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Synthesis, characterization and photocatalytic activity of crystalline Mn(II)Cr(III)-layered double hydroxide

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ABSTRACT

Photocatalytic decomposition of methylene blue was attempted over as-prepared Mn(II)Cr(III)-layered double hydroxide (LDH) containing Mn(II) and Cr(III) in 2:1 molar ratio. The LDH was prepared by the co-precipitation method, and was found to form at pH = 10 and at 80 °C following 24 h hydrothermal treatment. The Mn_2Cr-LDH thus obtained was structurally characterized by X-ray diffractometry, scanning electron microscopy and energy-dispersive X-ray spectroscopy. The Mn_2Cr-LDH displayed significant photocatalytic activity in the degradation of methylene blue under illumination with UV–vis light. The photocatalytic performance of the phase-pure and uncalcined Mn_2Cr-LDH is practically identical to that of the commercially available Degussa P25 TiO_2, and it was found to remain unaltered over five consecutive photocatalytic runs. The presence of the LDH structure in the composite is the prerequisite of the photocatalytic activity. Applying increasing calcination temperature, the LDH structure gradually collapses, and the Mn_2Cr-LDH transforms to photocatalytically inactive double oxide.

1. Introduction

The use of heterogeneous photocatalysis in various industrial processes steadily increases, and photocatalysts are in the process of becoming more and more popular in a variety of practical applications. Even though traditional (non-photoactive) catalysts are still predominate and are produced in much higher amounts, photocatalysts offer a viable and environmentally friendly alternative in, *e.g.*, cleaning industrial sewage [1,2].

Certain types of composite materials are capable of catalysing transformations of both organic and inorganic compounds in a photocatalytic way [3]. Layered double hydroxides (LDHs) were among those tested. At the early stage of these studies, it was shown that both the treatment of the composite compound before the reaction and the reaction conditions play crucial role in the photocatalytic efficiency [4,5]. Transition metal-containing LDHs are usually poorly crystalline materials [6,7], and as long as this is the case, photocatalysts of poor performance was possible to be prepared of them. On the other hand, with increasing crystallinity, the specific surface area of the photocatalyst inevitably decreases, which may also exert an adverse effect on the photoactivity [8,9].

In this work, our aims were (i) the synthesis of manganese-chromium containing LDH samples with optimal crystallinity and (ii) their use as photocatalysts in the degradation of methylene blue, as model compound.

The trivalent cation of choice was Cr(III), because of its expected photoactivity [10]. It has been already shown that ZnCr-LDHs, due to the presence of Cr(III), displays photocatalytic activity [10], which can be enhanced by doping it with Tb(III) [11] or including graphene in the composite [12]. Although the divalent cationic partner is most often Zn(II) in the layers, some examples for applying Cu(II), Ni(II) and even Mg(II) are known [10,13,14]. It is to be noted, however, that Cr(III)-containing LDHs were only seldom made [15,16] and details about the synthesis is even more scarcely

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communicated [16]. The reason is probably the difficulty in preparing phase-pure material [15].

Methylene blue is a cationic dye easily adsorbed over various materials like titanate nanowires [17], titanate nanotubes [18,19]. It was our choice in testing the photocatalytic activity of our MnCr-LDH preparation, since it proved to be useful substance in probing the photocatalytic properties of various LDH composite materials [20,21], recently.

2. Experimental

For obtaining sufficiently crystalline LDH, the synthesis parameters were necessary to be optimized first. The pH and the temperature used during the synthesis of the LDHs and the molar ratio of the two metal ions were suspected to be critical factors in terms of the efficiency of the photocatalyst prepared, but other processing parameters like those of the hydrothermal treatment are also known to greatly influence crystallization and photocatalytic efficiency. Accordingly, the following experimental parameters were systematically varied during the preparation: pH (from 8 to 11); the preparation temperature (from 25 to 80 °C), the ratio between the di-and the trivalent ions (from 2:1 to 4:1).[1] Both nitrate and chloride salts were used for the syntheses; however, chloride salts were omitted, as it was observed that the LDH did not precipitate from the reaction mixture if chloride salts were utilized. During a typical, *e.g.,* Mn_2Cr-LDH, synthesis *via* co-precipitation, a mixture of analytical grade $Mn(NO_3)_2 \times 4H_2O$ (30 mmol) and $Cr(NO_3)_3 \times 9H_2O$ (15 mmol) (both are Reanal products) was dissolved in 100 mL of distilled water, and was stirred at pH = 10 for 24 h. The pH was adjusted *via* adding a solution of 3 M NaOH to the system, the pH of which was monitored with a calibrated glass electrode. The suspension was filtered, washed with distilled water and the blackish-blue crystals were dried for 24 h *in vacuo* over P_2O_5. Hydrothermal treatment [22] was carried out in a closed Pyrex glass vessel at 80 ± 3 °C, using continuous stirring. The resulting suspension was filtered and dried for 24 h *in vacuo* over P_2O_5.

The materials prepared were characterized by various methods.

