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ARTICLE TYPE

Synthesis of high surface area mixed metal oxide from NiMgAl LDH precursor for Nitro-aldol condensation reaction

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We have investigated the effect of divalent metal cations on structural and catalytic activity of MgAl-layered double hydroxide (LDH), by partially substituting Mg^{2+} with M^{2+} (M^{2+}= Ni^{2+} and Co^{2+}) keeping metal to aluminium ratio (M^{2+}/Al^{3+}) =3 and Mg^{2+}/M^{2+} = 1.5. The LDH precursors were prepared by a coprecipitation method. The products were finally calcined at 450 °C for 4 h to obtain mixed metal oxides. The catalysts were characterized by powder X-ray diffraction (PXRD), Fourier transform infra-red spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) surface area techniques. The catalysts were then tested towards Nitro-aldol condensation reaction under different reaction conditions. The mixed metal oxide obtained from calcination of precursor NiMgAl LDH was found to be more efficient catalyst for Nitro-aldol condensation under solvent free condition at room temperature due to its high BET-surface area and pore volume.

Introduction

Nitro-aldol condensation, commonly known as Henry reaction is one of the most important C–C bond formation reactions and mostly used in bulk and fine chemical industries.[1] The product of the Henry reaction is also extensively used in many important syntheses including the synthesis of various biological compounds.[2,3] Usually, the product 2-nitroalkanol is produced by the aldol condensation of carbonyl compounds with nitroalkanes. The classical methods for the synthesis of this product use different bases including carbonate and bicarbonates. Formation of nitro-alkene by the elimination of water molecule from 2-nitroalkanol is one of the disadvantages of Henry reaction. Therefore, it is very much challenging to develop a green and economically cheaper solid base catalyst for selective synthesis of 2-nitroalkanol.

Layered double hydroxides (LDHs) are layered compound with structural similarities to hydrotalcite clays.[4-9] These compounds are also known as anionic clay[10-13] with the property of anion exchange due to which these compounds can be widely used in various fields as catalysts,[14-17] catalyst support,[18-20] and adsorbents.[21-24] They can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}\ (OH)_2]^{x+}\ (A^{n-}_{x/n})\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, x is the ratio of $M^{3+}/(M^{2+}+M^{3+})$, A^{n-} is anion that can be organic or inorganic by which excess positive charge in the layer can be compensated and m is the amount of water present in the interlayer.[25,26] Ternary LDHs exhibit better catalytic activity over precursor LDHs and greatly extend its application to various fields such as organic transformations,[27-29] photocatalysis etc.[30-32] These ternary compounds can be prepared by changing divalent or trivalent cation in the precursor LDHs. Calcination of LDHs give mixed metal oxides which can be used as basic catalysts in various organic transformations along with the advantages of high surface area and thermal stability.[33-37] Due to its simplicity, cost effectiveness and reusability, application of mixed metal oxides have drawn great importance in organic transformations.[38,39] The selective synthesis of 2-nitroalkanol by modified LDH has been investigated. However, catalytic performance of the mixed metal oxides from LDH precursor has not been well examined.

The aim of the present work is to prepare a green and environmentally benign solid base catalyst by partial substitution of $Mg^{2+}$with M^{2+} (M^{2+} = Ni^{2+}& Co^{2+}) ion in MgAl LDH. The synthetic method used to prepare LDHs is the co-precipitation method.[40] The synthesized and calcined catalysts were employed to test the catalytic activity for the nitro-aldol condensation reaction under solvent free condition at room temperature changing various reaction conditions.

Experimental Section

Materials

$Mg(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$, NaOH, Na_2CO_3 were purchased from Merck, Mumbai, nitromethane from G.S. Chemicals Testing Lab & Allied Industries, New Delhi; silica gel, iodine and solvents were purchased from RANKEM, New Delhi.

Synthesis of LDHs

LDHs were prepared by co-precipitation of an aqueous solution of metal nitrates- $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ with an aqueous solution of NaOH and Na_2CO_3 at a constant pH of (10±0.2) with M^{2+}/M^{3+} ratio of 3:1. After the formation of the precipitate, the gels were aged at 80 °C for 24 h. The solid product was then centrifuged, washed several times with distilled water until pH of the filtrate was 7 and then dried in the oven at 80 °C for 12 h. In MgAl LDH, Mg^{2+} was partially substituted by M^{2+} (M^{2+}= Ni^{2+} and Co^{2+}) keeping metal ratio M^{2+}/M^{3+} = 3 and of Mg^{2+}/M^{2+} = 1. The samples were calcined at 450 °C for 6 h in flowing air and the heating rate of 2 °C min^{-1}.

Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Multiflex instrument using nickel-filtered CuKα (0.15418 nm) radiation source and a scintillation counter detector. The intensity data were collected over a 2θ range of 5−70°. The crystallite size was calculated using Scherrer equation:

$$D = B\lambda/\beta_{1/2} \cos\theta$$

where D is the average crystallite size, B is the Scherrer constant (0.89), λ is wavelength of the X-ray beam, $\beta_{1/2}$ is the full-width at half-maximum (FWHM) of diffraction peak and θ is the diffraction angle. Elemental analyses for metal ions were performed using inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer, Optima 2100 DV). The solutions of the samples were prepared by keeping the samples to dry at 80 °C for 24 h and then dissolving the samples in (1:1) dil. HCl.[41] Infra-red spectra were measured in a FTIR spectrophotometer, Model Nicolet Impact I-410. Measurements are performed by pelletising the samples with KBr in the mid-infrared region. The TGA curves were obtained on a Thermal Analyzer (Model TGA-50, Shimadzu) instrument. The samples were heated from ambient temperature to 700 °C under N_2 flow. The heating rate in each case was kept at 10 °C min^{-1}. To study the surface topography, SEM analyses were carried out with “JEOL, JSM Model 6390 LV” Scanning Electron Microscopes, operating at an accelerating voltage of 15 kV. The Brunauer-Emmett-Teller (BET) surface areas were determined by N_2 adsorption using a Quantachrome Instruments (Model: NOVA 1000e). All the BET values in this study were measured within the precision of ± 5%. The pore size and pore volume is determined following Barrett-Joyner-Halenda (BJH) method in the same instrument. The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS 400 spectrometer taking Me_4Si as the internal standard in $CDCl_3$ and CD_3OD solvents. Preparative column chromatography was carried out with silica gel 60–120 mesh size and thin-layer chromatography (TLC) was carried out on glass plates with silica gel.

Catalytic activity

The nitro-aldol condensation reactions were performed under the solvent free conditions by taking 1 mmol of the aldehyde, 10 mmol of the nitromethane and 10 mg of the catalysts. For comparative study all reactions were carried out for 36 h and the reaction conditions were optimized by varying substituent, temperature and amount of catalysts. The reactions were monitored via thin layer chromatography and % conversions were obtained from ^1H and ^{13}C NMR analyses of the crude reaction mixture. To evaluate the catalytic activity more clearly, turnover frequency (TOF) of the catalysts were calculated using the general equation,

$$\mathrm{TOF} = \mathrm{TON} \times \frac{1}{\mathrm{Time\ (h)}}$$

where, TON refers to turn over number. For the turn over number calculations, number of active or basic sites was calculated by basicity measurements. In this method, a suspension of the 15 mg catalyst in a 2 ml toluene solution of phenolphthalein (0.1mg/ml) was stirred for 30 minutes and titrated with a toluene solution of benzoic acid (0.01M). The aqueous soluble amount of basic sites was determined by acid-base titration method reported previously.[42]

Results and Discussion

Characterization

Powder XRD patterns of LDHs are shown in Fig. 1(i). The formation of hydrotalcite (HT) type layered structure has been confirmed from the presence of sharp intense peaks at low 2θ angles and comparatively broad, less intense peaks at higher 2θ angles which match well with previous reports.[12,27] In case of all the synthesized LDHs, the diffraction peaks were observed approximately at 2θ values 11.6, 23.4, 34.8, 38.8, 46.3, 60.85 and 62.1° that could be assigned to (003), (006), (012), (015), (018), (110) and (113) reflections, respectively (JCPDS card no. 38-0478).[33] It has been observed that partial substitution of Mg^{2+} ions with Ni^{2+} and Co^{2+} affects the crystallization procedure which is well reflected from the broad and less intense peaks of both CoMgAl and NiMgAl samples in comparison to MgAl sample. The peaks for (015) and (018) reflections were not distinct in case of NiMgAl while the reflections at (015), (018), (110) and (013) were completely disappeared in CoMgAl. This can be attributed to the larger size of Co^{2+} (0.88 Å) and Ni^{2+} (0.83 Å) which could not accommodate well in the brucite layers. The effect can be understood from the calculation of lattice parameters and crystallite sizes. The value of lattice parameter ‘a’, which is a function of the average distance of metal ions within the layers can be obtained from the (110) reflection peak while ‘c’ parameter which is related to the thickness of the brucite-like layer and the interlayer distance can be obtained from the (003) reflection peak.[30] The lattice parameters ‘a’ ($a = 2d_{110}$) and ‘c’ ($c = 3d_{003}$) are calculated and summarized in Table 1. It is observed from the table that the ‘a’ parameter gradually increases in case of substituted LDH which can be due to the increased metal-metal distance on partial substitution of metal cations on MgAl LDH. However, the ‘c’ parameter increases in NiMgAl LDH while it decreases in case of CoMgAl LDH. This difference in lattice parameter ‘c’ can be attributed to the larger ionic radius of Co^{2+} (0.88 Å) than Ni^{2+} (0.83 Å).[12,27] Again the crystallite size of NiMgAl and CoMgAl are found to be less compared to that of MgAl LDH indicating the inclusion of larger cations in LDH layers resulting in the distortion of layered structure.[43]

Table 1

Chemical analysis, crystallographic data and crystallite size of mixed oxides.

