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Delaminated layered double hydroxides as catalysts for the Meerwein–Ponndorf–Verley reaction

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ABSTRACT

The Meerwein–Ponndorf–Verley (MPV) reaction involves the hydrogen-transfer reduction of a carbonyl compound by an alcohol used as hydrogen donor. The process is catalysed by both homogeneous and heterogeneous catalysts. The latter can be of the acid or basic type. In this work, we used delamination and ion-exchange in combination to obtain delaminated solids from layered double hydroxides (LDHs). Three Mg/Al LDHs (Mg/Al ratio = 2) containing carbonate, hydroxyl or dodecylbenzenesulphonate (DBS) as interlayer anion were prepared using a coprecipitation method or by rehydration of the solid obtained by calcinations of carbonate containing LDH. The X-ray diffraction patterns for LDHs exhibited the typical lines for LDHs intercalated with carbonate, hydroxyl or DBS ions. The DBS-containing LDH was delaminated by sonicating at 60 °C a suspension of this solid in 1-butanol. The DBS ions in the delaminated LDH could be exchanged by nitrate or hydroxyl ions by stirring a suspension of this delaminated LDH in 1-butanol containing an appropriate amount of $Ca(NO_3)_3$ of $Ca(OH)_2$, respectively. The resulting delaminated solids consisted of brucite-like nanolayers excess charge in which was countered by dodecylbenzenesulphonate, nitrate or hydroxyl ions. Some of these solids exhibited moderate catalytic activity in the MPV reaction of benzaldehyde with 2-propanol. The reaction was conducted at 82 °C (0.06 mol of 2-propanol was treated with 0.003 mol of benzaldehyde in the presence of 1 g of catalyst). Calcining at 450 °C the delaminated LDHs, however, provided solids with a high surface activity that made them highly effective catalysts for the reaction. The catalyst obtained by calcining delaminated LDH containing hydroxyl ions provided the best catalyst (100% conversion after 2 h of reaction) and has been used in the MPV reaction of other aldehydes with excellent results.

1. Introduction

Layered double hydroxides (LDHs) are compounds belonging to the anionic clay family. All are structurally identical with hydrotalcite $[Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O]$. This mineral in turn is similar to brucite $[Mg(OH)_2]$, where Mg^{2+} ions occupy octahedral positions and form infinite layers connected by hydrogen bonds. In hydrotalcite, some Mg^{2+} ions have been substituted by Al^{3+} ions, which introduces a charge deficiency that is offset by carbonate ions present in the interlayer region between octahedral layers [1]. However, the magnesium can also be substituted by other trivalent ions or even divalent ones and the interlayer ion can differ in nature. Therefore, the general formula of LDHs is $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_{x/m}]^{m-}{\cdot}nH_2O$, where M(II) and M(III) are a divalent and a trivalent metal, respectively, lying at octahedral positions of Mg^{2+} in brucite-like layers and A is the interlayer region – which can vary widely in nature and be either inorganic or organic. x, which denotes the ratio $M(II)/[M(II)+M(III)]$, typically ranges from 0.17 to 0.33 [1]. Calcining LDHs at 450 °C produces mixed oxides – of the Mg(Al)O type from hydrotalcite – that are often basic and useful as catalysts for condensation [2–4], Baeyer–Villiger [5–8] or reduction reactions [9–11], and also as metal supports [12–15]. In recent years, LDHs have also been used to obtain discrete brucite-like layers by delamination. One of the purposes of delaminating an LDH is to increase the accessibility of species to its brucite-like layers, which is highly restricted by the small size of the interlayer cavities. Delamination provides molecularly thick nanolayers [16] with ample free space for attack, which expands the catalytic scope of the solids. The procedure is usually applied to LDHs intercalated with an organic anion such as dodecylsulphate and involves attack with an appropriate solvent [17–20].

The reduction of unsaturated organic compounds with an organic molecule instead of hydrogen gas or a metal hydride as hydrogen donor, which is known as "hydrogen transfer", is widely documented [21]. Such is the case with the catalytic transfer of

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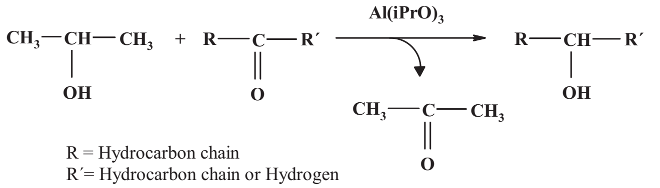


Scheme 1. General scheme for the Meerwein–Ponndorf–Verley reduction using $Al(iPrO)_3$ as catalyst.

