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ORIGINAL REPORT

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Layered double alkoxides a novel group of layered double hydroxides without water content

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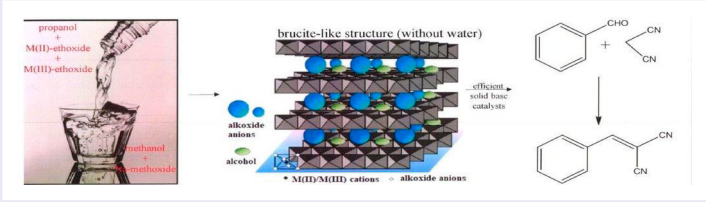
ABSTRACT

It has been generally accepted for long that water molecules are integral parts of layered double hydroxides (LDHs). It is even thought that in the absence of water molecules, there is no LDH structure. It is shown in this contribution that *via* the solvolysis of Mg- or Ca-alkoxides and Al-alkoxide with methanol or propanol and co-precipitated in methanolic methoxide, water-free LDH-like structures could be constructed. These novel LDH-like materials proved to be more active and selective catalysts in a Knoevenagel condensation than the corresponding 'classical' LDHs.



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KEYWORDS
Water-free LDH; colloidal phase co-precipitation; alkoxide–solvolysis; solid base catalyst

IMPACT STATEMENT

Synthesis, thought to be not possible to prepare, characterization and a catalytic application of water-free LDHs are described. Water molecules are replaced by small alcohol molecules in the interlayer space.

Introduction

Clearly proven by the over ∼30,000 articles published up to now since the nineties of the previous century that layered double hydroxides (LDHs), often called as anionic clays, became one of the most intensively studied material group.

Many scholars are working in this field, and this a broad one, spanning from intense research concerning the synthesis, modification and structural characterization of LDHs [1–6], through many applications like vehicles of medically important compounds [7–9] or polymer additives [10] to catalysis serving as catalysts either in their pristine layered forms [11–15] or after heat treatment forming mixed oxides with many vacancies [16–23].

MgAl- and CaAl-LDHs, the most frequently used representatives of the group, have positively charged brucite- and portlandite-like layers, respectively, with interlayer regions containing fully or partially hydrated charge-compensating anions [24]. Water molecules not only serve as the hydrate shells of the interlayer anions, but they are situated at different positions of the interlayer space attaching to the layers with intermolecular hydrogen bonds of varying strengths [25].

Some examples can be found in the literature that the decrease in the water-content can bring important

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benefits. Alkoxide and transition metal-containing systems behave as 2D materials, which are easy to exfoliate and re-build as ultrathin films [26]. These films are excellent candidates for energy storage and conversion. Furthermore, water-free ZnAl films have photoluminescence property [27]. Moreover, having high surface area with notable porosity, the alcohol-treated systems were found to be better absorbent than pure LDH [28].

As it has been mentioned already, water molecules establish hydrogen-bonded networks in the interlayer space of the LDH. However, in principle, hydrogen-bonded networks may also be made by small alcohol molecules. These molecules may form the solvate shell of the charge-compensating anions as well. Thus, we set out to attempt the preparation of LDH-like structures, where water molecules are expected to be replaced by small alcohol molecules. For the attempted syntheses, the solvolysis of Mg(II) and Al(III) ethoxides or Ca(II) and Al(III) ethoxides were performed in a variety of alcohols at various temperatures, and they were co-precipitated in methanolic methoxide. Here, mainly results obtained with the Mg(II) ethoxide–Al(III) ethoxide system will be shown, for details of the results concerning the Ca(II) ethoxide–Al(III) ethoxide system, see the Supplementary Material (SM, all figures, the table and the scheme start with 'S') file.

Materials and methods

Synthesis of CaAl- and MgAl-layered alkoxides

All chemicals used were of analytical grade Sigma–Aldrich products, and were applied without further purification.

