Insertion of electrochemically reduced Keggin anions into layered double hydroxides

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A new procedure is described to enable the charge on a Keggin ion to be modified to improve incorporation into layered double hydroxides. The procedure, involving electrochemical reduction, has been tested using the 12-molybdophosphate anion. Chemical analysis and PXRD data confirm that from the otherwise hydrolytically unstable and low charge anions which are unsuitable for intercalation within the basic matrix of MgAl–LDH, a species is obtained in which the stoichiometry is preserved and which yields a pillared LDH structure of 14.8 Å basal spacing.

Layered double hydroxides (LDHs) are synthetic phases of general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2][A^{m-}_{x/m}\cdot nH_2O]$, where M^{II} and M^{III} are the cations in the hydroxide layers and A^{m-} is the interlayer anion. The first report concerning the possibility of incorporating polyoxometalate species as the charge-balancing anions was contained in a patent by Woltermann.[1] Since then several different strategies for anion incorporation have been adopted, of which the most important are simple anion exchange procedures,[2,3] use of organic anion precursors,[4] reconstitution of calcined LDHs with or without organic preswelling agents,[5,6] anion exchange using wet LDH samples,[7] direct synthesis[8,9] and sol–gel technique.[10]

The isopoly- and heteropoly-metalates may adopt many different structures, depending on the number of condensing metal cations (so-called addenda), and heteroatoms.[11] One of the most studied heteropolyanions is the Keggin-type structure where twelve metal–oxygen octahedra form a shell surrounding a tetrahedrally coordinated heteroatom. The Keggin heteropolyanion is a bulky species of *ca.* 10 Å diameter. For the successful intercalation of a Keggin-type anion in an LDH compound two factors are of major importance. First, the heteropoly species should carry sufficient charge to compensate the excess positive charge of the hydroxide layer. In order for this to be possible and assuming a dense packing of heteropolyanions, the minimum negative charge on a Keggin-type heteropolyanion intercalated into a hydrotalcite of a $M^{II}_{0.67}M^{III}_{0.33}$ composition (and therefore of charge density $0.04\ e\ Å^{-2}$) should be at least 4. Second, the intercalated anion should be resistant to hydrolytic decomposition at the pH values required for the LDH stability. For this reason, in the intercalation experiments reported to date, highly charged heteropolytungstate anions have been principally investigated.[3,6–8,12–16] In contrast, since Woltermann's patent, no reports have appeared concerning the intercalation of heteropolymolybdates, probably as a result of their relatively poor stability against hydrolytic decomposition in other than strongly acidic conditions.[11]

In the present work we chose to study the interaction of the 12-molybdophosphate anion with the MgAl–LDH matrix. The $(PMo_{12}O_{40})^{3-}$ anion has all the disadvantages alluded to above, *i.e.* low charge and susceptibility to hydrolytic degradation in non-acidic conditions. Here, we show that both obstacles can be overcome by subjecting the anion to electrochemical reduction prior to exposure to the LDH. It is known that heteropolyanions undergo facile reduction by several electrons per Keggin unit, to give so-called heteropoly-blues, and that reduction renders the anions less acidic.[11,17] We took advantage of this to increase the negative charge on the $(PMo_{12}O_{40})^{3-}$ anion so as to produce a robust species better able to compensate the positive layer charge of the LDH matrix.

Experimental

Analytical-grade reagents were used for all preparations described in this work. Anionic exchange was used for insertion of heteropolyanions into the parent LDH compound.

The starting material, $[Mg_{0.67}Al_{0.33}(OH)_2](NO_3)_{0.33}\cdot nH_2O$, was prepared using a standard coprecipitation method. A solution containing 0.12 M $Mg(NO_3)_2$ and 0.06 M $Al(NO_3)_3$ dissolved in 50 ml distilled water was added dropwise to 100 ml of water at pH = 10 controlled by the dropwise addition of 2 M NaOH solution. The experiment was performed under nitrogen atmosphere to avoid contamination with carbon dioxide. The resulting white slurry was heated at 328 K for 24 h, washed with distilled water and dried in air at 333 K. The sample is further referred to as $MgAlNO_3$.

