SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
8 (2002)

PREPARATIONS OF CHLORIDE, NITRATE, AND SULFATE FORMS OF HYDROTALCITE-LIKE COMPOUNDS BY MODIFIED UREA METHOD

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Received June 13, 2002

A group of hydrotalcite-like compounds with a general formula $[M(II)_{1-x}Al_x(OH)_2]^{x+}(A^{n-}_{x/n})\cdot mH_2O$ *(M(II) = Co, Mg, Ni, and Zn;* $A^{n-} = Cl^-$, NO_3^-, CO_3^{2-}, *and* SO_4^{2-}; $x = 0.31 - 0.36$; $m = 0.5 - 0.7$*) were prepared by a precipitation from soluble salts in the presence of urea. This method, described previously for a preparation of compounds with* $A^{n-} = CO_3^{2-}$, *was modified so that pure hydrotalcite-like compounds with either M(II) = Zn, Ni, Co and* $A^{n-} = Cl^-$ *or M(II) = Zn, Co, and* $A^{n-} = NO_3^-$, *suitable for further ion exchanges, can be prepared. The prepared compounds were characterized by thermogravimetric analysis, IR spectroscopy and their cell parameters were determined from powder XRD data.*

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Introduction

Hydrotalcite-like compounds (HTlc) form a large class of inorganic materials with a general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}_{x/n})\cdot mH_2O$, where M(II) = Mg, Mn, Co, Ni, Zn, etc., M(III) = Al, Cr, Fe, etc., and A^{n-} is a charge compensating anion (CO_3^{2-}, Cl^-, SO_4^{2-}, NO_3^-, ClO_4^-, organic anions, iso- and heteropolyanions, etc.). These compounds are extensively studied as catalyst precursors and supports, anionic exchangers and sorbents [1–4]. Hydrotalcite-like compounds are the only known layered solids with positively charged layers and interlayer charge balancing anions that may be exchanged by ion-exchange processes. It is well known that carbonates are the most retained among the counterions of hydrotalcites. Therefore the preparation of HTlcs with other anions in the interlayer space from their carbonate form is very difficult. On the other hand, HTlcs containing chlorides or nitrates can be indicated as the best precursors for the exchange reactions [3].

Synthetic HTlcs are usually prepared by co-precipitation of the M(II) and M(III) salts with diluted NaOH and/or $NaHCO_3$ or Na_2CO_3 solutions. Poorly crystalline samples are often obtained, unless a low degree of supersaturation and relatively high temperatures are maintained during precipitation. A hydrothermal treatment is often used to obtain well-crystallized samples. HTlcs containing other anions than carbonate are usually prepared by anion exchange. Recently, Costantino and coworkers [5] used a precipitation from a homogenous solution. They found that the hydrolysis of urea in the presence of a mixture of M(II) and M(III) chlorides lead to a formation of HTlcs with a good crystallinity and a narrow distribution of the particle size. The authors report the preparation of carbonate forms of Zn-Al, Mg-Al and Ni-Al HTlcs. According to them, this method also works for the $Mg-Fe-CO_3$ and $Al-Li-CO_3$ hydrotalcites and some difficulties were observed when attempts to prepare hydrotalcites containing Cr(III) and Cu(II) cations were made.

The aim of this work is to prepare HTlcs by the above described method with inorganic anions other than carbonate which can serve as starting materials for anionic exchange with, for instance, organic anions.

Experimental

The reagents used were $AlCl_3\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$, $Al_2(SO_4)_3\cdot 18H_2O$, $NiCl_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $NiSO_4\cdot 7H_2O$, $CoCl_2\cdot 6H_2O$, $Co(NO_3)_2\cdot 9H_2O$, $CoSO_4\cdot 7H_2O$, $MgCl_2\cdot 6H_2O$, $Mg(NO_3)_2\cdot 6H_2O$ which were of analytical purity and used as received. ZnO was used as a source of Zn^{2+}, weighed amount of ZnO was dissolved in the stoichiometric amount of 5 M solution of corresponding acid.

