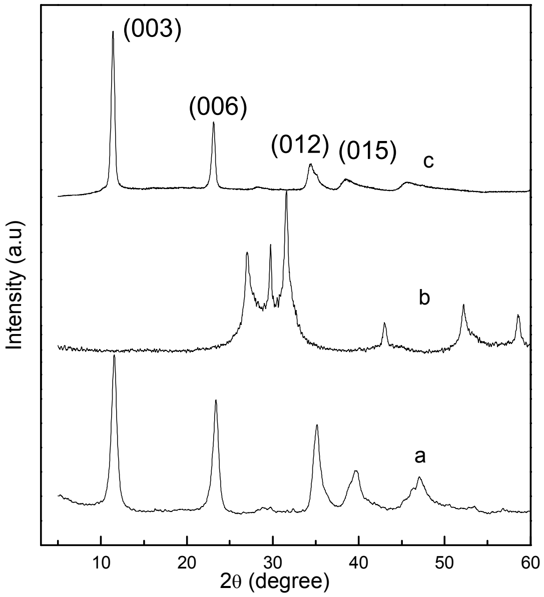


Fig.5 XRD pattern of (a) as-synthesized LDH (b) Calcined LDH (c) RH-Mg-Al LDH

In the calcined sample of Mg-Al LDH absence of peaks at 11°, 24° and 37° indicates collapse of the LDH structure and formation of oxide phase at 32°, 43° and 52° respectively (Fig.5b). RH-Mg-Al LDH showed similar reflections of LDH as synthesized (Fig. 5 a and c).

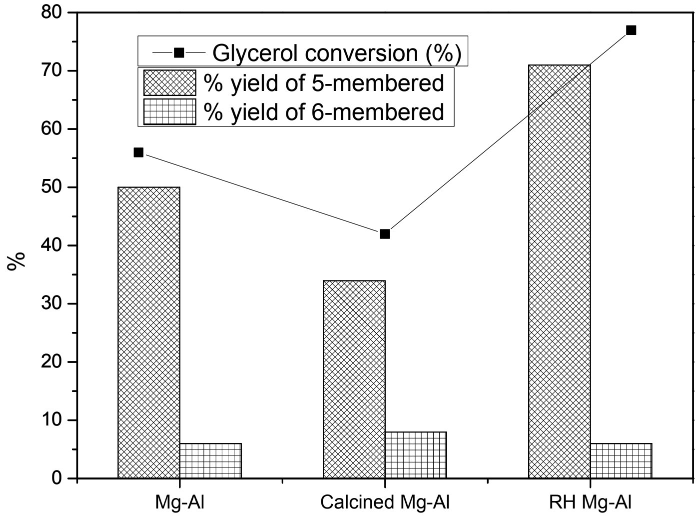


Fig.6. Acetalization of glycerol with different catalysts.
Reaction condition: reaction temperature, 140°C; mole ratio Gly:CA, 1:3; catalyst amount, 1g, reaction time, 60min; (MW).

In order to optimize the reaction conditions, various parameters like effect of reaction temperature, catalyst amount, mole ratio of the reactants and reaction time for acetalization of Gly with CA over RH-Mg-Al LDH were studied. Under optimized reaction conditions the reactions were carried out with 1 g RH-Mg-Al-LDH, Gly: aldehyde; ratio of 1:3 at temperature 140°C with microwave energy 900W for 1h. Results for various aldehydes are shown in Table.2. Acetalization of glycerol with cinnamaldehyde showed higher activity (about 77% conversion) with 96 % selectivity for 1,3-dioxalane and 4% for 1,3-dioxane. Higher reactivity of cinnamaldehyde is attributed to the presence of conjugated carbonyl group. Methoxy group in the anisaldehyde causes less conversion because of its electron donating nature rendering the carbonyl carbon less electrophilic.

Table.2. Acetalization of glycerol with various aldehydes.

Carbonyl Compounds	Conversion (%)	1,3-dioxalane (% Yield)	1,3-dioxane (% Yield)
Cinnamaldehyde	77	71	6
Benzaldehyde	56	51	8
Anisaldehyde	44	34	10
chloro-benzaldehyde	52	43	9
nitro-benzaldehyde	59	49	7

Reaction condition: reaction temperature, 140^{o}C; mole ratio Gly : CA, 1:3; catalyst amount, 1g, reaction time, 60min; RH-Mg-Al-LDH, MW

3.4 Basicity studies

The increased activity of the rehydrated sample is attributed to the recovery of its layered structure with increase in accessibility to significant extent of OH^- ions present on the surface and edge sites of the catalyst sample. This is supported by the TPD CO_2 profiles of as-synthesized and RH-Mg-Al LDH [Fig 7 and 8].