Catalysts	Atomic ratio		d_{003} (Å)	d_{110} (Å)	Cell parameters(Å)		Crystallite size (Å)	
	Starting	Analyzed #			c	a	003	110
MgAl	3:1	3:0.9	7.69	1.52	23.07	3.04	90	134
Ni^{2+}MgAl	1.5:1.5:1	1.5:1.47:0.9	7.87	1.53	23.61	3.05	63.5	113
Co^{2+}MgAl	1.5:1.5:1	1.5:1.48:1	7.68	1.55	23.04	3.09	54	70

Determined by ICP

As shown in Fig. 1(ii), the powder XRD patterns of the mixed oxides do not possess characteristic peaks corresponding to LDH, because on calcination, the layered structure gets collapsed and were converted to corresponding mixed oxides (ESI†).

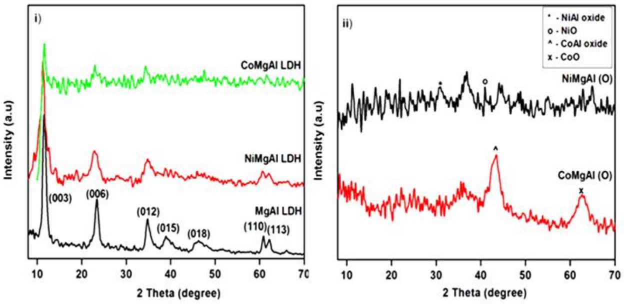

Fig. 1 X-ray powder diffraction patterns of i) LDHs and ii) mixed oxides.

The chemical compositions of LDHs were determined from the elemental analyses and presented in Table 1. The Table showed that the molar ratio of M^{2+}Mg/Al was close to 3 and that of M^{2+}/Mg (M^{2+} = Ni^{2+} or Co^{2+}) was 1:1 which nearly same as that of the starting solution.

The FTIR spectra of LDHs are shown in Fig. 2 (i). The bands at 3478.2 cm^{-1} and 1662.9 cm^{-1} can be assigned to the stretching and bending vibrations of -OH group of LDH layers and interlayer water molecule.[27,30] The sharp band observed at 1388.5 cm^{-1} is due to asymmetric stretching of CO_3^{2-} ion and broad peaks observed below 1000 cm^{-1} (500-800 cm^{-1}) are corresponds to M-O vibrations. [30]

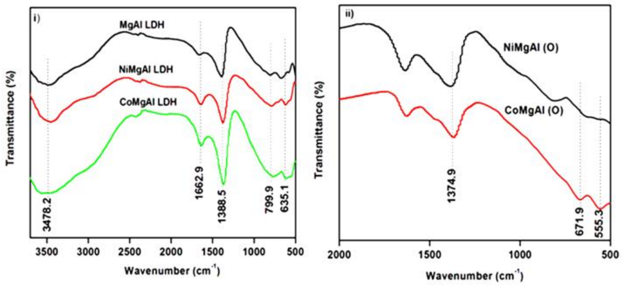

Fig. 2 FT-infrared spectra of i) LDHs and ii) mixed oxides.

In case of mixed oxides as shown in Fig. 2 (ii), the bands obseved at near 558.6, 672.4 and 811.9 cm^{-1}could be attributed to the vibration of metal-oxygen (M-O) bond. Moreover, the band at near 1376.9 cm^{-1} is due to the carbonate which may be arises from the adsorption of carbon dioxide from air on the surface of the metal oxides.[27]

The Thermogravimetric analysis of the precursor LDHs were carried out before calcination. From the TGA curve, shown in Fig. 3, two weight loss steps are observed. The first weight-loss can be observed in the temperature range of 50-200 °C which corresponds to the removal of water molecules absorbed on the surface and in the interlayer region of LDHs with weight loss of ~17.8 %. The second weight-loss step observed between 250-400 °C with weight-loss of ~19.5 % is due to the dehydroxylation of the brucite layer as well as the decomposition of the carbonate anions.[44]

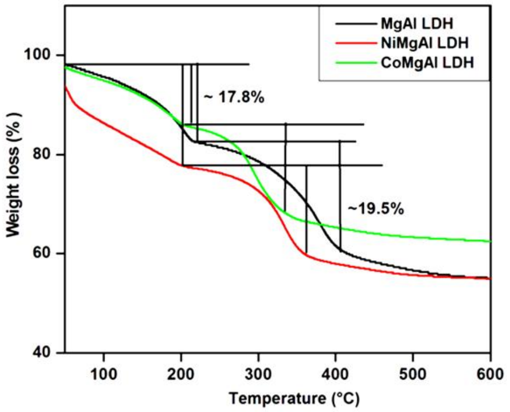

Fig. 3 Thermogravimetric curves of LDHs.

The SEM images of LDHs are presented in Fig. 4. Flat plate-like shapes are observed in case of MgAl LDH. Whereas, in case of NiMgAl and CoMgAl LDH, crystallites with large irregular particle size are observed which are due to agglomeration taking place on partial substitution of Mg^{2+} by M^{2+} (M^{2+}= Ni^{2+} and Co^{2+}) in MgAl LDH.

