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# Double bond isomerization of ethyl linoleate and vegetable oils to conjugated derivatives over LDH supported ruthenium catalyst

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MgAl-layered double hydroxides (LDHs) with different Mg/Al atomic ratios were prepared by co-precipitation and studied for the catalytic double bond isomerization of ethyl linoleate. Among them, MgAl4-LDH (Mg/Al atomic ratio of 4.0) showed maximum conversion (15%) and yield of isomerized products (9%) at 90 °C in presence of 1-butyl 3-methyl imidazolium chloride using toluene as solvent in 12 h. The catalytic performance improved significantly upon supporting 5% Ru on MgAl4-LDH that gave 42% conversion with 29% yield of isomerized product under similar conditions. However, while reusing, the catalyst showed a reduced yield (18%). $CO_2$-TPD studies revealed an increase in the amount of weak basic sites along with a decrease in the amount of high strength medium basic sites is probably the reason for this drop. Under the optimized conditions, vegetable oils were also converted to their corresponding conjugated oils though with lesser conversion and yields.

## Introduction

Due to the established drawbacks associated with traditional petroleum products, vegetable oils have gained interest for the production of valuable chemicals which are non-toxic and renewable in nature.[1] Vegetable oils/fats (lipids) have 50-70% of linoleic acid (LA), a long chain fatty acid (C18) in their triglyceride structure which has two *cis* double bonds located on carbon 9 and 12 respectively (non-conjugated positions). Conjugated linoleic acids (CLA; double bonds located on carbon 9 and 11 or 10 and 12) is the positional isomer of LA that has either cis (or) trans configuration (or) both located along the carbon chain.[2] CLA are well known food additives due to their health beneficial properties.[3] Biosynthesis of CLA in humans is insignificant. Hence, CLA has to be supplied to human body through diet. Synthetic CLA derivatives (Fig. 1) that are commercially available contains mixtures having equimolar amounts of c9,t11 and t10,c12 CLA with traces of t9,t11 and t10,t12 CLA. The presence of conjugated carbon-carbon double bonds in natural oils (CLA rich oils) is extremely important for their industrial application for the preparation of bio-based polymers, drying agents, and as coating agents in paints and inks.[3a]

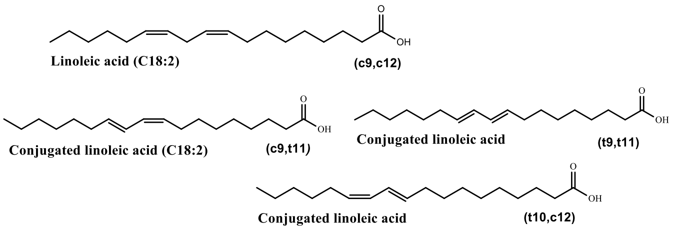

**Fig. 1** Structure of linoleic acid and conjugated linoleic acids

Possible synthetic routes of CLA/CLA rich oils are by the double bond isomerization of lipid derived linoleic acids/vegetable oils (or) dehydration of ricinoleic acid/castor oil by chemical (or) enzymatic methods.[4] Industrially, CLA are prepared by the double bond isomerization of linoleic acid using homogenous base catalysts at higher temperature under $N_2$ atmosphere.[5] Drawbacks such as difficulty in separation and non-reusability have created interest to look for alternative catalytic pathway to produce conjugated linoleates derivatives (fatty derivative/vegetable oils). CLA can be prepared from linoleates by consecutive reactions such as isomerization, saponification and neutralization with acid. Competitive reactions such as hydrolysis, transesterification and saponification make the same process not suitable for vegetable oils. Though few homogeneous metal complexes were studied for the isomerization reaction,[6] effective recovery of the complex and limited choice of solvent to solubilize the complexes are detrimental while using such systems. In order to overcome these problems, in recent years biphasic/multiphase reactions have gained interest for the preparation of CLA derivatives.[7]

In order to make the processes more eco-friendly, heterogeneous catalysts are targeted for the preparation of CLA derivatives. Mostly heterogeneous catalysts having transition metals are largely used for conjugating the double bonds in polyunsaturated fatty acids either in presence of hydrogen or in alcohols (transfer hydrogenation). Preferences are given for precious metals like Ru/Rh/Au- (or) base metal such as Ni containing catalysts for the preparation of these conjugated derivatives.[2,5,8] However, heterogeneous catalysts require harsher reaction conditions and often create a competition with hydrogenation and isomerization thereby make these processes more complicate. The concentration of hydrogen plays a key role in this reaction wherein controlled concentration leads to the formation of half-hydrogenated product and in turn results isomerized product. However, when used at higher concentration, instead of resulting half-hydrogenated product, complete hydrogenation occurs resulting saturated fatty acids/undesired hydrocarbons. Though, Ru/C is the most studied catalyst, in recent years studies are extended to different supports containing Ru catalysts for the isomerization reaction. It was also found that supports play a main role in changing the acidic/basic characteristics and diffusivity of the reactant molecule which are considered to be important factors for CLA preparation.[9]