Solid urea (25 g, molar ratio urea/(M(II) + M(III)) = 3.3) was added to 0.5

Table I Preparation condition, formulas and lattice parameters of HTlcs obtained

System	Method	Yield, %	pH	Formula	a (Å)	c (Å)
Zn-Al-Cl	A	-	8.5	HTlc-Cl + HTlc-CO_3	-	-
Zn-Al-Cl	B	84	5.6	$Zn_{0.64}Al_{0.36}(OH)_2(Cl)_{0.36}\cdot 0.5H_2O$	3.086	23.44
Zn-Al-NO_3	A	-	7.5	HTlc-NO_3 + HTlc-CO_3	-	-
Zn-Al-NO_3	B	85	5.6	$Zn_{0.67}Al_{0.33}(OH)_2(NO_3)_{0.37}\cdot 0.5H_2O$	3.077	26.70
Zn-Al-SO_4	A	-	7.7	HTlc-SO_4 + HTlc-CO_3 + $Al(OH)_3$	-	-
Zn-Al-SO_4	B	-	5.5	HTlc-SO_4 + $Al(OH)_3$	-	-
Ni-Al-Cl	A	88	7.5	$Ni_{0.69}Al_{0.31}(OH)_2(CO_3)_{0.155}\cdot 0.7H_2O$	3.065	23.83
Ni-Al-Cl	B	86	5.6	$Ni_{0.68}Al_{0.32}(OH)_2Cl_{0.32}\cdot 0.7H_2O$	3.046	23.70
Ni-Al-NO_3	A	85	7.6	$Ni_{0.69}Al_{0.31}(OH)_2(CO_3)_{0.155}\cdot 0.7H_2O$	3.073	23.84
Ni-Al-NO_3	B	-	5.9	HTlc-CO_3 + HTlc-NO_3	-	-
Ni-Al-SO_4	A	-	7.6	HTlc-SO_4 + $Al(OH)_3$	-	-
Ni-Al-SO_4	B	-	5.5	HTlc-SO_4 + $Al(OH)_3$	-	-
Co-Al-Cl	A	90	7.6	HTlc-Cl + HTlc-CO_3	-	-
Co-Al-Cl	B	88	5.6	$Co_{0.67}Al_{0.33}(OH)_2Cl_{0.33}\cdot 0.5H_2O$	3.079	23.45
Co-Al-NO_3	A	-	7.4	HTlc-CO_3 + HTlc-NO_3	-	-
Co-Al-NO_3	B	79	6.0	$Co_{0.65}Al_{0.35}(OH)_2(NO_3)_{0.35}\cdot 0.5H_2O$	3.078	26.62
Co-Al-SO_4	A	-	7.8	HTlc-SO_4 + $Al(OH)_3$	-	-
Co-Al-SO_4	B	-	5.4	HTlc-SO_4 + $Al(OH)_3$	-	-
Mg-Al-Cl	A	77	8.4	$Mg_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.165}\cdot 0.5H_2O$	3.046	22.71
Mg-Al-Cl	B	-	5.9	gel	-	-
Mg-Al-NO_3	A	76	8.0	$Mg_{0.64}Al_{0.36}(OH)_2(CO_3)_{0.18}\cdot 0.5H_2O$	3.043	22.81
Mg-Al-NO_3	B	-	6.1	gel	-	-

M aqueous solutions of metal salts (molar ratio M(II)/M(III) = 2) solutions (250 ml). The clear solutions were heated with stirring. The reaction mixture was either refluxed for 48 hours (method A) or heated at 90 °C with stirring in an open vessel for 48 hours (method B).

In the method B, a glass dish with a diameter of 15 cm was used as an open reaction vessel. The volume of the reaction mixture was kept constant by an automatic addition of distilled water. The apparatus for the automatic addition consisted in two metal electrodes immersed into the solution to indicate the level of the liquid, simple electronic circuit, and a pump connected to a water reservoir.

The compounds precipitated were decanted three times (250 ml CO_2-free distilled water), filtered, washed several times with CO_2-free distilled water and dried at 80 °C for two hours.

The content of the metal and chloride ions was determined by an energy-dispersive X-ray spectrometry (EDX) microanalysis. The content of the carbonate and nitrate anions was determined by C, N elemental analysis; the water content was determined by thermogravimetry. The yield of the products is given in Table I.

The powder data were obtained with an X-ray diffractometer HZG-4 (Freiberger Präzisionsmechanik, Germany) using CuKα radiation with discrimination of the CuKβ radiation by an Ni filter. CoKα radiation was used in the case of cobalt containing samples. Diffraction angles were measured from 5 to 80° (2θ). Silicium (a = 5.43055 Å) was used as an external standard.

The IR spectra were recorded on a Bio-Rad FTS spectrometer in a spectral range of 4000 – 500 cm^{-1}, using dry KBr powder containing 10 % of the sample. The resultant reflectance spectra were converted into the Kubelka–Munk format [6,7].