Water-free LDHs were prepared *via* the modified co-precipitation method: 0.015 mol of M(II) ethoxide and 0.0075 mol of M(III) ethoxide were solvolysed in 100 ml of methanol or ethanol or 2-propanol or propanol with constant stirring at 25 or 60°C for 24 h. The suspension obtained was dropped into a methanolic solution containing an appropriate amount of sodium methoxide to achieve the pH of precipitation. The 24 h room-temperature stirring of mixtures were followed by filtration, washing and drying (24 h, 25°C). All applied chemicals were water-free. The water contents of the solvents were removed using sodium-dosed distillation.

For comparison, nitrate-containing LDH samples were prepared by the co-precipitation method. As an example, for the synthesis of the pristine $Ca_2Al–NO_3^-$–LDH/$Mg_2Al–NO_3^-$–LDH samples, a mixture of $Ca(NO_3)_2 \times 4\ H_2O/Mg(NO_3)_2 \times 6\ H_2O$ (30 mmol) and $Al(NO_3)_3 \times 9H_2O$ (15 mmol) was dissolved in 100 ml of distilled water and was stirred at pH 13 (set by 3 M NaOH) for 12 h. The suspension was filtered and dried for 24 h at 60°C.

All operations were performed under N_2 atmosphere to avoid interlayer carbonate formation.

Characterization methods

Powder X-ray diffraction (XRD) patterns of the solid samples were recorded in the $2\theta = 5–60°$ range (θ is the incidence angle of the X-ray beam) on a Philips PW1710 instrument with a secondary monochromator, using CuKα ($\lambda = 0.1542$ nm) radiation with 4°/min scanning step.

The morphology of the composites was studied by scanning electron microscopy (SEM). The SEM images were made on an S-4700 scanning electron microscope (SEM, Hitachi, Japan) with accelerating voltage of 10–18 kV. EDX data were obtained with a Röntec QX2 energy dispersive microanalytical system from two different parts of the sample. The coupled system also provided with the elemental map.

More detailed images could be recorded by transmission electron microscopy (TEM). A FEI Tecnai^{TM} G2 20 X-Twin type instrument was used operating at an acceleration voltage of 200 kV.

A BIO-RAD Digilab Division FTS-65A/896 apparatus was available for IR spectroscopy measurements with 4 cm^{-1} resolution. The 4000–600 cm^{-1} ranges were recorded collecting 256 scans for each spectrum. Attenuated total reflection (ATR) mode was used for detection.

The ratio of metal ions was determined by Perkin Elmer Optima 7000DV Inductively Coupled Plasma Optical Emission (ICP-OES) spectrometer. Yttrium internal standard was used for each measurement. Before measurements, few milligrams of the samples measured by analytical accuracy were dissolved in 5 cm^3 cc. HCl. After dissolution, the samples were diluted with distilled water to 100 cm^3 and filtered.

Catalytic procedure for Knoevenagel condensation

Malononitrile (15.00 mmol), benzaldehyde (10.0 mmol) and dodecane as internal standard were mixed to get a clear solution using 3 cm^3 ethanol as solvent. The reaction was quenched after 1–120 min with 6N HCl in ice-cold conditions. The product was extracted with ethyl acetate ($3 \times 10\ cm^3$). The combined organic extracts were dried using anhydrous sodium sulphate, evaporated under reduced pressure, and assayed on a GC. Conversions in all cases were monitored with respect to the diminution of the aldehyde by gas chromatography. A Hewlett-Packard 5890 chromatograph equipped with

FID was employed for the analysis. The products were identified via using authentic samples.

Results and discussion

The effects of the solvents and the temperature of solvolysis for the material obtained from the solvolysis-co-precipitation of Mg(II) and Al(III) ethoxides are presented in Figure 1 through selected typical examples.