The deconvoluted TPD profiles of catalyst samples showed three peaks. The total basicity and basic strength distribution of the catalysts samples were assigned based on peak appeared with respect to temperature. The peak at 400-580^{o}C, related to desorption of CO_2 from the weak basic strength sites. The desorption peaks at 620-790^{o}C and 800-900^{o}C are attributed to medium and strong basic strength sites respectively. In the as synthesized sample of LDH, desorption peak at 400-580^{o}C is more intense compared to other peaks responsible for weak basic sites. However, after modification through rehydration, the intensity of this peak decreased and the peaks at 620-790^{o}C and 800-900^{o}C becomes more intense compared to the LDH sample as synthesized. The latter can be attributed to the partial conversion of weak basic sites into medium and strong basic sites. This could be due to the redistribution of OH groups during the rehydration process. Even the basicity as measured by the benzoic acid titration for the rehydrated sample was appreciably higher (181µmol/g) than the LDH sample as synthesized (124 µmol/g).Our observations are in line with study done by Alvarez et al., for rehydration of Mg-Al LDH under ultrasonication resulting in increased basicity of the LDH sample [56].

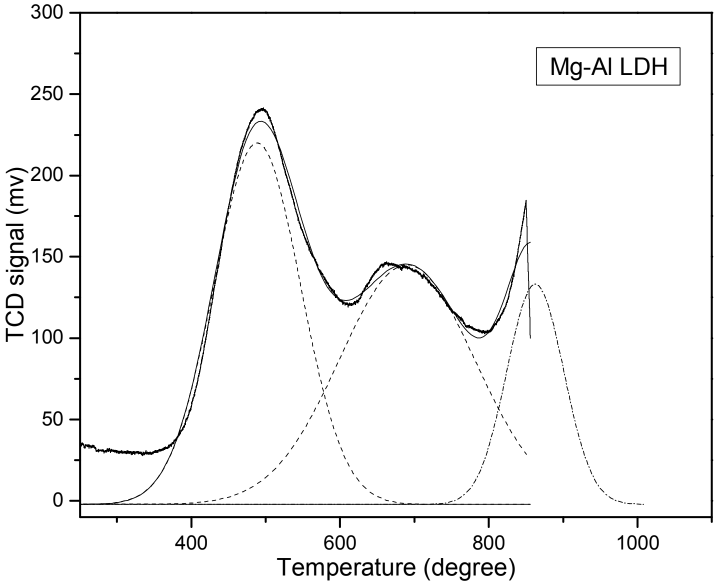


Fig.7 TPD CO_2 profile of Mg-Al LDH

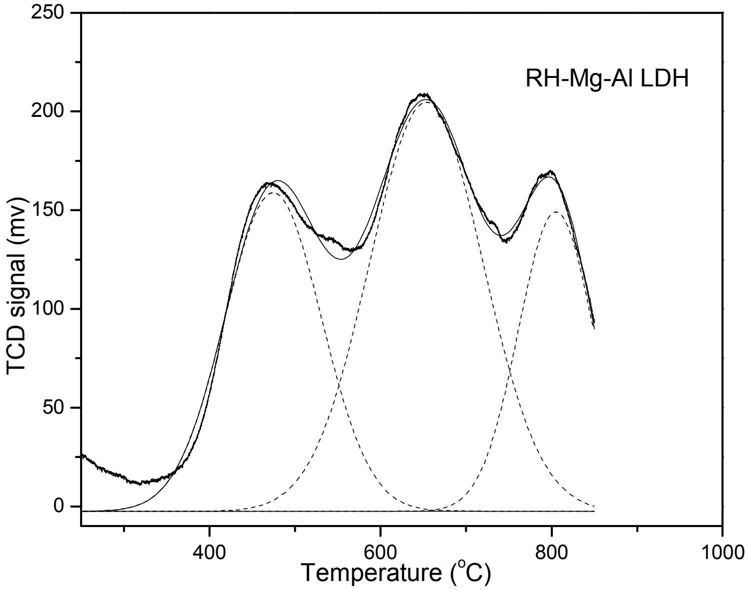
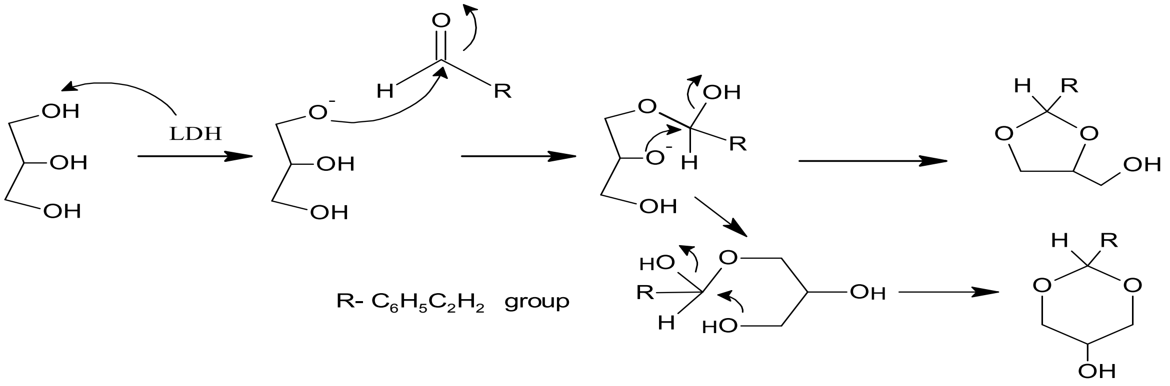