Results and Discussion

The Zn-Al, Mg-Al, Co-Al and Ni-Al HTlcs were prepared by the method A. During the refluxing of the reaction mixture, white crystals appeared in the condenser. These crystals were identified by XRD as NH_4HCO_3 (PDF 9-415). In some cases, a mixture of HTlcs containing both the carbonate form and the starting anion formed by the refluxing. It is obvious that the removal of the CO_3^{2-} ions from the solution can prevent the formation of the HTlc carbonate. This can be done easily by heating the reaction mixture in an open vessel and a simultaneous addition of water to keep the volume of the reaction mixture constant. In this way, we tried to prepare pure HTlcs containing chloride, nitrate and sulfate anions. The studied systems, the methods of preparation and the composition of the products are summarized in Table I. We observed that a part of M(II) ions remained in the solutions after some reactions. Therefore, the M(II)/M(III) ratio in the products is sometimes lower than in the starting mixture.

The precipitation of HTlcs starts at pH = 5.5 – 6; the pH value gradually increases during refluxing while it is almost constant in the case of heating in an open vessel (method B). The pH values of the reaction mixture at the end of the reaction (see Table I) ranged from 7.4 to 8.5 and from 5.4 to 6.1 for the methods A (refluxing) and B (open vessel), respectively. In the case of the preparation of Mg-Al HTlc by the method B, the pH values are too low to form hydrotalcite and only an amorphous product containing probably $Al(OH)_3$ is obtained.

Starting from chlorides, pure chloride forms of Zn-Al, Ni-Al, and Co-Al

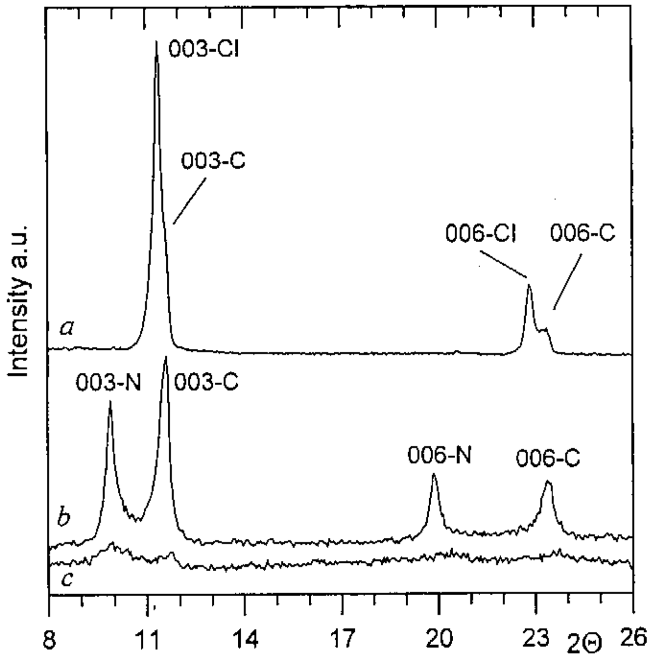

Fig. 1 Diffractograms (CuKα) of Zn-Al HTlc prepared by the method A from chlorides (a), nitrates (b) and sulfates (c)

HTlcs were obtained by the method B. A mixture of chloride and carbonate forms of Zn-Al and Co-Al HTlcs is usually formed using the method A. The presence of the chloride and carbonate forms of Zn-Al HTlc can be seen in the diffractogram (Figure 1-a), where (006) lines of both forms can be observed. Pure carbonate forms of Ni-Al and Mg-Al HTlcs were prepared by the method A that agreed with that proposed by Costantino [5].

Starting from nitrates, a mixture of the nitrate and carbonate forms of Zn-Al and Co-Al HTlcs is usually formed using the method A. The presence of the nitrate and carbonate forms of Zn-Al HTlc can be seen in the diffractogram (Figure 1-b) where (00*l*) lines of both forms are present. Pure nitrate forms of Zn-Al and Co-Al HTlcs are obtained using the method B whereas in the case of Ni-Al a mixture of nitrate and carbonate forms was prepared by this method. Pure carbonate forms are prepared in the system Mg-Al and Ni-Al using the method A.

Generally, both chloride and nitrate forms very easily transform to a carbonate form in water suspension by reaction with dissolved CO_2. When the nitrate form was washed with distilled water it changed completely to the carbonate form. Therefore the samples must be washed with CO_2-free distilled water. On the other hand, dry samples are relatively stable in air, the carbonate

