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Determination of the mechanism(s) for the inclusion of arsenate, vanadate, or molybdate anions into hydrotalcites with variable cationic ratio

Sara J. Palmer, Aurore Soisonard, Ray L. Frost *

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, Queensland, Australia

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ABSTRACT

Hydrotalcites with cationic ratios of 2:1, 3:1, and 4:1 were synthesised using the co-precipitation method. The mechanism of inclusion of arsenate, vanadate, and molybdate into these structures is investigated using the combination of X-ray diffraction, Raman spectroscopy, and thermal analysis. Results show that hydrotalcites with cationic ratios of 3:1 are thermally more stable then the 2:1 and 4:1 structures. The increase in thermal stability of the 3:1 hydrotalcite structures is understood to be due to the intercalation of arsenate, vanadate, or molybdate, by an increase in hydrogen bonds associated with the intercalated anion. The 3:1 vanadate hydrotalcite is the most thermally stable hydrotalcite investigated. It is observed that the predominant mechanism for inclusion of the three anionic species is adsorption for 2:1 and 4:1 hydrotalcites, and intercalation for the 3:1 hydrotalcite structures. The intercalation of arsenate, vanadate, and molybdate into the hydrotalcite structure increased the interlayer distance of the hydrotalcite by 0.14, 0.13, and 0.26 Å, respectively.

1. Introduction

Hydrotalcite ($Mg_6Al_3(OH)_{16}(CO_3)\cdot 4H_2O$) is a layered material comprised of metal cations (M^{2+} and M^{3+}) of similar radii randomly distributed in the octahedral positions, that form brucite-like structures ($Mg(OH)_2$). Substitution of divalent cations (Mg^{2+}) for trivalent (Al^{3+}) cations gives rise to a positively charged layer. In order to maintain electroneutrality, a suitable number of anionic species are required to neutralise the layer charge. This can be obtained by either intercalation of the anionic species into the interlamellar domain, or through adsorption of the anionic species on the external surface of the hydrotalcite surface. A variety of hydrotalcite-like compounds exist and are more commonly referred to as layered double hydroxides (LDH), with general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{m-}_{x/m}\cdot nH_2O$, where M^{2+} is a divalent cation, M^{3+} is a trivalent cation, and A an interlamellar anion with charge m^{-1}. The value of x needs to between 0.17 and 0.33 to ensure a LDH forms.

Anionic species intercalated into the interlayer region are mediated by: (i) coulombic forces between the positively charged layers and the negatively charged anions, and (ii) hydrogen bonding between the hydroxyl groups of anionic layers and interstitial water molecules [1,2]. In aqueous solutions containing a variety of anions, intercalation of a particular anion is dependent on the affinity of anions in solution. This affinity for the interlayer region is dependent on the combination of the anions charge density and size, where anions of higher charge density and smaller anionic radii are intercalated preferentially. An increase in anionic charge results in the electrostatic interactions between the positively charged hydroxide layer and the anion to become stronger, therefore rendering a more stable hydrotalcite. The interlayer region is relatively small, and therefore the physical size of the anion will dictate whether it is intercalated into the interlamellar domain.

The calcination of hydrotalcite, from temperatures of 350 to 800 °C, removes interlayer water, interlayer anions (carbonate anions), and hydroxyls. The result is the formation of periclase-like Mg, Al oxides. XRD studies have shown the collapse of the crystalline hydrotalcite to an amorphous magnesium oxide with aluminium ions dispersed as a solid solution [3–5]. The carbonate anions in the hydrotalcite structure decompose to carbon dioxide (CO_2) and O^{2-}, leaving the O^{2-} anions retained between the layers [6–9]. The thermal decomposition of hydrotalcites is as follows:

1. Removal of adsorbed water:
   (a) physio-absorbed on the external surface (up to 100 °C);
   (b) interlayer water (110–200 °C).
2. Dehydroxylation:
   (a) partial lost of OH groups in the brucite-like layer (~330 °C);
   (b) loss of OH groups bonded to intercalated anion (~360–380 °C).
3. Decarbonation:

* Corresponding author.
E-mail address: r.frost@qut.edu.au (R.L. Frost).

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(a) solvated CO_3^{2-} (~345 °C);
(b) carbonate bonded to the OH surface (~355 °C).

Thermal analysis using thermogravimetric techniques enables the mass loss steps, along with associated temperatures and mechanisms to be determined [10–18]. Thermo-analytical methods can provide a measure of the thermal stability of the hydrotalcite.

This investigation looks at the effect that the divalent/trivalent cationic ratio has on the thermal stability of hydrotalcites. The hydrotalcites synthesised in this investigation have '*x*' between 0.33 and 0.17. Raman spectroscopy and thermal analysis techniques have been combined to determine the mechanism involved in the removal of arsenate, vanadate and molybdate from aqueous solutions. The term inclusion is used to describe the intercalation or adsorption of these anionic species into/onto hydrotalcite structures. This work is used to help understand the stability of hydrotalcite structures with these variable Mg/Al ratios and the intercalation of these anionic species.

