



Cu(II)-amino acid–CaAl-layered double hydroxide complexes, recyclable, efficient catalysts in various oxidative transformations

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ABSTRACT

Intercalated composite materials were prepared with CaAl-layered double hydroxide as host and Cu(II)-amino acid (L-cysteine, L-histidine and L-tyrosine) complex anions as guests. Two methods (intercalation of the ligand first followed by constructing the complex; performing the complex first, then introducing it among the layers of the host) and optimization of the synthesis conditions were performed to obtain composites having the complex exclusively among the layers. The composite materials were structurally characterized by powder X-ray diffractometry, mid infrared (IR) spectroscopy with ATR (attenuated total reflectance) or photoacoustic detections, transmission and scanning electron microscopies and X-ray photoelectron spectroscopy. Structural features of the intercalant (coordination number, coordination sites) were elucidated by classical chemical and energy dispersive X-ray analyses, EPR (electron paramagnetic spectroscopy), X-ray absorption and far IR spectroscopies. Structural models based on these methods are also given. Catalytic activities, selectivities and recycling abilities of the substances were studied in the oxidation reactions of cyclohexene with peracetic acid and *in situ* formed iodosylbenzene as oxidants in the liquid phase. The catalysts were active in the Ullmann coupling reaction as well. The intercalated substances were found to be efficient and highly selective catalysts with very good recycling abilities.

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1. Introduction

Layered double hydroxides (LDHs), because of their relative ease of synthesis, represent inexpensive, versatile and potentially recyclable source of a variety of catalyst supports, catalyst precursors or actual catalysts. LDHs can be found in nature, but for applications they are usually synthesized. They have many representatives, and they have been classified [1]. Part of the hydroxaluminite supergroup is the hydrocalumite subgroup – the name giving mineral has the

formula of $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{A}\times n\text{H}_2\text{O}$ – having corrugated brucite-like main layers, which contain ordered arrangements of Ca^{2+} and Al^{3+} or other trivalent ions, seven- and six-coordinated, respectively, in a fixed molar ratio of 2:1. The layers are positively charged, which is compensated by interlayer anions. The anions are exchangeable with more or less difficulties, and even bulkier anions can also be introduced into the interlayer space.

Synthesis of LDHs is most often performed by a wet chemical method: co-precipitation of the LDH from the mixed solution of salt components by NaOH solution; however, mechanochemical routes for their preparation (for a recent original work and an even more recent review, see Refs. [2,3], respectively), occasionally, combined with ultrasound treatment, have been developed and applied [4]. The mechanochemical method worked well in

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the preparation of intercalated organic-inorganic host-guest complexes, too [5]. It is to be noted that the intercalated materials to be discussed here were made by the more commonly used direct anion exchange. The host was CaAl-LDH. The guests were Cu(II)-amino acid (L-cysteine, L-histidine and L-tyrosine) complex anions. Synthesis methods were optimized to arrive at composites having the complex exclusively among the layers. The comprehensively characterized organic-inorganic composites were used as catalysts in various oxidation reactions.

Metal complexes have already been incorporated in LDHs, and the early works have been reviewed [6]. Complexes of various transition metal ions (Ni(II), Co(II), Fe(II), Ir(III), Mo(IV, VI), Ru(II), ReO₂(V)) have been incorporated among the layers of LDHs; however, intercalated Cu(II) complex (the ligand was a phthalocyanine macrocycle) appears only once (the original Ref. [7]). Some works have been published since then, but real intercalation was only communicated in two papers [8,9]. The LDH and the ligands in the intercalated complexes were ZnAl-LDH and 2,2'-bipyridine-5,5-dicarboxylate [8], and MgAl-LDH and salicylidene-amino acid Schiff base with 1,10-phenanthroline or 2,2'-bipyridine [9]. Catalytic properties of the former intercalated complex were only studied [8]. Oxidation of styrene, ethylbenzene and cyclohexane produced benzaldehyde, acetophenone and a mixture of cyclohexanol and cyclohexanone, respectively, and the catalyst could be used for the second time as well.

However, the ligands have never been amino acids nor the host was CaAl-LDH in any of these works, and in this contribution, a more comprehensive structural characterization of the intercalated system is given than has been performed in the previous studies.

2. Experimental

2.1. Materials and the methods of synthesis

The LDH host containing nitrate anions as charge-compensating anions among the layers were prepared by co-precipitation method. It was synthesized as follows: a mixture of Ca(NO₃)₂ × 4H₂O (30 mmol) and Al(NO₃)₃ × 9H₂O (15 mmol) was dissolved in 100 ml of distilled water and was stirred at pH 13 for 12 h. The suspension was filtered and dried for 24 h.

