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Synthesis and characterization of macroporous MgAl LDH using polystyrene spheres as template

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Abstract

To overcome some limitations of LDH-type materials when prepared by conventional coprecipitation arising from poor diffusion and accessibility to active sites, however, prerequisites in many applications, these materials were designed as macroporous open structure. The preparation is adapted from the well-known 'inverse opals method' using polystyrene beads as template and successive impregnations of metal cations solutions into the voids. After NaOH addition, LDH-type phase is formed as proved by XRD and ^{27}Al NMR, and LDH replica is obtained either by dissolution of PS arrays or calcination–reconstruction process. Additionally, a large variety of anions may be incorporated, while keeping the 3D macropore ordering.

Keywords: A. Inorganic Compounds; B. Chemical Synthesis; C. X-ray diffraction; D. Nuclear magnetic resonance (NMR)

1. Introduction

The synthesis of ordered macroporous materials is a topical object of a lot of studies since, inherent to their open structure, they may be candidates for a wide range of applications that exploit high surface area structures, such as catalysis, molecular sieving, filtration technology and chemical sensors or biosensors conception.

In this study, we apply the well-known 'inverse opals method' to synthesize macroporous layered double hydroxides (LDHs); this process is found to be readily efficient in obtaining a large number of porous materials, but essentially for those presenting three-dimensional networks such as silica [1,2], metals [3,4], semiconductors [5], metal oxides [2,3,6], carbon [7] and polymers [8]. To the best of our knowledge, it is the first time that such a process is adapted to a two-dimensional complex system such as LDHs materials.

The synthetic procedure is based on the impregnation of precursors into the interstices of a polystyrene spheres crystal called 'opal'. This colloidal crystal is used as sacrificial template and is subsequently removed, thus creating macroporosity after precipitation of the desired material in the voids.

The anionic clays LDHs, also called hydrotalcite-like compounds [9], possess a layered structure of general formula: $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[X^{q-}_{x/q}(H_2O)_n]^{x-}$ that can be described by comparison to brucite-like layers. The positive charge created by the substitution of a part of the divalent cations by trivalent cations is compensated by the presence of anions in the interlayer space.

LDHs are useful in various fields of applications due to their ability to exchange anions and their behaviour as inorganic base. However, the conventional synthesis of LDH-type materials such as coprecipitation of metallic salts, and induced hydrolysis, do not allow a large control of the textural properties in term of morphology, particles size, specific area, pores structure. Since most of applications where LDH-type materials are concerned (catalysis, adsorption, bio-molecule immobilization, etc.) hinges on reactions at the interfaces solid/liquid and solid/gas, there is of great interest to imaging new synthesis route to obtain LDHs with more open structures, which would increase the diffusion properties as well as the accessibility to the active sites in the material. To date, only few works are dealing with the preparation of two-dimensional structured compounds based on nanostructured LDH thin films [10]. In this work, we described an alternative route to the synthesis of macroporous LDHs and some of their properties.

2. Experimental section

2.1. Synthesis of PS spheres ordered arrays

Monomer styrene was distilled before use to remove any traces of inhibitor. The initiator, potassium persulphate (KPS),

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was used as supplied. Deionised and decarbonated water was used. Colloidal suspensions were prepared by 'emulsifier-free' emulsion polymerization of styrene as described elsewhere [11]. Water (340 g) was poured into a reactor, kept at 70 °C, and stirred at constant speed (~350 rpm) using a twin paddled overhead stirrer. After 10 min, styrene monomer (40 g) was added to this solution, then KPS (0,1327 g) after 1 h. Finally, polymerization was performed under a nitrogen atmosphere for 28 h. Colloidal suspensions of monodisperse PS beads with a mean diameter in the range 150–800 nm have been synthesized. Colloidal suspensions with a weight fraction (wf) of solids in the range 0.5–9% remained suspended in their mother liquor until needed. To dispose the polystyrene spheres in closed-packed colloidal arrays, the suspension (2%wf) was centrifuged at 1200 rpm for 14 h. After removal of water, the resulting solid was air dried.

2.2. Preparation of LDHs inverse opals

Close-packed arrays of polystyrene spheres (~1 g) were deposited into an Erlenmeyer, and permeated with 6 mL of a water:ethanol mixture (1:1) solution of magnesium and aluminium chloride salts (1 M) with a ratio Mg^{II}/Al^{III} of 2, 3, 4 or 5. The excess of solution was removed by a slight filtration in Buchner funnel and the samples were dried.