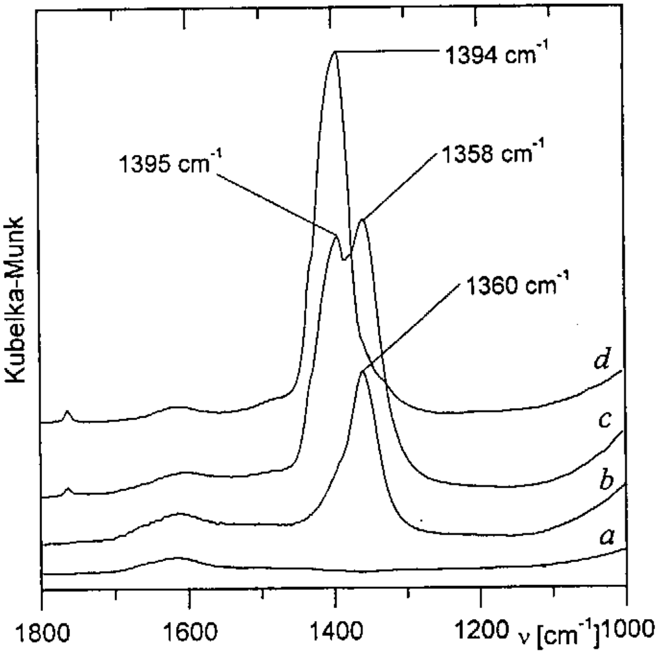

Fig. 2 IR spectra of Co-Al HTlcs prepared from chlorides by the methods B (a) and A (b) and from nitrates by the methods A (c) and B (d)

form was not observed even after 6 weeks.

The IR spectra confirm results obtained by the chemical analysis and X-ray diffraction. The spectra of the Co-Al samples prepared from chlorides and nitrates by both methods are given in Fig. 2. A band at 1355 cm^{-1} with a shoulder at 1400 cm^{-1} is characteristic of the carbonate ion in the interlayer space [8]. As follows from the IR spectra, the chloride form prepared by the method A contains significant amount of the carbonate ions (a band at 1360 cm^{-1}), whereas the sample prepared by the method B is a pure chloride form. A band at 1370 – 1390 cm^{-1} is characteristic of the nitrate ion [8]. The presence of bands at 1358 and 1395 cm^{-1} confirms that the sample prepared by the method A is a mixture of the nitrate and carbonate forms. On the other hand, the sample prepared by the method B is a pure nitrate form (only a band at 1394 cm^{-1} is observed).

Neither the method A nor the method B led to a pure sulfate form. In all cases the molar ratio SO_4^{2-}/Al^{3+} in the solid was found to be distinctly lower than 0.5 suggesting that the solid phase is probably contaminated with co-precipitated $Al(OH)_3$. Diffractograms of these products (Fig. 3) show broad diffraction lines indicating a low degree of crystallinity. In the case of Zn-Al HTlc, a formation of a mixture of the sulfate and carbonate forms was observed (Fig. 1 – c).

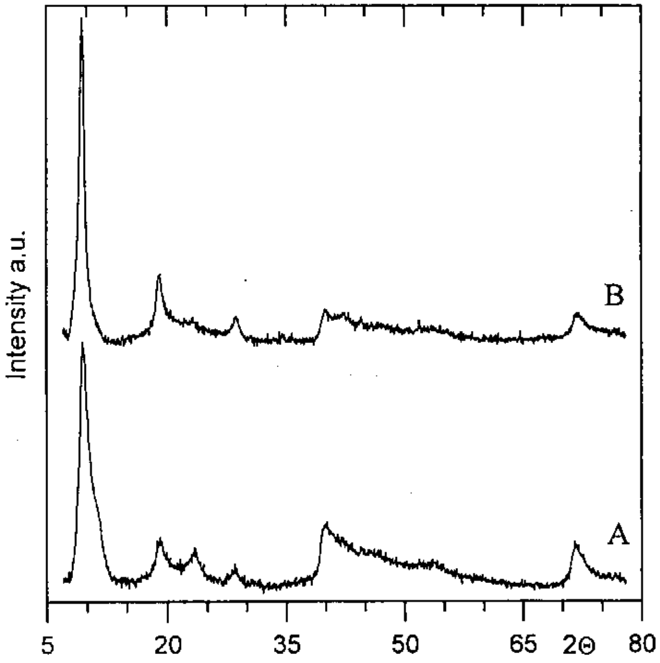

Fig. 3 Diffractograms (CoKα) of Co-Al HTlc prepared from sulfates by the methods A and B

It was found that the Zn-Cr HTlc carbonate form could be prepared by the urea method (both A and B), but the crystallinity of the product is very poor in both cases. The attempts to prepare Zn-Fe and Cu-Al HTlcs led only to a precipitation of FeO(OH) (PDF 34-1266) and $Cu_2Cl(OH)_3$ (PDF 25-269). The Li-Al system behaves similarly as the Mg-Al system. Using the method A, a carbonate form is prepared and an amorphous product containing probably $Al(OH)_3$ is obtained using the method B.

Acknowledgments

This work was supported by the Grant Agency of the Czech Republic (grants No. GA202/01/0520 and GV202/98/K002).

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