The porosity of the mixed oxides obtained by calcination of LDH precursors were investigated by nitrogen adsorption-desorption measurements. The Nitrogen adsorption-desorption curve showed that NiMgAl mixed oxide exhibit type IV isotherm with hysteresis loop H1 (Fig. 5) which is the characteristic of mesoporous material with regular pore structure [45] and along with an average pore size around 49.6 Å (inset of Fig. 5). However, in case of MgAl and CoMgAl mixed oxides, isotherm of type IV with combination of hysteresis loop H1 and H3[41,46] was observed

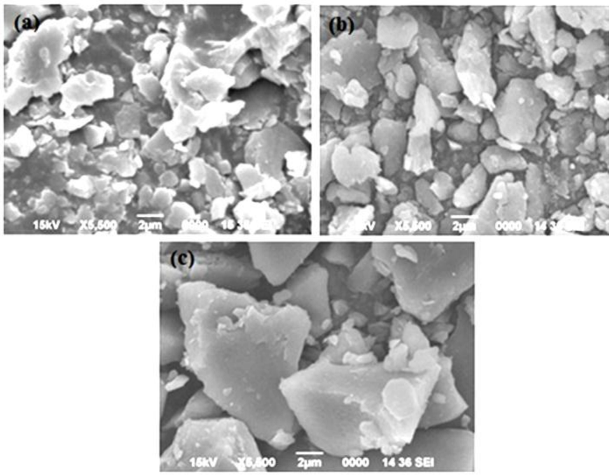

Fig. 4 Scanning electron micrographs of a) MgAl, b) CoMgAl and c) NiMgAl LDHs.

(ESI†, Fig. S1) and an average pore size around 88 and 107 Å (ESI†, Fig. S2). The BET surface areas and pore volumes of all the three mixed oxides were calculated and summarized in Table S1 (ESI†). From the table it can be observed that NiMgAl mixed oxide possessed high BET surface area and pore volume of 753 m^2/g and 279 cm^3/g, respectively. While in case of MgAl and CoMgAl mixed oxides; the observed surface area and pore volume were 561 m^2/g, 401 m^2/g, 0.974 cm^3/g and 0.937 cm^3/g, respectively. The high BET surface area and pore volume of the mixed oxides are due to the removal of adsorbed and interlayer water molecule and carbonate ions from the LDH layers at high temperature.

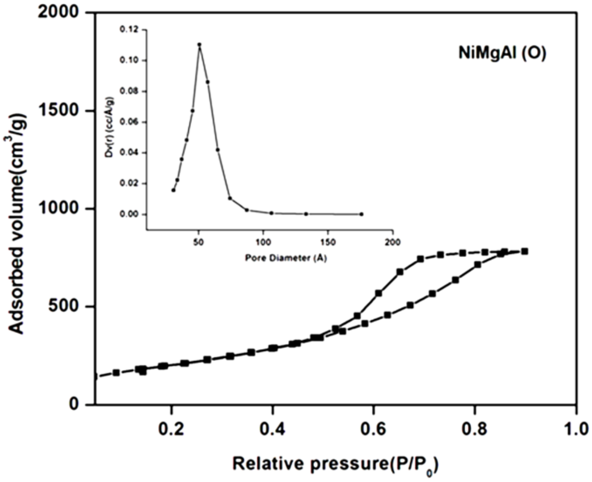

Fig. 5 Nitrogen sorption isotherms of NiMgAl mixed oxide; the inset shows pore size distribution.

Catalytic performance

To test the catalytic activity of the synthesized LDHs and mixed oxides, we first performed the reaction under solvent free condition by taking 1:10 molar ratio of 4-nitrobenzaldehyde and nitromethane in mmol scale and 10 mg of the catalyst at room temperature. From thin layer chromatography observation it was seen that good to excellent conversion to the product was obtained (84-94 %) for all the uncalcined catalysts but the time taken to complete the reaction was more (8-10 h) [Table 2]. Besides, we observed that partial substitution of metal ions on MgAl LDH further improved the catalytic activity. This increase in catalytic activity on partial substitution of metal ions can be explained on the basis of increased cell parameter ‘a’ and ‘c’ in case of NiMgAl and CoMgAl LDH (Table 1). The increased d value in case of NiMgAl LDH (d_{003} = 7.87) can be attributed to the superior catalytic activity providing increased basal spacing for the reaction to takes place between the two layers. However, performing the reaction under the same reaction conditions, it was observed that the reaction with calcined LDHs was much faster than the uncalcined LDHs and showed improvement of time giving 95-99 % conversion of the product within 2-6 hours with 100 % selectivity. Therefore, calcined catalysts were preferred over the uncalcined ones and all reactions were carried out further by mixed oxides. We have also observed from the table that in both the cases (uncalcined and calcined), NiMgAl LDH was found to be more efficient catalyst compared to that of MgAl and CoMgAl LDHs (entries 2 and 5, Table 2). The high surface area and large pore volume of the NiMgAl mixed oxide (Fig. 5) results in the superiority in catalytic activity over the other two mixed oxides for Nitro-aldol condensation reaction. Therefore, NiMgAl mixed oxide were considered as the best catalyst in this study.