Application of water-free methanol, ethanol and 2-propanol did give diffractograms resembling those of the LDHs; however, the crystallinity of the structures obtained were rather poor in methanol at both temperatures, and side-products were observed in both ethanol and propanol even at 25°C. On applying propanol, XRD pattern resembling crystalline layered material was observed at both temperatures with somewhat sharper reflections at 60°C. These patterns were indexed on the basis of nitrate-containing Mg_2Al–LDH (JCPDS#70-2151). The ICP-OES analysis (supported by EDX measurements as well) resulted in 2.05:1 actual molar ratios for the Mg(II):Al(III) (it is 1.85:1 for Ca(II):Al(III) ratio) indicating similarity between the newly and the classically prepared (co-precipitation in basic aqueous ethanol) structure.

The SEM image of the material prepared at 60°C using propanol revealed hexagonal morphology like the LDHs (image A of Figure 2), and the TEM image further verified that a material was formed with hexagonally-shaped platelet-like particles (image B of Figure 2).

Similar observations were made for the Ca(II) ethoxide–Al ethoxide system solvolysed in propanol at 60°C (see, SFigures 1 and 2).

All these findings verify that layered materials were formed, indeed.

Further supporting characterization was performed by SEM-EDX measurements, for the EDX spectra and the elemental maps, see SFigures 3 and 4, and cell parameter data for the layered materials are given in STable 1.

The thermal decomposition profile (SFigure 5(a)) contains a sharp weight loss at 346°C not seen in the thermograms of LDHs prepared by aqueous precipitation (thermal decomposition profile of MgAl–CO_3^{2-}–LDH is seen in SFigure 5(b) 3(b)). It is probably due to the decomposition of the interlayer alkoxide ions. The decomposition of the starting Mg(II)Al(III) ethoxide takes place under 300°C [29,30], i.e. the interlayer alkoxide ions are strongly fixed between the layers. The highest weight loss (30%) occurred at 120°C indicating the departure of interlayer propanol and methanol.

The TG/DTG thermograms for the Ca(II)Al(III) ethoxide can be found in the SM file as SFigures 6(a) and (b).

In the ATR-IR spectrum of the material prepared by solvolysis-co-precipitation from Mg(II) and Al(III) ethoxide (spectrum B of Figure 3) at 60°C, intense peaks are observed at around 1057 and 3645 cm^{-1} associated with CO stretching vibration and isolated OH stretching vibration of primary alcohol Another peak at around 1465 cm^{-1} was attributed to bending vibration of

