Synthesis, Structure, Adsorption Space and Magnetic Properties of Ni-Oxalate Metal Organic Frameworks

By

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Thesis

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Synthesis, Structure, Adsorption Space and Magnetic Properties of Ni-Oxalate Metal Organic Frameworks

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I want to dedicate this research to God who gave me the ability, time and strength to achieve this goal. To my parents, Wilfredo Rivera and Dimarie Maldonado, and my sisters, Charlotte Rivera, Chatterlyss Rivera, Chamylette Rivera and Challiette Rivera. To my grandmother, Cristina Rivera and my aunt, Milagros Maldonado. I am honored to belong to this family and thanks for your support, understanding and trusting in me. To my husband, Eric Maldonado, for motivating me to continue and never give up, thanks for your love and comprehension.

To all who collaborate with this research and are filled with joy with the culmination of this work.
Acknowledgements

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A technological alternative to adsorb carbon dioxide (CO₂) and minimize the greenhouse effect is the use of Metal Organic Frameworks (MOF's) (Ji et al. 2010). MOF's represent a new class of porous crystalline materials for which it is possible to design organic linkers and inorganic joints (Tranchemontagne et al. 2008). During this research there were synthesized 35 metal organic compounds using two modifications of the solvothermal process: The first procedure is at room temperature (27 °C) or heated at 70 °C, and the second was carried out under reflux conditions. The characterizations of the samples were accomplished with infrared Fourier Transform Spectrometry (DRIFTS), Raman Spectrometry (RS), Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD), adsorption and with a Vibrating Sample Magnometer (VSM). As the study consist in adsorption, the priority was given to the one that shows the higher weight loss obtained from the TGA and shows crystalline properties in XRD. From all the samples synthesized, the Ni-Ox-MOF displayed the highest weight lost and crystalline properties. The TGA data for Ni-OX-MOF display a 10% of weight loss and indicated that it has a pore volume. The adsorption analysis showed that the pore volume is $0.10 \pm 0.01 \text{cm}^3/\text{g}$. The XRD profile indicated that it is a layered compound. The DRIFTS, Raman and XRD data revealed that
each layer is formed by nickel cations linked by bisbidentate and bridging-bis-bidentate oxalate ligands and the DMF molecules are perpendicularly linked to the nickel cations to produce stacking. The Pawley fitting of the XRD profiles pointed out that the hydrated sample crystallizes in the P2₁/m space group. The cell parameters calculated are consistent with the proposed structure. The VSM study demonstrates that it is a paramagnetic material. And then was obtained a new Ni-Oxalic Metal Organic Framework compound (Ni-Ox-MOF). It was confirmed by using different databases that the Ni-Ox-MOF is unique and none studied in other research. The significance of this MOF is related to its porosity, that is, during degassing it releases water turning into a porous stable structure, showing notable magnetic properties. It’s very difficult achieve both characteristics in the same material, in the literature was found a small amount of MOF like it. In this case its porous properties, means that the electronic structure of nickel cations can be externally manipulated with adsorbed molecules. The material could be sensitive to small molecules; thereafter Ni-Ox-MOF possibly will be used as magnetic senor to trap \( \text{CO}_2 \) from the environment.
Resumen

CHRISTYMARIE RIVERA MALDONADO (BS, Chemistry)

Estudio de la Síntesis, Estructura, Adsorción y Propiedades Magnéticas del Enrejado Organometálico de Oxalato de Níquel. (mayo/2012)

Resumen de la Tesis de maestría en la Universidad del Turabo.

Tesis supervisada por el Dr. Rolando Roque-Malherbe

No. de páginas en el texto 63

Una alternativa novedosa para absorber dióxido de carbono (CO$_2$) y reducir el efecto invernadero en el ambiente, es el uso de enrejados organometálicos, conocido por sus siglas en inglés como MOF (Ji et al. 2010). Los MOF son materiales poroso cristalinos, en los cuales es posible enlazar materiales orgánicos e inorgánicos (Tranchemontagne et al. 2008). Durante esta investigación se sintetizaron 35 compuestos organometálicos realizando dos modificaciones a la síntesis solvotermal (Duan et al. 2006; Tranchemontagne et al. 2008) que se encontró en la literatura. El primer procedimiento se lleva a cabo a temperatura ambiente (27 ºC), si no reacciona, se calienta a 70 ºC en un horno por 24 horas. La segunda se realizo bajo condiciones de reflujo. La caracterización de las muestras se hizo utilizando la espectrometría infrarroja (DRIFT), espectrometría Raman (RS), análisis termogravimétrico (TGA), difracción de rayos X (DRX), adsorción con un Autosorb-1 y con un magnetómetro de muestra vibrante (VSM). Como el estudio consiste en adsorción, se buscó la muestra con más pérdida de peso reflejada en el TGA y que mostrara propiedades cristalinas en el DRX. De todas las muestras sintetizadas, el Oxalato de Níquel mostró la mayor pérdida de peso y las propiedades cristalinas necesarias para realizar la investigación. A este material se le
llamo Ni-OX-MOF. Los datos del TGA para él Ni-OX-MOF revelaron que es un material poroso y que tuvo una pérdida de peso de 10%. El análisis de adsorción mostró que el volumen de poro es de $0.10 \pm 0.01 \text{ cm}^3/\text{g}$. El difractograma del DRX indicó que es un compuesto en capas. Se observó en los datos de Raman e infrarrojo, que cada capa está formada por cationes níquel unidos por enlaces bisbidentados y puentes-bis-bidentados de oxalato; y que las moléculas de DMF están perpendicularly enlazadas a los cationes de níquel para unir las capas de los enlaces bisbidentados para formar una molécula bidimensional. El refinamiento con el método de Pawley señaló que la muestra hidratada cristaliza en el grupo espacial monoclinico $P2_1/m$. Los parámetros de la celda calculados son consistentes con la estructura propuesta. El estudio de VSM muestra que Ni-OX-MOF es un material paramagnético. Todos los resultados obtenidos demostraron que en esta investigación, se obtuvo un material nuevo. La importancia de este MOF, está relacionada con su porosidad y sus notables propiedades magnéticas. Es muy difícil sintetizar un MOF y lograr tener propiedades magnéticas y adsorbentes en un mismo material. Fueron muy pocos los materiales que se encontraron en la literatura con propiedades similares al Ni-Ox-MOF. Este material podría ser sensible a moléculas pequeñas, ya que su estructura puede ser manipulada externamente con moléculas adsorbidas. Lo cual indica que podría ser utilizado como un sensor magnético para atrapar y almacenar el $\text{CO}_2$ contaminante del medio ambiente.
Chapter One