LDHs intercalated with $(PMo_{12}O_{40})^{3-}$ anion was prepared by adding 0.5 g of parent LDH to 50 ml of water solution containing 0.5 mmol of $H_3PMo_{12}O_{40}$ (Fluka, p.a.). The mixture was left in air at room temperature for 1 h under continuous stirring. The final pH was *ca.* 4.0. The resulting solid was filtered, washed with distilled water, and dried at room temperature. The sample is further referred to as $MgAlPMo_{12}$.

To prepare the reduced $(PMo_{12}O_{40})^{7-}$ anion, a solution of 15 g of $H_3PMo_{12}O_{40}\cdot 30H_2O$ (*ca.* 7 mmol) in 66 ml distilled water, was placed in an electrochemical cell and reduced to a degree corresponding to the transfer of four electrons per each Keggin unit. The resulting reduced anion, characterized by a deep blue colour, can be thus described as $(PMo_{12}O_{40})^{7-}$. 0.5 g of the parent $MgAlNO_3$ was added to 5 ml of the blue solution diluted to 50 ml with distilled water. The mixture was stirred for 1 h at room temperature. The final pH was 4.0. The resulting blue solid was filtered, washed with distilled water, and dried at room temperature. The sample is referred to as $MgAlPMo_{12}$(reduced). PXRD patterns were obtained with a DRON-3 diffractometer using Ni-filtered Cu-Kα radiation.

Elemental composition of the samples was determined, after dissolution in concentrated nitric acid, using a ICP AES Perkin Elmer spectrometer.

Results and Discussion

Table 1 shows the atomic ratio of elements present in the brucite layer and in the interlayer obtained from the chemical

Table 1 Atomic ratio of elements in the brucite layer and in the heteropolyanion calculated from the chemical analysis data

	Mg	Al	P	Mo
Sample	brucite layer		heteropolyanion	
$MgAlNO_3$	2.07	1.00	–	–
$MgAlPMo_{12}$	1.55	1.00	1.00	4.50
$MgAlPMo_{12}$ (reduced)	1.51	1.00	1.00	11.20

analysis. In the parent $MgAlNO_3$ sample the Mg/Al ratio is close to the theoretical value. Upon exchange in the acidic medium both the $MgAlPMo_{12}$ and the $MgAlPMo_{12}$(reduced) sample become depleted of magnesium relative to the Al content, the degree of Mg dissolution being similar in both cases. There is, however, a substantial difference in the chemical composition of the heteropolyanion species retained by the two solids. In the case of the LDH exchanged with the $(PMo_{12}O_{40})^{3-}$ anion the Mo/P ratio of 4.5 is much lower than the stoichiometric value of 12 and points to a substantial degradation of the anion, possibly resulting in a mixture of species such as $(H_xPMo_9O_{34})^{(9-x)-}$ and $(H_yP_2Mo_5O_{23})^{(6-y)-}$.[11] On the other hand, the $MgAlPMo_{12}$(reduced) sample contains phosphomolybdate species whose composition is very close to the initial stoichiometry of the 12-molybdophosphate anion. The results of chemical analysis therefore indicate that the presence of four extra electrons in the electrochemically reduced 12-molybdophosphate anion brings about not only an increase of the overall negative charge on the anion, but also results in its enhanced hydrolytic stability.

