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Synthesis, structural elucidation and carbon dioxide adsorption on Zn (II) hexacyanoferrate (II) Prussian blue analogue

R. Roque-Malherbe*,[1], F. Lugo[1], R. Polanco

School of Science, University of Turabo, PO Box 3030, Gurabo, PR, 00778-3030, USA

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ABSTRACT

In the course of the last years hexacyanoferrates have been widely studied; even though, the adsorption properties of Zn (II) hexacyanoferrate(II) (labelled here Zn-HII) have not been thoroughly considered. In addition, soft porous crystals, i.e., adsorbents that display structural flexibility have been, as well, extensively studied, however this property has not been reported for Zn (II) hexacyanoferrate(II). In this regard, the key questions addressed here were the synthesis and structural characterization of Zn-HII together with the investigation of their low (up to 1 bar) and high pressure (up to 30 bar) adsorption properties, to found if these materials show structural flexibility. Then, to attain the anticipated goals, structural characterizations were made with: X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) and thermo-gravimetric analysis (TGA), simultaneously, with the investigation of the adsorption of carbon dioxide. As a result of the research process we concluded that the Zn-HII displayed $Fm\bar{3}m$ space group framework. Besides, the carbon dioxide adsorption investigation demonstrated the presence of the framework expansion effect together with an extremely high adsorption heat, properties that could be useful for the use of Zn(II) hexacyanoferrate(II) as an excellent adsorbent.

1. Introduction

Transition metal cyanides display structures assembled with transition metals, attached through the linear cyanide [1–10]. These compounds due to their magnetic [4], adsorption [5–8] and other properties are an important class of materials. Specially, metal hexacyanometalates are a notable group of transition metal cyanides. The basic component of the structure of hexacyanometallates, also known as PBAs is the linear, $-M' - C \equiv N - M - N \equiv C - M' -$ chain [6]. As a result, their structural framework is associated to the perovskite structure; even though, the metal centers are linked by the cyanide bridges instead of oxide ions [9]. Subsequently, since the basic structural element is straight, hence hexacyanometallates should crystallize in the cubic system, more precisely, in the $Fm\bar{3}m$ space group and in less extent in the $Pm\bar{3}m$[4]. Although, for some metals, specific distortions produce the crystallization of hexacyanometallates in the tetrahedral, $I4mm$, $I\bar{4}m2$ [7] and in less extent in other space groups [10].

It is necessary to remark that the presence of $[M'(X)\ (CN)_6]^{\mu-}$ vacancies produce a channel network, shaped by cavities, where the exchangeable metal, A, is located on these voids to generate charge balance [5,6]; acting, also, as charge centers capable to produce electrostatic interactions with the adsorbed molecules. Specifically, in the case of carbon dioxide; given that this molecule has a quadrupole moment it strongly interacts with the electric field gradients within the cavity [11].

In the specific case of hexacyanoferrates the generalized formula can be expressed as follows: $A\alpha M\beta[Fe(CN_6)]_\delta \cdot nH_2O$, is normally an alkaline metal, M, is in general a transition metal, ($Fe = Fe(X)$), $X = II\ or\ III$, and nH_2O are coordinated and loosely bound water molecules filling the $[Fe(X)\ (CN)_6]^{\mu-}$ vacancies, that forms the microporous framework [7,12].

During the last years the investigation of hexacyanometallates became an expanding research field; particularly, zeolite-like hexacyanometallates have received particular attention as porous solids for the adsorption of small molecules; as a result of their microporous framework [11]. Besides, a group of porous materials known as soft porous crystals (SPC) have been investigated on account of

* Corresponding author.
E-mail addresses: rroquemalh@aol.com, rolandoroquemalh@gmail.com (R. Roque-Malherbe).
[1] Present address: PO Box 2017, PMB 405, Las Piedras, PR 00771, USA.

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their structural flexibility [13–15]. These materials undergo different framework transformations produced by external stimuli, such as, mechanical stress, adsorption or temperature [13]. In the case where the outside stimulus is the interaction of the guest molecules with the framework, the structural transformations are manifested by the atypical adsorption-desorption isotherm patterns observed [14]. Particularly, gate opening effects are characterized by a big hysteresis loop between the adsorption and desorption branch of the isotherm [15].

Carbon dioxide is a good probe molecule to test framework transformations during adsorption, owing to the relatively high value of their quadrupolar moment ($Q_{CO_2} = -4.3 \times 10^{-42}$ C m^2 [16]); since, when it is adsorbed at low coverage become subjected to the dispersion, ϕ_D, repulsion, ϕ_R, and field gradient quadrupole, φ_{EQ} interaction energies [3]; where, $\phi_{EQ} = Q_{CO_2}/2\left(\partial E/\partial z\right)$; in which $\left(\partial E/\partial z\right)$, is the electric field gradient within the adsorption space [11].

PBAs are good adsorbents of small molecules [17–23]; hence, the main questions investigated here were, the synthesis and structural characterization of a Zn(II) hexacyanoferrate(II) (labelled Zn-HII); together, with the investigation of carbon dioxide adsorption in the low pressure (up to 1 bar) and high pressure (up to 30 bar) ranges, to investigate the structural transformations induced by adsorption in the framework of the tested Prussian blue analogue.

