

Nanostructured Layered Double Hydroxide aerogels with enhanced adsorption properties.

Souad Touati, Hela Mansouri, Abdelkader Bengueddach, André de Roy, Claude Forano, Vanessa Prevot*

Supporting Information

I. Experimental part

Preparation of sample

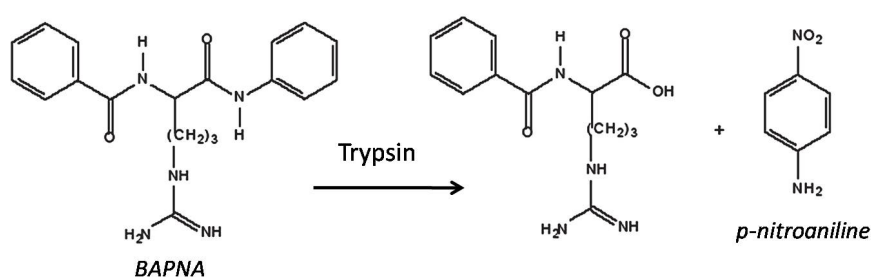
LDH samples were prepared by a fast coprecipitation method. An aqueous solution of metal salt (M^{II} and Al chloride with $M^{II}/Al = 2$ and metal ion concentration of 1 M) was quickly added to a flask containing 200 mL of deionised water. Simultaneously, a stoichiometric volume of a solution containing NaOH (2 M) and Na_2CO_3 (0.5M) was also added. After addition, the pH was checked and fixed at 10.0 ± 0.5 . The reaction was performed under vigorous magnetic stirring to ensure the homogeneity of the reaction medium. For the chloride intercalated Mg_2Al - compound, the same procedure was followed except that Na_2CO_3 was not added to the alkaline solution and reaction was performed under nitrogen atmosphere to avoid contamination with carbonate anions. Similarly, for the Mg_2Al -DDS preparation, the addition was carried out with a 0.1M aqueous solution of DDS, in absence of Na_2CO_3 and under N_2 . After complete addition of the metal salt solution, the slurry was aged during 15 min, washed by two dispersion/centrifugation cycles using deionised water to remove the reaction by-products from the materials. Then, aerogels were obtained by exchanging first the water for ethanol and then the ethanol for liquid CO_2 for 30 min which was further removed at supercritical conditions using Top Industry equipment. For SC treatment, the slurry was placed in an autoclave, and then the temperature and the pressure were slowly raised and adjusted to values above the critical point of CO_2 which are T_C 31°C and p_C 7.3 MPa. In this work, the temperature and the pressure were systematically fixed at respectively 80°C and 10 MPa. After 6h, the pressure was slowly decreased at constant temperature and the autoclave was cooled down, before to be opened. Note that LDH aerogels are recovered as a powder and not as a monolith because of the nature of the starting gel which is rather a physical gel than a chemical gel.

Adsorption experiment:

The adsorption reactions were carried out using a batch method at controlled temperature (20°C) by dispersion of 20 mg of Mg_2Al-CO_3 matrices in 10 ml of solution with trypsin concentrations ranging from 0 to 6.0 mg/mL. The solution was stirred at a constant speed (500 rpm) for 2 hours. Then, the solid was isolated by centrifugation (10000 $tr. min^{-1}$) and the trypsin concentrations in the supernatant were determined by monitoring the absorbance at $\lambda_{max} = 280$ nm.

Trypsin activity:

The activities of free and immobilized Trypsin (Tryp) were measured in aqueous solution at pH 7.5 by using an artificial substrate, the N-benzoyl-L-Arginine-p-nitroanilide (BAPNA). The hydrolysis of BAPNA by Tryp releases p-nitroaniline (see reaction 1) which was monitored spectrophotometrically at 410 nm. A typical experiment for free enzyme was carried out as follows: 3.0 mL of 1 mM Tryp solution was prepared in a Tris-HCl buffer medium (pH 7.5), 0.25 ml of 0.5 mM BAPNA solution was then added. Activities of the immobilized trypsin were performed on 0.25 ml suspension of biohybrid materials prepared with a Tryp/Mg₂-CO₃ weight ratio of 1:1. UV-Vis analyses were conducted to insure the absence of Tryp release in solution. The activities of free Trypsin, Mg₂Al-CO₃SC/Tryp and Mg₂Al-CO₃/Tryp were found to be respectively equal to 8.98 10⁻⁶ mol.min⁻¹.mg⁻¹, 2.74 10⁻⁶ mol.min⁻¹.mg⁻¹ and 1.22 10⁻⁶ mol.min⁻¹.mg⁻¹.



Reaction 1: Reaction of hydrolysis of BAPNA by trypsin.