Table 2

Nitroalkylation of 4-nitrobenzaldehyde with nitromethane catalyzed by mixed oxides at room temperature.[a]

Entry	Catalysts	Time (h)	Conversion (%)[b]
1	MgAl LDH	12	86
2	NiMgAl LDH	8	91
3	CoMgAl LDH	10	84
4	MgAl (O)	6	95
5	NiMgAl (O)	2	99
6	CoMgAl (O)	4	97

[a] Reactions were carried out with 1:10 molar ratio in 1 mmol scale of 4-nitrobenzaldehyde and nitromethane using 10 mg catalyst

[b] Determined from ^1H NMR data of crude mixture

After finding the best catalyst from our observation, we then studied the effect of various reaction parameters to optimize the reaction conditions for Nitro-aldol condensation reaction. At first we studied the temperature effect on the reaction by varying temperature from 25 °C (RT) to 60 °C (Table 3). It can be observed that on increasing the temperature upto 60 °C, the reaction time decreases from 2 h to 30 minutes. However, temperature does not have great effect over the conversion and we observed almost similar type of conversion in all cases. Therefore, it is convenient to use the greener path. So, the further studies were performed at room temperature under solvent free condition.

Table 3

Effect of temperature on Nitro-aldol condensation reaction of 4-nitrobenzaldehyde and nitromethane catalyzed by NiMgAl mixed oxide[a]

Entry	Temperature (°C)	Time (h)	Conversion (%)[b]
1	RT	2	99
2	40	1	98
3	60	30 min	99

[a] Reactions were carried out with 1:10 molar ratio in 1 mmol scale of 4-nitrobenzaldehyde and nitromethane using 10 mg catalyst

[b] Determined from ^1H NMR data of crude mixture

We next investigated the effect of amount of catalyst on reaction time and percentage conversion (Table 4). On increasing the catalysts amount from 5 to 15 mg, the % conversion increases along with decrease in reaction time. Further on increasing catalyst amount to 20 mg, it was observed that the reaction completed within 1h while conversion (%) was almost similar. So, we have selected 10 mg catalyst as our optimum amount for further studies at room temperature under solvent free condition.

Table 4

Effect of the amount of catalyst (NiMgAl mixed oxide) used in the conversion (%) of Nitro-aldol condensation reaction[a].

Entry	Catalyst (mg)	Time (h)	Conversion (%)[b]
1	5	4	95
2	10	2	99
3	15	2	98
4	20	1	99

[a] Reactions were carried out with 1:10 molar ratio in 1 mmol scale of 4-nitrobenzaldehyde and nitromethane using 10 mg catalyst

[b] Determined from ^1H NMR data of crude mixture

After getting optimizing conditions for Nitro-aldol condensation reaction, the reaction was then performed with variety of aldehydes, e.g. simple aromatic aldehydes, heterocyclic aldehyde and polycyclic aromatic aldehydes (Table 5). It is observed from the table that with changing the substituents, the amount of the % conversions are also getting changed. As expected, substrates with electron withdrawing groups give higher % conversion (97-99 %, entries 1-3, Table 5) while the % conversion become decreases (60-50 %) in case of the substrate with electron donating groups (entries 6-8). However it can be observed from the table that the reaction with polycyclic aldehydes gives better % conversion of 70-80 (entries 4-5).

Comparing our results with the reported one, we have observed that A. Cwik et al.[47] carried out Nitroaldol-reaction of aldehydes in the presence of non-activated Mg:Al 2:1 hydrotalcite. The reaction was performed at room temperature in methanol, tetrahydrofuran and nitromethane and best results were observed using nitromethane as solvent (20 mol equivalent). However, conversion was 95 % in 5 h. R. Manikandan et al.[48] Reported the synthesis and spectral characterization of three new nickel (II) complexes containing pyridoxal N(4)-substituted thiosemicarbazone ligands with triphenylphosphine. The new nickel (II) complexes were subjected as catalysts in the nitroaldol (Henry) reaction by employing various aldehydes with nitromethane in an ionic liquid medium. The reaction was carried out at room temperature for 5 h and the yield was observed to be about 52 %. However, on using ionic liquid as solvent medium, slight improve in the yield was observed from 52 to 64 %. The maximum yield of 92 % was observed in 12 h at 3.0 μmol concentration of the catalyst in 2 mL of methanol. M. Sutradhar et al.[49] reported the synthesis of a new cyclic binuclear Ni(II) complex, $[Ni_2(H_2L)_2]\cdot 4MeOH$ using the Schiff base N′[1],N′[3]-bis(2-hydroxybenzylidene) malonohydrazide (H_4L). A maximum conversion of ca. 93 % was obtained at 60 °C, for a 24 h reaction time, with 1 mol % loading of catalyst with the good syn:anti molar ratio of 72:28 was achieved.

Table 5

Nitro-aldol condensation reaction of nitromethane with different aldehydes.