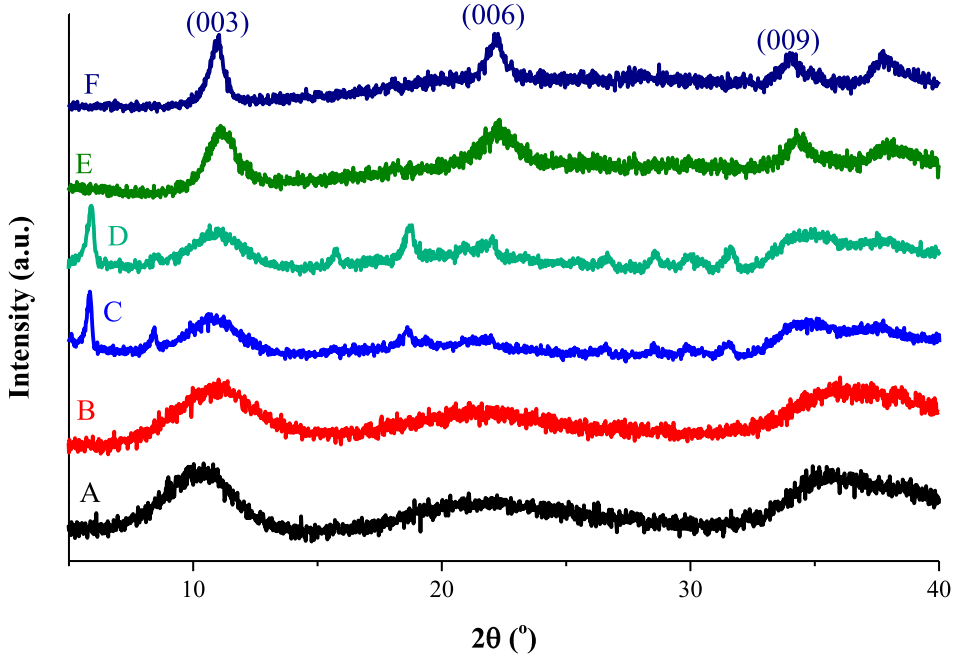

Figure 1. Selected XRD patterns obtained after the solvolysis-co-precipitation of Mg(II) and Al(III) ethoxides in (A) methanol at 25°C and (B) 60°C, (C) ethanol at 25°C, (D) 2-propanol at 25°C, (E) propanol at 25°C and (F) 60°C.

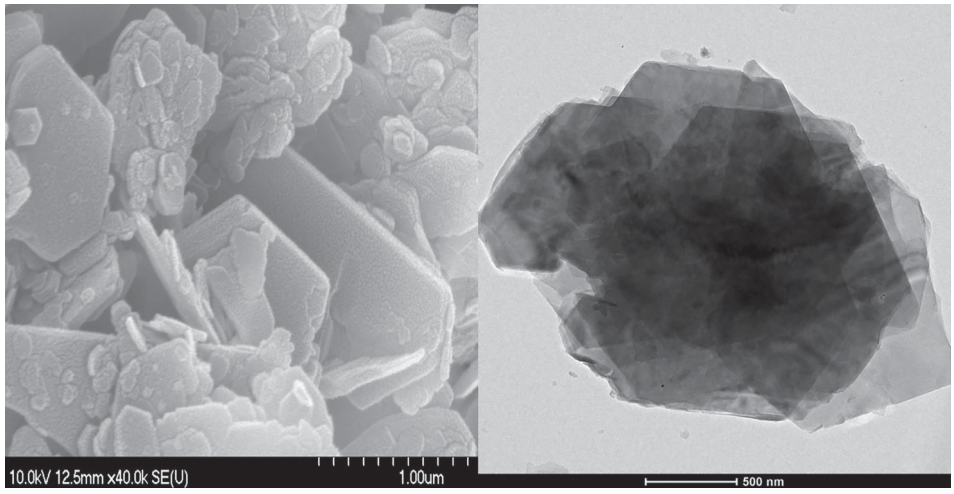

Figure 2. The (A) SEM and the (B) TEM images of the material prepared by solvolysis-co-precipitation of Mg- and Al-ethoxides at 60°C using propanol for solvolysis-co-precipitation.