Characterizations:

The zeta potential and the particle size were measured using a Malvern Zetasizer (Nano ZS). Powder X-ray diffraction patterns were recorded on a X'Pert Pro Philips diffractometer with diffracted beam graphite monochromator using Cu K α radiation source in the 2 θ range of 5-70° with a step of 0.013° and a counting time per step of 20 s. Attenuated Total Reflectance Fourier Transform infrared (FT-IR) spectra were measured in the range 400-4000 cm⁻¹ on a FTIR Nicolet 5700 spectrometer (Thermo Electron Corporation) equipped with a Smart Orbit accessory. SEM characteristics of the samples were imaged by a Zeiss supra 55 FEG-VP operating at 3 keV. Specimens were mounted on conductive carbon adhesive tabs and imaged after gold sputter coating to make them conductive. High-resolution transmission electron microscopy (HRTEM) images were taken using a JEOL JEM- 2100F microscope operated at 200 kV and coupled with an energy X-Ray spectrometer (EDS). Nitrogen adsorption-desorption were performed at -196 °C with a Micromeritics ASAP 2020. Before analysis, samples were pre-treated at 80 °C under vacuum for 12 h. The surface areas were estimated by using the Brunauer-Emmett-Teller method. To determine the water amount, thermogravimetric analyses (TGA) were recorded on a Setaram TG-DTA 92 instrument in the temperature range of 25-1000 °C, with a heating rate of 5 °C/min. Trypsin adsorption and activity were followed by UV-Vis spectroscopy using a Varian Cary 100 Scanning UV-VIS Spectrophotometer.

II. Complementary results

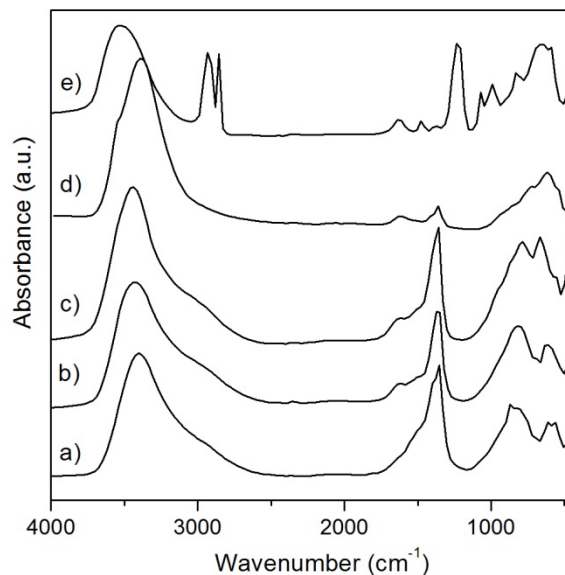


Fig. SI 1 : FTIR spectra of a) $\text{Co}_2\text{Al-CO}_3\text{SC}$, b) $\text{Ni}_2\text{Al-CO}_3\text{SC}$, c) $\text{Mg}_2\text{Al-CO}_3\text{SC}$, d) $\text{Mg}_2\text{Al-ClSC}$ and e) $\text{Mg}_2\text{Al-DDS}_{\text{SC}}$.

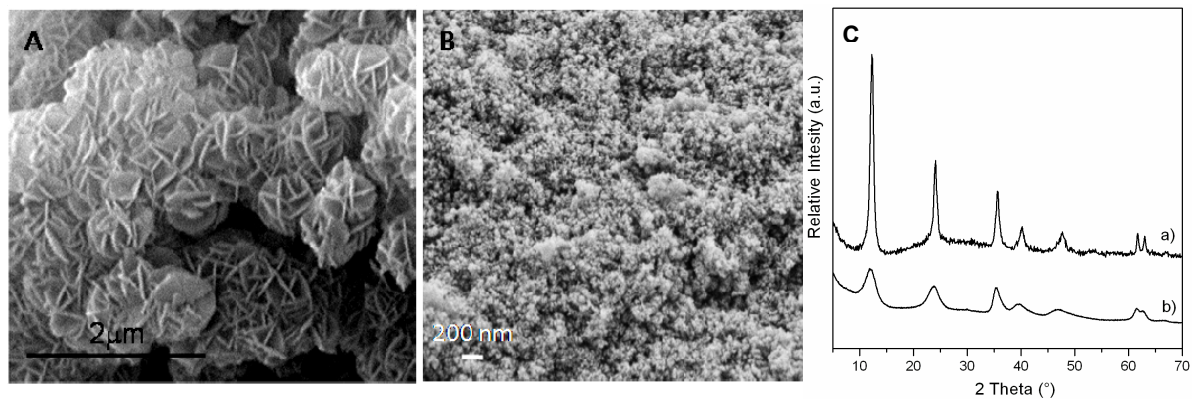


Fig. SI 2 : SEM images of $\text{Mg}_2\text{Al-CO}_3$ xerogel obtained A) by conventional pH constant coprecipitated and B) by flash coprecipitation and C) the corresponding PXRD patterns of a) $\text{Mg}_2\text{Al-CO}_3$ xerogel obtained by conventional pH constant coprecipitated and b) by flash coprecipitation.

