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Structure and adsorption properties of a porous cooper hexacyanoferrate polymorph

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ABSTRACT

The key questions addressed here were: the structure elucidation and the investigation of the adsorption space and framework expansion effect of a $Cu(II)$ hexacyanoferrate (III) polymorph (labeled Cu-PBA-I). The structural analysis was performed with a broad set of characterization methods. Additionally, a low and high pressure carbon dioxide adsorption investigation was performed, assuming, to comprehend the adsorption experiments, that the adsorbent plus the adsorbed phase were a solid solution. We concluded: that the Cu-PBA-I presented the following composition, $K_{1/4}Cu(II)[Fe(III)(CN)_6]_{3/4}\diamond_{1/4}nH_2O$, exhibited an antiferromagnetic behavior and displayed a thermally stable $I\bar{4}m2$ space group lattice in the degassed state. Moreover, the low pressure adsorption study allowed the calculation of the micropore volume, $W=0.09$ cm^3/g and the isosteric heat of adsorption, $q_{iso}=19$ kJ/mol; further, the high pressure adsorption data revealed an extremely high adsorption capacity owing to a framework expansion effect. Finally, the DRIFTS spectrum of adsorbed CO_2 displayed peaks corresponding to carbon dioxide physically adsorbed and interacting with electron accepting Lewis acid sites. Hence, was produced an excellent adsorbent which combine porosity and anti-ferromagnetism, antagonist properties rarely found together.

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1. Introduction

One essential characteristic of the sustainable development of the present and future Human society involve the economically and environmentally advantageous storage, separation and removal of small gas molecules, as for example: carbon dioxide, methane, ammonia and hydrogen, between others [1]. Particularly, for these purposes CO_2 occupies a special position; since their emissions cause global warming; because it influence the balance of received and emitted energy leading to the increase of the earth temperature, stimulating: sea level elevation, the increase in the oceans acidity and the strengthening of tropical storms, between other harmful effects [2].

One of the carbon dioxide emission sources is the burning of fossil fuels for industrial, transportation and other uses, since these processes releases large amounts of CO_2 into the atmosphere perturbing carbon steadiness in the earth that has been stable over hundreds of millions of years [3]. Hence, undoubtedly some approaches to reduce CO_2 emissions are urgently required to minimize climate change. In this regard, to reduce these emissions hydrogen as a clean fuel for transportation and industrial uses and methane as a car fuel, since it is considerably cleaner than petroleum, has been used [4,5]. In addition, the elimination of CO_2 from the chimney of power plants, presently a key source of emissions, is normally achieved by cooling and pressing the exhaust or by contacting the fumes across a fluidized bed of aqueous amine solution, however, both methods are expensive and ineffective [6]. Other methods based on chemisorption of CO_2 on oxide surfaces or adsorption within porous silicates, carbons, metal organic frameworks and other adsorbents have been pursued as means for CO_2 uptake [3–6]. However, the attainment of new adsorbents for carbon dioxide storage is still a vigorous research topic [5]. In this regard, transition metal cyanides [8–21] exhibiting structures assembled with transition metals, attached through the linear cyanide ion, as a consequence of their magnetism [14], physical adsorption [15–19] and other attributes [9–14], are a significant class of materials. In particular, metal hexacyanometalates isostructural to Prussian blue, namely Prussian blue analogs (PBAs), exhibit developed adsorption and magnetic properties between other characteristics [9,19–21].

The backbone of the structure of PBAs is the $-M\grave{}-C\equiv N-M-N\equiv C-M\grave{}-$ chain. This atomic sequence is straight hence PBAs typically crystallize in the cubic system,

specifically, in the $Fm\bar{3}m$ space group and in less extent in the $Pm\bar{3}m$ [19]. Even though, some PBAs crystalizes in the tetrahedral, $I\bar{4}m2$ [10] and $I4mm$ [18] space groups. Moreover, if $M' = Fe$ (III), and $M = M(II)$, the following, $A_xM(II)[Fe(III)(CN)_6]_z\diamond_{1-z}nH_2O$, generalized formula has been proposed to describe the stoichiometry of these materials [9], where the symbol, $\diamond$, indicates $[Fe(III)(CN)_6]^{\mu-}$ vacancies, generated together with the interstitial cations to produce charge balance in the framework. In this regard, some possible representatives compositions for these materials are [13], $AM(II)[Fe(III)(CN)_6]$ ($M/Fe = 1$), $M(II)[Fe(III)(CN)_6]_{2/3}\diamond_{1/3}nH_2O$ ($M/Fe = 3/2$) and $A_{1/4}M(II)[Fe(III)(CN)_6]_{3/4}\diamond_{1/4}nH_2O$ ($M/Fe = 4/3$), where the voids results to microporous frameworks.

The investigation of carbon dioxide physical adsorption [22] and the analysis of the infrared spectra of adsorbed CO_2 [23–25] are outstanding methods for the characterization of the porosity and surface chemistry of porous materials. Hence, the adsorption of this gas is an excellent tool for the investigation of the adsorption space of PBAs and other materials [26–31].

For the last years the investigation of PBAs became an expanding research field, specially, when materials with high thermal stability and porosity are produced [32–36]. Thereafter, the main questions investigated here were: the structural elucidation and the study of the adsorption properties and thermal stability of a porous $Cu(II)$ hexacyanoferrate (III) polymorph (labeled Cu-PBA-I) and the synthesis and characterization of the standard $Cu(II)$ hexacyanoferrate (III) (labeled Cu-PBA) for comparison.

2. Experimental section

The consumable chemicals were analytical grade. Water was bi-distilled.