X-ray diffractometry (XRD) was used to verify the success (or the failure) of the preparation of the LDHs, since LDHs are known to have characteristic XRD patterns. The XRD traces of the various samples were recorded on a Rigaku XRD-6000 diffractometer, using $Cu_{K\alpha}$ radiation (λ = 0.15418 nm) at 40 kV, 30 mA.

Scanning electron microscopy (SEM) was also employed to make the characteristic hexagonal morphology of the LDHs visible. The morphology of thin films was investigated using a Hitachi S-4700 scanning electron microscope with the accelerating voltage of 10–18 kV.

Energy dispersive X-ray (EDX) microspectroscopy gives a (semi)quantitative picture of the components in the material synthesized. EDX data were obtained on a Röntec QX2 energy dispersive microanalytical system from two different parts of the sample. The system was coupled to the SEM, and provided with the elemental map of the chosen region of the sample.

To identify interlayer anions, IR spectra of some selected samples were recorded. For this, a BIO-RAD Digilab Division FTS-65A/896 FT-IR spectrophotometer with 4 cm^{-1} resolution, using DRS technique was employed. Spectra in the 4000–600 cm^{-1} wavenumber range were recorded, but the most relevant 1850–600 cm^{-1} range will be displayed and discussed. 256 scans were collected for each spectrum.

The band gap of the material prepared was determined from the UV–vis spectrum registered on Ocean Optics USB4000 spectrometer with a DH-2000-BAL UV–vis-NIR light source measuring diffuse reflectance mode and using $BaSO_4$ as reference. The spectrum was analyzed with the SpectraSuite package. The band-gap energy was determined from the extrapolation of the straight section of the modified Kubelka-Munk function plotted *vs.* energy of the incident light. Bandgap determination was done only for the phase pure LDH, as this specimen was exclusively used for the photocatalytic tests.

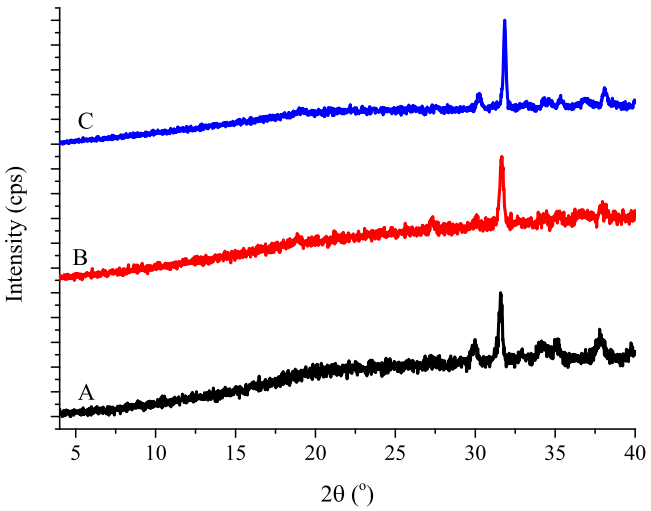

Fig. 1. XRD patterns for the solid substances obtained from a solution containing Mn(II) and Cr(III) in a molar ratio of 2:1 at various pH-s: A: pH = 9, B: pH = 10, C: pH = 11; the temperature of the reaction mixture was T = 25 °C.

For the photocatalytic tests, 1 mg of catalyst in 200 mL solution was used, the pH was controlled by a buffer based on KH_2PO_4 (0.15 M). To determine the best parameter set for the photocatalytic degradation, the pH of the solution (7–10), the temperature of the reaction mixture (8–50 °C) and the concentration of substrate, methylene blue that is (product of Aldrich Chemicals) were systematically varied. The photoreactor was an open Pyrex glass vessel. An OSRAM Power Star HCl-TC 70 W/WDL lamp (λ = 360–800 nm) was applied at a fixed position) for irradiating the reactor; the irradiation took place from vertical position, ca. 10 cm from the inlet of the vessel. The degradation of the dye was followed by UV–vis spectrometry on a Shimadzu UV–1650 spectrophotometer. Absorbance values at absorption maximum of methylene blue (665 nm) were recorded.

The X-ray photoelectron spectra (XPS) of the freshly prepared and the used samples were taken with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical electron energy analyzer (Germany) operated in the FAT mode. The excitation source was the Kα radiation of magnesium ($h\nu$ = 1253.6 eV) and aluminum ($h\nu$ = 1486.3 eV) anodes. The X-ray gun was operated at 180 W power (12 kV, 15 mA). The pass energy was set to 20 eV, the step size was 25 meV, and the collection time in one channel was 150 ms.

3. Results and discussion

3.1. Preparation and structural characteristics of the Mn_2Cr-LDH samples

During the preparative work, first, the synthesis of Mn_nCr-LDH with appreciable crystallinity was aimed at. As simple co-precipitation without hydrothermal post-treatment is reported to be a very efficient way of LDH preparation in general, therefore, this trivial synthesis route was initially employed [22,23]. As it is shown in Figs. 1–3 , *via* using this preparation method, the

[1] In the acronym used for the LDHs prepared, *i.e.,* Mn_nCr, n stands for the Mn:Cr molar ratio in the solid.

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