Fig.8 TPD CO_2 of RH-Mg-Al LDH

3.5 Plausible reaction mechanism:

According to literature, all the acetalization of glycerol reactions are carried out by using various Bronsted and Lewis solid acids with different carbonyl compounds [8-32]. In presence of solid acids, acetalization takes place through protonation of carbonyl oxygen of carbonyl compound followed by the nucleophilic addition of hydroxyl groups of the glycerol forming glycerol acetals through dehydration.

Present study shows that base catalysts such as LDHs are also effective in bringing out formation of glycerol acetals. Mg-Al LDH acts as base catalyst by removing the hydroxyl hydrogen of glycerol leading to generation of alkaoxy nucleophile as shown in scheme 2. It then readily attacks the available electrophilic carbonyl carbon of aldehyde forming cyclic acetals through dehydration.



Scheme.2 Possible reaction mechanism of LDH catalyzed acetals formation

3.6 Regeneration of spent catalyst:

To study the catalyst deactivation, RH-Mg-Al LDH was reused several (three) times under optimized conditions. After carrying out the reaction the used catalyst was separated by centrifugation after every cycle. It was then washed with methanol (5ml) and acetone to remove the adsorbed reactants and products on the surface of the catalyst, dried at 100°C for 2 h and then used for fresh batch of reaction. The structure of the catalyst was found to be unchanged after its use which was confirmed by XRD. Further the catalyst was used multiple times, the results of which are shown in the table.3. Conversion was found to decrease slightly for the fourth cycle. The partially deactivated catalyst was calcined at 450°C for 3 h and then rehydrated under MW irradiation in presence of N_2 atmosphere (2h, 100°C). The results (Table 3) show that the catalyst, apparently, regains its original layered structure with its initial activity (*Fifth cycle).

Table.3 Catalyst recyclability Studies

Cycles	Glycerol Conversion (%)
First cycle	77
Second cycle	77
Third cycle	76
Fourth cycle	64
Fifth cycle*	76

Reaction condition: reaction temperature, 140^{o}C; mole ratio Gly:CA, 1:3; catalyst amount, 1g, reaction time, 60min; (MW) *Fourth cycle catalyst sample calcined and rehydrated.

4. Conclusion: Acid catalyzed acetalization of glycerol into value added products can be brought about by base catalysts such as LDHs with equal ease. LDHs, being solid base catalysts, produce 5- and 6- membered acetals when glycerol is reacted with aldehydes. Hydroxyl groups, apparently present on the surface and edge sites of LDHs, act as basic sites for the acetalization. Calcination of LDH, leads to corresponding mixed metal oxides resulting in the loss of LDH structure. Microwave assisted rehydration is found to be very effective in restoring LDH structure of the calcined sample with improved basicity. The results show an improvement in the rate of acetalization by rehydrated Mg-Al-LDH compared to as-synthesized LDH sample. This is attributed to enhanced basicity after rehydration as supported by the TPD-$CO_{2.}$

Acknowledgement: The authors would like to thank the Principal and Governing Council of Bangalore Institute of Technology for the facilities provided and VTU for financial support.

References:

[1] C.H. Zhou, J. N. Beltramini, Y.X. Fan, G.Q. Lu, *Chem.Soc. Rev.*, 2008, 37, 527–549.

[2] P. Ferreira, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, *Appl. Catal. B: Environ.,* 2010, 98, 94–99.

[3] M.B. Guemez, J. Requies, I. Agirre, P.L. Arias, V.L. Barrio, J.F. Cambra, *Chem. Eng. J.,* 2013, 228, 300–307.

[4] C. Crotti, E. Farnetti, N. Guidolin, *Green Chem.,* 2010, 12, 2225–2231.

[5] X. Honga, O.M. Giverona, A.K. Kolaha, A. Orjuelab, L. Peereblooma, C.T. Liraa, D.J. Millera, *Chem. Eng. J.*, 2013, 222, 374–381.