2. Experimental

2.1. Synthesis of hydrotalcites

The hydrotalcites described in this investigation were synthesised using the co-precipitation method. Two solutions were prepared: a caustic solution and a mixed metal solution. The caustic solution contained 2 M NaOH and a combination of Na_2CO_3 and the sodium salt of the desired anion (e.g. Na_2MoO_4, $NaVO_3$, and $Na_2HAsO_4{\cdot}7H_2O$) to give a concentration of 0.2 M. Hydrotalcites with no anion apart from carbonate were prepared using 2 M NaOH and 0.2 M Na_2CO_3, while the hydrotalcites without carbonate were prepared using 2 M NaOH and 0.2 M Na_yX^{y-}. The mixed metal solution consists of 0.75 M Mg^{2+} ($MgCl_2{\cdot}6H_2O$) and 0.25 M Al^{3+} ($AlCl_3{\cdot}6H_2O$). This ratio of Mg^{2+} and Al^{3+} ions should result in the formation of a 3:1 hydrotalcite structure. For hydrotalcites with divalent/trivalent ratio equal to 2 the following concentrations were used: 0.66 M Mg^{2+} and 0.33 M Al^{3+}, while for a ratio of 4 the following mixture was prepared 0.80 M Mg^{2+} and 0.20 M Al^{3+}. The mixed metal solution was added at a steady rate to the caustic solution in a drop wise fashion using a separating funnel, with vigorous stirring. The resulting hydrotalcites are formed between a pH range of 9.5 and 10.5. A peristaltic pump was not used in the synthesis of these hydrotalcites, however, for a more crystalline structure a peristaltic pump is recommended. These hydrotalcites are prepared in open vessel reactors, therefore the dissolution of carbon dioxide to form carbonate in solutions is possible. The precipitated minerals were washed at ambient temperature thoroughly, with ultra pure water, to remove any residual salts (NaCl). The formation of NaCl reduces the concentration of chloride in solution, and therefore minimises possible contamination. The presence of chloride anions in solution may be intercalated into the hydrotalcite structure, however, the desired anions are intercalated preferentially.

2.2. X-ray diffraction

X-ray diffraction patterns were collected using a Philips X'pert wide angle X-ray diffractometer, operating in step scan mode, with CuK_α radiation (1.54052 Å). Patterns were collected in the range 3 to 90° 2θ with a step size of 0.02° and a rate of 30 s per step. Samples were prepared as a finely pressed powder into aluminium sample holders. The Profile Fitting option of the software uses a model that employs twelve intrinsic parameters to describe the profile, the instrumental aberration and wavelength dependent contributions to the profile.

2.3. Thermogravimetric analysis (TGA)

Thermal decomposition of the hydrotalcite was carried out in a TA® Instrument incorporated high-resolution thermogravimetric analyser (Series Q500) in a flowing nitrogen atmosphere (80 cm^3/min). Approximately 50 mg of sample was heated in an open platinum crucible at a rate of 2.0 °C/min up to 1000 °C. The synthesised hydrotalcites were kept in an oven for 24 h before TG analysis. Thus the mass losses are calculated as a percentage on a dry basis.

2.4. Raman spectroscopy

The crystals of hydrotalcite were placed on the stage of an Olympus BHSM microscope, equipped with 10× and 50× objectives and are part of a Renishaw 1000 Raman microscope system, which also includes monochromators, a filter system and a charge coupled device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a nominal resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Spectral manipulation such as baseline correction, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was undertaken using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz–Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

3. Results and discussion

3.1. X-ray diffraction (XRD)

All the hydrotalcites synthesised were identified as Mg/Al hydrotalcites by X-ray diffraction. EDX (energy-dispersive X-ray spectroscopy) confirmed the divalent/trivalent cationic ratios, Table 1. The hydrotalcites synthesised with carbonate, arsenate, vanadate, or molybdate were characterised by X-ray diffraction, which showed a single poorly crystalline phase (Fig. 1). The $d_{(003)}$ spacing for all the synthesised hydrotalcites were between 7.6 and 8.0 Å, which is commonly observed for hydrotalcite structures. Changes in the 003 reflection indicates a change in the interlayer distance of the hydrotalcite layers, where an increase in interlayer space results in a larger $d_{(003)}$ spacing. For the purpose of this investigation the arsenate, vanadate, and molybdate hydrotalcites will be compared to the carbonate hydrotalcite with the same Mg/Al ratio to determine changes in interlayer spacings.

The basal spacing for all the 2:1 hydrotalcites remained relatively the same, with an increase of only 0.04 being observed

Table 1
Elemental analysis of hydrotalcites with varying divalent/trivalent cationic ratios.

2:1		3:1		4:1	
Sample name	Mg/Al	Sample name	Mg/Al	Sample name	Mg/Al
2:1 HT-CO_3^{2-}	2.3	3:1 HT-CO_3^{2-}	2.8	4:1 HT-CO_3^{2-}	3.9
2:1 HT-$(VO_4)^{3-}$	2.3	3:1 HT-$(VO_4)^{3-}$	3.2	4:1 HT-$(VO_4)^{3-}$	3.8
2:1 HT-$(MoO_4)^{2-}$	2.3	3:1 HT-$(MoO_4)^{2-}$	3.3	4:1 HT-$(MoO_4)^{2-}$	4.0
2:1 HT-$(AsO_4)^{3-}$	2.2	3:1 HT-$(AsO_4)^{3-}$	3.2	4:1 HT-$(AsO_4)^{3-}$	4.0