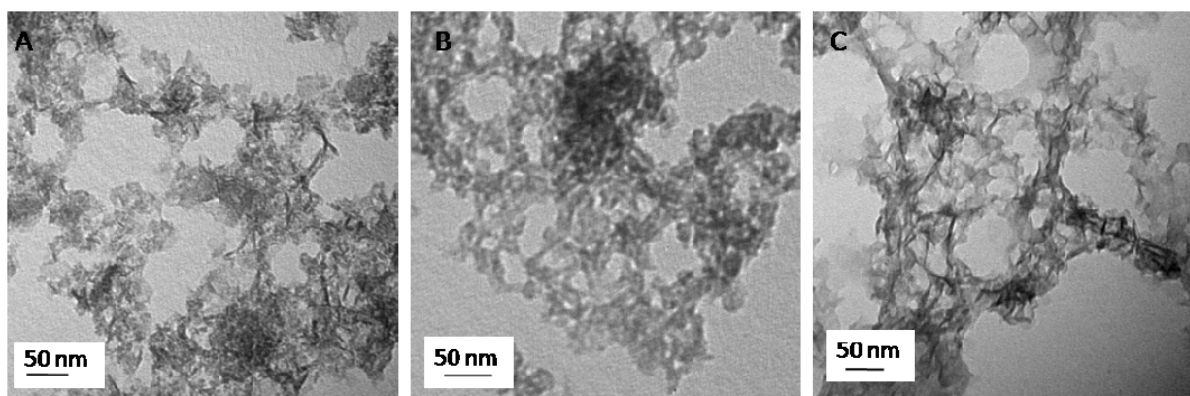


Fig.SI3: TEM images of A) $\text{Ni}_2\text{Al-CO}_3\text{SC}$ and B) $\text{Co}_2\text{Al-CO}_3\text{SC}$ and C) $\text{Mg}_2\text{Al-Cl}_{\text{SC}}$.

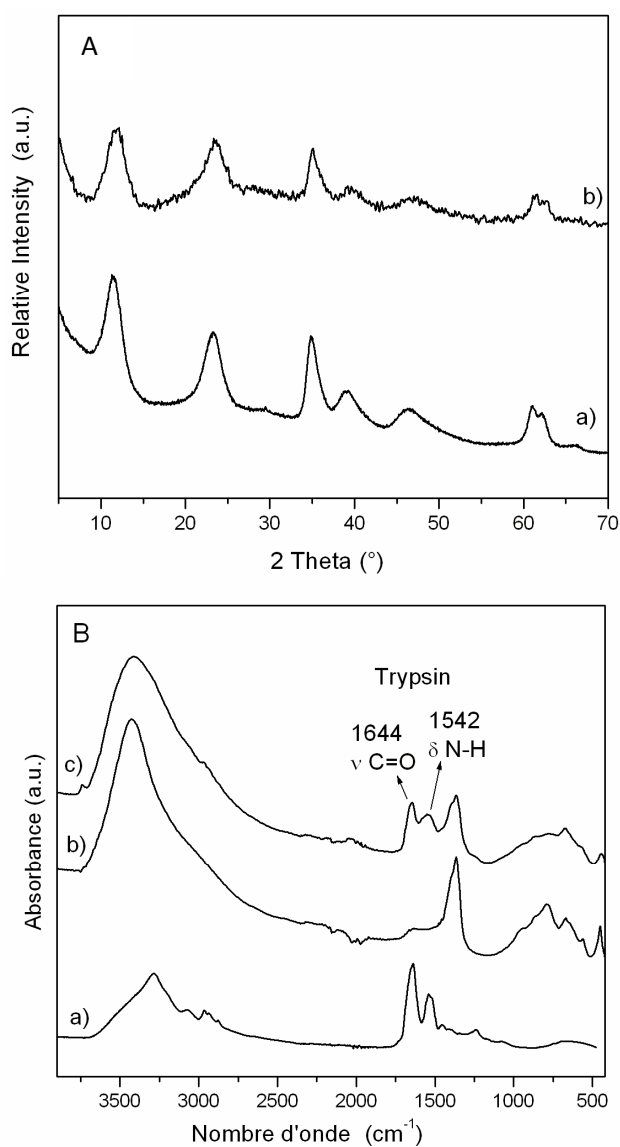


Fig. SEI 4:A) XRD patterns of $\text{Mg}_2\text{Al-CO}_3\text{SC}$ a) before adsorption and b) after trypsin adsorption and B) FTIR spectra of pure trypsin a), $\text{Mg}_2\text{Al-CO}_3\text{SC}$ b) before and c) after trypsin adsorption.