Entry	Substrate	Time (h)	Conversion (%)[a]
1	4-nitobenzaldehyde	2	99[b]
2	2-nitrobenzaldehyde	4	98
3	3-nitrobenzaldehyde	4	97
4	1-naphthaldehyde	20	76
5	Furfuraldehyde	20	70
6	4-hydroxybenzaldehyde	36	80
7	4-methylbenzaldehyde	36	78
8	Chloroaldehyde	36	91

[a] Determined by ^1H NMR data of crude mixture

[b] Isolated pure product

We have also studied the effect of calcination temperature on catalytic activity with the optimum reaction conditions. We have calcined the catalyst at a lower (350 °C) and at a higher (550 °C) calcinaton temperature to the reported one (450 °C). The sample calcined at 350 °C, showed low catalytic activity with 84 % conversion in 6 h (Table S2, ESI†). This lower calcination temperature leads to no any characteristic change in the layered structure. It can be considered as a dehydrated one with its basic sites occupied by CO_3^{2-} ions. Consequently, the BET surface area of the catalyst was relatively lower (584 m^2/g) that leads to the lower catalytic activity. On the other hand, the sample calcined at 550 °C, also exhibited lower activity with the 86 % conversion in 8 h (Table S2, ESI†). The high calcination temperature result in the phase transformation of mixed oxides into crystalline spinel phases which results in the lower BET surface area (566 m^2/g) and hence lower in catalytic activity.[7,50-54] The N_2 adsorption desorption graphs of NiMgAl (O) at 350 and 550 °C calcination temperature also followed type IV isotherm (Fig. S3, ESI†). The basic sites formed after calcination of LDHs at 450 °C were considered as the active sites in mixed metal oxides. The presence of different types of basic sites is related to –OH groups, O^{2-}-M^{n+} pairs and O^{2-} anions.[55-60]

The turnover frequency (TOF) of the mixed metal oxides is shown in Fig. S4 (ESI†). It can be seen from the figure that the TOF increases on partial substitution of metal cation with Mg^{2+} in MgAl mixed oxides and has been found to be maximum in case of NiMgAl (O) mixed oxide (149/h). While in case of MgAl (O) and CoMgAl (O), the TOF are 12.5 and 36/h respectively which are almost 11 and 4 times less than NiMgAl (O). This increase in TOF reflects the better catalytic performance of NiMgAl (O) mixed oxides for Nitro-aldol condensation reaction.

After testing the catalytic activity it is important to check the recyclability of the catalyst for their practical application. To test the recyclability we carried out the condensation reaction upto four cycles employing 10 mg of the catalyst and it was found that the catalyst become active up to 4 cycles as shown in Table S3 (ESI†). In the first 3 cycles, it took 2-3 h to complete the reaction with decrease in % conversion from of 96 to 92 %. However, after 3rd cycle, the time to complete the reaction become increased upto more than 4 h. Thus we observed that with increasing the number of cycles, the time taken to complete the reaction gradually increases along with decrease in catalytic activity. The reason for this decrease in catalytic activity of the catalyst may be due to the loss of catalyst during separation or deactivation of the active sites in the catalyst. The leaching of metals during recyclability of catalysts was observed. For this test, 1 mmol 4-nitrobenzaldehyde, 10 mmol nitromethane and 10 mg of the catalyst were taken in a round bottomed flask and stirred for 1 h at room temperature without any solvent. The catalyst was then filtered off and the experiment was continued with the filtrate for upto 24 h. It was observed that the conversion was remained unchanged indicating the absence of any metal in the filtrate.

Conclusions

In summary, we have synthesized high surface area mixed metal oxides from their precursor LDHs and also observed the influence of divalent metal cations on structural property and catalytic activity of MgAl LDH. The PXRD of all the as prepared LDHs revealed the formation of hydrotalcite (HT) type layered structure. The partial substitution of Mg^{2+} ions with Ni^{2+} and Co^{2+} affects the crystallization procedure which is well reflected from the broad and less intense peaks of both CoMgAl and NiMgAl samples in comparison to MgAl sample. The formation of mixed oxides can be revealed from the powder XRD patterns which possess no any characteristic peaks that corresponding to LDH. The mixed metal oxides were found to be catalytically more active towards Nitro-aldol condensation reaction under solvent free condition at room temperature with NiMgAl mixed oxide being more active. The high catalytic activity of NiMgAl mixed oxide can be attributed to the high BET surface area (753 m^2/g). The catalysts can be reused upto 4th cycle without any characteristics loss in its activity.

Spectral data

2-Nitro-1-(4-nitrophenyl) ethan-1-ol (ESI†, ^{1}H and ^{13}C spectra)
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (s, 1 H), δ 4.58-4.61 (m, 2H), δ 5.60-5.62 (m, 1H), δ 7.64(d, J_{HH} = 8.7 Hz, 2H), 8.27 (d, J_{HH} = 9.2 Hz, 2H); ^{13}C NMR (400 MHz $CDCl_3$): &0.0, 80.8, 124.2, 127.0, 145.4, 148.2 ppm.