Introduction

This research is intended to develop a feasible method to trap carbon dioxide (CO₂). The use of a cost effective carbon dioxide adsorption and storage methodologies, using non expensive chemical materials through the synthesis of Metal Organic Framework (MOF) may be attractive to industries and pharmaceuticals with high CO₂ emissions. The synthesis of MOF with adsorption characteristic will serve as a mechanism to decrease the degree of CO₂ contamination on the atmosphere and prevent human suffering. Carbon dioxide is the most powerful cerebral vasodilator known; inhaling large concentrations causes rapid circulatory insufficiency leading to coma and death. Low concentrations of carbon dioxide have been shown to cause increase in respiration and headache (Hoskin et al. 1990).

Is important get serious about reducing greenhouse gas emissions from energy production, deforestation, transport and industrial processes. The Earth is warming. Disasters occur as a result of people’s exposure to particular hazards and their degree of vulnerability. People in extreme poverty are in no position to withstand the additional burden of climate change. The literature shows a direct relation between the greenhouse effect and the higher emission of some gases like CO₂.

Carbon dioxide is a colorless, odorless, faintly acidic-tasting, and non-flammable gas at room temperature, with a molecular formula CO₂. The linear molecule consists of a carbon atom that is doubly bonded to two oxygen atoms, O=C=O. Carbon dioxide is the fourth most-abundant gas in the Earth’s atmosphere. Animals exhale carbon dioxide and a plant uses it in photosynthesis to convert it to sugars and other forms of energy.

There are various sources of CO₂ emissions, which are dominated by combustion of liquid, solid, and gaseous fuels. The amount of CO₂ consumption for organic chemicals
is relatively small compared to CO₂ emitted from fossil fuel combustion. However, CO₂ conversion and utilization should be an integral part of carbon management. Proper use of CO₂ for chemical processing can add value to the CO₂ disposal by making industrially useful carbon-based products. Studies on CO₂ conversion into carbon-based chemicals and materials are important for sustainable development. CO₂ conversion and utilization could also be positioned as a step for CO₂ recycling and resource conservation (Abrahams et al. 1991). Carbon dioxide thus can be chemically transformed from a detrimental greenhouse gas causing global warming into a valuable, renewable and inexhaustible carbon source of the future allowing environmentally neutral use of carbon fuels and derived hydrocarbon products (Rosi et al. 2005).

Metal organic materials (MOM’s) are compounds consisting of metal nodes and organic linkers. Specifically, MOMs presenting permanent porosity, that is, the so-called metal-organic frameworks (MOF), as well named porous coordination polymers (PCP’s) or microporous metal-organic frameworks (MMOF’s), or in the case where are magnetic, porous molecular magnets (PMM) (Stepanow et al. 2004; Rosi et al. 2005; O’Keeffe et al. 2008; Farha et al. 2010; Corma et al. 2010). These are a fascinating group of hybrid materials, appearing as crystalline lattices composed of inorganic nodes and multi-dentate organic linkers (Kinoshita et al. 1959; Hoskins et al. 1989; Desiraju 1989; Hoskins et al. 1990; Fujita et al. 1990; Abrahams et al. 1991; Abrahams et al. 1991; Fujita et al. 1994; Stepanow et al. 2004; Rowsell et al. 2004; Rosi et al. 2005; O’Keeffe et al. 2008; Farha et al. 2010; Corma et al. 2010) forming crystalline porous compounds, entailing strong metal-ligand interactions (Rowsell et al. 2004; Siberio-Perez et al. 2007).