To perform the corresponding experimental work the structural characterizations of the Zn-HII was done, by using X-ray diffraction (XRD); besides, a morphological study of the synthesized hexacyanoferrate was made with a scanning electron microscope (SEM); furthermore, the elemental composition was measured by means of the energy dispersive X-ray analysis (EDAX) facility included in the SEM; thereafter, the state of water in the Zn-HII material was investigated using thermo-gravimetric analysis (TGA), finally low and high pressure carbon dioxide adsorption was studied to closely examine the adsorption space of the produced hexacyanoferrate.

2. Experimental

2.1. Synthesis

The consumable chemicals were analytical grade. Water was bi-distilled. To start with, the synthesis of the Zn(II) hexacyanoferrate(II) material was performed as follows: were mixed 0.025 mol of solid potassium hexacyanoferrate(II) and solutions containing 0.025 mol of $Zn(NO_3)_2$ for 250 mL of water, at 70 °C, under constant stirring. Later, the formed precipitate was filtered, washed with distilled water and dried at 343 K for 24 h to get the sample labelled Zn-HII.

2.2. Methods

Firstly, the XRD profiles were gathered with a Bruker D8 Advance system in Bragg-Brentano vertical goniometer configuration. The 2θ angular measurements were made by applying steps of 0.01°. The X-ray radiation source was a ceramic Cu anode tube. Variable Soller slits were included and a Ni filter was placed, prior to the detector. Additionally, a LynxEye™ one-dimensional detector was used to produce large counting that resulted to high quality XRD profiles that can be accurately resolved by least square methods [17]. To confirm the assigned structure of the synthesized materials, the gathered XRD patterns were refined with the Pawley method. The computer program used to perform the Pawley refining processes was the Bruker DIFFRAC*plus* TOPAS™ software package. The emission profile used in the refining processes was shaped by two Lorentzians displaying the following parameters, $A_1 = 0.654$, $\lambda = 1.5406$ Å, $\Delta\lambda = 0.5$ mÅ and $A_2 = 0.346$, $\lambda = 1.5545$ Å, $\Delta\lambda = 0.63$ mÅ [23].

Secondly, the SEM study was carried out with a JEOL JSM-6360, whose electron beam acceleration voltage was 20 kV. The tested sample grains were homogeneously placed on a carbon tape and different spots were examined. Using these specifications different images of the studied materials were obtained. As well, the elemental chemical analysis of the as-synthesized and washed samples, were performed using an EDAX spectrometer coupled into the microscope. To improve the accuracy, five elemental compositions in different spots were measured, then calculated the average composition.

Afterwards, diffuse reflectance infrared Fourier transform spectra were gathered using a Thermo Scientific Nicolet iS10 FTIR spectrometer. The data were collected at a resolution of 4 cm^{-1} employing 100 scans per sample. The hydrated samples spectra were obtained at room temperature under N_2 flow (Praxair, 99.99%) at a rate of 50 cc/min. To get the spectra of the dehydrated samples, it were heated, to 100 °C, under a flow of N_2 (Praxair, 99.99%) at a rate of 50 cc/min for 2 h. The spectra of the dehydrated materials were then obtained at room temperature, under N_2 (Praxair, 99.99%) flow at a rate of 50 cc/min. In addition, DRIFTS spectra of carbon dioxide adsorbed in the PBA framework were obtained using as background the dehydrated sample at room temperature. After that, CO_2 (Praxair, 99.99%) flow at a rate of 50 cc/min for three minutes was passed through the dehydrated samples; then, the sample was purged under N_2 (Praxair, 99.99%) flow at a rate of 50 cc/min for one minute. The spectrum of the carbon dioxide molecule adsorbed on the PBA microporous framework, were then obtained at room temperature under N_2 flow.

Lastly, carbon dioxide (Praxair, 99.99%) adsorption was investigated at 273 K and 300 K in the low pressure (LP) range (pressure up to 1 bar) on samples degassed at 373 K for four hours in high vacuum (10^{-6} Torr) in a Quantachrome AS-1 automatic sorption analyzer. To measure the carbon dioxide (Praxair, 99.99%) adsorption at temperatures of 273 K, 300 K and 318 K on samples degassed at 373 K for four hours in high vacuum (10^{-6} Torr) in the high pressure range (pressure up to 30 bar) a Quantachrome iSorbHP-100 was used. The backfilling process was performed using helium (Praxair, 99.99%) in both cases.

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 using the method developed by Levenberg and Marquardt, making possible the calculation of the best fitting parameters.

3. Results and discussion

3.1. Synthesis

For the synthesis of the M(II) hexacyanoferrate (II) several methods have been reported during the last years; namely, precipitation, growth in a gel, growth on a solid alkali-metal ferrocyanide and others [17–22]. Here we applied a precipitation method to produce the Zn(II) hexacyanoferrate (II). In this regard, were mixed solid potassium hexacyanoferrate(II) and solutions containing of $Zn(NO_3)_2$ under constant stirring, to get after: precipitation, filtration, washing with distilled water and drying the sample labelled Zn-HII.

3.2. Structural elucidation

The average elemental composition, C_X, in molar per-cent for the synthesized hexacyaanoferrate (Zn-HII) is $C_K = 0.4(2)$; $C_{Fe} = 1.0(5)$; $C_{Zn} = 2.1$; giving that, the generalized formula can be expressed as follows: $A\alpha M\beta[Fe(CN_6)]_\delta \cdot nH_2O$, in which, *A*, an alkaline metal, *M*, a transition metal, such as, *Fe* = *Fe*(*X*)), *X* = *II or III*, and nH_2O are coordi-