hydrogen known as the Meerwein–Ponndorf–Verley (MPV) reaction [22]. The MPV reaction allows the highly selective reduction of aldehydes and ketones under mild conditions in the presence of a metal alkoxide such as aluminium isopropoxide as catalyst (see Scheme 1). However, the catalyst must be used in a large excess in order to obtain acceptable yields and removing excess alkoxide once the reaction has completed can be rather difficult. In recent years, a variety of acid and basic heterogeneous catalysts have been successfully used to avoid the need to remove the alkoxide from the reaction mass. Especially prominent among such catalysts are magnesium oxide [23–27] and calcined layered double hydroxides [28–32].

In this work, we delaminated an LDH intercalated with dodecylbenzenesulphonate (DBS) ion and subsequently exchanged DBS with nitrate or hydroxyl ions to obtain catalysts for use in the MPV reaction. The starting solid was an Mg/Al LDH with a metal ratio of 2 – which was previously found to be that providing the most active catalysts for this reaction [33]. The results obtained with the delaminated solids were compared with those provided by undelaminated LDHs containing carbonate or hydroxyl interlayer anions, calcination of which gave Mg(Al)O mixed oxides that were successfully used in MPV reactions in previous work [28,29,31–33].

2. Experimental

2.1. Preparation of layered double hydroxides

Three Mg/Al LDHs containing carbonate, hydroxyl or dodecylbenzenesulphonate (DBS) as interlayer ion were prepared. All three had an Mg/Al ratio of 2. The carbonate- and DBS-containing LDHs were prepared by using a coprecipitation method described elsewhere [34]. The method involves the dropwise addition, in nitrogen atmosphere, under vigorous stirring of an aqueous solution containing 0.2 mol of $Mg(NO_3)_2{\cdot}9H_2O$ and 0.1 mol of $Al(NO_3)_3{\cdot}9H_2O$ to another, aqueous solution of sodium carbonate or dodecylbenzenesulphonate. The pH of the mixture was kept at 10 by addition of 1 M NaOH. The resulting suspensions were heated at 80 °C for 24 h, filtered and washed with distilled, decarbonated water several times. The solids thus obtained from the carbonate- and DBS-containing LDHs were designated MgAl-CO_3 and MgAl-DBS, respectively. The hydroxyl-containing LDH was prepared from MgAl-CO_3. Calcining a carbonate-containing LDH at 450 °C destroys its layered structure; the process, however, can be reversed by rehydration because LDHs have a memory effect [1]. Our MgAl-CO_3 was calcined at 450 °C in a nitrogen atmosphere and then rehydrated at 100 °C by passing a nitrogen stream containing water vapour through it for 72 h. The resulting solid was designated MgAl-OH.

2.2. Delamination of MgAl-DBS

The DBS-containing LDH was delaminated by sonicating at 60 °C a suspension containing 1 g of solid in 250 mL of 1-butanol until it acquired a translucent appearance that remained stable over time; at that point, an LDH is seemingly completely delaminated [35,36]. Centrifugation of the translucent solution provided the solid named MgAl-DBS-DEL.

2.3. Ion-exchange of MgAl-DBS-DEL

DBS ions in the delaminated LDH were replaced by treating the above-described translucent solution with one of $Ca(NO_3)_2$ or $Ca(OH)_2$ to introduce nitrate or hydroxyl ions, respectively, in 1-butanol. In a typical run, an amount of 1 g of undelaminated LDH containing DBS anion (i.e. solid MgAl-DBS) was dispersed in 100 mL of 1-butanol and heated at 70 °C under sonication for 2 days. Then, the dispersion was allowed to cool and supplied with 20 mL of 1-butanol containing 0.085 mol of $Ca(NO_3)_2$ or $Ca(OH)_2$. The mixture was kept under vigorous stirring at room temperature for 24 h, which caused the formation of a precipitated solid that was identified as the calcium salt of DBS – therefore, Ca^{2+} ions acted as scavengers for DBS ions and facilitated their exchange with nitrate or hydroxyl ions in octahedral layers. The remainder was a translucent solution that remained stable over time. Finally, the solution was decanted and centrifuged to isolate the solid. The resulting solids were designated MgAl-NO_3-DEL and MgAl-OH-DEL.

2.4. Calcination of LDHs

Selected laminated and delaminated solids were calcined at 450 °C in the air for 8 h, using a temperature gradient of 1 °C/min. The resulting catalysts were named by adding 450 to the designation of the precursor; thus, the solid obtained by calcining MgAl-CO_3 was designated MgAl-CO_3-450.