Layered double hydroxides (LDHs; also referred as hydrotalcite-like (HT-like) materials) and their modified forms are well known solid catalysts and supports for many organic transformations.[10] Very recently Chen et al. reported the preparation of CLA from linoleic acid using oxides derived from ruthenium grafted-MgAl HT-like precursor as catalyst at high temperature (180 °C) under inert conditions and achieved 65% conversion.[11] Developing a catalytic system for the preparation of CLA (or) their derivatives from low quality feedstock and vegetable oils is the challenging area of research. Herein, we report the double bond isomerization of technical grade ethyl linoleate (EL) and vegetable oils to their corresponding conjugated derivatives over MgAl-LDH supported ruthenium as solid catalyst under mild reaction conditions (90 °C, atmospheric pressure and 12 h).

## Experimental

### Materials

The technical grade ethyl linoleate ($\geq$ 65%), $RuCl_3.xH_2O$, BMImCl ($\geq$98%), OMImCl ($\geq$ 97%), TBA ($\geq$98.5%) and TPAOH (~1.0 M) were purchased from Sigma-Aldrich. $BMImBF_4$ (99%), $BMImPF_6$ (99%) were purchased from Solvent Innovation. The ethyl linoleate has ~ 70% of linoleate species and ~ 20% of oleate species. Toluene was purchased from SD fine chemicals, India. All chemicals were used as such as without any further purification. The vegetable oils were purchased from local market. The fatty acid compositions of vegetable oils (ESI† Table S1) were determined by GC-MS after converting them into fatty acid methyl esters (Shimadzu, QP 2010). Technical grade ethyl linoleate is taken here as a model molecule for double bond isomerization reaction as most of the vegetable oils studied have almost similar fatty acid composition as that of this compound.

### Synthesis of LDH materials

MgAl-LDHs were synthesized by the co-precipitation under low supersaturation.[12] The samples are named as MgAlx-LDH where ‘x’ stands for nominal Mg/Al atomic ratio. Ru loaded LDHs were prepared through wet impregnation method in which MgAl4-LDH was dispersed into aqueous $RuCl_3$ soln. (different ratios) and stirred well for 3 h. Finally, the collected solid was washed well with water till the pH became neutral and denoted as y% Ru/MgAl4-LDH, where ‘y’ stands for wt.% of Ru. The as-synthesized LDHs were used as catalysts in this study, except otherwise explicitly stated.

### Characterization techniques

Elemental analysis of the synthesized materials was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES) on a Perkin Elmer, optima 2000 DV. Powder X-ray diffraction (PXRD) of the materials was carried out on a Rigaku Miniflex II system using Cu Kα radiation. The operating voltage and current were 30 kV and 15 mA, respectively. The step size was 0.04° with a step time of 0.2 s. Identification of the crystalline phases was made by comparing with the JCPDS files. FT-IR spectra were recorded in a Perkin-Elmer Spectrum-GX instrument, using KBr pellets; 100 scans were recorded with a nominal resolution of 4 $cm^{-1}$, which are accumulated and averaged to improve the signal-to-noise ratio. For FT-IR analysis of liquid samples, chloroform was used as solvent. In the case of EL treated ionic liquids, known quantities of EL and ionic liquids were taken in chloroform. Thermogravimetric (TG) analysis was done on Mettler Toledo instrument under nitrogen atmosphere from 50 to 800 °C at a heating rate of 10 °C/min. Basicity of the catalysts was measured using $CO_2$ temperature programmed desorption (TPD) on a Micromeritics Auto-Chem 2920 instrument.[13] $^1H$ NMR analysis was done using Bruker Avance DPX 200 instrument with the operating frequency of 200 MHz. For each analysis 16 scans were carried out with the flip angle of 90°.

### Isomerization reaction

Isomerization reactions were carried out in a 25 ml round-bottom (R.B.) flask fitted with water cooled condenser. Calculated amount of EL/oil was taken along with 5 ml of toluene as solvent. To that, calculated amount of catalyst and BMImCl were added. Then the R.B. flask was kept in an oil bath at 90 °C for 12 h with vigorous stirring (1100 rpm; Schott SLR stirrer, Germany to avoid mass transfer effects; temperature difference was ±2 °C between the oil bath and the reaction medium). After the reaction, the mixture was centrifuged to separate the catalyst. Water was added to remove BMImCl and the organic layer was extracted in hexane and mixture was subjected to rotary evaporation under reduced pressure. The solvent free sample (15-30 µL) was dissolved in $CDCl_3$ (500 µL) and analyzed by $^1H$ NMR using TMS as internal standard. The details about the analysis of product mixture are given in ESI† Fig.S1 & S2.

## Results and discussion

### Material characterization

Powder X-ray diffractions (PXRD) of the as-synthesized materials are shown in Fig. 2. All the materials exhibited pure hydrotalcite-like phase (JCPDS: 41-1428) without any X-ray detectable impurity phase. The materials show sharp and symmetric reflections at lower diffraction angles (peaks at $2\theta$= 11, 24 and 35° respectively) ascribed to the diffraction from the basal planes (003), (006) and (009). The broad asymmetric reflections at higher diffraction angles (peaks at $2\theta$= 38, 46 and 60° respectively) ascribed to the diffraction from the planes (105), (108) and (110).