[6] H. Serafim, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, *Chem. Eng. J.* 2011, 178 , 291-296.

[7] A.J. Showler, P.A. Darley, *Chem. Rev.* 1967, 67, 427–440

[8] G. Cherkaev, S.A. Timonin, G.F. Yakovleva, L. Shutikova, A.S. Mikhailova, L. D. Shapiro,

SU1, 1987, 337.

[9] M.J. Ashton, C. Lawrence, J.A. Karlsson, K.A.J. Stuttle, C.G. Newton, B.Y.J. Vacher, S. Webber, M.J. Withnall, *J. Med. Chem.*, 1996, 39, 4888–4896.

[10] T. Vu Moc, P. Maitte, *Bull. Soc. Chim. Fr.,* 1975, 9, 2558–2560.

[11] R.P. Radheshyam, V. Sumit, Jadhav, H.C. Bajaj, *Chem. Eng. J*, 2014, 235, 61-66

[12] B. Shubhangi, Umbarkar, T. V. Kotbagi, A.V. Biradar, R. Pasricha, J. Chanale, M.K. Dongare, A.S. Mamede, C. Lancelot, E. Payen,; *J. Mol. Catal. A Chem,* 2009, 310, 150-158

[13] P. Manjunathan, S.P. Maradur, A.B. Halgeri, G.V. Shanbhag, *J. Mol. Catal. A: Chem,* 2015, 396, 47-54

[14] A. Corma, M.J. Climent, H. García, J. Primo, *Appl. Catal.* 1990, 59, 333–336.

[15] R. Ballini, G. Bosica, B. Frullanti, R. Maggi, G. Sartori, F. Schroer, *Tetra. Lett.,* 1998, 39, 1615–1618.

[16] I. Rodriguez, M.J. Climent, A. Corma, S. Iborra, V. Fornés, *J. Catal.,* 2000, 192,441–447.

[17] M.J. Climent, A. Corma, A. Velty, M. Susarte*, J. Catal.,* 2000, 196, 345–351.

[18] L.T. Shuang, L.S. Hui, L.J. Tai,L.H. Zhang, *J. Chem. Res. Synop.,* 1997, 286–287.

[19] M. Csiba, J. Cleophax, A. Loupy, J. Malthete, S.D. Gero, *Tetra. Lett.,* 1993, 34,1787–1790.

[20] C. H. Zhou, H. Zhao, D. S. Tong, L. M. Wu & W. H. Yu, *Cat.Rev: Sci & Eng.*, 2013, 55, 369–453.

[21] M. J. Climent, A. Corma , S. Iborra, *Green chem- Rev.,* 2014,16, 516-547

[22] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner., 2008, 10, 1-140.

[23] H. Hartati, M. Santoso, S.Triwahyono, D. Prasetyoko., *Bulletin of Chem. Reac. Eng & Cat,* 2013, 8, 14-33.

[24] L. P. Ozorio, R. Pianzolli, M. B. S. Mota, C. J. A. Mota., *J. Braz. Chem. Soc.*, 2012, 23, 931-937.

[25] C. N. Fan, C. H. Xu, C. Q. Liu, Z. Y. Huang, J. Y. Liu, Z. X. Ye, *Reac. Kinet. Mech.Cat.,* 2012, 107, 189–202.

[26] T. E. Souza, M. F. Portilho, Priscila M. T. G. Souza, P. P. Souza, L.C. A. Oliveira, *Chem Cat.Chem*., 2014, 6, 2961-2969.

[27] C. Crotti, E. Farnetti, N. Guidolin, *Green Chem.*, 2010, 12, 2225-2231.

[28] L. Li, T. I. Koranyi, B. F. Sels, P. P. Pescarmona, *Green Chem.*, 2012, 14, 1611-1619.

[29] B. Mallesham, P. Sudarsanam, G. Raju, B. M. Reddy, *Green Chem.*, 2013,15, 478-489.

[30] B. L. Wegenhart, M. M. Abu-Omar, *Inorg. Chem*., 2010, 49, 4741–4743.

[31] B. Wang, Y. Shen, J. Sun, F. Xu, R. Sun, *RSC Adv*., 2014, 4, 18917-18923.

[32] M.Barbasiewicz, M. Makosza, *Org. Lettt.*, 2006, 8, 3745-3748.

[33] C.O. Kappe, *Angew. Chem. Int. Ed.,* 2004, 43, 6250–6284.

[34] P. Benito, I. Guinea, F.M. Labajos, J. Rocha, V. Rives, *Micropor. Mesopor. Mater.,* 2008, 110, 292–302.

[35] W.T. Reichle, *Solid State Ion.,* 1986, 22.1, 135–141.

[36] S. Velu, C.S. Swamy, *Appl. Catal. A.,* 1996, 145, 141-153.