2.5. Characterization techniques

The LDHs and their calcination products were characterized by using various instrumental techniques.

Elemental analysis of the solids was carried out by inductively coupled plasma-mass spectrometry on a Perkin–Elmer ICP-MS instrument under standard conditions.

All solids were subjected to X-ray diffraction analysis in order to check formation of LDH phases. Powder patterns were recorded on a Siemens D-5000 diffractometer using CuK_α radiation. Scans were performed over the 2θ range 5–70°, using a resolution of 0.02° and a count time of 2 s at each point.

Thermogravimetric analysis was performed on a Setaram Setsys 12 instrument by heating in an argon atmosphere from 25 to 800 °C at 10 °C/min.

BET surface areas were calculated from nitrogen adsorption–desorption isotherms obtained at −196 °C on a Micromeritics ASAP 2010 instrument. Samples were outgassed in vacuo at 100 °C for 12 h prior to use. The amount of CO_2 chemisorbed on each solid was measured on a Micromeritics 2900 TPD/TPR analyser. Prior to analysis, samples were heated at 450 °C in argon stream for 1 h. Measurements were made at room temperature by alternately passing argon an the same gas containing 5% CO_2 over each sample; the amount of chemisorbed CO_2 was calculated as the difference between the first adsorption peak (physisorbed plus chemisorbed CO_2) and the arithmetic mean of the adsorption and desorption peaks. Basicity was assessed under the assumption that one molecule of CO_2 was adsorbed at one basic site. The number of basic sites found was thus a measure of basicity.

2.6. Reaction conditions

The Meerwein–Ponndorf–Verley reaction was conducted in a two-necked flask furnished with a condenser and a magnetic stirrer. 2-Propanol (60 mmol) was treated with 3 mmol of the aldehyde

Table 1
Metal ratios and chemical formulae of the HTs.

LDH	Mg/Al[a]	Chemical formulae[b]
MgAl-CO_3	2.13	$Mg_{0.681}Al_{0.319}(OH)_2(CO_3)_{0.160}\cdot 0.62H_2O$
MgAl-DBS	1.97	$Mg_{0.663}Al_{0.327}(OH)_2(C_{12}H_{23}C_6H_4SO_3)_{0.168}\cdot 0.15H_2O$
MgAl-OH	2.13	$Mg_{0.681}Al_{0.319}(OH)_2(OH)_{0.320}\cdot 0.71H_2O$

[a] Metal ratios as determined by ICP-MS.
[b] Crystallization water was determined thermogravimetrically.

and the reaction mixture heated at reflux temperature with stirring (1000 rpm). The reaction was started by introducing 1 g of freshly calcined catalyst. The reaction products were analysed by GC–MS, using an HP 5890 gas chromatograph furnished with a Supelcowax 30 m × 0.32 mm column and equipped with an HP 5971 MSD instrument using helium as carrier gas and an injector temperature of 250 °C. Each chromatographic run was performed with an amount of sample of 0.1 μL and the following temperature gradient: (1) 80 °C for 5 min, (2) 80–150 °C ramp at 10 °C/min and (3) 150 °C for 20 min. Under these conditions, the retention time for benzaldehyde and benzyl alcohol was 6.84 and 5.18 min, respectively. To present the results we have used the conversion and selectivity values defined as:

$$\text{Conversion}\,(\%) = \frac{\text{mol of converted aldehyde}}{\text{mol of initial aldehyde}} \times 100$$

$$\text{Selectivity}\,(\%) = \frac{\text{mol of obtained alcohol}}{\text{mol of obtained alcohol} + \text{mol of subproducts}} \times 100$$

3. Results and discussion

3.1. Characterization of catalysts

Table 1 shows the metal ratios and empirical formulae of the three synthetic LDHs. As can be seen, the experimental ratios were quite consistent with the theoretical value [2]. The calcination–rehydration process had no effect on the metal ratio, which was thus identical for MgAl-OH and MgAl-CO_3.

