Study of Carbon Dioxide Adsorption on a
Cu-nitroprusside Polymorph

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Thesis

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Study of carbon dioxide adsorption on a

**Cu-nitroprusside polymorph**

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Dedications

I dedicate this thesis in the first place to the one who guide and care of all my steps, God. To my parents who gave me the tolos and skills to become the person that I’m. Specialy to my husband who motivates me in hard times when I felt to abandonate my dreams, for being my support in this long trip, I love you.
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I wish to thank Dr Roque who trust me and who given me the opportunity haved worked in his laboratory. To Dr Schaffner who has assisted me with the administrative steps for complete my master. To the entire laboratory staff for given me all the materials needed to complete this research. I also want to thanks to Prof Karlo Malave-Llamas, for beliving in my work and for his tips, necessary for the completion of this project. Besides I acknowledge the financial support provided by the US Department of Energy through the Massie Chair project at the University of Turabo and to the National Science Foundation CHE-0959334 for financial support of this project.
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Abstract

FRANCES N LUGO ALVARADO. (MS, Master of Environmental Science)

Study Of Carbon Dioxide Adsorption On Nitroprussides \( \text{Cu[Fe(CN)}_5\text{NO]}^2 \) Polymorph
(March/2012)

Abstract of a master thesis at the Universidad del Turabo.
Thesis supervised by Professor Rolando Roque-Malherbe PhD.
No. of pages in text 58

A rigorous evaluation of the structure of the nitroprusside can lead to a better understanding of this material. Nitroprusside porous materials offer a micro-porous environment able to achieve the adsorption of other molecules. The TGA, DRIFTS and a Pawley fitting of the XRD powder results indicate that the hydrated and in situ dehydrated polymorph crystallizes in the orthorhombic space group Pnma. Meanwhile, the \( \text{CO}_2 \) isosteric heat of adsorption appears to be independent of loading with an average value of 30 kJ/mol. This translates to a physisorption type interaction, where the adsorption energy corresponding to wall and lateral interactions are mutually compensated to produce apparently homogeneous adsorption energy. The somewhat high adsorption energy is probably due to the confinement of the \( \text{CO}_2 \) molecules in the nitroprusside pores. Statistical Physics and the Dubinin theory for pore volume filling allowed model the \( \text{CO}_2 \) equilibrium adsorption process in Cu-nitroprusside. A DRIFTS test for the adsorbed \( \text{CO}_2 \) displayed a peak at about 2338 cm\(^{-1}\) that was assigned to a contribution due to physical adsorption of the molecule. Another peak found at 2362 cm\(^{-1}\) evidenced that, in addition to the physically adsorbed carbon dioxide was also found in
the spectra of carbon dioxide adsorbed on the nitroprusside, that this molecule interacts with the Cu$^{2+}$ acting as an electron accepting Lewis acid site forming the following adduct: \[ Cu^{2+} \cdot \cdot \cdot O = C = O. \] The structural characterization of the tested material allowed us to conclude that: the dehydration behavior of the obtained polymorph is typical of the stable \textit{Pnma Cu-nitroprusside} polymorph. The importance of the thesis is to report a \textit{Pnma} stable Cu-nitroprusside polymorph obtained by the precipitation method that can adsorb contaminants like carbon dioxide, sulfur dioxide and ethanol. These contaminants are important because we can reduce the anthropological effects. The material could be used like a filter and gas sensor for reduce this contaminant from our atmosphere.
Resumen

FRANCES N LUGO ALVARADO. (MS, Maestría en Ciencias Ambientales)

Estudio de la Absorción del Dióxido de Carbono en el polimorfo de Nitroprusiato de Cu[Fe(CN)₅NO]²⁻ (marzo/2012)

Resumen de tesis de maestría de la Universidad del Turabo.
Tesis supervisada por el Profesor Rolando Roque-Malherbe PhD.

No. de páginas en texto: 58

Una evaluación rigurosa de la estructura del nitroprusiato puede conducir a un mejor entendimiento de este material. Nitroprusiato es un material que ofrece un ambiente micro-poroso capaz de adsorber moléculas gaseosas. Los estudios de TGA, y un ajuste de Pawley de los resultados de difracción de polvo de rayos X indican que la hidratación y deshidratación in-situ del polimorfo de nitroprusiato de cobre cristaliza en el grupo espacial Pnma ortorrómbico. Por otro lado, el calor isoterico de adsorción de CO₂ parece ser independiente de la carga con un valor de 30 kJ / mol. Esto se traduce en una interacción de absorción física, donde la energía de absorción corresponde a interacciones con las paredes y a las interacciones laterales del material mutuamente compensado para producir energía de adsorción homogénea. La energía de adsorción algo elevada es probablemente debido al confinamiento de las moléculas de CO₂ en los poros del nitroprusiato. Física estadística y la teoría de Dubinin para el llenado de el volumen de poros fue el modelo que permitió conocer el proceso de equilibrio de absorción de CO₂ en el Cu-nitroprusiato. La prueba de DRIFTS sirvió para conocer la
absorción de CO₂, donde mostró un pico alrededor de 2338 cm⁻¹ que fue asignado a adsorción física de la dicha molécula. Otro pico que se encontró alrededor de 2362 cm⁻¹ evidencia que en adición a la absorción física de dióxido de carbón este interactúa con el Cu²⁺ actuando como un aceptador de electrones en Lewis acid site formando la siguiente cadena \( \text{Cu}^{2+} \cdot \cdot \cdot O = C = O \). La caracterización del material evaluado nos permite concluir que el comportamiento del polimorfo deshidratado es típico de un polimorfo estable perteneciente al grupo especial \( Pnma \). La importancia de esta tesis es reportar una nitroprusiato de Cu estable obtenido por el método de precipitación que puede absorber contaminantes como dióxido de carbón, dióxido de azufre y etanol. Estos contaminantes son importantes para reducir los efectos antropológicos en nuestro ambiente. Este material puede ser usado como filtro o sensores para reducir la contaminación a nuestra atmósfera.
Chapter One

Introduction

The synthesis and characterization of porous nitroprussides is the main objective of this thesis. Nitroprusside is an octahedral ferrous center surrounded by five bound cyanide ligands and one linear nitric oxide ligand. This material display porous frameworks built from, structure units bridged though, $M^{2+}$, cations, by means of the CN$^-$ ligands (Mullica et al. 1991, 1992; Kaye and Long 2005). Porous materials offer a micro-porous environment to make them able for the adsorption of different molecules. The relevancy of these substances consists on the variety of its crystalline structures and its porous system topologies useful for the storage of a variety of molecules, being of particular interest, the carbon dioxide (CO$_2$), sulfur dioxide (SO$_2$) and ethanol (CH$_3$CH$_2$OH) molecule. CO$_2$ is, in particular, very important; since it is a greenhouse gas which contributes to global warming.