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Notes and references

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†Electronic Supplementary Information (ESI) available: XRD analysis and textural properties of mixed oxides, effect of calcinaton temperature on Nitro-aldol reaction, Recyclability test, N_2 adsorption-desorption isotherms and pore size distribution of MgAl and CoMgAl mixed oxides, N_2 adsorption-desorption isotherms of NiMgAl mixed oxide at different calcination temperature, Turnover frequency (TOF) plot of mixed metal oxides, ^{1}H and ^{13}C NMR spectra of the pure product. See DOI: 10.1039/b000000x/

1 B. M. Choudary, B. Kavita, N. S. Chowdari, B. Sreedhar and M. L. Kantam, *Catal.Lett.*, 2002, **78**, 373-377.
2 B. M. Choudary, M. L. Kantam, C. V. Reddy,K. K. Rao and F. Figueras, *Green Chem.*,1999, **1**, 187-189.
3 R. Devi, R. Borah and R. C. Deka, *Appl. Catal. A: Gen.*, 2012, **433–434**, 122–127.
4 S. Miyata, *Clays Clay Miner.*, 1983, **31**, 305-311.
5 I. Y. Park, K. Kuroda and C. Kato, *J. Chem. Soc. Dalton Trans.*,1990, pp. 3071-3074.
6 I. C. Chisem and W. Jones, *J. Mater. Chem.*, 1994, **4**, 1737-1744.
7 V. R. L. Constantino and T. J. Pinnavaia, *Inorg. Chem.*, 1995, **34**, 883-892.
8 S. Zhu, S. Jiao, Z. Liu, G. Pang and S. Feng, *Environ. Sci.: Nano*, 2014, **1**, 172-180.
9 K. Klemkaite, I. Prosycevas, R. Taraskevicius, A. Khinsky and A. Kareiva, *Cent. Eur. J. Chem.*, 2011, **9**, 275-282.
10 Y. Zhao, F. Xiao and Q. Jiao, *J. Nanotechnol.*, 2011, 1-6.
11 M. del Arco, S. Gutierrez, C. Martin and V. Rives, *Inorg. Chem.*, 2003, **42**, 4232-4240.
12 S. Velu, K. Suzuki, S. Hashimoto, N. Satoh, F. Ohashi and S. Tomura, *J. Mater. Chem.*, 2001, **11**, 2049-2060.
13 S. Mandal, D. Tichit, D. A. Lerner and N. Marcotte, *Langmuir*, 2009, 25, 10980-10986.
14 R. Sen, S. Bhunia, D. Mal, S. Koner, Y. Miyashita and KI. Okamoto, *Langmuir*, 2009, **25**, 13667–13672.
15 M. L. Kantam, B. M. Choudary, C. V. Reddy, K. K. Raoand F. Figueras, *Chem. Commun.*, 1998, 1033-1034.
16 L. Mohapatra, K. M. Parida, and M. Satpathy, *J. Phys. Chem.C*, 2012, **116**, 13063−13070.
17 N. Baliarsingh, K. M. Parida and G. C. Pradhan, *Ind. Eng. Chem. Res.*, 2014, **53**, 3834-3841.
18 J. R. Ruiz, C. Jiménez-Sanchidrián and M. Mora, *Tetrahedron*, 2006, **62**, 2922–2926.
19 J. W. Boclair, P. S. Braterman, B. D. Brister and F. Yarberry, *Chem. Mater.*, 1999, **11**, 2199-2204.
20 J. C. Villegas, O. H.Giraldo, K. Laubernds and S. L. Suib, *Inorg. Chem.*, 2003, **42**, 5621-5631.
21 S. Mandal, D. Tichit, D. A. Lerner, and N. Marcotte, *Langmuir*, 2009, **25**, 10980–10986.