The Fourier transformed infrared (FT-IR) spectra of all the as-synthesized materials are shown in ESI† Fig. S3. The main

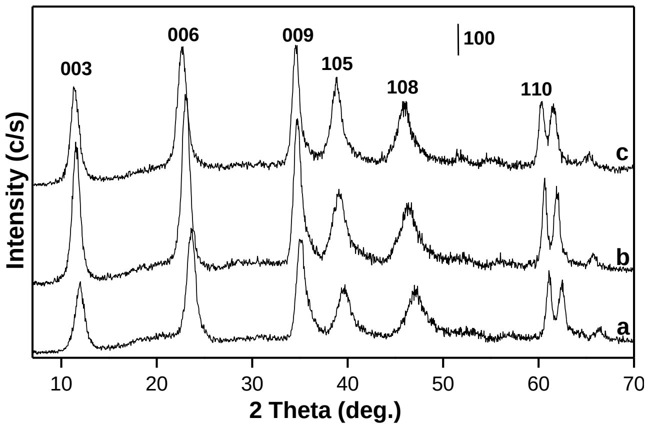

**Fig. 2** PXRD patterns of (a) MgAl2-LDH, (b) MgAl3-LDH, (c) MgAl4-LDH

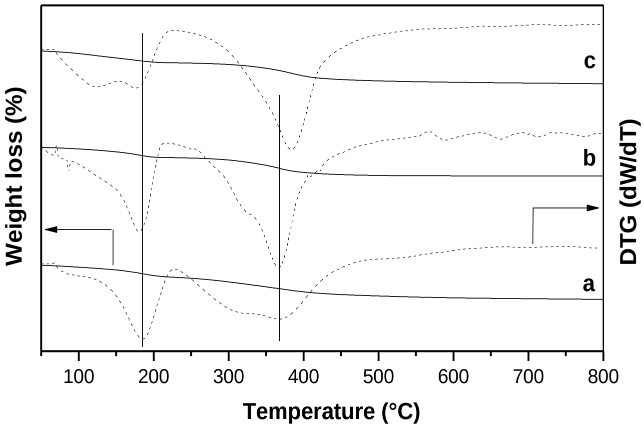

**Fig. 3** TG and differential thermogravimetric (DTG) profile of (a) MgAl2-LDH, (b) MgAl3-LDH, (c) MgAl4-LDH

absorption band around 3500-3600 cm$^{-1}$ is attributed to the hydrogen bonding stretching vibrations of the -OH group in the brucite like layer. The carbonate anion in the symmetric environment in the interlayer is characterized by $D_{3h}$ symmetry with three IR active absorption bands at 1350-1380 cm$^{-1}$ ($\nu_3$), 850-870 cm$^{-1}$ ($\nu_2$) and 670-690 cm$^{-1}$ ($\nu_4$). All as-synthesized materials showed the presence of these carbonate vibrations. Band appeared around 1650 cm$^{-1}$ corresponds to the bending vibration of water molecules. The elemental chemical analysis and lattice parameters of the materials along with the calculated formula are given in the ESI† Table S2. The Mg/Al ratios in the solids nearly matched well with the starting solutions and slight variation may be due to preferential precipitation/solubility variation of the hydroxides of the cations.[14]

### Catalytic reactions of MgAl-LDHs

Double bond isomerization of EL was studied over MgAl-LDHs as catalyst in presence of 1-butyl 3-methyl imidazolium chloride (BMImCl) using toluene as solvent at 90 °C for 12 h and the results are given in Table 1. Initially, studies were performed at 110 °C at which loss of solvent was observed. Hence, the temperature was reduced and fixed at 90 °C for all catalytic measurements. Blank reaction (reactant and solvent) resulted 8% conversion with 3% yield of isomerized products. Though, conversion is same while varying Mg/Al nominal ratio in LDH material, higher yield of isomerized products (15%) was obtained with MgAl4-LDH as catalyst. It may be mentioned here for clarity that in some cases the conversion value did not match with the sum of the yield of both products (isomerized and hydrolysed) as the calculation for the yield considers conjugated protons formed from both ester and hydrolysed derivatives. The reason for the formation of higher amount of hydrolysed products is possibly due to the presence of structurally different water molecules in MgAl4-LDH, as inferred from the well-defined first weight loss in TG and their differential (Fig. 3) profile, generally attributed to the physisorbed and structural/intercalated water molecules.[15] It is well known that BMImCl is basic and has propensity to trap moisture thereby facilitates the hydrolysis reaction. Thus, the presence of water molecules in as-synthesized LDH and hygroscopic nature of ionic liquid cooperatively contribute to the formation of hydrolyzed products along with the desired product. Further increase in the reaction time (48 h) while using MgAl4-LDH catalyst gave 32% hydrolyzed product indicates longer reaction time is favourable for hydrolysis rather than for