The greenhouse gases are constituted by water vapor, CO$_2$, methane, nitrous oxide, ozone and chlorofluorocarbons. The accumulation of these gases form a dense layer that function as an absorbent of the radiation from the sun; if the absorption of the radiation is larger cause the effect of global warming. Global warming is the raise in the average temperature of the Earth due to the increasing concentration of greenhouse gases in the atmosphere. The SO$_2$ is a volatile, colorless liquid that has a slight odor. Large concentration on this gas could result in respiratory problem; central nervous system effects and could affect the metabolism. This gas also affects the environment with the acid rain. Acid rain is a precipitation that is unusually acidic; that it possesses elevated
levels of hydrogen ions. It can have harmful effects on plants, aquatic animals, and infrastructure. Acid rain is caused by emissions of carbon dioxide, sulfur dioxide and nitrogen oxides which react with the water molecules in the atmosphere to produce acids. Another gas CH₃CH₂OH is a volatile, flammable, colorless liquid. Large concentration may cause serious risk of suffocation when in confined areas. Today ethanol is one of the fuel option but the National Academy of Sciences has found that corn ethanol production increases greenhouse gas emissions.

The significance of the nitroprussides rests on the capacity for the sequestration of gases on the porous frameworks. CO₂ is an excellent probe molecule to study adsorption on microporous materials (Reguera et al. 2008). Specifically, CO₂ adsorption data is an excellent tool for measure the micropore volume and adsorption interactions (Roque-Malherbe 2010, 2007). Additionally, a very useful tool for the study of the physical and chemical properties of solid surfaces is the infrared spectra of adsorbed CO₂, since this molecule is a small and weakly interacting probe adsorbate (Reguera et al. 2008).

1.1 Goals of the Research

The creation of new materials for the adsorption of gaseous pollutant is very important because a significant reduction of the concentration of this gas in the helps Earth atmosphere. Human activities produce emission of gases, helping in the retention of more heat in the environment and climate changes. Factories, power plants, cars, planes, thermoelectric, industries and homes each emit relatively small amounts of different gases. The accumulations of small amount of all this activities create a large effect in our environment. Variation on the synthesis of adsorption materials could lead the creation of better absorbent of gases. This would be a significant advance in the
creation of new filters/collectors for the absorption of gaseous pollutant in the air. Diminutions of emissions will help on reducing the impact of this phenomenon that is commonly accepted to be responsible for global warming effects.

The capability for the gaseous pollutant sequestration within the porous networks promises not just significant advancements in global efforts for the reduction of pollutant levels and their known environmental impact, but also appear a series of favorable economical opportunity. Carbon dioxide, ethanol and sulfur dioxide is, in particular, are very important, since it is a greenhouse gas which contributes to global warming.

Some environmental applications for the adsorption of gaseous pollutant are molecular sieve and gas sensor. Molecular sieve is a material that contains tiny pores of a precise and uniform size that is used as an adsorbent for gases and liquids (Breck 1964). Could absorb molecules small enough to pass through the pores are adsorbed while larger molecules are not (Roque Malherbe 2010). Other application for this material is Gas sensor this is a tool which detects the existence of various gases within an area, usually as part of a safety system. This type of apparatus is used to detect a gas leak and is important because there are many gases that can be harmful to environment and humans. Gas sensor can be used to detect combustible, flammable and toxic gases, and oxygen depletion (Thomas Publishing Company 2003).

Creation of new porous materials with more pore volume from new synthesis parameter could amplify the possibility of the absorbents. This contribution is important for the removal of gaseous pollutant of environment. Providing more choices to environmental scientists for the remediation can greatly assist in managing the environment.
1.2 Studies Objectives

The structure of Cu-nitroprusside has been previously studied (Mullica et al. 1991; Reguera et al. 1996; Balmaseda et al. 2003; Reguera et al. 2008). With respect to the structure at, is normally accepted that nitroprussides exhibit a marked polymorphic nature (Balmaseda et al. 2003; Reguera et al. 1996); then, minor changes in the synthesis process of these materials could lead to materials with fairly different properties. In the present thesis the structural characterization of a Cu-nitroprusside polymorph synthesized by the precipitation method applying relatively concentrated solutions in order to get atypical characteristics, that is, a different polymorph will be carried out.

The adsorption properties of Cu-nitroprusside have been barely studied (Reguera et al. 2008; Balmaseda et al. 2003). The adsorption properties of a Cu-nitroprusside polymorph in order to carefully explore the geometry of the adsorption space and the intensity of the adsorption field and as well potential applications of this material as adsorbent applying carbon dioxide as a probe molecule will be studied. To accomplish our objectives, the synthesized samples were studied using: energy dispersive X-ray spectroscopy (EDAX), thermogravimetric analysis (TGA), X-ray diffraction spectroscopy (XRD), diffuse reflectance infrared Fourier transform spectrometry (DRIFTS), and adsorption of carbon dioxide at 273 K and 295 K.

1.3 Research Hypothesis

The hypothesis of this research is that by modifying the synthesis procedures of nitroprussides such as Cu[Fe(CN)_5NO] will result in a porous material that could absorb CO₂ molecules and the formation of distinctive space group crystals. Because the synthesis is different, a carefully characterization is required to identify the polymorph
and its adsorption properties. We will also evaluate the role of the type of cooper salts (Cu(SO₄) and Cu(NO₃)₂ in the synthesis. We hypothesized that because the same cation (Cu²⁺) is used the effect of the typed of salt will be minimum or negligible.
Chapter Two

Literature Review

2.1 Nitroprusside Description

Transition metal cyanides nitroprussides (Mullica et al. 1991, 1992; Kaye and Long 2005) display frameworks assembled with the transition metals, bridged through the linear cyanide ion. This structure possesses interesting properties, such as, physical adsorption (Mullica et al. 1992; Kaye et al. 2008), light induced phenomena (Gadet et al. 1992), magnetism (Reguera et al. 1996) and other properties that make these materials an interesting class of porous coordination polymers. Nitroprussides (pentacyanonitrosylferrates), are a group of metal cyanides, consisting of porous frameworks built from: \([\text{Fe(CN)}_5\text{NO}]^{2-}\), structure units bridged through, metal, cations, by means of the \(\text{CN}^{-}\) ligands (Kate and Long 2005; Mullica et al. 1991, 1992). In this tridimensional framework the \(\text{O}\) atom at the end of the \(\text{NO}\) ligands, remains permanently free (Vertelman et al. 2008) and the metal, cation normally coordinates to one or more water molecules while the rest of the water molecules are hydrogen-bonded to the metal-coordinated water molecules (Ohkoshi et al. 2010; Pejakovic et al. 2000). These nitroprusside at the same time are filling the adsorption space (pore volume) formed by the array of the nitroprusside framework. Therefore, after thermal dehydration both the coordinated, hydrogen-bonded or zeolitic water molecules are detached, leading to materials with a channel system suitable for the adsorption of small molecules (Mullica et al. 1991, 1992; Mullica et al. 1989; Manoharam and Hamilton 1963).
2.2 Background Studies