X-Ray diffraction patterns of the parent LDH and the exchange products are shown in Fig. 1. Assuming a layer thickness of *ca.* 4.8 Å and the Keggin ion diameter of 9.8 Å, the basal spacing after intercalation should be *ca.* 14.6 Å. Fig. 1(a) shows the XRD pattern recorded for the parent $MgAlNO_3$ compound. The 001 harmonics of the basal spacing, *i.e.* 8.87 and 4.42 Å, are clearly visible. The patterns obtained for 12-molybdophosphate-exchanged samples are presented in Fig. 1(b), (c). It may be seen that as a result of reaction in both cases the reflections characteristic of the parent compound have disappeared and are replaced by new reflections. However, in the pattern produced by the $MgAlPMo_{12}$ sample, no trace of the reflection at *ca.* 14.6 Å, corresponding to the value expected for the Keggin ion–LDH intercalate appears. Instead, there are strong peaks at 11.1 and at 4.96 Å which might be regarded as 00*l* reflections of a poorly ordered layer structure, the disorder possibly resulting from the presence of decomposed anions of different sizes and compositions. The 1.52 Å ($2\theta = 60.3°$) reflection shows that the skeleton of the Mg–Al hydroxide layer has been retained. The XRD powder pattern of $MgAlPMo_{12}$(reduced) sample intercalated with the electrochemically reduced species is different and shows that upon intercalation the desired product has been formed [Fig. 1(c)]. Here, a low-angle reflection at 14.8 Å appears, along with higher-order reflections at 7.44, 4.89 and 3.70 Å, characteristic of an LDH structure pillared with Keggin anions.

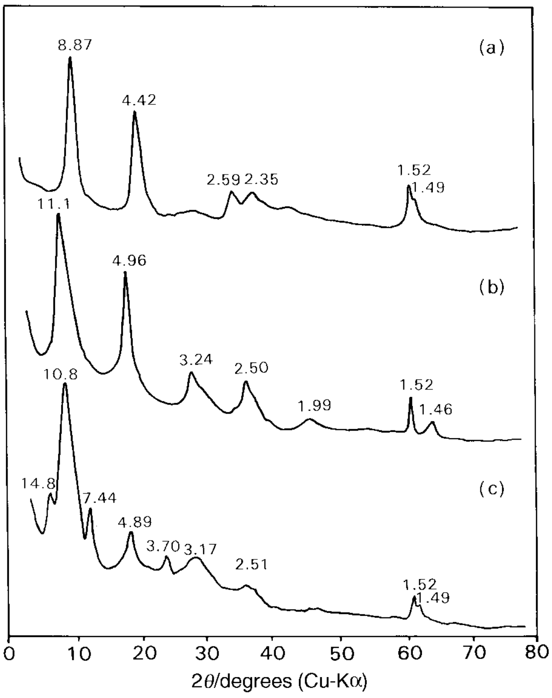

Fig. 1 XRD powder patterns of (a) $MgAlNO_3$, (b) $MgAlPMo_{12}$, (c) $MgAlPMo_{12}$ (reduced)

In addition to the pattern expected for the exchanged LDH matrix, a broad peak with a maximum around 10.8 Å also appears. This type of XRD pattern is frequently encountered in LDHs intercalated with isopoly- and/or heteropoly-oxometalates in acidic medium.[7,9,12,13,16,18] The origin of the broad reflection has been frequently discussed over the years. It has been assigned either to a polyoxometalate salt impurity formed by reaction of the extracted magnesium (and some aluminium) with the polyoxometalate anions used in the intercalation experiment[12,16] or to a defect LDH structure resulting from acid damage.[7] In the case of materials prepared in the present work the former hypothesis seems improbable, since it is not likely that Mg or Al will form insoluble salts with 12-molybdophosphate anions.[19]

Both chemical analysis and the PXRD data show that the use of electrochemically reduced 12-molybdophosphate anions changes dramatically the outcome of the intercalation experiment. From anions predictably unsuitable for intercalation within the basic matrix of MgAl–LDH species are obtained that preserve their stoichiometry and give the pillared LDH structure of 14.8 Å basal spacing. The results of this work open new opportunities in the preparation of polyoxometalate–LDH intercalates and extend the range of heteropolyanions which may be inserted. The method also offers simple means to control the pillar density, by appropriate choice of the extent of reduction of the heteropoly-blue anion.

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