Fig. 1 shows the XRD patterns for the LDHs. That for MgAl-CO_3 exhibited the typical lines for an LDH with intercalated carbonate ions and hence for natural hydrotalcite [37]. Calcination at 450 °C destroyed the layered structure and led to the formation of an Mg(Al)O mixed oxide structurally identical with periclase MgO [1]. Rehydration of the oxide under the above-described conditions restored the original LDH structure, albeit with hydroxyl as interlayer ion. The XRD pattern for this solid (MgAl-OH) was also similar to that for natural hydrotalcite; lines, however, were taller and narrower than those for MgAl-CO_3 by effect of its increased crystallinity. Finally, the pattern for MgAl-DBS was similar to that reported in the literature [38]. The shift to higher 2θ values in the $(0\,0\,l)$ reflections was assigned to the presence of DBS ions in the interlayer region. The 2θ value for the (0 0 3) reflection was used to calculate the lattice distance (viz. the sum of one brucite-like layer and one interlayer spacing), which was obviously dependent on the nature and orientation of the interlayer ion and the degree of hydration of the LDH [1]. The distance was 0.762 nm for MgAl-CO_3, 0.768 nm for MgAl-OH and 3.12 nm for MgAl-DBS.

As noted under Experimental, all LDHs were delaminated in 1-butanol. This solvent was chosen on the grounds of its increased boiling point relative to water and hence of its efficiently removing all interlayer water molecules hindering delamination of the LDHs [16,17]. This is seemingly the key to effective exfoliation of LDHs. 1-Butanol molecules gradually enter the interlayer region with the aid of ultrasound and cause it to swell to a point where discrete layers are separated. Once the LDH has been thoroughly delaminated, the suspension becomes translucent, which can be checked by centrifuging it and analysing the solid by XRD spectroscopy. Fig. 2 shows the XRD pattern for the centrifuged solid, which was named MgAl-DBS-DEL. As can be seen, the solid exhibited no baseline reflection, which confirms that the LDH structure was completely destroyed. There was, however, a halo at low 2θ values that was assigned to dispersion of disordered aggregates of exfoliated nanolayers [35] in addition to a signal at $2\theta = 60°$ due to the 11 side of a hexagonal two-dimensional unit cell ca. 30.4 nm in size suggesting that two-dimensional layers in the LDH preserved their crystal order after delamination.

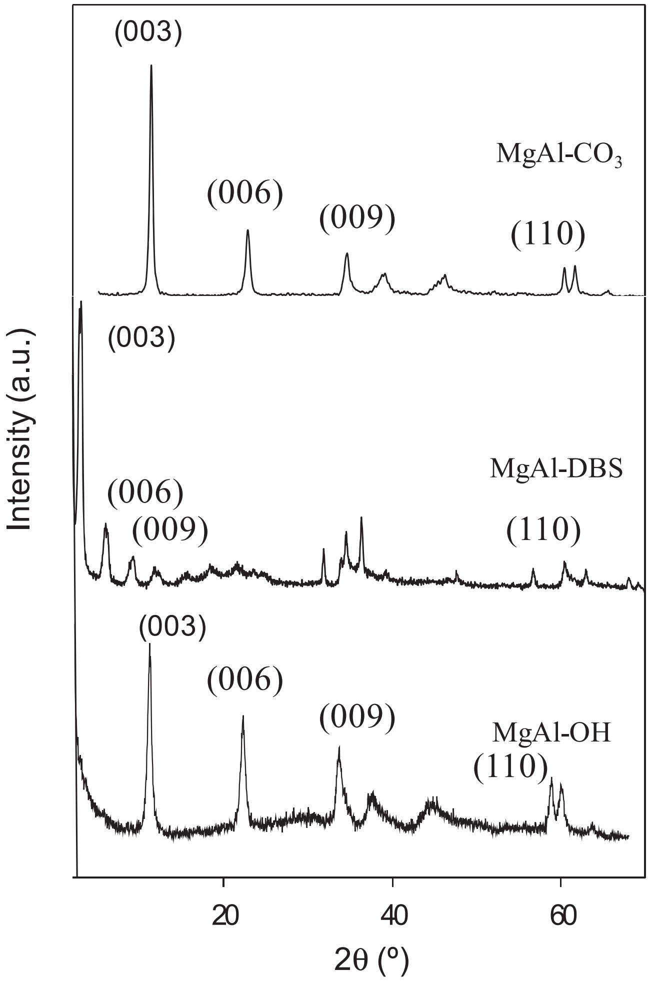


Fig. 1. XRD patterns for synthesized LDHs.

Once the procedure was checked to completely delaminate the DBS-containing LDH, we exchanged it with nitrate and hydroxyl ions. Fig. 2 shows the XRD patterns for the two new solids, named MgAl-NO_3-DEL and MgAl-OH-DEL, respectively. As can be seen, ion-exchange caused no relamination of the materials. A qualitative elemental analysis of the exfoliated solids revealed the complete absence of organic matter and sulphur, and hence that they were completely ion-exchanged.