The structure of Cu-nitroprusside (Cu-NP) has been studied for nearly two decades (Ohkoshi et al. 2010; Lima et al. 2010), but their polymorphic nature still requires more effort for a complete understanding of the properties of these materials. Stable Cu-NP crystallizes, in the Pnma space group with a framework where Fe atoms are coordinated by five CN ligands and a NO group and Cu atoms are coordinated by five CN and a H$_2$O molecule, and the second water molecule is H-bonded to the coordinated water (Ohkoshi et al. 2010). In the case of the hydrated Cu-NP fresh precipitates, however, there are reported a mixture of two tetragonal phases (Lima et al. 2010) and a polymorph crystallizing in the space group Amm2, where Fe atoms are coordinated to five CN ligands and a NO group, while the Cu atoms are coordinated by four CN and two H$_2$O molecules (Manoharam and Hamilton 1963). Additionally, it has been reported that the dehydrated species obtained on heating Amm2 Cu-nitroprusside phase experiences a transformation to, an anhydrous, tetragonal space group I4mm phase (Mullica et al. 1991,1992). The stable phases are orthorhombic (Pnma) dihydrates for (Mn$^{2+}$, Fe$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$) and face-centred cubic (Fm$\overline{3}$ m) tetrahydrates for Co$^{2+}$ and Ni$^2$ (Reguera et al. 1996).

The highest capacity absorption of CO$_2$ adsorption isotherm at 0 °C was observed for Cu>Ni>Cd>Zn (Reguera et al. 2008). The capacity of absorption and the pore volume are related with the molar volume of the CO$_2$ in Cu>Cd>Ni>Zn nitroprusside (Balmaseda et al. 2006). Other results from Balmaseda reveal that the precipitated sample of Cu-NP form a layer structure which on heating loses occurs a structural transformation to an anhydrous tetragonal phase from a orthorhombic (Balmaseda et al. 2003). The small
pores are inaccessible to be an absorbent material (H₂O, CO₂, and N₂) (Balmaseda et al. 2003). This phenomenon is attributed to a large polarization of the nitrosyl ligands.

Stretching of the ligands CN in the infrared can be used as a sensor of the affinity by the N end of the CN group, the frequency order are Cu (2203) > Ni (2192) > Zn (2190) > Cd (2180) (Reguera et al. 2008). These materials were obtained from the mixing of 0.01 aqueous solutions of sodium nitroprusside and transition metal salts. The precipitated material was filtrared (Reguera et al. 2008). In order to obtain the stable polymorph the time for aging the sample is five years (Reguera et al. 2008). Others researchers do the synthesis with the same concentration with a long time of aging (Balmaseda et al. 2003).
3.1 Materials and Synthesis Procedure

All the consumed chemicals were analytical grade without additional purification. The water used in the synthesis process was bi-distilled. The syntheses were performed following a very simple methodology, specifically, the precipitation method, consisting of mixing 0.1 M aqueous solutions of $Na_2[Fe(CN)_3NO].2H_2O$ and of nitrates and sulfates of the divalent transition metal, that is, $Cu(NO_3)_2$, and $Cu(SO_4)$. The formed fresh precipitates were then separated, washed successively with distilled water, and dried at 70°C and aging for three days (Figure 3.01). Finally, two samples were obtained, that is: No.1, which was synthesized with the $Cu(NO_3)_2$ solution and No.4 produced with the $Cu(SO_4)$ solution. The specific difference of the synthesis procedure applied here was, that, relatively concentrated solutions, were used in order to study, if this fact, yield products with different properties (Figure 3.01).

3.2. Characterization Methods.

The energy dispersive X-ray spectroscopy (EDAX) of the Cu-nitroprusside samples was carried out by SEM with a JEOL Model JSM-6390LV electron microscope (Figure 3.02), equipped with an energy dispersive X-ray analysis detector SUTW sapphire, to make the elemental chemical analysis. The acceleration of the electron beam was 15 kV. The sample grains were glued with silver colloid to the sample-holder.

The TGA (Figure 3.03) testing process was carried out with a TA, Q-500 equipment (Roque-Malherbe 2010). To make the TGA test, the samples were placed into
Figure 3.01. Diagram of synthesis process.
a ceramic sample holder, which is suspended from an analytical balance. Then, the sample holder was heated according to a predetermined thermal cycle, that is: the temperature was linearly scanned, from 25 to 300 °C, at a heating rate of 5 °C /min, in a flow of 100 ml/min of the purge gas that is pure N₂. The data collection, the temperature control, the programmed heating rate, and the gas flow control, were automatically controlled by the software of the TA, TQ500 TGA. The TGA data was collected as a Wt. % versus T (°C) profile, where: \( \text{Mass\%} = \left( \frac{M_t}{M_0} \right) \times 100 \), is the per-cent ratio of the sample mass during the thermal treatment, \( M_t \), and the initial mass of the sample \( M_0 \).

To get the diffuse reflectance infra-red Fourier transform spectra, was applied a Thermo Scientific Nicolet iS10 FTIR spectrometer with the Smart Collector for diffuse reflectance analysis and the Environmental Chamber for the smart collector. The spectra were collected with a resolution of 4 cm\(^{-1}\) and were made 100 scans per sample. Additionally, previous to get the sample spectrum, a background with KBr (FTIR pure, provided by Nicolet) located in the sample holder of the environmental chamber was made applying the same conditions used to get the samples spectra. The samples were heated, at 100 °C, under N₂ (Praxair, 99.99 %) flow at a rate of 50 cc/min during 2 hours and the spectra of the dehydrated materials were obtained with the sample inside the environmental chamber, at room temperature, under N₂ (Praxair, 99.99 %) flow at a rate of 50 cc/min at 30 °C. To get the IR spectra of carbon dioxide adsorbed inside the Cu-nitroprusside framework the background taken was the nitroprusside sample dehydrated at 100 °C and then cooled to 30 °C. Thereafter, was passed a flow of \( \text{CO}_2 \) (Praxair, 99.99 %) at a rate of 50 cc/min during 3 minutes. Then, the samples were purged under N₂ (Praxair, 99.99 %) flow at a rate of approximately 50 cc/min during one minute. Finally,
the spectra were obtained with the sample inside the environmental chamber to get the spectra of the carbon dioxide molecule adsorbed on the nitroprusside microporous framework at 30 °C under N₂ flow.