**Table 1.** Catalytic activity of MgAl-LDHs[a]

| Catalyst | Conversion (%) | Yield (%) | | Surface area (m$^2$/g) | Pore volume (cm$^3$/g) |
|---|---|---|---|---|---|
| | | Isomerized products | Hydrolyzed products | | |
| Blank | 8 | 3 | 0 | - | - |
| MgAl2-LDH | 15 | 9 | 3 | 105 | 0.20 |
| MgAl3-LDH | 15 | 9 | 2 | 150 | 0.29 |
| MgAl4-LDH | 15 | 15 | 10 | 115 | 0.23 |
| MgAl4-LDH[b] | 44 | 9 | 32 | - | - |
| MgAl4-LDH[c] | 13 | 8 | 5 | - | - |
| Without catalyst | 10 | 2 | 2 | - | - |
| Without ionic liquid | 10 | 3 | 8 | - | - |

[a]EL = 250 mg, Toluene = 5 ml, BMImCl = 40 wt.% w.r.t. EL, Catalyst = 20 wt.% w.r.t. EL, Temp. = 90 °C, Time = 12 h; [b]48 h; [c]Reconstructed LDH (Preparation method is given in ESI†).

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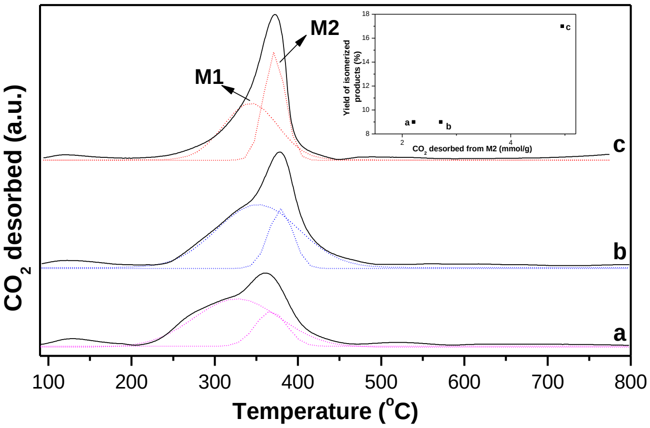

**Fig. 4** $CO_2$-TPD profiles of (a) MgAl2-LDH, (b) MgAl3-LDH, (c) MgAl4-LDH; Inset: correlation between high strength medium basic sites (M2) of catalysts with yield of isomerized products

the desired isomerization reaction. Incidentally, reaction performed using reconstructed MgAl-LDH showed 13% conversion with 8 and 5% yield of isomerized and hydrolysed products respectively. Reaction without catalyst (or) without ionic liquid gave 2 (or) 3% yield of isomerized product respectively, similar to blank reaction and these results suggests possible co-operative effect of the catalyst along with ionic liquid to obtain the desired isomerized product. Basicity is one of the main parameters that might enhance the isomerization efficiency of the catalysts. In order to find the relation between the basicity with the yield of isomerized product, $CO_2$ temperature programmed desorption (TPD) studies were done for MgAl-LDHs.

### $CO_2$-TPD studies

$CO_2$-TPD profiles of MgAl-LDH catalysts are given in Fig. 4. All materials exhibited less intense and high intense desorption peaks in the temperature range of 100-170 °C and 230-420 °C corresponds to desorption from weak and medium strength basic sites respectively. MgAl2-LDH and MgAl4-LDH exhibited a weak (less intense) and broad desorption peak at 460-570 °C corresponds to desorption from strong basic sites that were not present in MgAl3-LDH. Upon increasing the Mg/Al atomic ratio from 2 to 4, the intensity of the desorption peak of the medium strength basic sites increased and became sharper suggests more and nearly uniform basic sites are present in MgAl4-LDH material.

Peak maximum temperature, the amount of $CO_2$ desorbed from each kind of basic sites along with the total and intrinsic basicity are given in Table 2. Though, strong basic sites are not present in MgAl3-LDH, its catalytic activity was nearly similar to MgAl2-LDH suggests dispensable nature of these sites for this reaction. If one were to look carefully at the profile of medium strength basic sites, it is apparently clear that at least two different basicity sites with varying strengths could be seen and are categorized here as M1 and M2 where M1 are low strength medium basic sites where desorption occurs in the temperature window of 220-330 °C and M2 are high strength medium basic sites where desorption occurs in the range 330-430 °C. A decrease in the strength of weak basic sites was found when Mg/Al atomic ratio increased with concomitant increase in the yield of the isomerized product possibly suggests the presence of these sites facilitate the undesired reactions and thus MgAl4-LDH that had the lowest amount of these sites exhibited the highest yield of isomerized product.

