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Research paper

New insight into the preferred valency of interlayer anions in hydrotalcite-like compounds: The effect of Mg/Al ratio

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ABSTRACT

Magnesium-aluminum hydrotalcite-like compounds with molar ratios of Mg/Al ranging from 1.93 to 6.63 were synthesized and characterized with elemental analysis, XRD, SEM, TG/MS, XPS, ^{27}Al solid state MAS NMR, ^{13}C solid state CP MAS NMR, and vibrational spectroscopy (FTIR and Raman). The results of physico-chemical studies show that the materials are free of impurities and consistently point to the steady evolution of the interlayer anion composition upon increase of Mg/Al ratio. In particular, it is observed that the growing content of magnesium within the hydrotalcite layer is accompanied by the gradual substitution of dinegative interlayer carbonate anions with mononegative bicarbonates and/or nitrates. The observation contradicts the generally accepted view that the hydrotalcite-like structures have greater affinities for multivalent anions compared with monovalent ones. It is argued that in materials with low degree of Al for Mg substitution, hence larger distance between the charge generating sites, compensation by monovalent anions enhances Coulombic interactions within the hydrotalcite-like structure.

1. Introduction

Hydrotalcite-like compounds (Htlc), also referred to as anionic clays or layered double hydroxides, are described by the general molecular formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-}_{x/n})\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, x is the molar ratio $M^{3+}/(M^{2+} + M^{3+})$, A^{n-} is an exchangeable anion of charge n, and m indicates the content of water of hydration. Htlc are widely studied because of their potential as ion exchangers, sorbents, catalysts and catalyst precursors, as well as building blocks and/or templates in engineering of advanced materials (Cavani et al., 1991; Rives, 2001; Costantino et al., 2008; Wang and O'Hare, 2012; Forano et al., 2013). A number of studies demonstrated that the hydrotalcite interlayer chemistry is strongly dependent on the M^{2+}/M^{3+} ratio, which controls the layer charge density, so that the nature, packing and orientation of intercalated species may be appropriately tuned (Kwon et al., 1988; Kooli et al., 1996; Newman and Jones, 1998; Xu and Zeng, 2001a; Khan and O'Hare, 2002; Leroux and Taviot-Guého, 2005; Evans and Slade, 2006; Li and Duan, 2006; Wang and Wang, 2007; Goh et al., 2008; Theiss et al., 2014). There is also a general agreement that Htlc have higher affinity towards anions with higher charge density (Miyata, 1983; Dutta and Puri, 1989; Cavani et al., 1991; You et al., 2001; Das et al., 2006; Sun et al., 2015). In particular divalent anions are favored over monovalent anions, with CO_3^{2-} having the greatest preference for the Htlc structure.

Magnesium-aluminium Htlc, related to the naturally occurring mineral, belong to the most studied compounds. This is predominantly due to the strong basic properties of these materials, which can be easily tuned, the chief tool being the modification of the relative amount of structure-forming cations. This feature makes the Mg-Al Htlc very attractive for catalytic applications, and the materials, used as received or as mixed oxides obtained by calcination, show excellent catalytic properties in a number of base-catalyzed reactions (Sels et al., 2001; Figueras, 2004; Zhang et al., 2008). The present work was prompted by our studies of the eco-friendly Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone with the use of hydrogen peroxide/nitrile system (Olszówka et al., 2016). The reaction is catalyzed by basic catalysts and we investigated the impact of Mg/Al ratio on the yield of ε-caprolactone (Olszówka et al., 2017). Physico-chemical characterization of the catalysts revealed an unexpected feature, indicating that

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upon increase of the Mg/Al ratio, the well-known affinity of the materials towards multivalent anions, in particular CO_3^{2-}, ceases to play the dominant role and the layer charge compensation occurs preferentially via interaction with the available monovalent anions. This new aspect of Mg-Al Htlc structural chemistry, studied for the impurity free Mg-Al hydrotalcite-like materials with x ranging from 0.131 to 0.341, is described in the present work.

2. Experimental

2.1. Materials

Mg-Al hydrotalcite like compounds with nominal Mg/Al ratio = 2, 3, 4, 6, 8, were synthesized by the co-precipitation method. In general, an aqueous solution containing suitable molar amounts of magnesium and aluminium nitrates was added dropwise to an aqueous solution of Na_2CO_3 at pH = 10, at 55 °C, under vigorous stirring (550 rpm). The rate of reagents addition was ca. 1 ml/min and the variation of pH from the desired value did not exceed ± 0.05. The amount of carbonates from sodium carbonate used during synthesis was twice that of nitrates from aluminium nitrate. The pH was kept constant by dropwise addition of 2 M NaOH. It is known that the synthesis of Mg-rich hydrotalcite-like solids, with $x < 0.2$ is difficult, as it is, in general, accompanied by formation of impurities such as brucite or basic magnesium carbonates (Cavani et al., 1991; Di Cosimo et al., 1998; Michalik et al., 2008; Takagaki et al., 2010). In the course of our work we found that elimination of the precipitate ageing step helped to minimize the risk of additional phases formation. For this reason the precipitates were separated from the mother liquor straight after synthesis and washed with water by centrifugation. Specimens were dried overnight at 50 °C in an oven. The samples were referred to as Mg_xAl, where x = Mg/Al nominal ratio.