The X-ray diffraction experiment was carried out with a Bruker D8 Advance system in Bragg- Brentano vertical goniometer configuration (Figure 3.04). The angular measurements were made with reproducibility (Theta/2Theta) of: ± 0.0001 degree, applying steps of 0.01 degree from 5 to 60 degree to get 5500, intensity versus angle XRD profiles that could be accurately resolved by least square methods. The X-ray radiation source applied was a ceramic X-ray diffraction Cu anode tube type KFL C 2K of 2.2 kW, with long fine focus. A variable computer-controlled motor driven divergence slit with 2.5° Soller slit was included to allow to keep the irradiated area on the sample surface constant. Previous to the detector a Ni filter was placed to eliminate Cu-K_β radiation. The applied detector was a LynxEye™ one-dimensional detector for X-ray diffraction, based on Bruker AXS’ compound silicon strip technology. This detector increases measured intensities, without sacrificing resolution and peak shape in approximately 200 times compared with a point detector with identical data quality. This fact together with the small step, bring us excellent XRD profiles to be mathematically treated. To carry out high temperature measurements in vacuum the Anton Paar high temperature stage HTK-1200N was applied. This high-vacuum chamber is designed to be used in the range from room temperature up to 1200 °C. The sample is mounted on an alumina sample holder and just below the sample the temperature sensor is located. The HTK 1200N allows operation under high vacuum with the help of a vacuum system for Anton Paar stages.
Carbon dioxide adsorption at 273 K and pressure up to 1 atm was carried out in an upgraded Quantachrome Autosorb-1 automatic volumetric physisorption analyzer (Figure 3.05). The measurements at 298 K and pressures up to 7 atm. were obtained with a Micromeritics ASAP 2050 static volumetric adsorption system. The adsorption isotherms of CO$_2$ (Praxair, 99.99 %) at 273 K and 298 K were obtained in samples degassed at 573 K during three hours in high vacuum ($10^{-6}$ Torr). The backfilling process was carried out using helium (Praxair, 99.99 %) as a backfill gas in both cases.
Figure 3.02. Energy dispersive X-ray spectroscopy (EDAX) and SEM with a JEOL Model JSM-6390LV electron Microscope, Central Electron Microscope Unit RCMI Program, Medical Sciences Campus, University of Puerto Rico.
Figure 3.03. The Company TA Instrument model TA, Q-500 used for Thermo Gravimetrical Analysis (TGA).
Figure 3.04. Thermo Scientific Nicolet iS10 FTIR spectrometer with the Smart Collector used for diffuse reflectance analysis and the Environmental Chamber for the smart collector.
Figure 3.05. The Bruker D8 Advance model used for X-ray diffraction system in Bragg-Brentano vertical goniometer configuration.
Figure 3.06. The Quantachrome Autosorb-1 used for automatic volumetric physisorption analysis.
4.1 EDAX and TGA Results

Elemental chemical analysis of the nitroprusside samples were carried out with a SEM equipped with an energy dispersive X-ray analysis detector. The measurement yielded: $Fe/Cu \approx 1/1$ in accordance with the formula unit of this nitroprusside, i.e. $Cu[Fe(CN)_3NO] \cdot xH_2O$. The water amount $xH_2O$ was estimated using TGA measurements (Mullica et al. 1991; Mullica et al. 1992). The thermal gravimetric profile is shown in Figure 4.01, while the derivative of this profile is presented in Figure 4.02 and 4.03. It is evident that at relatively low temperatures, that is, below 100 °C the water is released in two steps. This fact was confirmed in Figure 4.02 and 4.03 where this shape was resolved in two peaks. These peaks can be related, sequentially, to the liberation of hydrogen-bonded water and coordinated water respectively. The total weight lost during to water elimination corresponds to approximately 11 wt. %, or about 2 $H_2O$ molecules per formula unit. Consequently, the formula unit of the tested Cu-NP should be (Mullica et al.1992)

Meanwhile the obtained nitroprusside appears to be stable from 100 to 200 °C as evidenced by the absence of any appreciable changes in that region of the TGA profile. Finally, the weight lost observed after at 200 °C could be related to the decomposition of the nitroprusside by the liberation of the structural NO and CN groups contained in the framework (Mullica et al. 1991). It should be mentioned that the previously reported results are typical of the $Pnma$ Cu-NP polymorph, which is the stable form of this
Figure 4.01. TGA profiles of samples: No. 1 and No. 4.
Figure 4.02. Derivative of the TGA profiles of samples: No.1.
Figure 4.03. Derivative of the TGA profiles of samples: No. 4.
nitroprusside (Mullica et al. 1992) obtained by the slow diffusion tube methodology (Mullica et al. 1989; Mullica et al. 1991). However, the polymorph tested here was obtained by the precipitation method. It is our assessment that was produced the stable Pnma, as a consequence of the addition of powdered solid Na$_2$[Fe(CN)$_5$NO]•2H$_2$O to the corresponding copper(II) salt.

4.2 DRIFT Results

DRIFT spectra of the Cu-NP sample (hydrated and dehydrated) in the range between: 1400-2400 cm$^{-1}$ and 3200-3800 cm$^{-1}$, are shown in Figure 4.04. IR data in the range between: 1400-2400 cm$^{-1}$, in inorganic compounds, contain information about the framework vibrations and those in the range 3200-3800 cm$^{-1}$ include information related, essentially, with the hydration water (Nakamoto, 1997).

Figure 4.04 shows the vibrations observed in the range between: 1400-2400 cm$^{-1}$, which are related with the $\nu$(CN) stretching vibration at around 1610 cm$^{-1}$, a 1950 cm$^{-1}$ band corresponding to $\nu$(NO) stretching vibration and a 2200 cm$^{-1}$ band due to $\delta$(Fe$-$C$\equiv$N) vibration (Holzbecher et al. 1971; Aymonino, 1988; Mullica et al. 1991; Mullica et al. 1992; Benavente et al. 1997). All these vibrations are maintained after dehydration (Figure 4.04) with only minor shifts, excluding the $\nu$(CN) stretching vibration corresponding to the unlinked cyanide which disappears. It is necessary to state that this band possibly vanish because all the CN are linked in the dehydrated state Balmaseda et al. 2003). Vibrations related to the water molecules contained in the nitroprusside are usually present in the 3200-3800 cm$^{-1}$ range. In Figure 4.04 are these contribution are characterized by one broad the 3250-3400 cm$^{-1}$ range and a narrow one at around 3650 cm$^{-1}$. It is a very well known fact that the hydrogen bonded water, shows
a broad stretching, $\nu(OH)$, absorption bands approximately in the range between: 3250-3400 cm\(^{-1}\) (Nakamoto 1997). On the other hand, the coordinated water exhibits a comparatively narrow band around 3650 cm\(^{-1}\) (Holzbecher et al. 1971). Both bands disappear after dehydration.