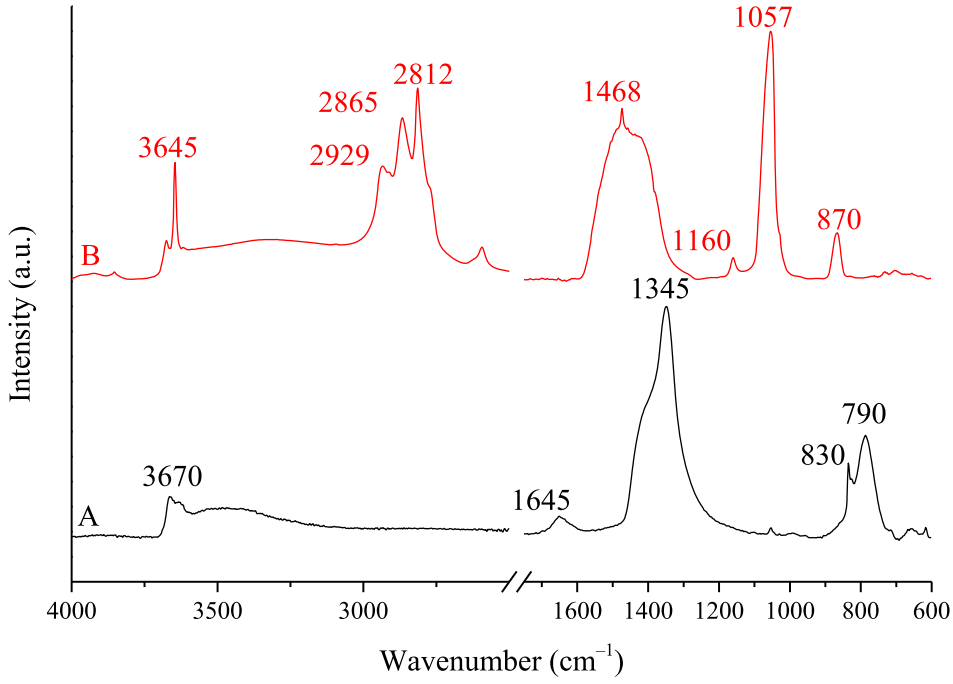

Figure 3. IR spectra of (A) MgAl–NO_3^-–LDH and (B) MgAl–LDA prepared by solvolysis-co-precipitation of Mg(II) and Al(III) ethoxides at 60°C.

CH (alkane) of alcohol [31]. Other characteristic peaks centred at about 2800–3000 cm^{-1} were related to CH_3 stretching vibrations of alcohols [32,33]. Peaks at 1160 and 870 cm^{-1} can be identified as CO stretching and CH_2 bending vibrations of longer chain alcohol (e.g. propanol), respectively [34].

Most importantly, the IR spectrum of the material does not contain the typical water H–O–H bending vibration around 1645 cm^{-1}, which is clearly detectable in the IR spectrum of the MgAl–NO_3^-–LDH sample made by aqueous precipitation (spectrum A of Figure 3). In addition, in the high wavenumber region, a new peak at about 3400–2600 cm^{-1} was registered for the water-free sample composing of C–H stretching and the interlayer O–H stretching vibration modes typical of hydrogen-bonded systems [35] confirming that hydrogen-bonded alcohol molecules substituted the water molecules in this structure. The deconvoluted spectrum is displayed in Figure 4.

Similar assignation can be provided for CaAl–LDA.

These observations verify that indeed, a water-free layered substance is in our hands. This observation holds for

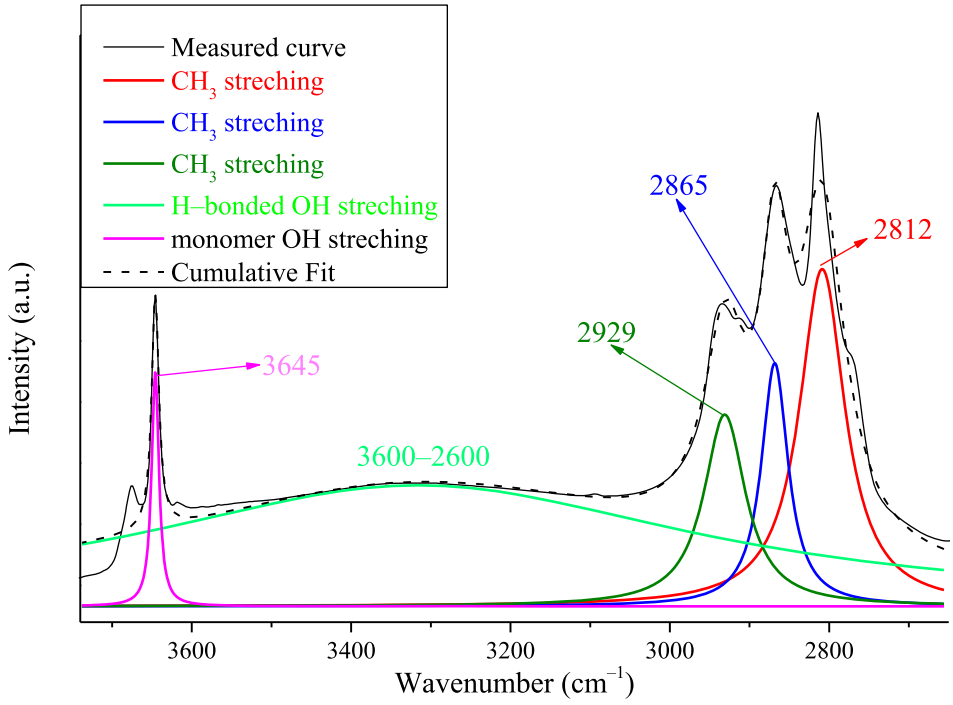

Figure 4. Deconvoluted IR spectrum of MgAl–LDA in the 3750–2550 cm^{-1} range.

the CaAl system as well (SFigure 7). From now on, these substances are going to be called water-free MgAl–LDA and water-free CaAl–LDA.