Furthermore, if one were to look M2 basic sites (Table 2), a reasonable correlation could be made between the amount of to enable this reaction, a combination of absence of weak basic sites that possibly promote undesired reactions such as hydrolysis and the presence of high strength medium basic sites (M2 sites) are necessary to obtain high yield of isomerized product. Using MgAl4-LDH as the preferred catalyst, amount of BMImCl was varied to find the role of ionic liquid for this reaction and the results are given in ESI† Table S3. An increase in the amount of ionic liquid increased the conversion of the reaction; but the yield of isomerized products were optimum up to 40 wt.% of ionic liquid (with respect to EL) and thereafter remained the same. Common basic compounds such as tributylamine (TBA) and tetrapropylammonium hydroxide (TPAOH) gave higher conversion namely 63 and 25% respectively, however witnessed with poor yield of isomerized product, and with many undesired products along with hydrolysed products.

### Catalytic activity of some of the commercial catalysts

Catalytic activity of MgAl4-LDH was compared with commercially available catalysts such as alumina, metal oxides for the double bond isomerization of EL and the results are given in Table 3. Basic catalysts such as basic alumina and MgO gave around 15% conversion with 7% yield of isomerized

**Table 2.** $CO_2$-TPD results of MgAl-LDHs

| Catalyst | Weak | | Medium | | Strong | | Total $CO_2$ desorbed (mmol/g) | Intrinsic basicity (mmol/m$^2$)[a] |
|---|---|---|---|---|---|---|---|---|
| | $T_1$ (°C) | $CO_2$ desorbed (mmol/g) | $T_2$ (°C) | $CO_2$ desorbed (mmol/g) | $T_3$ (°C) | $CO_2$ desorbed (mmol/g) | | |
| MgAl2-LDH | 132 | 0.61 | 361 | 10.55 *(8.33&2.21)*[b] | 484 | 0.82 | 11.97 | 0.11 |
| MgAl3-LDH | 127 | 0.37 | 381 | 12.32 *(9.61&2.71)*[b] | - | - | 12.69 | 0.09 |
| MgAl4-LDH | 122 | 0.34 | 373 | 11.52 *(6.57&4.95)*[b] | 477 | 1.1 | 12.95 | 0.11 |

[a] Intrinsic basicity is calculated as total $CO_2$ desorbed per unit surface area; [b] $CO_2$ desorbed from low strength (M1) and high strength medium basic sites (M2).

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**Table 3.** Catalytic activity of commercial catalysts[a]

| | Catalyst | Conversion (%) | Yield (%) | |
|---|---|---|---|---|
| | | | Isomerized products | Hydrolyzed products |
| *Base catalysts* | MgAl4-LDH | 15 | 15 | 10 |
| | Basic alumina[b] | 17 | 7 | 0 |
| | MgO[c] | 15 | 7 | 0 |
| | CaO[d] | 46 | 2 | 36 |
| *Acid catalysts* | Acidic alumina[b] | 6 | 2 | 2 |
| | Sulphated zirconia[d] | 0 | 0 | 0 |
| *Other catalysts* | Neutral alumina[b] | 19 | 6 | 3 |

[a]EL = 250 mg, Toluene = 5 ml, BMImCl = 40 wt.% w.r.t. EL, Catalyst = 20 wt.% w.r.t. EL, Temp. = 90 °C, Time = 12 h; [b]Purchased from Sd fine, India Ltd.; [c]$MgCO_3$ calcined at 500 °C/5 h; [d]$CaCO_3$ calcined at 700 °C/5 h; [d]Gifted from Dr. B.Tyagi's research group, CSIR-CSMCRI.

products without hydrolyzed products. Though, CaO gave higher conversion of 46%, it ended mainly with hydrolyzed products. Acidic alumina gave 6% conversion with 2% yield of isomerized product. Interestingly, sulphated zirconia did not show any activity for this reaction. Neutral alumina gave 6% yield of isomerized product. These results indicate that basic catalysts are active for this reaction than acidic catalysts. Among the catalysts studied MgAl4-LDH showed higher activity for the double bond isomerization reaction and was taken as parent/support material for further modification.

### Catalytic reactions of MgAl4-LDH supported Ru catalysts

In order to further increase the yield of isomerized products and having known that ruthenium is an active catalyst for isomerization,[2,5,8c,8e,16] it was supported on MgAl4-LDH through impregnation at different loadings and were studied for this reaction (Table 4). Inductively coupled plasma optical emission spectrometry (ICP-OES) results of 5% Ru/MgAl4-LDH revealed that only 2.6% Ru was loaded on the LDH support and for 0.5% and 1% Ru/MgAl4-LDHs were 0.1 and 0.16 % of Ru respectively. An increase in the % of Ru loading increased the conversion of EL and the yield of isomerized products ($^1H$ NMR given in ESI† Fig.S4). A maximum conversion of 42% with the yield of 29% was obtained with the 5% Ru loaded MgAl4-LDH. Interestingly, this catalyst did not give hydrolysed products. TG-DTG (ESI† Fig. S5) profile of this catalyst showed the presence of one kind of water molecules that might not involve/facilitate the hydrolysis reaction. The higher activity of the material is probably due to high dispersion of ruthenium on the LDH surface.[17] It is known that ruthenium is highly active for double bond isomerization reaction due to the presence of free d-orbitals that can interact with π-bonds of linoleic acid and also activate the adjacent C-H bond present in it.[8e]

