



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

As-prepared and intercalated layered double hydroxides of the hydrocalumite type as efficient catalysts in various reactions

Pál Sipos^{a,b}, István Pálinkó^{a,c,*}^a Materials and Solution Structure Research Group, Institute of Chemistry, University of Szeged, Aradi Vértanúk tere 1, Szeged, H-6720 Hungary^b Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, Szeged, H-6720 Hungary^c Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary

ARTICLE INFO

Article history:

Received 28 August 2016

Received in revised form 7 October 2016

Accepted 1 December 2016

Available online xxx

Keywords:

Layered double hydroxides

Synthesis methods

Structural characterization

Oxidative transformations

Cross-aldol dimerization-condensation

Activities

Selectivities

Recycling abilities

ABSTRACT

The activities of the research group in the synthesis, characterization and, especially catalytic applications of layered double hydroxides (LDHs) of the hydrocalumite type are reviewed placing the work in literature context. In the project, CaFe- and CaAl-LDHs and their intercalated varieties were synthesized with wet chemical, mechanochemical and ultrasonically-assisted mechanochemical methods, and their structural characterization was performed with state-of-the-art methods. Metal ion [Mn(II), Cu(II), Fe(III) or Ni(II)]-amino acid (L-tyrosine, L-histidine or L-cysteine)–CaAl-LDH composites were also prepared and characterized. The as-prepared LDHs and composites were applied in a wide range of reactions like epoxidation/oxidation of olefins with or without additional functionality, the Baeyer-Villiger oxidation, cross-aldol dimerization–condensation or the Ullmann-type coupling reactions. The activities, selectivities and recycling abilities of the catalysts were investigated.

© 2016 Elsevier B.V. All rights reserved.

1. The main structural features and use of layered double hydroxides

In the last decades, layered double hydroxides (LDHs) in the following) received increased attention due to their wide-ranging applications, and to the relative ease of their availability and functional modification. They can be used as flame retardants [1], efficient adsorbents [2,3] or models of supramolecular systems [4,5]. LDHs also have considerable potential in health care; they can be applied as antacids, medicine stabilisers and even as transportation vehicles in delivering drug molecules [6]. They are good catalysts in, e.g., transesterification and hydrogenolysis reactions, in the synthesis of chiral metal complexes, and certain representatives have photocatalytic activity, too [1,7]. Finally, they are frequently used as catalysts of base-catalyzed transformations in their layered forms or, more frequently, after calcination (then the layered structure is lost) [8–10].

Generally speaking, the formula of an LDH may be given as $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{m-}_{x/m}nH_2O]^{x-}$, where M^{2+} and M^{3+} represent the di- and trivalent metal ions, $x = M^{3+}/[M^{2+} + M^{3+}]$ and A^{m-} are the interlayer anions with charge m [11]. It can be deduced from brucite, a lamellar $Mg(OH)_2$, where the divalent metal ions are partially and isomorphously substituted by trivalent (or, occasionally, tetravalent – e.g., Zr^{4+} , Sn^{4+}) cations. The excess positive charge of the layers is usually compensated by simple and exchangeable inorganic anions situated among the layers together with interlayer water molecules [12,13]. The variation of these anions gives numerous opportunities to modify the physical and chemical attributes of LDHs. Besides varying the interlayer anions, the ratio of the di- and trivalent metal ions in the layers can often be altered, and this may also modify the structural and catalytic characteristics of the LDH [14,15].

LDHs have peculiar properties. One of them is the so-called memory effect [16–18]. It is known that the layered structure is lost on heat treatment, but it is nearly completely regained under rehydrating conditions. There are some limitations though, the most important is that calcination temperature should not be too high. The actual upper limit of temperature depends on the specific LDH; however, generally speaking, at calcination temperature higher than 773 K, there is no return to the layered structure.

* Corresponding author at: Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720, Hungary.

E-mail address: palinko@chem.u-szeged.hu (I. Pálinkó).

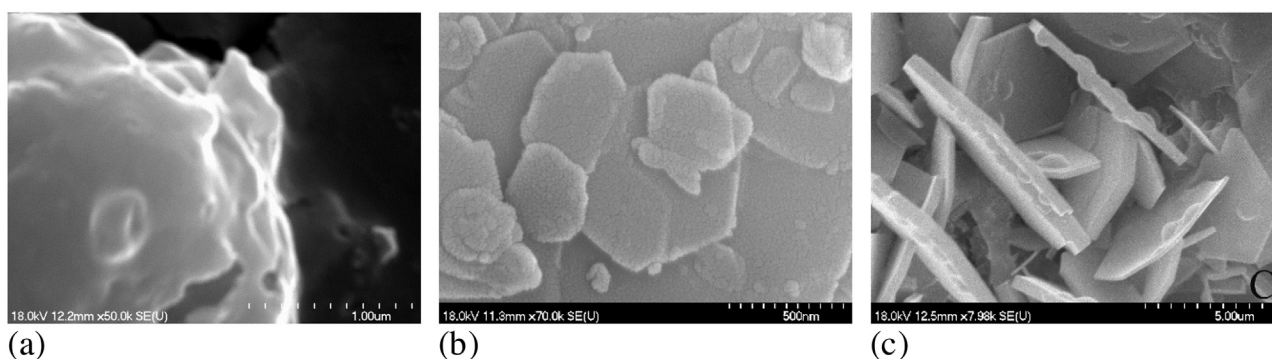


Fig. 1. The typical morphologies of (a) CaSn-, (b) CaAl- and (c) CaFe-LDHs.