The Metal organic Frameworks (MOF) first arose through the study of zeolites. Those appear due to a modification of the synthesis of zeolites. The MOF first reported was in the Cambridge Structural Database (CSD) in 1978, this is software for database access for structure visualization and data analysis, and structural knowledge bases. The
center and connection method for the synthesis of extensive framework materials was developed in the first years of the last decade of the 20th century fundamentally by Robson and Hoskins (Hoskins et al. 1989; Hoskins et al. 1990; Abrahams et al. 1991; Abrahams et al. 1991), Fujita (Fujita et al. 1990; Fujita et al. 1994), Desiraju (Desiraju 1989) and others (Stepanow et al. 2004; Rosi et al. 2005; O’Keeffe et al. 2008; Farha et al. 2010; Corma et al. 2010). Descriptions of this kind of materials were presented by Kinoshita and collaborators more than fifty years ago (Kinoshita et al. 1959). The selection of a concrete metal node, regularly determine the structure of the resulting framework and the diverse coordination numbers with the favored geometries of the metal (Stepanow et al. 2004; Rosi et al. 2005; O’Keeffe et al. 2008; Farha et al. 2010). Between these materials those with shows permanent porosity are the most interesting ones. This characteristic is the one that normally lead to great pore volumes, specific surface areas and low densities (Farha et al. 2010; Corma et al. 2010). Some of these materials have shown potential applications in gas storage (Dinca et al. 2005; Murray et al. 2009; Li et al. 2009; Furukawa et al. 2009), molecular separation (Farha et al. 2010), ion exchange (Min et al. 2000), catalysis (Ma et al. 2009; Corma et al. 2010), together with luminescence (Allendorf et al. 2009) and magnetism (Kurmoo 2009).

The perfect gas-storage MOF should have high adsorption capacity and fast kinetics at workable temperatures, and the gas should interact strongly enough with the material that it is not lost from the solid on storage but not so strongly that it cannot be released from the material for use at the required time. They show promising potential for hydrogen, methane, nitrogen and CO₂ storage. MOF’s adsorbed, and store without significant loss, large quantities of materials. MOF’s are the major candidates that might meet the U.S. Department of Energy requirements for vehicular gas storage (Millward et al. 2005). The literature shows that MOF could store as much CO₂ as would be stored in nine tanks that do not contain MOF. By comparison, a tank filled with porous carbon one of the current
state of the art materials for capturing CO$_2$ in power plant flues would hold only four tanks worth of CO$_2$. MOF can be made in large quantities from low cost ingredients. (Tranchemontagne et al. 2008) Be effective, low-cost way of reducing CO$_2$ emissions, according to Yaghi. Tens of thousands of MOF have been synthesized and structurally characterized; however, only a few of them have been tested for their adsorption properties. Selective adsorption has been observed in less than about seventy MOF, mostly based in on gas adsorption isotherms (Li et al. 2008).

Based in the porosity of the frameworks, several groups have successfully studied the magnetic properties of the materials. The majority of magnetic frameworks are those containing paramagnetic metal centers and in particular, the first row transition metals (V, Cr, Mn, Fe, Co, Ni and Cu) (Kurmoo 2008). To construct porous magnets, is required distance within interaction range. A key point is to fulfill effective magnetic exchange pathways in the porous MOF.

PMM and molecule-based magnets, (M-BM’s) (Castillo et al. 2001; Nowicka et al. 2007; Coronado et al. 2008) are primarily characterized by the chemical nature of its organic and metallic constituents and their spatial configuration. In this sense, the bis-chelating coordination capacity of the oxalate ion and its facility to generate magnetic interaction between metallic centers has made it a valuable and flexible option in the design of diverse molecule-based magnetic compounds (Coronado et al. 2008). The magnetic properties of oxalato-bridged complexes are outstanding owing to the capacity of the oxalate ligand to assume different bridging modes, together with its ability to take part in strong magnetic exchange by mediating electronic effects between paramagnetic metal ions (Castillo et al. 2001). That is, the oxalate anions which have four potential donor sites, is very attractive as a linker due to its ability to form framework structures and participate in strong magnetic exchange).
One aim of the scientists is to develop bifunctional novel materials. The importance of this material is the dual function obtained even though the combination of porosity and magnetism is a complicated undertaking; because porosity is associated to long bridging, whereas magnetic exchange needs short distances (Nowicka et al. 2007). In this case its porous properties, means that the electronic structure of nickel cations can be externally manipulated with adsorbed molecules. The material could be sensitive to small molecules; thereafter, used as a magnetic sensor to trap CO\textsubscript{2} from the environment.

In the present research it is described the synthesis, structural characterization, study of the porous structure, surface chemistry and magnetic properties of a new Ni-oxalate metal organic frameworks (Ni-Ox-MOF). To accomplish the proposed objectives, the material was designed by: applying a concrete synthesis methodology and the synthesized materials were carefully studied by diffuse reflectance infrared Fourier Transform Spectrometry (DRIFTS), Raman Spectrometry (RS), Thermogravimetric Analysis (TGA), structure analysis by X-Ray Diffraction (XRD), adsorption of carbon dioxide at 273K and magnetochemistry with a Vibrating Sample Magnetometer (VSM). Searches in different databases as: Journal of American Chemical Society, Cambridge Structural Database, Database for Australian National University for MOF, among others; showed that the material studied in this investigation is unique and none observed in other investigation.
Chapter Two
Experimental Data

2.1 Materials and Synthetic Procedure.

The literature shows four different conditions to synthesize the MOF's:

1. Hydrothermal - All chemicals are prepared using water as a solvent, and heated at a temperature that fluctuates between 70 °C to 220 °C, from 6 hours up to 6 days (Fang et al. 2008).

