



Thermal behaviour of Cu–Mg–Mn and Ni–Mg–Mn layered double hydroxides and characterization of formed oxides

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Abstract

Thermal behaviour of synthetic Cu–Mg–Mn and Ni–Mg–Mn layered double hydroxides (LDHs) with M^{II}/Mg/Mn molar ratio of 1:1:1 was studied in the temperature range 200–1100 °C by thermal analysis (TG/DTA/EGA), powder X-ray diffraction (XRD), Raman spectroscopy, and voltammetry of microparticles. Powder XRD patterns of prepared LDHs showed characteristic hydrotalcite-like phases, but further phases were indirectly found as admixtures. The Cu–Mg–Mn precipitate was decomposed at temperatures up to ca. 200 °C to form an XRD-amorphous mixture of oxides. The crystallization of CuO (tenorite) and a spinel type mixed oxide of varying composition Cu_xMg_yMn_zO₄ with Mn⁴⁺ was detected at 300–500 °C. At high temperatures (900–1000 °C), tenorite disappeared and a consecutive crystallization of 2CuO·MgO (gueggonite) was observed. The high-temperature transformation of oxide phases led to a formation of Cu^I oxides accompanied by oxygen evolution. The DTA curve of Ni–Mg–Mn sample exhibited two endothermic effects characteristic for hydrotalcite-like compounds. The first one with minimum at 190 °C can be ascribed to a loss of interlayer water, the second one with minimum at 305 °C to the sample decomposition. Heating of the Ni–Mg–Mn sample at 300 °C led to the onset of crystallization of oxide phases identified as Ni_xMg_yMn_zO₄ spinel, (Ni,Mg)O oxide containing Mn⁴⁺ cations, and easily reducible XRD-amorphous species, probably free Mn^{III,IV} oxides. At 600 °C (Raman spectroscopy) and 700 °C (XRD), the (Ni,Mg)₆MnO₈ oxide with murdochite structure together with spinel phase were detected. Only spinel and (Ni,Mg)O were found after heating at 900 °C and higher temperatures. Temperature-programmed reduction (TPR) profiles of calcined Cu–Mg–Mn samples exhibited a single reduction peak with maximum around 250 °C. The highest H₂ consumption was observed for the sample calcined at 800 °C. The reduction of Ni–Mg–Mn samples proceeded by a more complex way and the TPR profiles reflected the phase composition changing depending on the calcination temperature.

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1. Introduction

A controlled thermal decomposition of hydrotalcite-like compounds (layered double hydroxides, LDHs), represented by the general formula $[M_1^{II}{}_{1-x}M_x^{III}(\text{OH})_2]^{x+}[A_{x/n}^{n-} \cdot y\text{H}_2\text{O}]^{x-}$ where M^{II} and M^{III} are divalent and trivalent metal cations and A^{n-} is an n -valent anion, gives finely dispersed mixed oxides of M^{II} and M^{III} usable in various applications. For example, many hydrotalcite-like compounds are used in heterogeneous catalysis as precursors for preparation of mixed oxide-based catalysts, whose catalytic performance strongly depends on the way of their thermal treatment (Cavani et al., 1991; Vaccari, 1998). Therefore, the thermal behaviour of the hydrotalcite-like compounds is studied in detail. In addition, the precursors of more complex oxide mixtures may essentially affect their final composition. For example, calcination of mixture of Mn nitrates with other transition metal salts yields primarily β - MnO_2 and subsequently cubic Mn_2O_3 , while homogeneous precursors of hydrotalcite-type yield preferentially mixed oxides at relatively low temperatures.

A great number of studies on thermal decomposition of layered double hydroxides was performed with synthetic Mg–Al hydrotalcite (Reichle et al., 1986; Hibino et al., 1995; Hudson et al., 1995; Bellotto et al., 1996; Rives, 2001). Two characteristic processes accompanied by a considerable weight loss and an endothermic effect can be observed during hydrotalcite heating: the release of interlayer water at 150–250 °C and the thermal decomposition at 350–600 °C, with a simultaneously proceeding transformation of the hydroxyl and carbonate groups into water and carbon dioxide, respectively. A new MgO phase starts to form above 400 °C and MgAl_2O_4 spinel crystallization is detected at 900 °C and higher temperatures. Thermal decomposition of the other hydrotalcite-like compounds containing various M^{II} and M^{III} metal cations can also be characterized by two endothermic transitions mentioned above. Both these transitions depend qualitatively and quantitatively on many factors, especially on the chemical composition (the nature and relative amounts of the M^{II} and M^{III} cations and the type of anions), the sample crystallinity, and the atmosphere used during decomposition. After dehydroxylation, the layered crystal

structure collapses and predominantly amorphous mixed oxides are obtained. A gradual crystallization of the oxides at higher temperatures can be observed and a $M^{II}M_x^{III}O_4$ spinel-like phase and/or divalent metal oxides $M^{II}O$ are usually detected in the powder XRD patterns. The ill-organized mixed oxides display generally three broad diffraction maxima corresponding to the future strongest lines of the spinel-like phase. Therefore, they are also called pre-spinel oxides and it is possible that the transformation from the layered structure to this oxide phase is topotactic (De Roy et al., 2001). In some cases, the transformation of primary oxides and the formation of new oxide phases could be observed at high temperatures. For example, the heating of copper-containing hydrotalcite-like compounds leads to the formation of CuO and/or Cu^{II} containing spinel-like phase. At least partial decomposition of Cu^{II} oxides takes place at temperatures above 900 °C and new Cu^I-containing oxide phases are formed (Kovanda et al., 2001). The transformation of primarily formed oxides was also observed during heating of the Ni–Mn hydrotalcite-like compounds (Barriga et al., 1996; Kovanda et al., 2003).

A large number of various M^{II} – M^{III} layered double hydroxides was prepared and reported in the literature. However, only a few papers reported on hydrotalcite-like compounds containing manganese. The layered double hydroxides occurring in nature, Mn^{II} –Al (charmarite) and Mg– Mn^{III} (desautelsite), were described by Chao and Gault (1997) and Dunn et al. (1979), respectively. Hansen and Taylor (1991) prepared the Mg–Mn layered double hydroxide of desautelsite type by air oxidation of MnCO_3 suspended in $\text{Mg}(\text{NO}_3)_2$ solution at constant pH ~9 and also by coprecipitation of Mg^{2+} and Mn^{2+} containing solution in strongly alkaline conditions. Fernandez et al. (1994) studied the thermal stability of Mg–Mn hydrotalcite-like compound prepared by the coprecipitation of $\text{Mg}(\text{NO}_3)_2$ and MnCl_2 solution in alkaline NaOH/ Na_2CO_3 solution. According to the temperature-programmed reduction (TPR), the main part of Mn^{2+} (84%) was oxidized to Mn^{3+} during the synthesis. The calcination of the Mg–Mn hydrotalcite-like compound caused its thermal decomposition at 390 °C, which was followed by the formation of an amorphous material. Crystallization of MgO and Mg_2MnO_4 spinel was

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