[37] S. Kannan, S. Velu, V. Ramkumar, C.S. Swamy, *J. Mat. Sci.,* 1995, 30, 1462-1468

[38] W. Feitknecht, M. Gerber, Helvetica, *Chimica Acta ,* 1942, 25, 106–137.

[39] J.R.O. Gomez, O.G.J. Aberasturi, B.M. Madurga, A.P. Rodrıguez, C.R. Lopez, L.L.Ibarreta, J.T. Soria, M.C.V. Velasco, *Appl. Catal. A.,* 2009, 366, 315-321.

[40] M. Malyaadri, K. Jagadeeswaraiah, P.S. Prasad, N. Lingaiah, *Appl. Catal. A.,* 2011, 401, 153-157

[41] N.J. Venkatesha, B.S. Jai Prakash, Y. S. Bhat, *Catal. Sci. Technol.,* 2015, 5, 1629-1637

[42] S. Ramesh, B.S. Jai Prakash, Y.S. Bhat, *Appl. Clay. Sci.*, 2010, 48, 159–163.

[43] R. Gedye, F. Smith, K. Westaway, H. Ali, L. Laberge, R. Rousell, *Tetrahedron Lett.,* 1986, 27, 279–282

[44] R.J. Giguere, T.L. Bray, S.M. Duncan, G. Majetich, *Tetrahedron Lett.*, 1986, 27, 4945–4948.

[45] M.B. Gawande, S.N. Shelke, R. Zboril, R.S. Varma, *Acc. Chem. Res.,* 2014, 47, 338–1348.

[46] S.A. Galema, *Chem. Soc. Rev*., 1997, 26, 233–238.

[47] P. Lidström, J. Tiemey, B. Wathey, J. Westman, *Tetrahedron.,* 2001, 57, 9225–9283.

[48] L. Perreux, A. Loupy, *Tetrahedron.,* 2001, 57, 9199–9223.

[49] C.O. Kappe, Angew. *Chem. Int. Ed.,* 2004, 43 6250–6284

[50] C.O. Kappe, D. Dallinger, *Mol. Divers.,* 2009, 13, 71–193.

[51] A. De La Hoz, A. Diaz-Ortiz, A. Moreno, *Chem. Soc. Rev.*, 2005, 34, 164–178.

[52] N.E. Leadbeater, M. Marco, *Angew. Chem. Int. Ed.,* 2003, 42, 1407–1409

[53] R.K. Arvela, N.E. Leadbeater, M.S. Sangi, V.A. Williams, P. Granados, R.D. Singer, *J. Org. Chem.,* 2005, 70, 161–168

[54] D. Michael, P. Mingos, D.R. Baghurst, *Chem. Soc. Rev.*, 1991, 20, 1–47.

[55] N.J. Venkatesha, B.M. Chandrashekara, B.S. Jai Prakash, Y.S. Bhat, *J. Mol. Catal. A: Chem,* 2014, 392, 181-187

[56] M.G. Alvarez, R.J. Chimentao, F. Figueras, F. Medina, *Appl. Clay Sci.,* 2012, 58, 16-24

Figures:

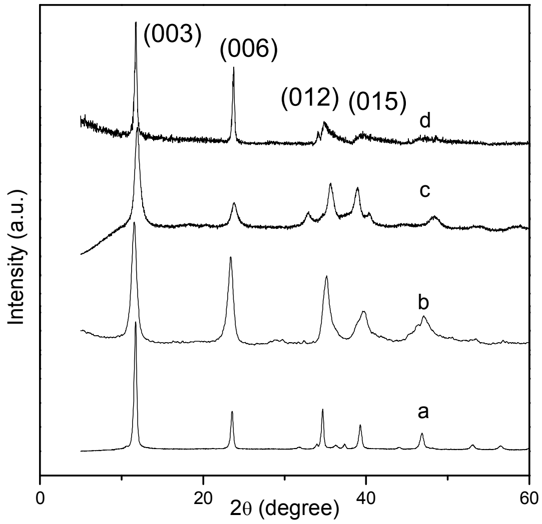


Fig.1 XRD pattern of different LDHs. (a) Zn-Al (b) Mg-Al (c) Cu–Al (d) Co-Al

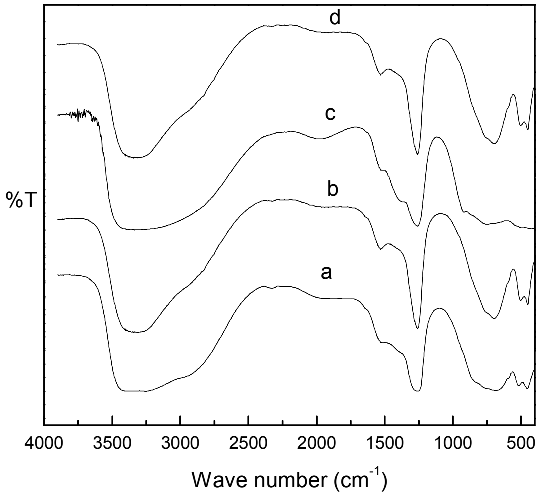


Fig. 2. FT-IR Spectra of different LDHs (a) Zn-Al,(b) Mg-Al, (c) Cu-Al, (d) Co-Al