2. Solvothermal - All chemicals use a solvent other than water, and prepare it from 4 °C to 250 °C, from 6 hours to 28 days (Tranchemontagne et al. 2008; Duan et al. 2006).

3. Biphasic solvothermal - Inorganic salts are dissolved in water and organic compounds are dissolved in an organic solvent and carefully layered above the aqueous solution. This is then sealed and heated at 70 °C to 150 °C, from 6 hours to 28 days (Kondo et al. 2010).

4. Sol-gel synthesis- Inorganic salts and template are dissolved into a sodium silicate solution. The organic linker is dissolved in water and carefully layered above the gel layer. This is allowed to sit at room temperature, from 6 to 20 days (Hermes et al. 2007).

The four methods were developed by scientist to obtain porous metal organic materials (MOF), with highly crystalline structures and a large variety of extended porous frameworks with a considerable range of pore sizes and functionalities. All of them are based in a basic procedure; where by dissolve a metal salt and a ligand are possible obtain a MOF. The difference between each method lies in the physical conditions or materials used to prepare it. Refer to figure 2.01 to observe a general MOF syntheses flowsheet.
Figure 2.01. A MOF's Synthesis Flowsheet. This is the main procedure to which is applied different conditions to obtain a MOF.
In the present project the solvothermal method (Rosi et al. 2005) was slightly modified to get a new material. This procedure was made by two different ways. The first method used was a modified solvothermal process at room temperature (27 °C) or heated at 70 °C, using dimetilformamide (DMF) as solvent. To make it different to the original process, was added triethylamine (Et$_3$N) 70.3M in dimethylformamide (DMF) and Hydrogen Peroxide (Figure 2.02).

![Figure 2.02. The Modified Solvothermal Process: Method One. This picture present the scheme used in process one to synthesize MOF.](image)

The second procedure is by refluxing the reaction mixture, showed in figure 2.03, without H$_2$O$_2$, using heat to accelerate the precipitation. The solid formed precipitates from the solution in hours. The solutions that slowly react at the first modified solvothermal process, now precipitates in a couple of hours, less than 6 hours. For this process several approaches were used, trying to obtain a MOF with adsorbent properties.

All the chemicals used were analytical grade without additional purification. The water used in the synthesis process was bi-distilled. The Ligands are: Maleic acid, Fumaric acid, Succinic acid, L-Tartaric acid, 1,2-trans-ciclohexanebicarboxylic acid, 1,4-trans-ciclohexanebicarboxylic acid, 4,4-bipyridine, Mandelic acid, Glutaric acid, Adipic acid, Malonic Acid and Oxalic acid. In the table 2.01 is presented the formula, the common name, IUPAC name and the carbon chain of dicarboxylics acids used for this research.
Figure 2.03. MOF synthesis under refluxing conditions. This picture shows the equipment required to use the refluxing method identified by the red color: Thermometer, Stand, Safety Adapters, Magnetic Stir Bar, Round Flask, Hot plate/Stirrer, Clamp, Water condenser. Also shows were is water in and out; this is represented by blue color.
Table 2.01. Table of the Dicarboxylic Acids used on this research; the formula, carbon quantity and common name.

<table>
<thead>
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<th>Common name</th>
<th>IUPAC name</th>
<th>Carbon Quantity</th>
<th>Formula</th>
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<tbody>
<tr>
<td>Oxalic acid</td>
<td>ethanedioic acid</td>
<td>2</td>
<td>C₂H₂O₄</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>propanedioic acid</td>
<td>3</td>
<td>C₃H₄O₄</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>Butanedioic acid</td>
<td>4</td>
<td>C₄H₆O₄</td>
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<tr>
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<td>C₆H₆O₆</td>
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<td>Maleic acid</td>
<td>(Z)-Butenedioic acid</td>
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<td>pentanedioic acid</td>
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<td>C₅H₈O₄</td>
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<tr>
<td>Adipic acid</td>
<td>hexanedioic acid</td>
<td>6</td>
<td>C₆H₁₀O₄</td>
</tr>
<tr>
<td>Mandelic acid</td>
<td>2-Hydroxy-2-phenylacetic acid</td>
<td>8</td>
<td>C₈H₆O₃</td>
</tr>
<tr>
<td>1,4-Cyclohexane dicarboxylic acid</td>
<td>Cyclohexane-1,4-dicarboxylic acid</td>
<td>8</td>
<td>C₈H₁₂O₄</td>
</tr>
<tr>
<td>Bipyridine</td>
<td>4,4-Bipyridine</td>
<td>10</td>
<td>(C₅H₄N)²</td>
</tr>
</tbody>
</table>

The metal salts used were (Table 2.02): zinc nitrate (Zn(NO₃)²), cobalt nitrate (Co(NO₃)²), lead nitrate (Pb(NO₃)²), iron nitrate (Fe(SO₄)²), mercury nitrate (Hg(NO₃)²), cadmium nitrate Cd(NO₃)², copper nitrate (Cu(NO₃)²), and nickel nitrate Ni(NO₃)².