Firstly, the synthesis of the standard $Cu(II)$ hexacyanoferrate(III) was carried out following the recipes reported in literature [19] to get the sample labeled Cu-PBA. Secondly, the synthesis of the $Cu(II)$ hexacyanoferrate(III), different to the standard one, took place by mixing 0.025 mol of solid potassium hexacyanoferrate (III) and solutions containing 0.025 mol of $Cu(NO_3)_2$ in 250 mL of water, at 70 °C, under constant stirring, next, the formed precipitate was filtered, washed with distilled water and dried at 343 K for 24 h to get the sample labeled Cu-PBA-I.

Next, X-Ray diffraction (XRD) profiles were collected (Bruker D8 Advance) using a Bragg–Brentano vertical goniometer configuration. The angular measurements were made using steps of 0.01°. The X-ray radiation source was a ceramic X-ray diffraction Cu anode tube type KFL C 2K. In addition, a Soller slit was included and a Ni filter was placed prior to the detector. Also, a LynxEye™ one-dimensional detector was used for X-ray detection.

Afterwards, the scanning electron microscopy (SEM) images were obtained at 20 kV (JEOL, JSM-6360) for sample grains placed on a carbon tape. At the same time as, elemental chemical analysis was performed using the energy dispersive X-ray analysis (EDAX) included in the SEM.

Subsequently, the thermo-gravimetric analysis (TGA) testing process was carried out (TA, Q-500). The sample and holder were heated according to a predetermined thermal cycle from 25 to 700 °C at a heating rate of 5 °C/min while flowing 100 ml/min of pure N_2 (Praxair, 99.99%). The TGA profiles were collected as a wt% versus T (°C) graphic, where $wt\% = (M_t/M_0) \times 100$ is the percent-ratio of the sample mass for the thermal treatment M_t and the initial mass of the sample M_0.

Afterward, diffuse reflectance Fourier transform infrared spectrometry (DRIFTS) spectra were gathered (Nicolet iS10). The spectra were collected at a resolution of 4 cm^{-1} employing 200 scans per sample in a high temperature infrared cell. The hydrated samples spectra were obtained at room temperature under N_2

flow at 50 ml/min rate. To get the spectra of the dehydrated samples it were heated at 473 under a flow of N_2 at 50 ml/min rate for 2 h. Then, the spectra of the degassed materials were obtained at room temperature, under N_2 flow. Similarly, a Raman spectrum was taken with a Renishaw Raman microspectrometer RM2000 system equipped with a Leica microscope using a $20\times$ objective and a charge-coupled device (CCD) detector. Then, the spectrum was obtained with a laser line at 532 nm, generated by a Spectra Physics EXCELSIOR solid state diode laser, in the range of 100–3500 Raman Shift (cm^{-1}) with an integration time of 15 s per scan, averaging 15 scans.

Later, the magnetization curve (M versus H) was collected at room temperature (300 K) in the vibrating sample magnetometer (VSM) (Lakeshore 7400). To perform the test, the powder sample was weighted, located on the sample holder and subsequently was generated the ramp -2.2–2.2 T and backward.

Lastly, carbon dioxide (Praxair, 99.99%) adsorption was investigated at 300 K and pressure up to 1 bar (LP) (Quantachrome AS-1) and at 300 K and pressure up to 30 bar (HP) (Quantachrome iSorbHP-100), on samples degassed at 423 K for three hours in high vacuum (10^{-6} Torr). The backfilling process was performed using helium (Praxair, 99.99%). Furthermore, the DRIFTS spectrum of carbon dioxide adsorbed in the Cu-PBA-I was collected utilizing as background the dehydrated sample at room temperature. After that, a CO_2 flow at a rate of 50 ml/min for three minutes was passed through the dehydrated samples, next, the sample was purged under N_2 flow at a rate of 50 ml/min for one minute, and then a spectrum of the carbon dioxide molecule adsorbed on the Cu-PBA-I adsorption space was obtained at room temperature under N_2 flow.

Finally, the curve fitting processes were performed with the analysis and peak separation software PeakFit® (Seasolve Software Inc., Framingham, Massachusetts) based on a least square procedure [37]. The program made possible the calculation of the best fitting parameters in the case of curve fitting. For peak separation the software made possible the calculation of the band parameters, i.e., intensity, peak position and half-band-width using for the spectrum fitting Lorentzian functions.

3. Results and discussion

3.1. Structural characterization of the synthesized CU-PBA-I

First of all, the powder XRD profiles of the as-synthesized Cu-PBA and Cu-PBA-I were collected and resolved into separate Bragg components using the Pawley powder pattern decomposition method, by means of the Bruker AXS TOPAS® powder X-ray diffraction analysis software. The profiles were fitted assuming the $Pm\bar{3}m$ space group (SG) for the Cu-PBA (Fig. 1a) [23] and the tetragonal $I\bar{4}m2$ SG for the Cu-PBA-I (Fig. 1b) respectively. Likewise, in Table 1 are reported the refined parameters. The profile of the Cu-PBA and the refined cell parameters (Table 1) agreed with the XRD data previously published [19]; meanwhile, the crystallographic information reported for the Cu-PBA-I, indicated that was produced a different polymorph.

Secondly, three SEM images corresponding to the Cu-PBA-I material were collected (Fig. 1a–c). These images exhibited the formation of particles of 60 μm shaped by aggregates of 0.5–1 μm formed by the 25 nm Cu-PBA-I crystallites. In addition, EDAX elemental chemical analysis of the Cu-PBA-I was performed (see Fig. 1d). In this regard, the elemental composition was calculated as the average of ten tests similar to those reported in Fig. 1d. Thereafter, the average concentration plus the calculated standard deviation (σ) expressed in molar per-cent was calculated and reported in Table 2 (Fig. 2).