As noted earlier, calcining an Mg/Al LDH provides a basic Mg(Al)O mixed oxide. Fig. 3 shows the XRD patterns for the solids MgAl-CO_3-450, MgAl-OH-450, Mg/Al-OH-DEL-450 and Mg/Al-NO_3-DEL-450. All exhibited the typical signals for a periclase MgO phase [1].

The solids were characterized in textural and surface chemical terms via N_2 physisorption and CO_2 chemisorption tests. Table 2 shows the specific surface area as determined with the BET method, and the number of basic sites, for each calcined solid. As can

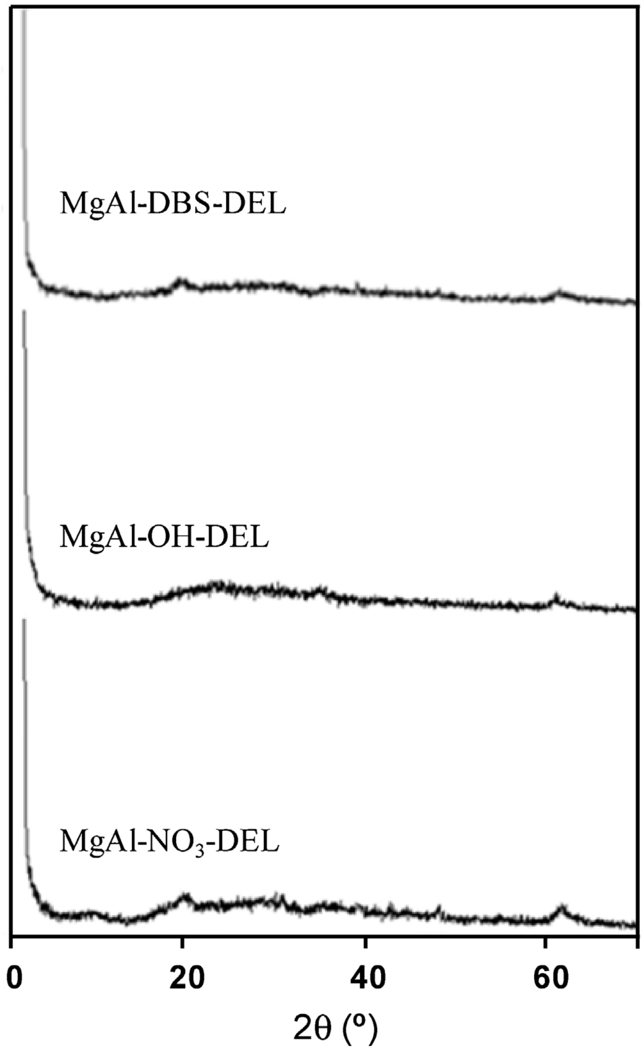


Fig. 2. XRD patterns for delaminated LDHs.

Table 2
Specific surface area, of the synthetized solids and their calcination products and number of basic sites of the calcined solids.

Solid	S_{BET} (m^2/g)[a]	n_b (μmol CO_2)[b]
Mg/Al-CO_3	71	n.d.
Mg/Al-OH	59	n.d.
Mg/Al-DBS	3	n.d.
Mg/Al-DBS-DEL	5	n.d.
Mg/Al-OH-DEL	67	n.d.
Mg/Al-NO_3-DEL	66	n.d.
Mg/Al-CO_3-450	107	348
Mg/Al-OH-450	149	361
Mg/Al-OH-DEL-450	198	403
Mg/Al-NO_3-DEL-450	176	372

[a] Specific surface area.
[b] Number of basic sites (n.d. = non determined).

be seen, intercalating DBS ions dramatically reduced the specific surface area of the solid by effect of the organic molecules covering the surface of brucite-like layers and hindering access of any others. The specific surface area of the LDH containing interlayer carbonate was consistent with reported values for similar solids [28]. The calcination–rehydration process caused a slight decrease in specific surface area. On the other hand, delamination increased the area of MgAl-OH, albeit only slightly. MgAl-NO_3 was similar to MgAl-OH in this respect, but the DBS-containing LDH had a very low specific surface area relative to them. Consistent with reported results [28], calcination at 450 °C invariably increased surface areas. The increase was especially marked in the mixed oxides obtained from the delaminated solids. As regards basic sites, delamination and subsequent calcination led to the formation of more basic solids (particularly MgAl-OH-450).