In general DRIFTS results correlate well with the TGA data. That is, IR absorption bands in the 3200-3800 cm\(^{-1}\) range are related to hydrogen-bonded water and coordinated water respectively. Then, the IR profile in this range is also characteristic of the stable \textit{Pnma} polymorph of Cu-NP (Mullica et al. 1992). For hydrated Cu-NP fresh precipitates as was previously stated, there are reports of at least two polymorphs (Balmaseda et al. 2003). The polymorphic nature of nitroprussides is associated to the way that \textit{CN} and \textit{H}_2\textit{O} ligands are coordinated to the cation \textit{M} (Mullica et al. 1991, Mullica et al. 1992; Reguera et al. 1996). In the case of the stable \textit{Pnma} polymorph of Cu-NP, five cyanide groups and one water molecule are bonded to the Cu cation and the other water molecule is hydrogen-bonded to the coordinated water molecule (Mullica et al 1992). The polymorph normally obtained from fresh precipitates, crystallizes in the \textit{Amm2} space group, where the Cu atoms are coordinated by four \textit{CN} and two \textit{H}_2\textit{O} molecules (Balmaseda et al. 2003). This is not the case here and therefore we must suspect that our synthesized Cu-NP crystallizes in the orthorhombic \textit{Pnma} space group. However, in order to substantiate this hypothesis we must consider a thorough XRD analysis.

4.3 XRD Results

Figure 4.06 shows the XRD profile gathered for the hydrated Cu-NP sample in the range between: 5-60° in 2θ. In order to resolve the powder XRD profile into separate
Figure 4.04 DRIFTS spectra of sample No.1 hydrated and dehydrated.
Figure 4.05 XRD profiles of the hydrated Cu-NP sample.
Bragg components and in the absence of any concrete structural model was applied the pattern decomposition method (Torraya 1989). More concretely was applied the Pawley whole-powder pattern decomposition (WPPD) method (Pawley 1984). This method can refine the unit cell parameters and decompose the whole powder pattern into individual reflections (Torraya 1989). The concrete computer program used to carry out the calculations was the Bruker DIFFRACplus TOPAS™ software.

Figure 4.06 shows the resulting fitting of the hydrated Cu-NP powder pattern for the orthorhombic Amm2, I4mm and Pnma space groups. Table 4.01 collects the cell parameters, the cell volume and the R factor. The obtained data (Table 4.01) show a good fitting for both the Amm2 polymorph (Reguera et al. 2008) and Pnma stable polymorph (Mullica et al. 1991). However, a somewhat better fitting was obtained for the orthorhombic Pnma space group. This result together with TGA and DRIFTS data presented above allow us to reasonably propose that the tested Cu-NP crystallizes, in the hydrated state, in the orthorhombic Pnma space group with: \(a = 14.41534\, \text{Å}, \ b = 6.99627\, \text{Å}, \ c = 10.38027\, \text{Å}\) cell parameters.

As was previously stated, it has been reported that dehydrated Amm2 Cu-nitroprusside polymorph experiences a phase transformation to an anhydrous, tetragonal space group I4mm phase upon heating, (Reguera et al. 2008). Figure 4.07 shows the fittings of the XRD profile of the dehydrated Cu-NP sample at 100 \(^\circ\)C for 2 h. in vacuum and collected at room temperature also in vacuum inside the high temperature cell for the orthorhombic I4mm and Pnma space groups. Table 4.01 also shows the corresponding cell parameters, cell volume and R factor. The obtained results demonstrate a good fitting for the I4mm space group and an excellent fitting for the Pnma space group. That is, a
Figure 4.06 Pawley refinements of the XRD profile of sample No.1 hydrated.
Table 4.01. Cell Parameters and Cell Volume Calculated with the Resolved Powder Patterns Applying the Pawley Whole-Powder Pattern Decomposition Method.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrated</td>
<td>7.207195</td>
<td>6.99623</td>
<td>10.38031</td>
<td>1046.89</td>
<td>Amm2</td>
<td>0.242</td>
</tr>
<tr>
<td>Hydrated</td>
<td>14.41534</td>
<td>6.99627</td>
<td>10.38027</td>
<td>1047.122</td>
<td>Pnma</td>
<td>0.193</td>
</tr>
<tr>
<td>Dehydrated</td>
<td>7.11529</td>
<td>7.11529</td>
<td>10.93799</td>
<td>533.76</td>
<td>I4mm</td>
<td>0.231</td>
</tr>
<tr>
<td>Dehydrated</td>
<td>14.83321</td>
<td>12.2363</td>
<td>9.89889</td>
<td>1796.15</td>
<td>Pnma</td>
<td>0.139</td>
</tr>
</tbody>
</table>

better fitting was obtained for the orthorhombic Pnma space group. Thereafter, as a consequence of the better fitting of the refined XRD data; and the fact that the Pnma phase is the stable phase of Cu-NP, we propose that the polymorph studied here crystallized in the anhydrous state in an orthorhombic space group Pnma phase, with the following cell parameters: \( a = 14.83321 \, \text{Å} \), \( b = 12.2363 \, \text{Å} \), \( c = 9.89889 \, \text{Å} \). However, this assignment is some sense in contradiction with the disappearance of the ν-CN band corresponding to the unlinked CN; since, this fact is characteristic of the transition from the orthorhombic Amm2 phase to the I4mm tetragonal phase during dehydration (Balmaseda 2007). In this regard, we can give an explanation to this fact by the enlargement of the parameter b of the orthorhombic dehydrated Pnma (Table 4.01) which indicates a phase transformation during dehydration to a cell similar to the tetragonal I4mm.
4.4 Carbon dioxide adsorption study

The framework of the Cu-NP contains distorted octahedral metal centers that are linked by cyanide bridging in a staggered way creating micropores that pervades the crystal lattice (Mullica et al. 1991). This framework looks as a stack of rippled sheets connected by cyanide bonds and consequently we are dealing with a microporous crystalline adsorbent showing a 3-dimensional channel system (Balmaseda et al. 2003) with pore diameters in the range of the carbon dioxide molecular diameter (carbon dioxide is a molecule with an ellipsoidal form 5.4 Å long and a diameter of 3.4 Å) (Omi et al. 2005).

We should expect adsorption of carbon dioxide molecules in the synthesized Cu-NP in the anhydrous state. To prove that the tested Cu-NP adsorbs carbon dioxide, Figure 4.08 shows logarithmic in P and linear in the amount adsorbed adsorption isotherms of carbon dioxide at 273 K and 298 K on the Cu-NP sample. This material was pre-activated at 100 °C, a temperature high enough to release all the water present in the micropores as indicated by the TGA data. Meanwhile, to demonstrate that the equilibrium adsorption process is typical of a microporous adsorbent, Figure 4.09 shows Dubinin-Radushkevitch (D-R) plots. Since, an immense amount of experimental data indicates that the adsorption process in the micropore range is very well described by the Dubinin-Radushkevitch (D-R) adsorption isotherm equation (Roque-Malherbe 2007; Roque-Malherbe 2009). The Dubinin-Radushkevitch (D-R) adsorption isotherm equation can be represented in a log-log scale, as follows: \( \ln(n_a) = \ln(N_a) - \left(\frac{RT}{E}\right)^2 \ln\left(\frac{P_0}{P}\right)^2 \), describing the relation between the amount adsorbed, \( n_a \), and the inverse of the relative pressure, i.e., \( \frac{P_0}{P} \); where, \( E \) is a parameter named the characteristic energy of adsorption and, \( N_a \), is the maximum amount.
Figure 4.07 Pawley refinement of the XRD profile of the dehydrated Cu-NP sample.
Figure 4.08 Carbon dioxide adsorption isotherms of samples: No.1 and No.4 at 273 K and 298 K.
Figure 4.09 Semi-logarithmic plot (a). Dubinin-Radushkevitch (D-R) plot.
adsorbed in the micropore volume.