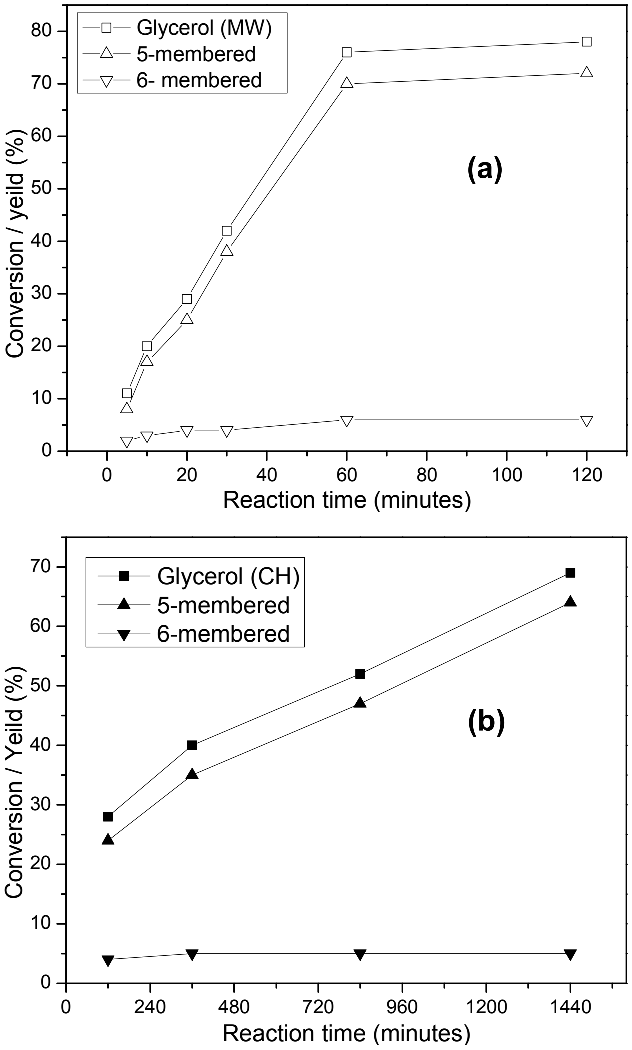


Fig.3 Acetalization of Gly with CA under (a) microwave (MW) and (b) conventional (CH) heating. Reaction condition: catalyst amount, 1 g; mole ratio Gly: CA, 1:3; temperature, 140^{0}C.

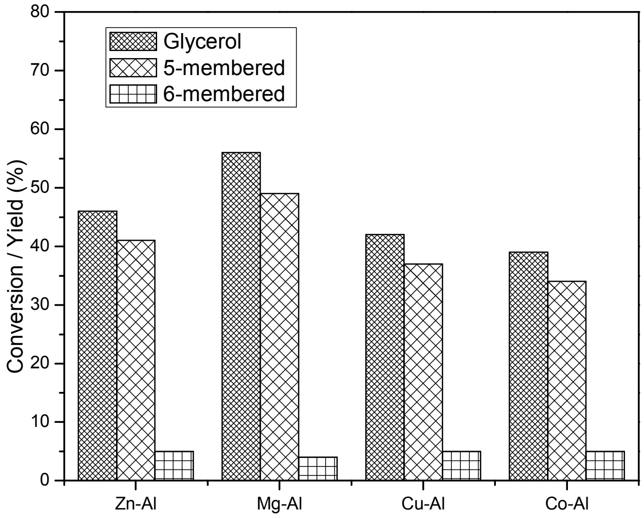


Fig.4 Acetalization of Glycerol with cinnamaldehyde(CA) with different LDH catalysts. Reaction condition: reaction temperature, 140°C; mole ratio Gly:CA, 1:3; catalyst amount, 1g, reaction time, 60min; (MW)