Oxides derived through calcination of 5% Ru/MgAl4-LDH showed 38% conversion with 22% yield of isomerized product which is comparatively lesser that as-synthesized 5% Ru/MgAl4-LDH. Commercially available Ru/C and Ru/$Al_2O_3$ catalysts gave 10% yield of isomerized products with the conversion of 8 and 25% respectively. These results suggest the influencing role of support on the yield of the desired product. For comparison purpose, catalytic activity of commercially available Rh/$Al_2O_3$ was also studied which gave 9% yield of isomerized product with 10% conversion indicates the superiority of Ru catalysts for the preparation of isomerized products under the studied conditions. Subsequently, 5% Ru/MgAl4-LDH was chosen as the active catalyst for further

**Table 4.** Catalytic activity of Ru containing catalysts[a]

| Catalyst | Conversion (%) | Yield (%) | |
|---|---|---|---|
| | | Isomerized products | Hydrolyzed products |
| 0.5% Ru/MgAl4-LDH | 6 | 2 | 3 |
| 1% Ru/MgAl4-LDH | 17 | 2 | 7 |
| 5% Ru/MgAl4-LDH | 42 | 29 | 0 |
| 5% Ru/MgAl4-CLDH[b] | 38 | 22 | 0 |
| 5% Ru/C | 8 | 10 | 2 |
| 5% Ru/$Al_2O_3$ | 25 | 10 | 3 |
| 5% Rh/$Al_2O_3$ | 10 | 9 | 0 |
| 5% Ru/MgAl4-LDH[c] | 23 | 13 | 11 |
| 5% Ru/MgAl4-LDH[d] | 35 | 6 | 24 |
| 5% Ru/MgAl4-LDH[e] | 42 | 1 | 37 |

[a]EL = 250 mg, Toluene = 5 ml, BMImCl = 40 wt.% w.r.t. EL, Catalyst = 20 wt.% w.r.t. EL, Temp. = 90 °C, Time = 12 h; [b]Calcined at 500 °C for 5 h in air; [c]$BMImBF_4$; [d]$BMImPF_6$; [e]OMImCl.

studies. Time variation studies were done and the results are given in ESI† Table S4. Increase in the reaction time increased the conversion of EL and yield of isomerized products wherein maximum conversion and yield of isomerized products was achieved in 12 h and hence chosen for further studies. Reactions carried out lower temperatures (25, 45 and 75 $^{o}$C) showed lesser conversion (18-25%) with higher yield of hydrolysed products (5-15%).

### Catalytic activity in different ionic liquids

Different ionic liquids such as 1-butyl-3-methyl imidazolium tetrafluoroborate ($BMImBF_4$), 1-butyl-3-methyl imidazolium hexafluorophosphate ($BMImPF_6$) and 1-methyl-3-octyl imidazolium chloride (OMImCl) were screened for this reaction under the optimized conditions (Table 4). Both 1-butyl-3-methyl imidazolium ionic liquids gave lesser yield of isomerized product with moderate conversion than BMImCl. The variation in the activity could be due to variation in the hydrophobicity of these ionic liquids[18] which in turn have influence on the yield of hydrolysis products. $BMImPF_6$ has lesser interaction with water molecules present in the system and therefore showed a higher yield of hydrolysed product than $BMImBF_4$. Further, as the chain length increases from butyl to octyl in the case of alkyl methylimidazolium ionic liquids hydrophobicity increases[19] while the catalytic activity in OMImCl although showed similar conversion (42%) as that of BMImCl, however gave 37% yield of hydrolysed products.

To unravel such variations, $^1$H NMR analysis of the mixtures of EL with ionic liquids was carried out and are given in ESI† Fig. S6. EL treated with BMImCl clearly indicated the influence on the double bond in EL as evidenced by the change in the intensity ratio of the proton peaks appeared at 5.4-5.2 ppm while the same was not observed for EL treated with OMImCl. Further, the peak appeared at 4.3 ppm in the case of mixture of EL with OMImCl suggests strong interaction with $–OCH_2$ protons of EL that facilitates the formation of hydrolysed products. FT-IR analysis further supported NMR results where a significant change in the intensity and position of the bands was observed at ~2925 and ~2850 cm$^{-1}$ corresponding to asymmetric stretching band of C-H in $CH_2$ and –C=C in EL in presence of BMImCl (ESI† Fig. S7) while such change was not seen with OMImCl. Formation of new bands in the spectra is likely due to the contribution from ionic liquids.