The synthetic procedure applied for Ni-Ox-MOF was, the modified solvothermal process at room temperature (27 °C), it was showed in Figure 2.04. The concrete synthesis procedure was as follows:
Table 2.02. Table of the Metal Salts used on this research; the common name and formula.

<table>
<thead>
<tr>
<th>Common name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc nitrate</td>
<td>Zn(NO$_3$)$_2$</td>
</tr>
<tr>
<td>Cobalt nitrate</td>
<td>Co(NO$_3$)$_2$</td>
</tr>
<tr>
<td>Lead nitrate</td>
<td>Pb(NO$_3$)$_2$</td>
</tr>
<tr>
<td>Iron nitrate</td>
<td>Fe(SO$_4$)$_2$</td>
</tr>
<tr>
<td>Mercury nitrate</td>
<td>Hg(NO$_3$)$_2$</td>
</tr>
<tr>
<td>Cadmium nitrate</td>
<td>Cd(NO$_3$)$_2$</td>
</tr>
<tr>
<td>Cooper nitrate</td>
<td>Cu(NO$_3$)$_2$</td>
</tr>
<tr>
<td>Nickel nitrate</td>
<td>Ni(NO$_3$)$_2$</td>
</tr>
</tbody>
</table>

-A 70.3 mM solution of Et$_3$N in DMF was prepared.

-A 0.01 mol of Ni(NO$_3$)$_2$ is dissolved in 50.0 ml of DMF and 0.01 mol of C$_2$H$_2$O$_4$ (oxalic acid) is added and dissolved.

-To the above solution is added 29.0 ml of H$_2$O$_2$ (50%) was added slowly while stirring manually.

-The reaction mixture is cooled between 5-10 °C and 24.1 ml of Et$_3$N 70.3 mM was added slowly in a period of 5 to 10 minutes.

-After the addition of the Et$_3$N the flask is sealed and placed in the hood for one week at room temperature (27 °C).

-The solid formed was vacuum filter in a
Büchner's funnel washed with two portions of methanol and 5.0 ml of bi-distilled water.

- It was placed in the oven at 70 °C for 24 hours.
- The solid obtained was pulverized and characterized using XRD, IR and RAMAN spectroscopy, TGA analysis and others.

To characterize the synthesized materials in different equipments a few gases were used such as: pure Potassium Bromide (KBr), provided by Nicolet; for adsorption isotherms of carbon dioxide (CO\textsubscript{2} Praxair, 99.99%) and helium (He\textsubscript{2} Praxair, 99.99%); to hydrated and dehydrated samples in spectra, was used a nitrogen flow (N\textsubscript{2} Praxair, 99.99%).

2.2. Characterization Methods.

For this research is required found a sample with crystalline properties and highest porosity, because both are characteristics of a MOF with adsorbent properties. Once was obtained the material with these characteristics, will proceed to make specific studies to characterize the sample with the instrumentation will be described below.

As the focal point for this research is got a sampler with crystalline properties, the first analysis was done to all samples was the X-ray diffraction (XRD), showed in Apendix A-1.01. Tests were carried out using a Bruker D8 Advance system in a Bragg- Brentano vertical goniometer configuration. The angular measurements were made with a (Theta / 2Theta) of: ± 0.0001 degree reproducibility, 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 was a ceramic X-ray diffraction Cu anode tube type KFL C 2K of 2.2 kW, with long fine focus. A LynxEye™ one-dimensional detector was employed. This detector is based on Bruker AXS compound silicon strip technology and increases measured
Figure 2.04. The synthesis to prepare Ni-Ox-MOF: (A) Sample dissolved (B) Sample reacting under the hood at room temperature (27 °C). (C) Sample was filtered (D) Pulverize (E) Dry it on a desiccator (F) Identified and put on a corresponding container.
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 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 (Roque-Malherbe et al. 2011).

The second main point for this investigation is found a sampler with the highest porosity, because it was made the Thermogravimetric Analysis (TGA) showed in Appendix A-1.02. Testing process was carried out with a TA, Q-500 instrument. Samples were placed onto a ceramic sample holder suspended from an analytical balance. The sample and holder were heated according to a predetermined thermal cycle, that is: the temperature was linearly scanned, from 25 to 350 °C, at a heating rate of 5 °C/min, in a flow of 100 ml/min of pure nitrogen. The data collection, temperature control, programmed heating rate, and gas flow, were automatically controlled by the software of the instrument. The TGA data was collected as a Weight (%) versus Temperature (°C) profile. The focal point for this research is found a sampler with the highest weight loss in the TGA.