CaAl-LDH, a member of the hydrocalumite supergroup, belongs to the hydrocalumite subgroup [19]. In this material, the aluminium ion has the expected octahedral coordination; however, the calcium ion, due to its increased size relative to magnesium ion is heptahedrally coordinated [20]. Single crystal X-ray diffraction measurements revealed two possibilities for occupying the seventh coordination site. For half of the calcium ions, it is the water molecule, while for the other half, it is the carbonate ion coordinated *via* one of the oxygens in the CaAl–CO₃-LDH composite [21]. The hydrocalumites can readily be synthesised, the most frequently used techniques are the co-precipitation, the urea and the sol-gel methods, all of them take place in solution, and apply soluble salts of metal ions as starting materials [22–25]. Another well-known preparation way is the hydration of the solid 3CaO·Al₂O₃ double oxide [26,27]. Finally, CaAl-LDHs can be prepared mechanochemically, either by manual grinding or milling of the suitable precursors [28].

The overwhelming majority of the relevant papers concerns layered double hydroxides; however, there are some describing three or more cationic components. Many ternary layered hydroxides (in the following, they will be called layered triple hydroxides, abbreviated as LTHs like for CoNiAl-LTH [29]) have been prepared and structurally characterized [30–35]. Homogenous cation distribution is typical in those ternary systems, which are related to common LDHs like MgAl-LDH, ZnAl-LDH [36] or CaAl-LDH [37], and either the di- or the trivalent ion was replaced in part.

2. Methods used for structural characterization

Powder X-ray diffractometry (XRD) is a major characterizing tool in LDH chemistry. XRD patterns are typical of LDHs, and the basal distance (interlayer space plus the thickness of one layer) and its change due to functionalization can be directly determined. Diffraction peaks can be identified by means of the JCPDS (Joint Committee of Powder Diffraction Standards) database.

High-resolution transmission electron microscopy can be used for verifying the formation of the layered structure, and, occasionally, direct measurements of the thickness of the layer and the interlayer spacing are possible.

Scanning electron microscopy is generally applied to examine the morphology of the CaFe- and CaAl-LDH samples (Fig. 1). They are coated with a few nanometres gold layer in order to get sharper images.

The actual Ca/Fe or Ca/Al metal ratios in the samples can be determined with energy dispersive X-ray analysis (EDX) measurements.

LDHs have typical thermal behaviour. Thermogravimetric measurements usually reveal three distinctive forms of water molecules. Physisorbed and interlayer water molecules are generally removed in the 100 °C–150 °C and 175 °C–325 °C ranges,

respectively, while water from the dehydration of structural OH groups and their closely associated (hydrogen bonded) water molecules leave between 350 °C to 475 °C. This ‘high-temperature form’ is frequently called ‘structural water’, although it exists in the form of OH groups in the layer, but it goes away as water on dehydration. The water forms can be distinguished with dielectric relaxation spectroscopy (DRS), and rehydration of the dehydrated LDH can also be monitored this way [17,18].

The Fourier-transform infrared (FT-IR) spectroscopy can be used for monitoring the interlayer anions, and, of course, some structural features of the LDHs can also be visualized.

For the identification of metal(ion)–O(S and/or N) vibrations, the far IR spectra are suitable. The difficulty lies in the scarcity of vibration–wavenumber correlation data. Purpose-made probe complexes can give the necessary correlation data [38].

XAS (X-ray absorption spectroscopy) is a synchrotron-based method with very useful characterization possibilities for the LDH host as well as the intercalated anions, especially if those are metal (ion) complexes. Coordination parameters (coordination number, geometry, bond distances, oxidation state) can be deduced from the near edge (XANES – X-ray absorption near edge spectroscopy) as well as the extended regions (EXAFS – extended X-ray absorption fine structure) [39,40]. The method is element (ion) specific and the range of elements, which can be studied depends on the capabilities of synchrotron facility.

EPR spectroscopy can be used for gathering information on the structure of the metal complexes if the metal or its ionic form is EPR active.

Mössbauer spectroscopy is a very appropriate method to map the immediate surrounding of a Mössbauer active nucleus. Unfortunately, there are not so many of them. In our case; however, in CaFe-LDH we have a nucleus like that, thus, ⁵⁷Fe Mössbauer spectroscopy was proved to be a very powerful structural characterization tool [15,41,42].

It is important to mention that although sophisticated instruments usually give significant structural information, the results of more traditional chemical analysis methods (concentration measurements of metal ions as well as amino acid ligands, after digesting the intercalated LDH [39,40]) are also indispensable in putting together the jigsaw puzzle of the complex structure of an intercalated LDH.

3. Syntheses methods of LDHs and their intercalated varieties

There are many routine ways of preparing LDHs [11,43]. One of the most often used methods is the co-precipitation of two (or more) precursors with a base, for instance, and most often, with an aqueous solution of NaOH at constant pH. For CaAl-LDH, the resulting material has typical X-ray diffractogram (see, also the indexing)

Download English Version:

<https://daneshyari.com/en/article/6504489>

Download Persian Version:

<https://daneshyari.com/article/6504489>

[Daneshyari.com](https://daneshyari.com)