Further, TG-DTG analysis was done for the used catalysts performed in presence of ionic liquids after first cycle (ESI† Fig. S8). It clearly showed the loss of water molecule in the catalyst for the reaction carried out in OMImCl which may facilitate the formation of hydrolysed products. In addition, temperature for the second weight loss, associated with structural decomposition, shifted to lower values indicates structural collapse (or) loss in crystallinity of the catalyst for the reaction performed in OMImCl. PXRD of the fresh and used catalysts conducted in presence of ionic liquids after first cycle are given in Fig. 5. Complete structural loss (as the sample became nearly amorphous) was seen for the catalyst for the reaction performed in OMImCl while LDH phase was retained for the recovered catalyst for the reaction performed in BMImCl. FT-IR studies corroborated the structural loss as elucidated by the disappearance of the characteristic band of carbonate appear around 1370 cm$^{-1}$ for the used catalyst for the reaction carried out in presence of OMImCl after first cycle (ESI† Fig. S9).

### Stability of the catalyst

In order to find the stability of the catalyst, appropriate amount of the catalyst was taken in toluene and stirred well at 90 ºC for 12 h. After recovering the catalyst, the supernatant solution was mixed with calculated amount of EL and BMImCl and kept at 90 ºC for 12 h to assess homogeneous contribution, if any. It showed 14% conversion of EL with 5% yield of isomerized

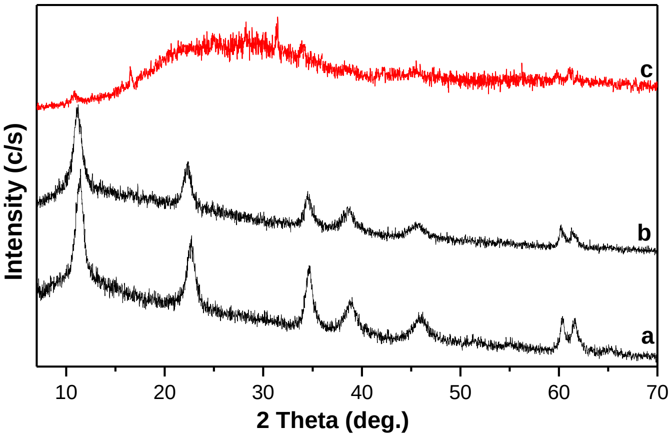

**Fig. 5** PXRD patterns of fresh and recovered catalysts (a) 5% Ru/MgAl4-LDH, (b) 'a' after first cycle in BMImCl, (c) 'a' after first cycle in OMImCl

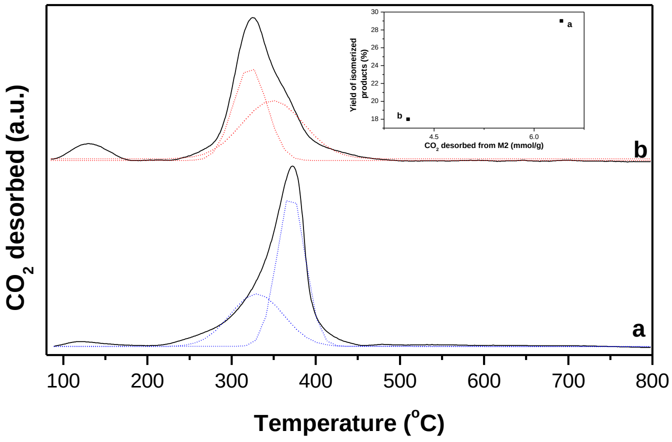

**Fig. 6** $CO_2$-TPD profiles of (a) 5% Ru/MgAl4-LDH, (b) 'a' after first use; Inset: correlation between high strength medium basic sites (M2) of fresh and used catalysts with yield of isomerized products

**Table 5.** $CO_2$-TPD results of fresh and used catalysts

| Catalyst | Weak | | Medium | | Total $CO_2$ desorbed (mmol/g) | Intrinsic basicity (mmol/$m^2$)[a] |
|---|---|---|---|---|---|---|
| | $T_1$ (°C) | $CO_2$ desorbed (mmol/g) | $T_2$ (°C) | $CO_2$ desorbed (mmol/g) | | |
| 5% Ru/MgAl4-LDH | 125 | 0.29 | 373 | 10.68 *(4.27&6.41)*[b] | 10.97 | 0.15 |
| Recovered catalyst | 131 | 0.73 | 335 | 8.74 *(4.63&4.11)*[b] | 9.46 | 0.19 |

[a]Intrinsic basicity is calculated as total $CO_2$ desorbed per unit surface area; [b]$CO_2$ desorbed from low strength (M1) and high strength medium basic sites (M2).

products suggests minor contribution possibly through leaching of metal ions during the reaction. However, ICP-OES analysis of the product mixture inferred insignificant leaching of metals from LDH (<0.2% Mg & Al; Ru% is below the detection limit). These results confirm the stability of the supported catalyst.