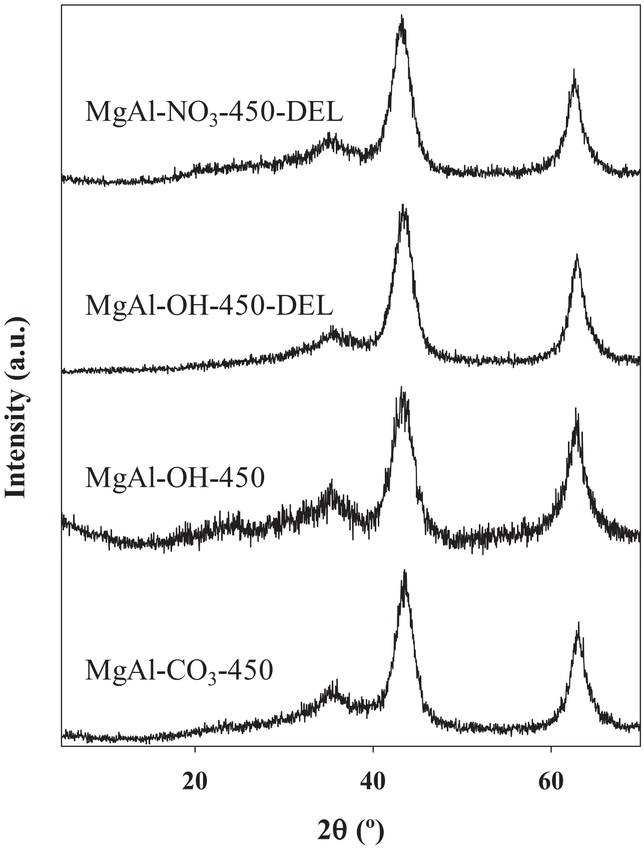


Fig. 3. XRD patterns for calcined LDHs.

3.2. Meerwein–Ponndorf–Verley reaction

All synthetic LDHs and their calcination products were tested as catalysts in the MPV reaction of benzaldehyde with 2-propanol as hydrogen donor. In previous work [28], we found the MPV reactions of aldehydes and ketones in the presence of mixed oxides obtained from Mg/Al hydrotalcites to exhibit a linear correlation between the natural logarithm of the concentration of the carbonyl compound and the reaction time (i.e. the reaction to be first-order in the aldehyde or ketone concentration). Fig. 4 shows the temporal variation of the conversion to benzyl alcohol with the four most active catalysts. As can clearly be seen, the slopes of the curves for the catalysts obtained from delaminated solids were greater than those for the catalysts obtained by calcining undelaminated solids. Table 3 shows the initial catalytic activity in mmol benzyl alcohol per hour per gram of catalyst and the rate constant, in addition to conversion and selectivity data. As noted earlier, the initial catalytic activity was greater for the solids obtained by calcining delaminated solids than for those from calcined undelaminated solids. The selectivity was 100% or very close to this value with all catalysts.

The reaction develops via a concerted process involving both benzaldehyde and the donor (alcohol), and the formation of a six-membered cyclic intermediate adsorbed on the catalyst surface (see Scheme 2) [22,39,40]. This mechanism is similar to that

Table 3
Catalytic activity, rate constant and conversion to benzylalcohol obtained in the Meerwein–Ponndorf–Verley reaction of benzaldehyde with 2-propanol.[a]

Solid	r_a[b]	k[c]	Conversion (%)[d]	Selectivity (%)[e]	t (h)[f]
Mg/Al-CO_3	–	–	0	–	24.0
Mg/Al-OH	0.08	0.002	65	96	24.0
Mg/Al-DBS	–	–	0	–	24.0
Mg/Al-DBS-DEL	–	–	0	–	24.0
Mg/Al-OH-DEL	0.17	0.009	79	95	24.0
Mg/Al-NO_3-DEL	0.19	0.012	82	96	24.0
Mg/Al-CO_3-450	1.32	0.869	96	98	3.5
Mg/Al-OH-450	1.89	1.034	98	100	3.5
Mg/Al-OH-DEL-450	5.40	2.142	100	100	2.0
Mg/Al-NO_3-DEL-450	4.73	1.633	97	100	2.0

[a] Reaction conditions: $T = 82\,^\circ C$; 0.003 mol of benzaldehyde; 0.06 mol of 2-propanol; 1 g of catalyst.
[b] Catalytic activity at 10% conversion, in mmol of benzylalcohol·h^{-1} g^{1}.
[c] Rate constant, in h^{-1}.
[d] Conversion to benzyl alcohol.
[e] Selectivity to benzylalcohol.
[f] Reaction time.