It is necessary to state now that the equilibrium adsorption process of vapors in complex porous systems takes place approximately as follows (Roque-Malherbe 2007; Roque-Malherbe 2009) first, micropore filling, where the adsorption behavior is dominated nearly completely by the interactions of the adsorbate, and the pore wall; after that, at higher pressures, external surface coverage, consisting of monolayer, and multilayer adsorption on the walls of mesopores, and open macropores, and finally capillary condensation in the mesopores. We are working in the micropore filling pressure range, $0.0008 < P/P_0 < 0.02$, then we are far from surface coverage, that normally takes place in the $0.05 < P/P_0 < 0.4$ range, and farther from capillary condensation that is the cause of adsorption hysteresis. Consequently, our isotherm is completely reversible, thereafter, we don’t need to get the desorption isotherm.

The isotherms (Figure 4.09) were also employed for the calculation of the isosteric heat of adsorption, $q_{iso}$, using the Clausius-Clapeyron equation:

$$q_{iso} = RT^2 \left[ \frac{d \ln P}{dT} \right]_{T_i} \approx RT^2 \left[ \frac{d \ln P}{dT} \right]_{n_a} \approx RT_2 \left( \frac{T_2 - T_1}{T_2 - T_1} \right) \left( \frac{P_2 - P_1}{n_a} \right)$$

Where, $\Gamma = n_{ad}/n_{Ab}$, is the ratio number of moles of the adsorbate, $n_{ad}$, and the adsorbent $n_{Ad}$ in the system adsorbate-adsorbent for a microporous material (Roque-Malherbe, 1987; Roque-Malherbe, 2000; Roque-Malherbe, 2007), $n_a$, is the amount adsorbed in mmol/g, $T_i$ is the temperature and $P_i$ the equilibrium adsorbate pressure at constant loading. Results of the calculations made with equation “1” are reported in Figure 4.10.
From these results it is possible to conclude that, \( q_{iso} \), is nearly constant with respect to the variation of the amount adsorbed, \( n_a \). The mean and standard deviation of the values of: \( q_{iso} \), reported in Figure 4.11 are \( 30 \pm 3 \) kJ/mol. This fact requires an explanation. During adsorption in micropores, as was previously stated, the adsorption behavior is initially, at very low relative pressure, dominated almost entirely by the interactions of the adsorbate and the pore wall, afterward, at higher pressures, lateral interactions between adsorbate molecules are also present (Roque-Malherbe 2007). The process of adsorption is normally energetically heterogeneous as long as the adsorption field inside the micropore is heterogeneous and depends upon the position of the adsorbate inside the adsorption space. That is, the isosteric heat of adsorption should be a decreasing function of the micropore volume recovery, \( \theta = n_a / N_m \) (Roque-Malherbe, 2007). However, in some cases the energetically heterogeneous character of the process is masked by the presence of lateral interactions, which provoke the homogeneization of the adsorption field. That is the adsorption energy corresponding to wall and lateral interactions are mutually compensated to produce, an apparently, homogeneous adsorption energy.

The number reported for the isosteric heat of adsorption corresponds to a relatively high amount of adsorption energy. It compares well with values reported for silicalite, a 10MR molecular sieve showing the MFI framework type. To be precise the experimental isosteric heat of adsorption measured for the adsorption of carbon dioxide on silicalite at 296-306 K, in the range: \( 0.1 < n_a < 1.5 \) mmol/g, yields an average a value for, \( q_{iso} \), of \( 28 \) kJ/mol (Dunne et al. 1996). In addition, for a set of different amorphous silica materials, the isosteric heat of adsorption measured for the adsorption
Figure 4.10 Isosteric heat of adsorption versus amount adsorbed profile corresponding to the adsorption of carbon dioxide on samples No.1 and No.4.
of carbon dioxide at 297 K in the micropore region produces values for \( q_{iso} \), around 28 kJ/mol (Roque-Malherbe et al. 2010).

Similarly, the isosteric heat of adsorption for the adsorption of carbon dioxide at 297 K on Na-SAPO-34 molecular sieve yielded similar values for \( q_{iso} \) (Arevalo-Hidalgo et al. 2010). It is a very well known fact that the interaction between an adsorbent and a molecule like carbon dioxide, that show a noticeable quadrupolar moment, \( Q_{CO_2} = -4.3 \times 10^{-42} \text{ C.m}^2 \) (Buckingham 1963), comprises a combination of dispersive and electrostatic attractive interactions (Roque-Malherbe et al. 2010). It is widely accepted that carbon dioxide interact with microporous frameworks through dispersion and quadrupole interactions (Dunne et al. 1996; Bai et al. 2003; Arevalo-Hidalgo et al. 2010; Roque-Malherbe et al. 2010). In the case of interest here this is the case as will be below further discussed.

Statistical Physics (Roque-Malharbe 2007) and the Dubinin theory of volume filling (Bering et al. 1972) are usually applied to to mathematically model the equilibrium adsorption process in microporous crystalline materials; such as: zeolites, metal organic frameworks (MOFs) and other porous coordination polymers, as nitroprussides and then deduce a isotherm equations \( \theta = n_a / N_m \) (Roque-Malherbe 1984; De la Cruz et al. 1989; Roque-Malherbe 2007; Roque-Malherbe 2009; Roque-Malherbe 2010). To develop the model of interest here (Roque-Malherbe 1984; De la Cruz et al. 1989; Roque-Malherbe 2009), the adsorption space was considered energetically homogeneous and the adsorption process was considered as a 3-D volumetric occupation of the adsorption space (Bering et al. 1972) and not as a 2-D surface covering process such as the one described by traditional Langmuir processes. The isotherm equation for immobile and mobile adsorption with
lateral interactions deduced by means of the Grand Canonical Ensemble (Roque-Malherbe 2007) following the conditions previously imposed, has the following form (Roque-Malherbe 1984; Roque-Malherbe 2009):

$$\theta = \frac{n_a}{N_a} = \frac{KP}{1 + KP}$$

(2)

$$K_I = K_0 \exp \left( \frac{[E_0^g - E_0^a]}{RT} \right) \exp \left( \frac{k\theta}{RT} \right)$$

(3)