For constructing the Cu-amino acid anions among the layers, two methods were used, similarly to that of the Mn(II)-amino acid anion-CaAl-LDH, published recently [10], and repeated here for the Cu(II)-containing derivatives. In *Method 1*, the amino acid anions were intercalated first, and it was followed by the introduction of the Cu²⁺ anions. In the first step, 2.5 × 10⁻⁴ moles of L-cysteine, L-histidine or L-tyrosine were used for the intercalation. The copper ions were introduced in the solution in various amounts (the molar ratio of the amino acid and the copper ions varied from 1:2 to 1:8). In order to identify the optimum conditions, the solvents (aqueous ethanol, aqueous acetone or water) and the pH (from 7.5 to 9.5) were also varied. Designation of composites prepared with *Method 1* will be CaAl-Cu(II)-amino acid anion-LDH. In *Method 2*, the Cu(II)-amino acid complexes were prepared separately applying the same amounts and ratios and varying the solution and the pH in the same way as in *Method 1*. Then, the solution containing the complex was used for the intercalation. Designation of the composites prepared with *Method 2* will be Cu(II)-amino acid anion-CaAl-LDH.

All synthetic operations were performed under N₂ protecting gas to exclude airborne CO₂ reacting with the water content of the LDH forming carbonate ion, which readily intercalates inhibiting the introduction of any other anion.

All the applied compounds were the products of analytical grade from Sigma-Aldrich (Germany), and they were used as received.

2.2. Methods of structural characterisation

X-ray diffraction (XRD) patterns of the fresh and used samples were recorded by a Miniflex II diffractometer (Rigaku, Japan) using Cu_{Kα} radiation (λ = 0.15418 nm) at 40 kV, 30 mA.

The layered structures of the freshly prepared and the used intercalated materials were studied by a TECNAI G₂20 X-TWIN transmission electron microscope (TEM, FEI, Germany, 200 kV accelerating voltage).

Morphologies of the pristine and the intercalated samples were investigated using an S-4700 scanning electron microscope (SEM, Hitachi, Japan) with accelerating voltage of 10–18 kV. E(nergy)Dispersion X(-ray) analysis data were obtained with a QX2 energy-dispersive microanalytical system (Röntec, Germany) from two different parts of the sample. The coupled system was applied for providing with elemental maps.

For BET measurements, a NOVA3000 instrument was applied (Quantachrome, USA). The samples were flushed with N₂ at 100 °C for 5 h to clean the surface of any adsorbents.

X-ray absorption measurements (X-ray absorption spectroscopy – XAS) were carried out on the K-edge of copper at beamline I811 of MAXIV-lab (Lund, Sweden). This is a superconducting multipole wiggler beamline equipped with a water-cooled channel cut Si(111) double crystal monochromator delivering at 10 keV, approximately 2 × 10¹⁵ photons/s/0.1% bandwidth with horizontal and vertical FWHM of 7 and 0.3 mrad, respectively. A beam-size of 0.5 mm × 1.0 mm (width × height) was used. The incident beam intensity (I₀) was measured with an ionization chamber filled with a mixture of He/N₂. Higher order harmonics were reduced by detuning the second monochromator to 70% of the maximum intensity. Data collection was performed in the fluorescence mode. The samples were placed in Teflon spacers closed with Kapton tape windows. Data were treated by the EXAFSPAK software package [11].

Combination of three different infrared (IR) techniques was applied for determining the positions of the amino acid anions and/or the anionic forms of the complexes. The instrument for recording the spectra was a Digilab Division FTS-65A/896 FT-IR (BIORAD, USA) spectrophotometer with 4 cm⁻¹ resolution. The 4000–600 cm⁻¹ wavenumber range was recorded, but the most relevant 1850–600 cm⁻¹ range is displayed and discussed. 256 scans were collected for each spectrum. The spectra of each sample were taken in the diffuse reflectance mode (observing both the surface and the bulk of the samples) and using a MTEC 200 photoacoustic (PA) detector (scan speed of 2500 Hz – exploring the composition of the bulk) as well as a single reflection diamond ATR accessory (detecting organic material on the surface of the LDH).

For the identification of Cu–O(S and/or N) vibrations, the far IR spectra were recorded with a Digilab Division FTS-40 (BIORAD, USA) vacuum F(ourier)T(ransform)–IR spectrophotometer (4 cm⁻¹ resolution, 256 scans). The Nujol mull technique was used between two polyethylene windows (the suspension of 10 mg sample and a drop of Nujol mull).

E(lectron)P(aramagnetic)R(esonance) spectroscopy was used for gathering information on the structure of the complexes. The spectra were recorded with a EleXsys E500 (BRUKER, Germany) spectrometer (microwave frequency 9.51 GHz, microwave power 12 mW, modulation amplitude 5 G, modulation frequency 100 kHz) in quartz EPR tubes at room temperature. Approximately 10 mg of samples were used for each measurement, and their spectra were recorded without any additional sample preparation. All recorded EPR spectra were simulated by an EPR computer program [12].

The amounts of metal ions between the layers were measured by an IRIS Intrepid II ICP-OES (Thermo Fisher Scientific, USA) spectrometer. Before measurements, a few milligrams of the intercalated complexes measured by analytical accuracy were digested

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