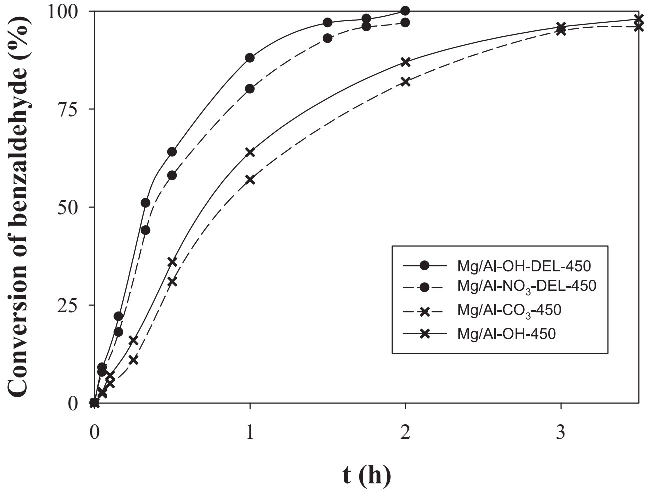
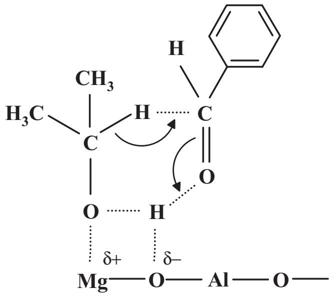


Fig. 4. Temporal variation of the conversion to benzyl alcohol in the MPV reaction of benzaldehyde with 2-propanol as catalysed by varios catalysts. Reaction conditions: $T = 82\,^\circ C$; 0.003 mol of benzaldehyde; 0.06 mol of 2-propanol; 1 g of catalyst.

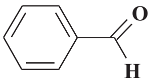
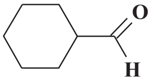
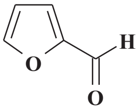
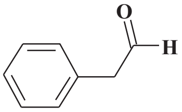
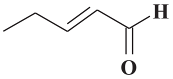
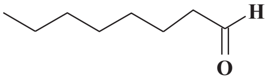


Scheme 2. Proposed mechanism for Meerwein–Ponndorf–Verley reaction of benzaldehyde with 2-propanol over calcined Mg/Al LDH.

reported for the same process with a Lewis acid catalyst such as beta zeolite [41–43]. In this case, the first step of the process involves chemisorption of the hydrogen-donor alcohol at a Lewis acid site (Al^{3+} ion). This results in the formation of a surface alkoxide that is assumed to be the activated hydrogen donor. Subsequent coordinative interaction of the carbonyl compound with this acid site causes the formation of a six-membered transition state similar to that of Scheme 2. This mechanism was subsequently confirmed by Peters et al. [44] using deuterated 2-propanol. Therefore, the activity of a solid acting as a catalyst for the reaction will be closely related to its surface chemical properties. As can be seen from Table 3, the LDHs intercalated with carbonate and DBS were inactive in the reaction (conversion after 24 h in their presence was zero). On the other hand, the solid intercalated with hydroxyl ions was active and exhibited 50% conversion after the same reaction time. One plausible explanation for these results is the difference in accessibility to basic sites between solids. Basicity in LDHs can be ascribed to Brönsted sites (viz. hydroxyl groups at the edges of brucite-like layers). According to Winter et al. [45], the basicity of carbonate-, oxalate- and hydroxyl-containing LDHs is related to the accessibility of reactant molecules to these hydroxyl groups. Calcining and rehydrating a carbonate-containing LDH leads to a new, structurally distorted LDH as reflected in its XRD pattern. The distortion causes Brönsted basic sites at the edges of brucite-like layers to be more readily accessed by reactant molecules than in carbonate- or DBS-containing LDHs, which are much more crystalline. Therefore, the solid MgAl-OH must possess a greater catalytic activity than MgAl-CO_3 and MgAl-DBS. The solid obtained by delaminating and ion-exchanging MgAl-DBS (i.e. MgAl-DBS-DEL) continued to be inactive in the reaction, probably because of the steric hindrance posed by the long hydrocarbon chains bonded to the brucite-like layers. With MgAl-OH-DEL and MgAl-NO_3-DEL, conversion was much higher than with undelaminated MgAl-OH, however. These results can be ascribed to the solids consisting of discrete brucite layers being more accessible by the reagents than the corresponding layered solids. In addition, solids containing an organic anion have a very low specific surface area. In any case, conversions were rather poor as a result of the catalytic effect involving Lewis basic sites. For this reason, we used the calcined LDHs and delaminated solids, which were Mg(Al)O mixed oxides containing Lewis O^{2-} sites.