The metal salt impregnated crystal (~1 g) was immersed into a 2 M sodium hydroxide aqueous solution (6 mL) to achieve the templated LDH precipitation. After removal of excess solution, the samples were washed with water, and then dried.

The organic phase in the LDH-beads composite was extracted by three successive toluene soakings (1 g/10 mL). Alternatively, polystyrene was also removed from the composite by calcination using a tubular furnace under a slow air stream (~2 L/min). Samples were heated from room temperature to 400 °C for 14 h. The calcined samples were finally immersed in deionised water for a day, and dried.

2.3. Preparation of LDHs by coprecipitation method

The synthesis conducted at constant pH was carried out at 60 °C under magnetic stirring and under nitrogen gas. A mixed solution of 0.66 M $MgCl_2$, $6H_2O$ and 0.33 M $AlCl_3$, $6H_2O$ was added dropwise to a reactor previously filled with decarbonated water. A 2 M NaOH solution was concomitantly added in order to keep the pH constant at 10. After complete addition of the metal salts, the precipitate was aged in the mother solution for 48 h. The precipitate obtained was then centrifuged, washed twice in water by centrifugation and finally dried at room temperature.

2.4. Anionic exchange

Composite, 25 mg, heated at 400 °C in tubular furnace was immersed immediately after heating into 50 mL of 0,1 M aqueous solutions containing the desired anion (dodecylsulphate, chloride, sulphate) for a day under nitrogen atmosphere, then washed with water and dried.

2.5. Characterization

SEM characteristics of the samples were imaged by a JEOL 5190 microscope operated at 15 keV. Powder X-ray diffraction (XRD) experiments patterns were carried out with a Siemens D501 X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5415$ Å) and fitted with a graphite back-end monochromator. FTIR spectra were collected on a Perkin–Elmer 16PC spectrophotometer using KBr pellets. ^{27}Al ($I = 5/2$) solid state NMR experiments were performed with a 300 Bruker spectrometer at 78.20 MHz. The experiments were carried out using magic angle spinning (MAS) condition at 10 kHz and a 4 mm diameter size zirconia rotor. For ^{27}Al nuclei, $Al(H_2O)_6^{3+}$ obtained after dissolution of $AlCl_3$ in water was used as a reference. Short radio frequency pulses associated to a recycling time of 2 s were used. Chemical shifts are not corrected from the second order quadrupolar effect, which induces shift to lower frequency. The particle size was measured with a Malvern Zetasizer (Nano ZS) from dilute samples of PS sphere suspensions.

3. Results and discussion

Fig. 1 is a schematic outline of the 'inverse opals method' which was used for synthesis of macroporous LDHs using polystyrene (PS) opals as template. The hydrotalcite solid $Mg_2Al(OH)_6(CO_3)_{0.5}$ described in this study is obtained by co-precipitation of divalent and trivalent metallic cations; taking place inside the voids of the PS colloid crystal after successive infiltrations.

Templates usually used are beads of silica or polymers (PS, PMMA, copolymers). PS spheres were chosen because they can be easily removed by dissolution or after a slight calcination. The results obtained by Zetasizer confirm that emulsifier-free emulsion polymerization produces very monodisperse PS spheres (polydispersity index lower than 0.09), and that these beads are negatively charged with a zeta potential in the range −50 mV/−15 mV. The crystallization of opal is controlled by repulsive electrostatic forces between spheres. It is possible to induce crystallization by centrifugation. The SEM pictures (Fig. 2) allowed us to verify that monodisperse beads are disposed in closed-packed arrays. The both cubic-close-packed and face-centered cubic lattices are observed on these arrays. It should be noted that the rotation speed should not be too high to ensure a good order, high speed rotation results in excessive densification of PS crystal and impedes the filling with precursors, furthermore small ordered areas [12] would be obtained.

The resulting opal is infiltrated by a precursor solution containing Mg and Al chloride salts. In order for the precursors solution to diffuse between the closely packed polystyrene spheres and then to fill satisfactorily the colloidal voids, a mixture ethanol:water (1:1) was used as solvent. After drying, the solid network is formed by soaking in sodium hydroxide. Note that soaking times should be long enough, more than 6 h, to obtain well crystallized LDH.