2.2. Methods

Powder X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert PRO MPD powder diffractometer, using Cu Kα radiation (40 kV, 30 mA) selected by a nickel monochromator in the diffracted beam, with a step size of 0.02°/min. The uncertainty in determination of the cell parameters was < 0.05% of the determined value. Crystallinity of the synthesized catalysts was established by using Scherrer equation. The calculation uncertainty is about 10% of the D_{hkl} value. Deconvolution of superimposed XRD reflexes was carried out using lorentzian functions and Fityk 0.9.8 software [Wojdyr, 2010]. Morphology of the materials was characterized with JEOL JSM-7500F Field Emission Scanning Electron Microscope. K575X Turbo Sputter Coater was used for coating the studied samples with chromium. The content of C and N in the samples was determined with use of an elemental analyzer Vario EL III. The uncertainty of the measurement was < 2% for C, and < 4% for N of the determined values. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for determination of Mg and Al. The measurements were carried out by using a Perkin-Elmer OPTIMA 2100DV equipment, after dissolution of samples in a 1:1 (v/v) mixture of concentrated HCl and HNO_3 acids, the measurement uncertainty being < 5% for both elements. X-ray Photoelectron Spectroscopy (XPS) spectra were obtained with a hemispherical analyzer (SES R4000, Gammadata Scienta) and Mg Kα X-ray source (1253.7 eV). The system was calibrated according to ISO 15472:2010. The electron binding energy scale (BE) was calibrated for C 1s core excitation at 285.0 eV. The spectra were fitted with the Casa XPS 2.3.15 software, using Gaussian/Lorentzian functional (70:30) and Shirley-type background. The uncertainty of the quantitative XPS elemental analysis was < 0.5%. Solid state ^{27}Al Magic-Angle-Spinning Nuclear Magnetic Resonance (MAS-NMR) spectra were measured on the APOLLO console (Tecmag) at the magnetic field of 7.05 T produced by the 300 MHz/89 mm superconducting magnet (Magnex). A Bruker HP-WB high-speed MAS probe equipped with the 4 mm zirconia rotor and KEL-F cap was used to spin the sample at 8 kHz. The resonance frequency of 78.068 MHz, and a single 2 μs rf excitation pulse corresponding to π/6 flipping angle in the liquid was applied. The number of averages was 1000, with the acquisition delay equal to 1 s. The frequency scale in ppm was referenced to 1 M solution of $Al(NO_3)_3$. A homemade nonlinear regression SPECMACS program operating in the Linux environment was used to deconvolute the spectra. Lorentzian lineshapes were applied in the fitting procedure, which required to set the number of components and their initial positions. The uncertainties of parameters determined in the deconvolution procedure are equal to 0.5 ppm, 1 ppm, and 3% for the line positions, linewidths, and relative intensities, respectively. The ^{13}C solid-state CP MAS NMR spectra of the samples were acquired at the basic resonance frequency of 125.76 MHz, on a Bruker Avance III 500 MHz WB spectrometer operating at a magnetic field of 11.7 T. The experiments were performed using 4 mm zirconia rotors. The ^{1}H-^{13}C CP MAS NMR spectra were recorded with a contact time of 2 ms, at a spinning rate of 5.5 kHz and a 5 s recycle delay. Typically, 2048 transients were accumulated for a spectrum. Chemical shifts are quoted in parts per million (ppm) from external TMS. Fourier transform infrared (FTIR) absorption spectra were recorded using transmission mode with Nicolet 6700 spectrometer under atmospheric conditions. Spectra of samples were recorded as KBr pellets in range of 4000–400 cm^{-1} at a spectral resolution 2 cm^{-1}. Raman spectra were collected with a DXR Raman microscope (Thermo Scientific) using 532 nm excitation laser wavelength, and spectral resolution 2 cm^{-1}. Thermal analysis was carried out in flowing synthetic air, using the Netzsch STA 449F3 Jupiter apparatus. 20 mg samples were heated from 20 to 1000 °C, at 10 °C min^{-1} heating rate. The uncertainty of the TG analysis was < 1% of the determined values. Simultaneous analysis of the evolved gases was carried out with a quadrupole mass spectrometer Netzsch QMS 403C Aëolos. The uncertainty of the quantitative CO_2 and NO determination was < 2% of the determined values. The basicity of the catalysts was assessed by measuring the pH of aqueous suspension of 0.15 g of each member of the Mg_2Al-Mg_8Al series in 10 ml of deionized water at room temperature (Glazneva et al., 2008). The uncertainty of the pH determination was < 0.5% of the determined value.

3. Results and discussion

3.1. SEM, XRD, XPS characterization

SEM analysis shows that grains of all hydrotalcite-like materials belonging to the Mg_2Al-Mg_8Al series display predominantly plate-like morphology, typical for Mg-Al hydrotalcite-like compounds (Fig. 1).

XRD patterns of the synthesized materials are gathered in Fig. 2. All diffractograms are typical of a hydrotalcite structure (ICSD ref. code 086655). There is no indication of any other crystalline phase, in particular no trace of the reflections characteristic of $Mg(OH)_2$ or basic magnesium carbonate phases, even in the sample with the nominal Mg/Al ratio equal 8. The XRD patterns have been indexed on the basis of a hexagonal unit cell, and the unit cell parameters a and c, determined from the expression $a = 2d_{110}$ and $c = 3d_{003}$, are listed in Table 1. The position of the non-basal reflex (110), used for the determination of parameter a, represents the mean cation–cation distance in the brucite-like layer, and, in view of different Shannon (1976) effective ionic radii of Mg^{2+} and Al^{3+} (0.54 Å vs. 0.72 Å), carries information about the degree of Al for Mg substitution x (Cavani et al., 1991). Fig. 3 shows that there is a linear dependence of parameter a on the degree of substitution with aluminium x, the slope of the line and the y-intercept (0.3124 nm) being very similar to those reported earlier (Brindley and Kikkawa, 1979; Kaneyoshi and Jones, 1999). The effect indicates that in the investigated range of x, the brucite layer composition changes in a continuous manner, which is consistent with the conclusion as to the essentially phase pure character of the synthesized materials, at least