Thin films of multimetallic layered double hydroxides obtained by the sol-gel method

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Introduction

In recent years, because of the structural anisotropy inherent to layered materials, worthwhile efforts have been reported on the formation of transparent thin films from layered double hydroxides (LDH).[1-3] LDHs are a class of naturally occurring anionic clays, represented by the general formula: $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2]A^{n-}_{x/n}\bullet mH_2O$.[4] These materials have been studied as catalysts or catalyst precursors to a great extent for the past few decades. In addition, LDHs have found a wide range of scientific and technological applications. A sol-gel method is presented in this paper, by which various compositions of binary and ternary LDHs were accomplished. Solids thus obtained revealed small particle size and a high degree of intercalation of alkoxy groups in the interlayer region. These characteristics enabled the formation of thin films by the dipping technique, resulting in continuous, transparent, highly homogeneous and well adhered films.

Materials and Methods

Binary LDH compounds were prepared by dissolving aluminum tri-*sec*-butoxide (ATB) in alcohol at 70 °C under constant stirring. Nitric acid was then added dropwise. Afterwards, the system was taken to room temperature, and acetic acid (AA) was added to complex the aluminum alkoxide. One hour later, the temperature was lowered to 0 °C, and a 0.3 M solution of the divalent cation (magnesium methoxide, nickel acetate, nickel nitrate, copper nitrate, zinc nitrate, or cobalt nitrate) in ethanol was added drop wise. The system was taken to room temperature in constant stirring for 18 h. For ternary LDHs, magnesium methoxide was added before the divalent metal precursor. Films were formed by dip-coating technique using a glass slide. The molar ratios of reactants were ATB:ROH = 1:60, ATB:HNO_3 = 1:0.03, ATB:AA = 1:1~3, M^{II}:M^{III} = 3. For ternary samples, 15% wt. of the second divalent cation was used.

Results and Discussion

Previous studies on MgAl LDHs prepared by this method revealed that alkoxy groups, from the alcohol employed as solvent, are located in the interlayer region; the corresponding XRD patterns showed broad peaks from an LDH structure.[4] The intercalation degree was found to be MgAl-E>MgAl-P>>MgAl-B. EDS analyses revealed spatial distribution of Mg, Al, and C throughout the films, the MgAl-E being more uniform than the MgAl-P. In view of the fact that both films have the same morphology and very similar particle and crystal sizes, the greater uniformity of MgAl-E is most likely related to its higher intercalation degree. This hypothesis is supported by the fact that the MgAl-B films, with the lowest intercalation degree, were by far less homogeneous and non-transparent. Thus, ethanol was chosen as solvent for the synthesis of multimetallic LDH thin films.

LDH films have been observed to develop a preferred orientation that may have significant effects on film properties, especially in the case of anisotropic crystal structures. Two-dimensional (2-D) image (background) and corresponding integrated diffraction pattern of LDH films with various compositions are displayed on Figure 1. *001* and *002* reflections, which are characteristic of hydrotalcite-like materials, appeared in all cases. In-plane reflections ($h, k \neq 0$), which appear above 2θ ~35°, were not observed. These results are evidence for extremely well oriented LDH films. Crystallite size from Scherrer equation on d_{001} reflection is between 49 to 226 Å, depending on the chemical composition and the precursors employed. Accordingly, as the particles become smaller, the chemistry is dominated by the surface atoms, as they represent a large portion of the total structure.[3] The increase in surface-to-surface interactions, along with the intercalation of alkoxy groups and the consequent expansion in the interlayer region produces well oriented films. These factors also affect the adhesion properties of the LDHs, so films adhere well to polar substrates such as glass. On the other hand, SEM images revealed a smooth, uniform deposit on the glass slide, with film thickness depending on several parameters, mainly, the relative amounts of water and acetate groups; and the ageing time of the sols, which has a direct influence on viscosity, due to continued condensation and cross-linking reactions.

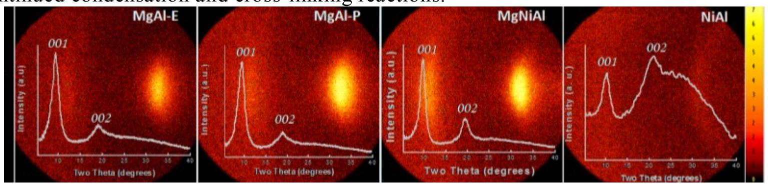

Fig. 1. 2-D (background) and corresponding XRD pattern from LDH films. The right-hand bar indicates intensity.

Significance

To sum up, we have presented a sol-gel method by which various binary and ternary LDHs were synthesized, whose unique features enabled the formation of continuous, transparent, highly oriented and well adhered thin films. Also, a simple way to control the film's thickness was proposed. These films could be used in a wide variety of scientific and technological fields; for instance, in optics, as functional coatings and membranes, for the development of sensing devices, as catalysts in microreactor coatings, in the development of organic-inorganic nanocomposites, etc.

References

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