INTERCALATION COMPOUNDS OF ALUMINUM HYDROXIDE

V. P. Isupov

Crystalline aluminum trihydroxides Al(OH)₃ (gibbsite, bayerite, and nordstrandite) can serve as layered intercalation matrices in which metal salts are arranged in a specific way. Small cations (lithium, magnesium, and transition metals) lie in the octahedral voids of aluminum hydroxide layers, and water molecules are located between the layers. This localization of small cations gives rise to the molecular sieve effect, where alkaline and alkaline earth cations (Na⁺, K⁺, Ca²⁺, etc.), which are large relative to the octahedral voids, are not intercalated into aluminum trihydroxides. In the first step of lithium salt intercalation, the cations, the anions, and the water molecules are incorporated into the interlayer space of aluminum hydroxide with subsequent transition of lithium into the voids of the layer.

INTRODUCTION

According to current knowledge, intercalation processes are reversible topotaxial chemical reactions in which guest molecules (atoms, ions) are intercalated into a solid matrix [1]. Interest in these processes arises from the possibility of synthesizing new compounds possessing a set of physicochemical properties which may not be obtained by using traditional chemical methods of synthesis. Therefore, it is certainly of interest to seek new intercalation systems (host matrix+ guest molecules), investigate the mechanism of their formation, and reveal their applications. The majority of works in this field were devoted to intercalation into systems with two-dimensional host matrix. Analysis of the literature data on intercalation systems containing various matrices and guest molecules shows that intercalation into layered structures is characterized by incorporation of guest molecules into the interlayer space [1-28]. Thus molecules with parameters and geometries differing by dozens of angstroms can be intercalated into the same layered matrix, that is, the molecular sieve effect is absent.

On the other hand, there are many compounds with layered structure which are capable of incorporating small guest molecules not only between but also inside the layers. Examples are well known compounds such as dioctahedral aluminosilicates (kaolin minerals, montmorillonite, etc.) containing octahedral voids in the layers.

Thus our knowledge about intercalation into layered matrices may be significantly improved by investigating the possibility and the mechanism of synthesis of intercalation compounds by fixing guest molecules not only in the interlayer space but also in molecular voids inside the layers. Among layered type matrices whose layers contain voids, of special interest are crystalline aluminum trihydroxides (gibbsite, bayerite, nordstrandite). The principal structural motif of the trihydroxides is two-dimensional layers linked by hydrogen bonds. The layer consists of two nets of close-packed hydroxide ions. The aluminum ions occupy two thirds of the total number of octahedral voids in this packing, and the remaining voids (whose radius is 0.60-0.70 Å) are unoccupied [29-34]. In contrast to dioctahedral aluminosilicates [3, 11], the octahedral voids are not screened by the silicon oxygen net and have no direct exit to the interlayer space. Therefore, one can assume that this size and easy access to the voids permit accommodation of small cations (lithium, aluminum, magnesium, nickel, cobalt) without significant deformation of the layer. Indeed, localization of small cations in the octahedral voids between close-packed hydroxide ions without pronounced deformation of the packing is observed for brucite Mg(OH)₂, hydrotalcite, and manasseite Mg₆Al₂(OH)₁₆CO₃·4H₂O [35-40].

voids are too small to accommodate larger cations (sodium, calcium, potassium, etc.) without marked deformation of the close packing, one can expect the molecular sieve effect of intercalation into layered matrices, not observed previously. Finally, as is known from the literature, amorphous aluminum hydroxides are effective selective sorbents of lithium salts from composite salt media [41-44]. Although the nature and mechanism of selective sorption are not known, one can think that they are associated with intercalation processes. This set of data suggests that crystalline aluminum trihydroxides can act as intercalation matrices with molecular sieve properties, capable of fixing small cations inside the hydroxide layer. The introduction of such cations into a solid must be accompanied (for the solid to preserve its electroneutrality) by either intercalation of anions into the interlayer space or by cation exchange. Therefore, it is of interest to study the possibility and the mechanism of synthesis of intercalation compounds by fixation of guest molecules (metal cations) not only in the interlayer space but also inside the matrix layers (crystalline aluminum hydroxides as matrices) and to examine the possibility of the molecular sieve effect during the intercalation. These investigations were carried out at the Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences.