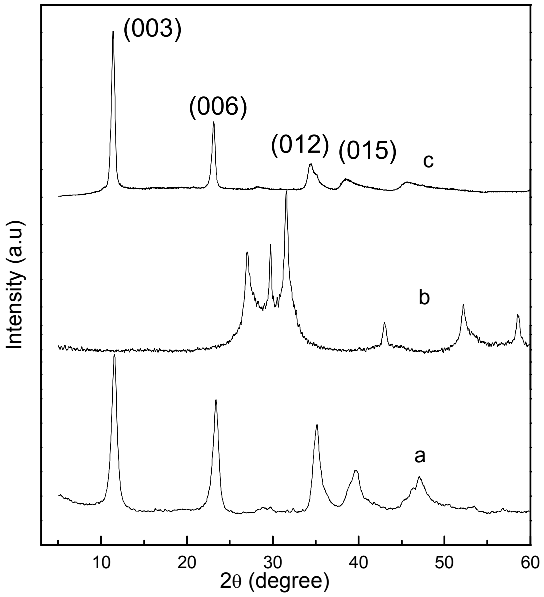


Fig.5 XRD pattern of (a) as-synthesized LDH (b) Calcined LDH (c) RH-Mg-Al LDH

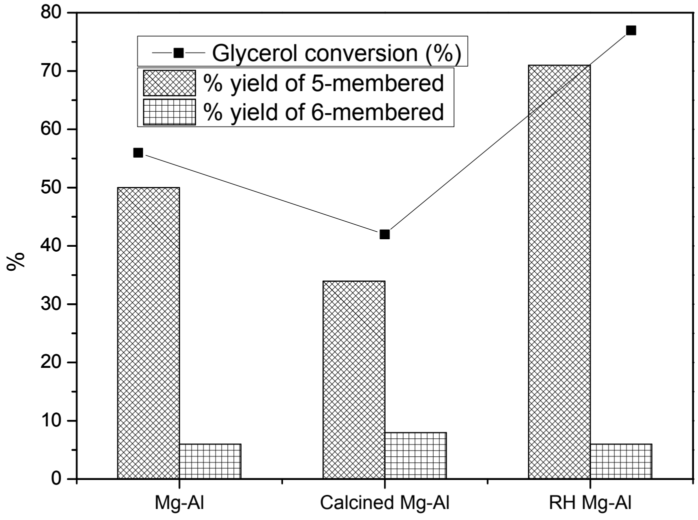


Fig.6. Acetalization of glycerol with different catalysts.
Reaction condition: reaction temperature, 140^{o}C; mole ratio Gly:CA, 1:3; catalyst amount, 1g, reaction time, 60min; (MW).

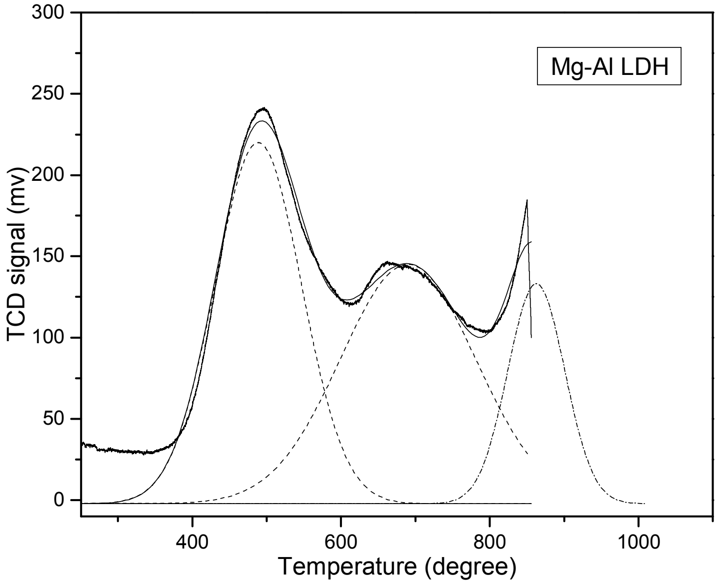


Fig.7 TPD CO_2 profile of Mg-Al LDH

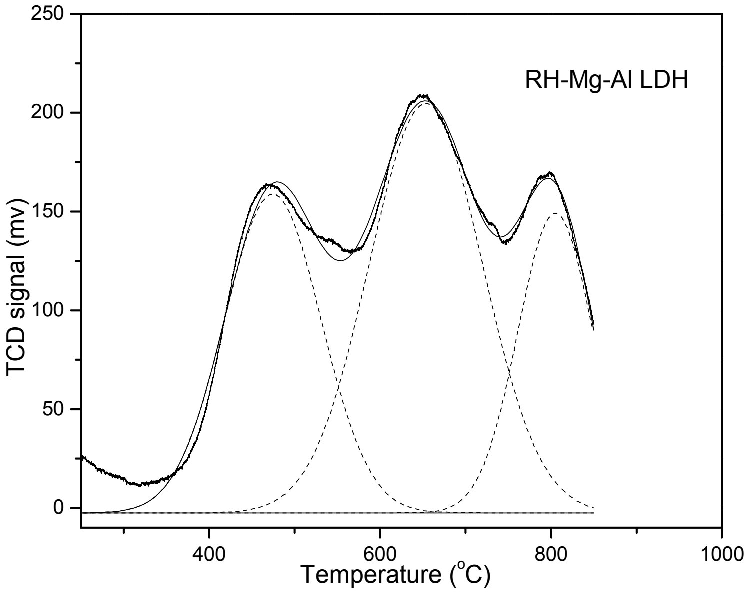


Fig.8 TPD CO_2 of RH-Mg-Al LDH

Tables:

Table.1 Basicity of as synthesized and modified LDH.