Once the sample was selected, DRIFTS was performed in the Infrared Spectrum (showed in Appendix A-1.03). Diffuse reflectance infrared Fourier transform spectra (DRIFTS) 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. A background, with pure KBr, applying the same conditions used to get the samples spectra was always made previous to sample collection. The hydrated samples spectra were obtained at room temperature under N₂ flow at a rate of 50 cc/min. To get the spectra of the dehydrated samples, it was heated, to 100 °C, under a flow of N₂ at a rate of 50 cc/min
for 2 hours. The spectra of the dehydrated materials were then obtained at room temperature, under N₂.

As a complementary technique, was used a Raman Spectrum (RS) (Refer to Appendix A-1.04 to observe the Raman instrumentation used). The Raman analysis were taken with a Renishaw Raman microspectrometer RM2000 system, showed in Appendin A-1.04, is equipped with a Leica microscope using 20x objective and with a charge-coupled device (CCD) detector. A spectrum was obtained with laser lines at 532 and 785 nm. The 785 nm laser excitation line was provided by a model PI-ECL-785-300-FS, Process Instruments, Inc., Salt Lake City, UT. The 532 nm excitation source was a Spectra Physics EXCELSIOR solid state diode laser. Raman spectra were collected in the range of 100-3500 Raman Shift (cm⁻¹), with an integration time of 10s per scan. The Raman spectra were the result of the average of 3 scans.

The fitting process of the Raman and DRIFTS spectra were performed with the peak separation and analysis software PeakFit (Seasolve Software Inc., Framingham, Massachusetts) based on the least square procedure, in order to calculate the best fitting parameters, peak positions, and amplitudes, and peak half width.

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, is showed in Appendix A-1.05. The adsorption isotherms of CO₂ at 273 K and 298 K were obtained for samples degassed at 573 K for three hours in high vacuum (10⁻⁶ Torr). The backfilling process was carried out using helium in both cases.

DRIFTS spectra of carbon dioxide adsorbed in the sample selected were obtained using as background the dehydrated sample at room temperature. That is, a background, of the dehydrated sample applying the same conditions used to get the adsorbed samples spectra were always made previous to sample collection. After that, CO₂ flow at a rate of 50 cc/min for three minutes was passed through the dehydrated samples; afterward, the
sample was purged under N\textsubscript{2} flow at a rate of 50 cc/min for one minute. Spectra of the carbon dioxide molecule adsorbed on the MOF were then obtained at room temperature under N\textsubscript{2} flow.

The magnetic measurements were obtained in the vibrating sample magnetometer (VSM), Lakeshore 7400 Series, showed in Appendix A-1.06. The magnetization curve, magnetization (M) versus field strength (H) was carried out at room temperature (300 K). The powder sample was weighted, located in the sample holder and then applied the ramp from -2.2 to 2.2 T (T=Tesla) and thereafter in backward direction.
Chapter Three

Results and Discussion

3.1 Synthesis

With the center and connection methodology, in the present work it was synthesized 35 different metal organic materials. The Table 3.01 shows detailed each reaction and the observations after the characterization in the TGA and XRD. The figure 3.01 showed the XRD data of the nickel oxalic material and other three materials also synthesized with nickel, in this is seen as a sample was determined amorphous or crystalline material. The samples were crystalline if it had a defined pattern of peaks and was amorphous when the sample had no peaks arranged, by the XRD data the nickel oxalic material showed crystalline properties. The TGA obtained data showed that the sample with the highest weight loss is the nickel oxalic material. Refer to figure 3.02 to see the comparison of nickel oxalic material with other three samples also synthesized with nickel. The 35 samples were compared to each other, but in this research only were presented three additional samples synthesized with nickel as an example; because the amount of documentation was massive and the idea was to facilitate the way was token the conclusion that the nickel oxalic sample was right one. In accordance with the above information, nickel oxalic product is crystalline and porous.

The Ni-Ox-MOF was Porous Molecular Magnet (PMM); the synthesis process was repeated, changing slightly the steps described in section 2.1, in order to test the reproducibility of the synthesis process. The synthesis procedure showed itself extremely delicate, that is, minimal changes produced a non-porous material.
Figure 3.01. The example of crystalline and amorphous materials founded in the XRD data. The figure showed the XRD data of the nickel oxalic material and other three materials also synthesized with nickel, in this is seen as a sample how was determined amorphous or crystalline each material.
Figure 3.02 The example of different issues founded in the TGA Data: The sample of Ni(NO$_3$)$_2$ + Succinic acid, represented by the purple color, shows no weight loss and a decomposition at 150 °C; The sample of Ni(NO$_3$)$_2$ + Maleic acid, represented by the green color, shows a 8% of weight loss and a decomposition at 210 °C; The sample of Ni(NO$_3$)$_2$ + Oxalic acid, represented by the red color, shows a 11% of weight loss and a decomposition at 200 °C; Ni(NO$_3$)$_2$ + ciclohexanedicarboxylic acid, represented by the red color, shows a 5% of weight loss and a decomposition at 120 °C.
Table 3.01: Table of the metal organic materials synthesized and the observations of each reaction.