Where, $K_0$ is a constant for $T = \text{const}$, different for the mobile and immobile cases, $E_0^g$ is the reference energy state for the gas molecule, $E_0^a$, is the reference energy state for the adsorbed molecule in the homogeneous adsorption field inside the cavity or channel, $k$, is a constant characterizing the lateral interactions, and, $\theta = n_a/N_a$, where, $n_a$, is the amount adsorbed and, $N_a$, is the maximum amount adsorbed in the volume of the micropore. Equation “2” is a Fowler-Guggenheim Type (FGT) adsorption isotherm equation; but, describing a volume filling rather than a surface coverage. For $k = 0$ equation “2” reduces to a Langmuir Type (LT) adsorption isotherm equation, but still well describing a volume filling instead of a surface coverage. Then, for $k \approx 0$, we can plot the LT equation:

$$n_a = \frac{N_a KP}{1 + KP}$$

(4)

Where: $K$ is a constant for $T = \text{const}$, that could be estimated with the help of a least square non-linear fitting process. The fitting process was carried out with the peak separation and analysis software PeakFit (Seasolve Software Inc., Framingham, Massachusetts) based on the least square procedure (Draper and Smith 1989), and the results are gathered in Table 4.02. This method allowed for reliable measurement of the
micropore volume \( W_{MP} = N_a V_L \); in which, \( V_L = 41.3 \, cm^3/g \) is the molar volume \( CO_2 \) at 273 K) for the studied polymorph.

The FGT isotherm equation type can be also written as follows:

\[
\ln \left( \frac{\theta}{1-\theta} \right) = \ln K + \frac{k\theta}{RT} \tag{5}
\]

A fit of this isotherm is shown on Figure 4.11 and the parameters are gathered in Table 4.03. This plot experimentally establishes that \( k \approx 0 \). Therefore, it is our assessment that the analysis of the adsorption data with the help of the LT type adsorption isotherm for volume filling is very accurate.

Now, with the values calculated for: \( K \), at two different temperatures (Tables 4.02 and 4.03) and the following expression (Nakamoto 1997):

\[
K = K_0 e^{\frac{q_{iso}(0)}{RT}} \tag{6}
\]

We can estimate the isosteric heat of adsorption for zero loading \( q_{iso}(0) \). The obtained value, \( q_{iso}(0) = 36 \pm 3 \, kJ/mol \), is close to the average value measured with the help of the isosteric method. It is necessary state now that the values of \( K \) calculated by plotting equations. “6” (Table 4.02) and “7” (Table 4.03) are equivalent within the experimental error. This fact indicates the consistency within the obtained data.

The micropore volume data (Table 4.02) evidence an increase in the micropore volume with increasing temperature from \( W_{MP}^{CO_2} = 0.153 \, cm^3/g \) at 273 K to \( W_{MP}^{CO_2} = 0.181 \, cm^3/g \) at 298 K. This fact explains the large amount of adsorption of carbon dioxide at 298 K and 6.7 atm. measured (\( n_a = 0.122 \, g/g \), that is: 12.2 Mass %). Since, the framework of the orthorrombic \( Pnma \) polymorph resembles a stack of rippled sheets
interconnected by cyanide bonds (Mullica et al. 2003), it is possible to assume that the distance between sheets increases with temperature causing the observed increase in the micropore volume with rising temperature.

The pore size of the orthorhombic framework of the tested nitroprusside is close to the kinetic diameter of the carbon dioxide molecule. This fact causes an effect named confinement (Derouane et al. 1992; Yang et al. 2001; Roque-Malherbe 2008) or surface interaction potential overlapping that favors relatively strong dispersion and repulsion interactions between the framework of the adsorbent and the adsorbed molecule. This force, combined with the interaction between the quadrupole moment of the carbon

Table 4.02. Microporous Volume Calculated by Fitting the Langmuir-Type (LT) Isotherm for Volume Filling in a Microporous Adsorbent in Linear Form to the Obtained Adsorption Data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ [K]</th>
<th>$R^2$</th>
<th>$W_{\text{MP}}^{\text{CO}_2}$ [cm$^3$/g]</th>
<th>$K$ [gTorr/mmol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-NP</td>
<td>273</td>
<td>0.9999</td>
<td>0.154</td>
<td>0.00119590</td>
</tr>
<tr>
<td>Cu-NP</td>
<td>298</td>
<td>0.9996</td>
<td>0.185</td>
<td>0.00030256</td>
</tr>
</tbody>
</table>

dioxide molecule and the nitroprusside framework electric field gradient, which is as well enhanced by the confinement, are the major contributions to the adsorption energy. Then, the confinement effect justifies the relatively high value measured for the adsorption energy in a physical adsorption process that binds the carbon dioxide molecule inside the
Figure 4.11. Plots for the corroboration of the Langmuir-type adsorption isotherms for volume filling in the adsorption of carbon dioxide on samples No.1 and No.4.
Table 4.03. Parameters Calculated by Fitting the Fowler-Guggenheim Type (FGT) Isotherm in Linear Form to the Obtained Adsorption Data

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ [K]</th>
<th>$k$</th>
<th>$\ln K$</th>
<th>$q_{\text{iso}}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-NP</td>
<td>273</td>
<td>0.0049</td>
<td>-6.721</td>
<td>36 ± 3</td>
</tr>
<tr>
<td>Cu-NP</td>
<td>298</td>
<td>0.0056</td>
<td>-8.058</td>
<td>36 ± 3</td>
</tr>
</tbody>
</table>

nitroprusside micropores, by the influence of the dispersive forces and the attraction of the quadrupole interaction (Roque-Malherbe 2010). Calculations made with the help of the Horvath-Kawazoe method and applying the Saito-Foley equations (Roque-Malherbe 2007; Roque-Malherbe 2009) for cylindrical pores in silica have shown that these forces; specifically, London forces and quadrupole interactions, contributes about 90% of the whole interaction (Roque-Malherbe 2010). To get information about further contributions to the interaction between the nitroprusside framework and the carbon dioxide molecule further DRIFTS studies were made. In this regard, a DRIFTS spectrum of carbon dioxide adsorbed on the tested polymorph at 300 K was obtained.

The resolved carbon dioxide IR spectrum (deconvoluted by fitting three Lorentz functions with the help of a least square procedure (Draper and Smith 1989) and the corresponding data are reported in Figure 10 and Table 4.04 respectively. This spectrum shows that the carbon dioxide molecule has some direct interactions with the nitroprusside framework; as evidenced by the presence of three peaks in the observed experimental absorption band. The free carbon dioxide molecule belongs to the $D_{xh}$ point group symmetry, showing four fundamental vibration modes, that is: the symmetric stretching,
$\nu_1$ (1338 cm$^{-1}$) the doubly degenerate bending vibration, $\nu_{2a}$ and $\nu_{2b}$ (667 cm$^{-1}$), and the asymmetric stretching vibration $\nu_3$ (2349 cm$^{-1}$) (Lavalley 1996; Xamena and Zecchini 2002).