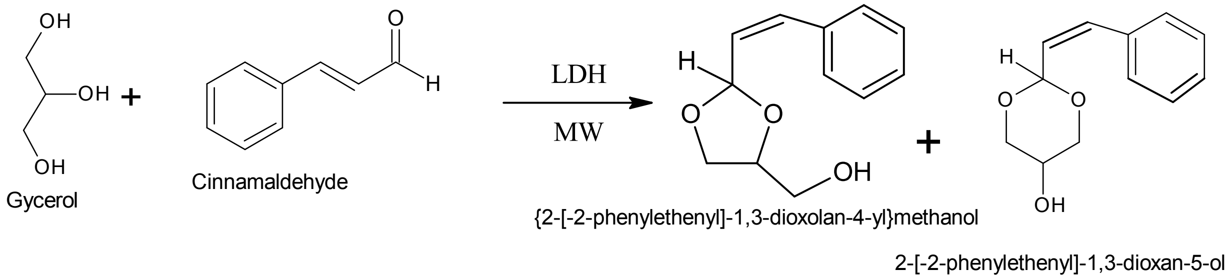
Catalyst	Basicity density (µmol/g)	% Conversion of of Gly
Zn-Al	112	46
Mg-Al	124	56
Cu-Al	105	42
Co-Al	98	39

Table.2. Acetalization of glycerol with various aldehydes.

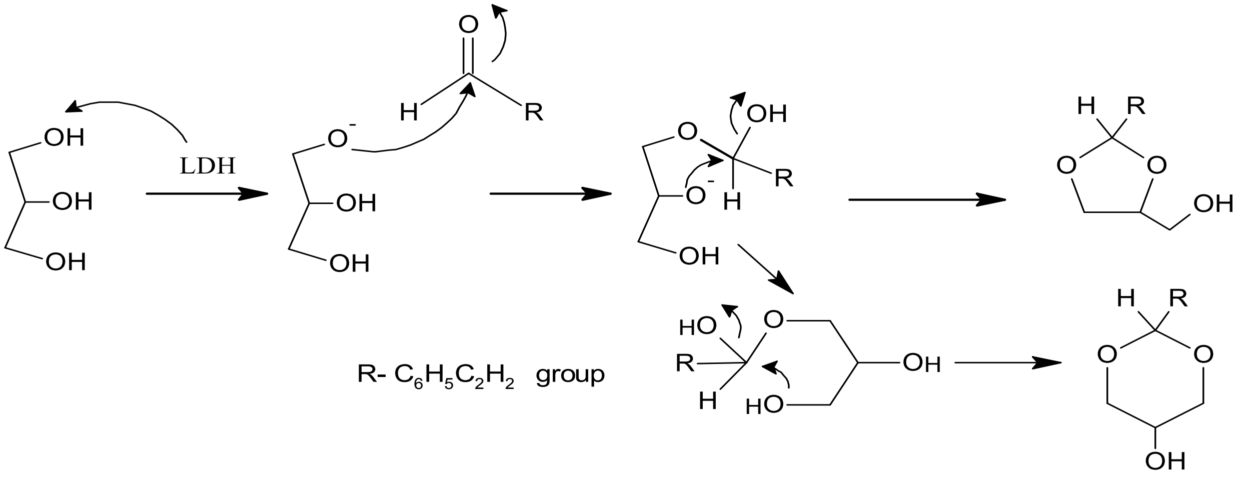
Carbonyl Compounds	Conversion (%)	1,3-dioxalane (% Yield)	1,3-dioxane (% Yield)
Cinnamaldehyde	77	71	6
Benzaldehyde	56	51	8
Anisaldehyde	44	34	10
chloro-benzaldehyde	52	43	9
nitro-benzaldehyde	59	49	7

Reaction condition: reaction temperature, 140^{o}C; mole ratio Gly : CA, 1:3; catalyst amount, 1g, reaction time, 60min; RH-Mg-Al-LDH, MW

Schemes:



Scheme.1: Acetalization reaction of glycerol with cinnamaldehyde.



Scheme.2 Possible reaction mechanism of LDH catalyzed acetals formation