22 L. Ai, C. Zhang, and L. Meng, *J. Chem. Eng. Data*, 2011, **56**, 4217–4225.
23 N. Kannan, M. M. Sundaram, *Dyes Pigments*, 2001, **51**, 25–40.
24 K. Morimoto, K. Tamura, N. Iyi, J. Ye, H. Yamada, *J. Phys. Chem.* Solids, 2011, **72**, 1037–1045.
25 R. P. Bontchev, S. Liu, J. L. Krumhansl, J. Voigt and T. M. Nenoff, *Chem. Mater.*, 2003, **15**, 3669-3675.
26 K. M. Parida, M. Sahoo and S. Singha, *J. Mol. Catal. A: Chem.*,2010, **329**, 7-12.
27 N. N. Das and S. C. Srivastava, *Bull. Mater. Sci.*, 2002, **25**, 283-289.
28 N. N. Labidi, A. Ghorbel, D. Tichit and G. Delahay, *React. Kinet.Catal.Lett.*, 2006, **88**, 261-268.
29 Z. Houa and T. Yashima, *Appl. Catal. A: Gen.*, 2004, **261**, 205–209.
30 K. Parida, L. Mohapatra and N. Baliaarsingh, *J. Phys. Chem. C*, 2012, **116**, 22417-22424.
31 K. Parida, M. Satpathy and L. Mohapatra, *J. Mater. Chem.*, 2012, **22**, 7350-7357.
32 R. K. Sahu, B. S. Mohanta and N. N. Das, *J. Phys. Chem.* Solids, 2013, **74**, 1263–1270.
33 F. Cavani, F. Trifiro and A.Vaccari, *Catal. Today*, 1991, **11**, 173-301.
34 F. Kovanda, T. Grygar, V. Dorničák, T. Rojka, P Bezdička and K. Jirátová, *Appl. Clay Sci.*, 2005, **28**, 121– 136.
35 T. Shishido, M. Sukenobu, H. Morioka, M. Kond, Y. Wanga, K. Takaki and K. Takehira, *Appl. Catal. A: Gen.*, 2002, **223**, 35–42.
36 L. Chmielarz, P. Kustrowski, A. Rafalska-Łasocha and R. Dziembaj, *Thermochim. Acta.*, 2003, **395**, 225–236.
37 W. Xie, H. Peng and L. Chen, *J. Mol. Catal. A: Chem.*, 2006, **246**, 24–32.
38 M. B. Gawande, R. K. Pandey and R. V. Jayaram, *Catal. Sci. and Tech.*, 2012, **2**, 1113-1125.
39 C. Yuan, H. B. Wu, Y. Xie, and X. W. Lou, *Angew. Chem. Int. Ed.*, 2014, **53**, 1488–1504.
40 W. T. Reichle, *Solid States Ionics*,1986,**22**, 135-141.
41 F. Li, X. Jiang, D. G. Evans and X. Duan, *J. Porous Mater.*, 2005, **12**, 55–63.
42 J. M. Fraile, N. Garcia, J. A. Mayoral, E. Pires and L. Roldan, *Appl. Catal. A: Gen.*, 2009, **364**, 87-94.
43 W. Trakarnpruk, *J. Met. Mat. Min.*, 2012, **22** 131-136.
44 P. Deka, R. C. Deka and P. Bharali, *New J. Chem.*, 2014, **38** 1789-1793.
45 B. Naik, S. Hazra, V. S. Prasad and N. N. Ghosh, *Catal. Commun.* 2011, **12**, 1104-1108.
46 M. An, J. Cui and L. Wang, *J. Phys. Chem. C*, 2014, 118, 3062-3068.
47 A. Cwik, A. Fuchs, Z. Hell and J.-M.Clacens, *Tetrahedron*, 2005, **61**, 4015–4018.
48 R. Manikandan, P. Anitha, G. Prakash, P. Vijayan and P. Viswanathamurthi, *Polyhedron*, 2014, **81**, 619–627.
49 M. Sutradhar, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Catal. Commun.*, 2014, **57**, 103–106.
50 M. K. Ram Reddy, Z. P. Xu, G. Q. (Max) Lu, and J. C. Diniz da Costa, *Ind. Eng. Chem. Res.*, 2006, **45**, 7504-7509.
51 N. D. Hutson, S. A. Speakman and E. A. Payzant, *Chem. Mater.*, 2004, **16**, 4135-4143.
52 W. Yang, Y. Kim, K. T. Liu, M. Shahimi and T. T. Tsotsis, *Chem. Eng. Sci.*, 2002, **57**, 2945-2953.
53 D. Tichit, M. N. Bennani, F. Figueras and J. R. Ruiz, *Langmuir*, 1998, **14**, 2086-2091.
54 M. Bellotto, B. Rebours, O. Clause, J. Lynch, D. Bazin and E. Elkaïm, *J. Phys. Chem.*, 1996, **100**, 8535-8542.
55 C. Noda Pérez, J. L. F. Monteiro, J. M. L. Nieto and C. A. Henriques, *Quim. Nova*, 2009, **32**, 2341-2346.
56 A. Corma, S. Iborra, J. Primo and F. Rey, *Appl. Catal. A*, 1994, **114**, 215-225.
57 M. J. Climent, A. Corma, S. Iborra and J. Primo, *J. Catal.*, 1995, **151**, 60-66.
58 M. J. Climent, A. Corma, S. Iborra, K. Epping and A. Velty, *J. Catal.*, 2004, **225**, 316-326.
59 C. Noda Pérez, C. A. Pérez, C. A. Henriques and J. L. F. Monteiro, *Appl. Catal. A*, 2004, **272**, 229-240.
60 J. I. Di Cosimo, V. K. Díez, M. Xu, E. Iglesias and C. R.Apestegía, *J. Catal.*, 1998, **178**, 499 510.

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Graphical Abstract

Synthesis of high surface area mixed metal oxide from NiMgAl LDH precursor for Nitro-aldol condensation reaction

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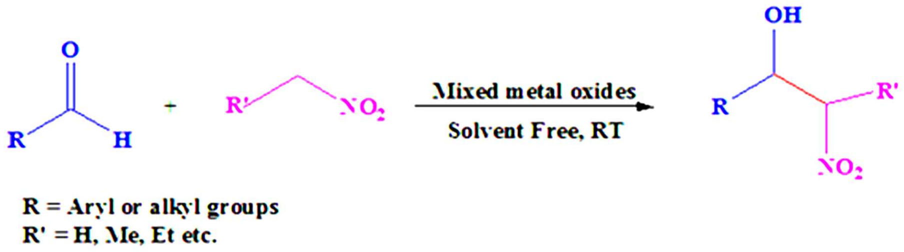

R = Aryl or alkyl groups
R' = H, Me, Et etc.

NiMgAl mixed oxide catalyzes Nitro-aldol condensation reaction at room temperature under solvent free condition exhibiting 99 % conversion.