The storage time of LDA was 9 months in air. To our surprise, the degradation product could be isolated as Li methylcarbonate analogous structure by IR spectroscopy (SFigure 8). All the characteristic vibrations, such as the asymmetric (1590 cm^{-1}) and symmetric (1468 cm^{-1}) stretching vibrations of O–C–O in the monomer, the same vibration modes related to the dimer form (1405, 1361 cm^{-1}) as well as the out-of-plane bending vibrations (873, 830 cm^{-1}) proved the formation of metal methylcarbonate [36]. This observation indirectly supports that the synthesis of water-free LDA was successful, because this coordination compounds have already been produced by the interaction of inorganic methoxides (e.g. lithium methoxide) with CO_2 in (non-aqueous) methanol [37].

MgAl–LDHs prepared by the conventional aqueous co-precipitation method only displayed appreciable catalytic activities in the Knoevenagel condensation between benzaldehyde and malononitrile (SScheme 1) after heat-treatment [38] or doping with base [39] or in the presence of water [40]. Even after doping, the selectivity towards the condensation product was not 100%.

However, both water-free substances proved to be efficient, recyclable catalysts being fully selective towards the condensation reaction (Figure 5). For the optimization of catalyst loading, solvent used and reaction temperature, see, SFigure 9, STable 1, SFigure 10, respectively.

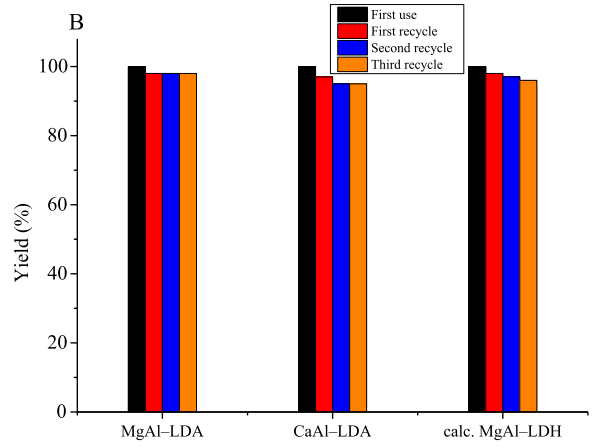

Figure 5. The yield of the Knoevenagel reaction over the various LDH-structured systems and the reusability of the materials. Conditions: benzaldehyde (10.0 mmol) and malononitrile (15.0 mmol); solvent-free, $m_{cat} = 0.2$ g, T = 75°C.

The addition product was fully transformed to the condensation product, which did not react any further, i.e. no Michael adduct could be observed. Hydrotalcites and hydrocalumites needed activation [37–41], while our water-free LDHs worked in their as-synthesized forms and under mild conditions (small amounts of catalysts, low reaction temperature, free of solvent and short reaction time).

Conclusions

On the basis of experimental results presented, it was shown that the generally accepted belief that LDHs must contain water molecules, can be circumvented. LDH-like structures could be prepared free of water by applying short-chain alcohols as the agents for solvolysis. XRD patterns and electron microscopy images and IR spectroscopy revealed ordered structures with hexagonally shaped morphologies, i.e. structures analogous to those of LDHs and water-free environments. The water free, as-prepared LDH-like substances proved to be active, highly selective and recyclable catalysts in the Knoevenagel condensation of benzaldehyde and malononitrile under mild reaction conditions unlike the analogous LDHs, which needed activation of some sort.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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