INTERACTION OF CRYSTALLINE ALUMINUM TRIOHYDROXIDES WITH METAL SALT SOLUTIONS

Interaction of Metal Salts with Gibbsite

In studies of the interaction of polycrystalline samples of gibbsite with concentrated aqueous solutions of metal (Li, Na, K, Ca, Mg, Ni, Co, Cu, Sr) chlorides it was found that under conditions of experiment (salt concentration to saturated solution, temperature from room temperature to 360 K, time up to 8 h) reaction occurs only in the case of lithium salts [45, 46]. The possibility of gibbsite reaction with lithium salts was shown independently in [47]. The diffractograms of the products of interaction showed new reflections, differing from those of gibbsite. Their position did not change, but the intensity increased with the synthesis temperature, the concentration of lithium salts, and reaction time. In certain conditions, gibbsite reflections vanished, and new compounds formed, whose X-ray diffraction diagrams are shown in Fig. 1 [48-51]. During the interaction, the specific surface of the solid considerably increases compared to that of the starting gibbsite, and the crystal morphology of the solid changes. The starting gibbsite is represented by spherule-like concretions of prismatic crystals with hexagonal planes. The size of the prismatic crystals comprising a concretion varies (in height and in the base plane) from 5-10 to several dozens microns. The crystal morphology of the starting substance indicates pronounced genetic defectiveness of the prismatic crystals of the concretion; the defects include cracks, growth steps, and blocking of crystals. Complete transformation of gibbsite leads to decomposition of concretions into prismatic crystals and partitioning of the latter into blocks. The latter have dimensions $m \times n \times p \leq 10$, where $m$, $n$, and $p$ vary from 0.5 to 5 µm. The blocks consist of plates several tenths of a micron in thickness. The specific surface of the products is 3-5 $m^2/g$ and is markedly greater than the specific surface of the starting gibbsite (0.1-0.2 $m^2/g$). The X-ray diffractograms contain intense reflections with multiple interplanar distances, indicating that the structure of the products is lamellar. The Li/Al atomic ratio in the products is 0.5, and the molar ratio of lithium to anion is 1 for $X = Cl^-$, $Br^-$, $I^-$, NO$_3^-$, and 2 for SO$_4^{2-}$. In the IR spectra of the products (Fig. 2), one can observe the bands characteristic of the stretching vibrations of OH groups, deformation vibrations of Al–OH and water molecules, and stretching vibrations of the Al–O bond of the Al–O$_6$ complex [48, 52, 53]. In the high-resolution $^{27}$Al NMR spectra, the chemical shift values indicate the presence of aluminum with an oxygen octahedral environment [52]. Thus IR and NMR spectroscopy data testify that the octahedral environment of aluminum typical of the starting gibbsite is preserved in the interaction. The above set of data permits one to infer an equation defining the interaction of gibbsite with lithium salts: $Li_nX+ 2nAl(OH)_3+ pH_2O = Li_nX \cdot 2nAl(OH)_3. pH_2O$ (BALH–X). The water content in the synthesized compounds depends on storage conditions and varies from 0.5 to 4 molecules.

The effects of lithium salt concentration, temperature, dispersivity and defectiveness of the solid phase, and the type of solvent on the degree of gibbsite conversion into BALH–X are reported in [52-61].

The dependence of the extent of gibbsite conversion into BALH–X on the concentration of lithium salts is a sigmoid curve (Fig. 3) [53-55]. At low concentrations, the degree of conversion is insignificant. As the concentration increases to certain values, the degree of conversion increases sharply and changes slightly as the concentration increases further. Thus a quantitative transformation of the starting aluminum hydroxide into an intercalation compound obviously