### Recycle studies

In reusability studies, after the completion of the first cycle of the isomerization reaction, the reaction mixture was collected by decantation. In the case of EL isomerization, catalyst stuck on the walls of the flask during reaction while using BMImCl in the reaction medium (the same was not observed in the case of isomerization of vegetable oils). Collected catalyst was washed well with toluene to remove the oily material and kept in an oven for drying at 110 °C for 1-2 h. Then, the fresh reactant mixture (EL and BMImCl) was added to the same flask and the reaction was carried out under the optimized reaction conditions. Though the catalyst showed almost similar conversion during second cycle, the yield of isomerized product decreased to 18 from 29%. The conversion of EL decreased to 17% with 4% yield of isomerized products during the third run (ESI† Table S5). Both fresh and used catalysts showed similar PXRD pattern (Fig. 5 a & b) as well as FT-IR spectra (ESI† Fig. S9 a & b) suggest the retention of phase after first cycle. Surface area of fresh and used catalysts were 75 and 51 m²/g respectively suggests the reduced activity of the catalyst during the second run is probably due to decrease in the surface area.

In order to discern relationship with the basicity, $CO_2$-TPD studies were done for fresh and used catalysts and the TPD profiles are given in Fig. 6. Both the catalysts exhibited less intense desorption peaks in the range of 100-180 °C and high intense desorption peak in the range of 250-450 °C which corresponds to weak and medium strength basic sites respectively. Peak maximum temperature, the amount of $CO_2$ desorbed from each kind of basic sites along with total and intrinsic basicity are given in Table 5. The amount of weak basic sites increased for the used catalyst (0.73 mmol/g) compared to fresh catalyst (0.29 mmol/g) suggest the possible occurrence of undesired reaction as explained earlier and thus in turn results reduced yield of the isomerized products. Furthermore, a significant change in amount of medium strength basic sites was observed for the recovered catalyst whose peak maxima also shifted to lower temperature. Though, $CO_2$ desorbed from low strength medium basic sites (M1) were almost similar for both fresh (4.27 mmol/g) and used (4.63 mmol/g) catalysts, a noticeable change was observed in high strength medium basic sites (M2) between them (fresh catalyst - 6.41 mmol/g; used catalyst - 4.11 mmol/g). It is thus evident that a decrease in the amount of high strength medium basic sites leads an activity drop for the used catalyst (inset in Fig. 5). To summarize, Ru species present in the catalyst augmented by the basic functionality of LDH support along with cooperative contribution of ionic liquid in tandem are responsible for the activity for both fresh and reused catalysts wherein presence of relatively larger amount of weak basic sites and reduced amount of high strength medium basic sites are the reasons for the decreased yield of isomerized products for the used catalyst.

### Reaction with oils

After the successful optimization of double bond isomerization in EL using 5% Ru/MgAl4-LDH as solid catalyst, work was extended for some vegetable oils and the results are given in Table 6. Compared to EL, vegetable oils showed lesser conversion and yield of isomerized products under the studied conditions. Sunflower oil and once cooked oil showed ~15 and 14% conversion with 14 and 13% yield of conjugated oils

**Table 6.** Isomerization of vegetable oils[a]

| Name of the vegetable oil | Conversion (%) | Yield of conjugated oil (%) |
|---|---|---|
| Sunflower oil | 15 | 14 |
| Once cooked (sunflower) oil | 14 | 13 |
| Doubly cooked (sunflower) oil | 12 | 9 |
| Corn oil | 10 | 6 |
| Soybean oil | 7 | 3 |
| Gingelly oil | 5 | 4 |

[a]Oil = 125 mg, Toluene = 5 ml, BMImCl = 40 wt.% w.r.t. oil, Catalyst (5% Ru/MgAl4-LDH) = 20 wt.% w.r.t. oil, Temp. = 90 °C, Time = 12 h.

respectively. Doubly cooked oil gave 12% conversion with 9% yield of conjugated oil possibly due to lesser linoleate content (compared to once cooked oil). Corn and soybean oil gave 10 and 7% conversion with 6 and 3% yield of conjugated oil respectively. Gingelly oil gave 5% conversion with 4% yield of conjugated oil. Under the studied conditions, hydrolysis reactions are possible; but none of the oils showed hydrolysed product (glyceryl proton peak area remained constant in $^1$H NMR). However, small peaks appeared in the region of 3-4 ppm in $^1$H NMR analysis indicates formation of some unknown products along with isomerized product

## Conclusions

Among MgAl-LDHs with different Mg/Al atomic ratios, MgAl4-LDH showed a high yield of isomerized product (15%) for the double bond isomerization of ethyl linoleate. $CO_2$-TPD results bestowed that presence of high strength medium basic sites (referred here as M2 sites) along with lesser amount of weak basic sites are necessary to facilitate this reaction. 5% Ru/MgAl4-LDH gave 42% conversion with 29% yield of isomerized product at 90 °C in 12 h. During recycle, a decrease in the product yield was noticed and $CO_2$-TPD studies revealed similar variation in the distribution of basic sites that augment our earlier inference. Studies extended to some vegetable oils showed 5-15% conversion with 3-14% yield of conjugated oils.

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### Notes and references

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† Electronic Supplementary Information (ESI) available: [FT-IR of catalysts and reactant with ionic liquids, TG-DTG analysis of catalysts, $^1$H NMR of product mixture and reactant with ionic liquids, calculation methods, elemental analysis of LDHs, ionic liquid amount variation studies and composition of oils]. See DOI: 10.1039/b000000x/

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