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cd(NO$_3$)$_2$ + Fumaric acid + H$_2$O$_2$ (50 %) + DMF + Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)</td>
<td>No present significant weight loss in TGA</td>
</tr>
<tr>
<td>2. Cd(NO$_3$)$_2$ + Succinic acid + H$_2$O$_2$ (50 %) + DMF + Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)</td>
<td>Poor crystalline properties</td>
</tr>
<tr>
<td>3. Cd(NO$_3$)$_2$ + Maleic acid + H$_2$O$_2$ (50%) + DMF + Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)</td>
<td>Amorphous Material</td>
</tr>
<tr>
<td>4. Co (NO$_3$)$_2$.6H$_2$O + Fumaric acid + H$_2$O$_2$ (30 %) + DMF+ Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)</td>
<td>No Reaction was obtained</td>
</tr>
<tr>
<td>5. Cu(NO$_3$)$_2$ + Maleic acid + (30%)+DMF+Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)</td>
<td>Amorphous Material</td>
</tr>
<tr>
<td>6. Fe(SO$_4$) + Fumaric acid + H$_2$O$_2$ (50 %) + DMF + Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)</td>
<td>Amorphous material</td>
</tr>
<tr>
<td>7. Fe(SO$_4$) + Maleic acid+ H$_2$O$_2$ (30 %) + DMF + Et$_3$ N (70.3 mM in DMF); at room temperature (27 °C)</td>
<td>Amorphous material</td>
</tr>
<tr>
<td>8. Fe(SO$_4$) + Succinic acid + H$_2$O$_2$ (30 %) + DMF + Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)</td>
<td>Amorphous material</td>
</tr>
<tr>
<td>9. Fe(SO$_4$) + L-Tartaric acid + H$_2$O$_2$ (30%)+DMF+ Et$_3$N (70.3mM in DMF); at room temperature (27°C)</td>
<td>No Reaction was obtained</td>
</tr>
<tr>
<td>10. Hg(NO$_3$)$_2$ + L-Tartaric acid + H$_2$O$_2$ (50%) + DMF + Et$_3$N (70.3mM in DMF); at room temperature (27°C)</td>
<td>No present significant weight loss in TGA</td>
</tr>
<tr>
<td>11. Hg(NO$_3$)$_2$ + Maleic acid+ H$_2$O$_2$ (30 %)+DMF+ Et$_3$N (70.3 m in DMF); at room temperature (27 °C)</td>
<td>Amorphous material</td>
</tr>
<tr>
<td>12. Ni(NO$_3$)$_2$.6H$_2$O + Oxalic acid + H$_2$O$_2$ (50 %)+DMF+ Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)</td>
<td>Present Crystalline characteristics and weight loss in TGA</td>
</tr>
<tr>
<td>13. Ni(NO$_3$)$_2$.6H$_2$O + Fumaric acid + H$_2$O$_2$ (30 %) + DMF + Et$_3$N (70.3 m in DMF); at room temperature (27 °C)</td>
<td>No Reaction was obtained</td>
</tr>
<tr>
<td>14. Ni(NO$_3$)$_2$.6H$_2$O + Succinic acid + H$_2$O$_2$ (30 %)+DMF+ Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)</td>
<td>No present significant weight loss in TGA</td>
</tr>
</tbody>
</table>
15. **Ni(NO$_3$)$_2$.6H$_2$O + Maleic acid + H$_2$O$_2$ (30 %)+DMF+ Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)**
   Amorphous material

16. **Pb(NO$_3$)$_2$ + Maleic acid + H$_2$O$_2$ (50 %) + DMF + Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)**
   Amorphous material

17. **Pb(NO$_3$)$_2$ + Succinic acid + H$_2$O$_2$ (50 %) + DMF + Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)**
   No present significant weight loss in TGA

18. **Pb(NO$_3$)$_2$ + Oxalic acid + H$_2$O$_2$ (50 %) + DMF + Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)**
   No present significant weight loss in TGA

19. **Pb(NO$_3$)$_2$ + 1,4-ciclohexanedicarboxilic acid+ H$_2$O$_2$ (30 %) + DMF + Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)**
   No present significant weight loss in TGA

20. **Zn(NO$_3$)$_2$.6H$_2$O + Oxalic acid + H$_2$O$_2$ (30 %) + DMF + Et$_3$N (70.3 mM in DMF); at room temperature (27 °C)**
   No present significant weight loss in TGA

21. **Co (NO$_3$)$_2$.6H$_2$O + Fumaric acid + (30 %)+ DMF+Et$_3$N (70.3 mM in DMF) (Heated 70 °C)**
   Poor crystalline properties

22. **Cu(NO$_3$)$_2$ + Fumaric acid + H$_2$O$_2$ (30 %)+ DMF+Et$_3$N (70.3 mM in DMF) (Heated at 70 °C)**
   No Reaction was obtained

23. **Cu(NO$_3$)$_2$ + Maleic acid + (30 %)+ DMF+Et$_3$N (70.3 mM in DMF) (Heated at 70 °C)**
   No present significant weight loss in TGA

24. **Cu(NO$_3$)$_2$ + Succinic acid + (30 %)+ DMF+Et$_3$N (70.3 mM in DMF) (Heated 70 °C)**
   No present significant weight loss in TGA

25. **Cu(NO$_3$)$_2$ + Fumaric acid + H$_2$O$_2$ (30 %)+ DMF+Et$_3$N (70.3 mM in DMF) (Heated at 70 °C)**
   No Reaction was obtained