Table. 4.04. Resolved Peaks Positions of the DRIFTS Spectra of Carbon Dioxide Adsorbed on the Tested Cu-nitroprusside.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\chi^1_c$ [cm$^{-1}$]</th>
<th>$A_1$ [%]</th>
<th>$\chi^2_c$ [cm$^{-1}$]</th>
<th>$A_2$ [%]</th>
<th>$\chi^3_c$ [cm$^{-1}$]</th>
<th>$A_3$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-NP</td>
<td>2321</td>
<td>0.26</td>
<td>2338</td>
<td>0.28</td>
<td>2362</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The $\nu_2$ and $\nu_3$ modes are infrared active, whereas $\nu_1$ is only Raman active, in the free molecule (Xamena and Zecchini 2002). However, when a carbon dioxide molecule interacts with a surface it is not longer a free molecule, and its symmetry is lowered. As a result the $\nu_1$ mode becomes infrared active, and a small band is observed (Goodman et al. 2005), whereas the other modes undergo moderate changes in wave number (Xamena and Zecchini 2002).

The asymmetric stretching vibration, $\nu_3$, of the adsorbed carbon dioxide molecule was observed at 2338 cm$^{-1}$ (Figure 4.12 and Table 4.04). This band corresponds to carbon dioxide physically adsorbed (Goodman 2009) onto the nitroprusside framework surface. The smaller band at about 2321 cm$^{-1}$ is normally assigned to a combination band (Goodman et al. 2005), while, the absorption band observed at around 2338 cm$^{-1}$, is the result of the attachment of the confinement of the carbon dioxide molecule and thereafter
Figure 4.12. DRIFT spectrum of carbon dioxide adsorbed on sample No.4.
the frequency shift and explains the band observed at 2338 cm$^{-1}$ and the combination band. This state of the carbon dioxide molecule is equivalent to one of zeolitic water.

In addition there is observed another band observed at 2362 cm$^{-1}$, that should correspond to adsorption of carbon dioxide on an electron accepting Lewis acid site (Lavalley 1996). An example of this type of adducts was recently reported (Llewellyn et al. 2008), in a study of the adsorption of carbon dioxide in the molecular organic framework MIL-100, where a $\nu_3$ band was found at 2351 cm$^{-1}$ and assigned to a the following species: $Cr^{3+} \cdots O = C = O$. In our case the band at 2362 cm$^{-1}$ should characterize the interaction of the carbon dioxide molecule with the Cu$^{2+}$ located in the framework of the Cu-nitroprusside forming following adduct: $Cu^{2+} \cdots O = C = O$. This state of the carbon dioxide molecule is equivalent to that of coordinated water.

The DRIFTS data indicates the existence of two adsorption states for the carbon dioxide molecule, one of them a state where the molecule interacts with the Cu$^{2+}$ located in the framework of the Cu-NP which acts as an electron accepting Lewis acid site (Knozinger and Huber 1998). The Lewis acid-base reaction results in more or less stable adducts, whose steadiness can be effectively explained by the model of the hard and soft acids and bases scheme (Pearson 1997). That is, an acid-base adduct is produced by the charge transfer from the HOMO of the base to the LUMO of the acid (Mebs et al. 2010).

In our case the importance of this finding is related to the fact that the Cu$^{2+}$ is located in the framework of the Cu-NP in a site accessible to adsorbed molecules. Therefore, it is possible to assume that an acid-base interaction between Cu$^{2+}$ and small basic molecules producing a charge transfer which could be detected for example by a change in the magnetic susceptibility (Zentkova et al. 2004) of the nitroprusside. Besides,
this Cu$^{2+}$ site is intrinsically a catalytic site (Corma and Garcia, 2005)

The adsorption of carbon dioxide has been recently studied on a dehydrated Prussian blue analogue $\text{Co}^{II}_{3}\text{Co}^{III}(CN)_6\text{Co}^{III}$ (Windisch et al. 2009; Windisch et al. 2010) (Windisch et al. 2009, 2010) with the help of DRIFTS. It was found an infrared band at 2340 cm$^{-1}$ that was assigned to adsorbed carbon dioxide and reported the following enthalpy of adsorption $\Delta H_{ad} = -23 \pm 3$ kJ/mol (Windisch et al. 2009). These results are similar to the data reported in this thesis.
Chapter Four

Summary

A thorough structural characterization of the synthesized Cu-NP was necessary in order to unambiguously identify the studied polymorph among possible variants. TGA and DRIFTS techniques were employed to study the dehydration process in the as-synthesized Cu-NP polymorph. It was shown that such dehydration process is characteristic of the stable orthorhombic \textit{Pnma} Cu-NP. Fitting the XRD powder profile data via the Pawley method, indicates that the hydrated polymorph, crystallizes in the orthorhombic \textit{Pnma} space high temperature XRD group ($a = 14.41534$ Å, $b = 6.99627$ Å, $c = 10.38027$ Å). Meanwhile, the best fitting for the \textit{in situ} XRD profile of the anhydrous phase indicate that it also crystallizes in the orthorhombic space group \textit{Pnma} ($a = 14.83321$ Å, $b = 12.23268$ Å, $c = 9.89889$ Å).

A carbon dioxide adsorption study was used to calculate the corresponding isosteric heat of adsorption, indicating an average interaction of 30 $kJ/mol$ and nearly independent of loading. This indicates that the adsorption space of the studied material is apparently energetically homogeneous and the adsorption field is fairly strong within the physisorption range. Furthermore, it appears that the high adsorption interaction energy is the result of the confinement of the carbon dioxide molecule in the nitroprusside framework pores.

Applying Statistical Physics methods, particularly the Grand Canonical Ensemble and the Dubinin theory for pore volume filling, allowed us to develop a set of isotherm equations suitable for the quantification of carbon dioxide adsorption onto the tested Cu-NP. The thorough calculations demonstrated that the studied polymorph showcase an
increase of the micropore volume with an increase in temperature which correlates with the high adsorption amount observed at 298 K and 6.7 atm.

A DRIFTS study revealed a band at ca. 2338 cm\(^{-1}\) probably related to carbon dioxide physically adsorbed carbon dioxide onto the surface of the nitroprusside framework micropores. The state of the carbon dioxide molecule is similar to zeolitic water. In addition a peak observed at 2362 was related to an interaction of carbon dioxide with Cu\(^{2+}\) which probably act as an electron accepting Lewis acid site according to the following adduct: \(\text{Cu}^{2+} \cdot \cdot \cdot O = C \cdot O\). This state of the carbon dioxide molecule should correlate to that of coordinated water.

In general this study indicates that the studied polymorph should be considered a suitable adsorbent material for gases due to the available micropore volume and adsorption interaction within the adsorption space. It is hypothesized that upon dehydration small guest molecules could interact with Cu\(^{2+}\) and changes its magnetic properties resulting this in a potential platform for the development of gas sensors.


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