Table 3 shows the conversions to benzyl alcohol obtained with the LDHs and delaminated solids calcined at 450 °C. Clearly, the mixed oxides obtained by calcination of hydrotalcites are much more effective catalysts for the MPV reaction than are their uncalcined precursors. This is consistent with the proposed reaction mechanism [39,22]. Thus, based on Scheme 2, the hydrogen transfer takes place via a concerted process where 2-propanol and the carbonyl compound are absorbed onto the catalyst surface to form a six-membered cyclic intermediate. The surface of these solids can be assumed to contain pairs of strong Lewis basic sites (O^{2-} ions) and Lewis acid sites (coordinatively unsaturated Mg^{2+} and Al^{3+} ions). Therefore, the ability to adsorb 2-propanol molecules will increase with increasing number of sites; as a result, the solid with the greatest number of basic sites can be expected to be the best catalyst and that with the smallest the one giving the lowest conversions. In previous work [46], our group found the MPV reduction of citral in the presence of catalysts consisting of mixed oxides of magnesium and a trivalent metal to be directly related to the

Table 4
Results obtained in the MPV reaction of aldehydes with 2-propanol using MgAl-OH-DES-450 and MgAl-OH-450 as catalysts.[a]

Entry	Reactant	MgAl-OH-DES-450		MgAl-OH-DES-450	
		Conversion (%)[b]	*t* (h)[c]	Conversion (%)[b]	*t* (h)[c]
1		100	2.0	98	3.5
2		100	3.0	96	4.8
3		100	1.9	98	3.3
4		97	3.0	96	4.2
5		100	3.0	100	5.0
6		98	3.0	98	5.0

[a] Reaction conditions: $T = 82\,^{\circ}\mathrm{C}$; 0.003 mol of aldehyde; 0.06 mol of 2-propanol; 1 g of catalyst.
[b] Conversion to alcohol.
[c] Reaction time.

surface basicity of the oxides. In fact, our most active catalyst was also the most basic. The catalytic activity and conversion results of Table 3 are also strongly correlated with the basicity results of Table 2: the most active solids were those containing the largest populations of basic sites.

In order to check whether this catalytic behaviour applied to all solids, we conducted the reaction by using other substrates and MgAl-OH-DES-450 and MgAl-OH-450 as catalysts. Table 4 shows the conversion obtained with the two catalysts after different reactions times. Irrespective of the nature of the hydrocarbon chain of the aldehyde, the catalyst obtained by calcining the delaminated solid provided increased conversion values at shorter reaction times than that obtained from the undelaminated solid.

Finally, we assessed catalyst regeneration and recycling by using the most active catalyst, MgAl-OH-DES-450, in the reaction of benzaldehye with 2-propanol. To this end, we initially used the catalyst as isolated by filtering from the reaction mixture. The conversion values thus obtained were very poor. This led us to regenerate it by washing with methanol (25 mL/g catalyst) four times and calcination at 450 °C for 2 h. Under these conditions, conversion in successive reuses was similar to that obtained with fresh catalyst (*viz.* 100% within 2.5 h).

4. Conclusions

An Mg/Al LDH containing dodecylbenzenesulphonate as interlayer ion was efficiently delaminated in the presence of 1-butanol and ultrasound. The exfoliated solid was ion-exchanged to obtain discrete LDH nanolayers the excess positive charge in which was countered by nitrate or hydroxyl ions. These solids provided moderately good results as catalysts in the Meerwein–Ponndorf–Verley (MPV) reduction of benzaldehyde with 2-propanol (conversions at 24 h were in the region of 80%). In any case, they clearly surpassed the solids obtained from undelaminated LDHs containing carbonate or hydroxyl interlayer anions, which were inactive in the reaction and exhibited 50% conversion only after 24 h, respectively. These results can be explained in terms of accessibility of hydroxyl groups at layer edges, which are Brönsted basic sites. In highly crystalline LDHs, accessibility to such sites is poor but increases when the crystal lattice is distorted; hence, MgAl-OH, with a reduced crystallinity, was active in the reaction, whereas MgAl-CO_3 was completely inactive. Delamination facilitated access of the reactant molecules to hydroxyl ions at layer edges in the LDHs, thereby increasing conversion in the MPV reaction. Calcining layered and delaminated LDHs at 450 °C produced mixtures of Mg(Al)O double oxides with a high surface basicity of the Lewis type. The calcined solids exhibited excellent (quantitative or nearly quantitative) conversion after only 2 h of reaction.

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