26. **Ni(NO$_3$)$_2$ + 1,2-cis-ciclohexanebicarboxilicacid + H$_2$O$_2$ (50 %) DMF+Et$_3$N (70.3 mM in DMF) (Heated at 70 °C)**
   No present significant weight loss in TGA

27. **Ni(NO$_3$)$_2$ + 1,4-cis-ciclohexanebicarboxilicacid + H$_2$O$_2$ (50 %)+DMF+Et$_3$N (70.3 mM in DMF) (Heated at 70 °C)**
   No present significant weight loss in TGA

28. **Pb(NO$_3$)$_2$ + Succinic acid + H$_2$O$_2$ (50 %)+DMF+Et$_3$N (70.3 mM in DMF) (Heated at 70 °C)**
   No present significant weight loss in TGA

29. **Pb(NO$_3$)$_2$ + Maleic acid + H$_2$O$_2$ (50 %) + DMF + Et$_3$N (70.3 mM in DMF) (Heated at 70 °C)**
   No present significant weight loss in TGA

30. **Zn(NO$_3$)$_2$.6H$_2$O + Fumaric acid + H$_2$O$_2$ (30 %) + DMF + Et$_3$N (70.3 mM in DMF) (Heated at 70 °C)**
   Amorphous Material

31. **Ni(NO$_3$)$_2$ + 1,4-trans-ciclohexanebicarboxilicacid + Adipic acid + DMF (Reflux at 160 °C)**
   Poor crystalline properties
32. Ni(NO₃)₂ + Mandelic acid + DMF; Reflux at 160 °C  
33. Ni(NO₃)₂ + Oxalic acid + DMF; Reflux at 160 °C  
34. Ni(NO₃)₂ + 1,4-trans-ciclohexanedicarboxilic acid + DMF; Reflux at 160 °C  
35. Ni(NO₃)₂ + 1,2-trans-ciclohexanedicarboxilic acid + DMF; Reflux at 160 °C  

Amorphous Material

The idea behind the synthesis procedure was to use oxalate anion in order to create a 2D layer. To produce the layered structure, Et₃N was introduced to neutralize the oxalic acid. The H₂O₂ was used to accelerate the reaction, introduce water in the framework and oxidize a fraction of the Ni²⁺ to Ni³⁺. DMF was not only the solvate, also acted as a shaping molecule.

The layered framework makes possible the combination of paramagnetic nodes at short distances within the layer associated with long bridging distances in the direction of the layer stacking. Explicitly, it is possible the combination of magnetism and porosity, since we have magnetic exchange because of the short distances in the layer and porosity due to long bridging in the stacking direction.

3.2. Structural analysis of the Ni-Ox-MOF

3.2.1. DRIFTS and RS study

The DRIFTS spectra of the Ni-Ox-MOF sample as-synthesized and degassed at 75 °C in the range between: 500-4000 cm⁻¹ are shown in Figure 3.03. The main IR active vibrations observed in the range between: 500-2000 cm⁻¹ are the ν(CO) asymmetric stretching vibration, at 820 cm⁻¹; the ν(CO) symmetric stretching vibrations, located at 1321 and 1361 cm⁻¹ and between 1500-1700 cm⁻¹ the ν(OCO) broad band. These are the
Figure 3.03. DRIFTS Spectra of Ni-Ox-MOF. The picture showed the DRIFTS of the as-synthesized and degassed at 75°C Ni-Ox-MOF. A) Showed the vibrations observed in the Ni-Ox-MOF as synthesized. B) Shows the vibrations obtained after the Ni-Ox-MOF as synthesized was degassed at 75 °C. C) Shows the vibration produced by adsorbed water from the as synthesized material after degassing.
distinctive IR bands of the bis-bidentate oxalate-bridging (Figure 3.04) ligand (Tuero et al. 1991). These bands are, with minor shifts, maintained after dehydration at 75 °C. The band at 1469 cm$^{-1}$, also very well noticed in the Raman spectrum (Fig. 3.05), correspond to the $\nu(C = O)$ of the DMF (Fig. 3.04). Additionally, the band 1020 cm$^{-1}$ corresponds to the $\nu(CN)$ stretching vibration of DMF (Olejnik et al. 1971).

In the range between 2750-3800 cm$^{-1}$ are observed the vibrations related to the water and the DMF included in the Ni-Ox-MOF. In this range are evidenced three broad bands. The band in the range: 3200-3700 cm$^{-1}$ correspond to the stretching, $\nu(OH)$ vibration produced by adsorbed water. This band disappears after degassing at 75 °C (see in Fig 3.03 the difference spectrum). The other two bands in the range 2750-3200 cm$^{-1}$ do not disappear after degassing at 75 °C. Since, these two, relatively broad bands, also found in the Raman spectrum, are produced by $\nu(CH)$ and $\nu_s(NCH_3)$ vibrations corresponding to DMF (Olejnik et al. 1971).

Two very important features of the Raman spectrum are the bands located at 528 cm$^{-1}$ and 588 cm$^{-1}$. The band located at 528 cm$^{-1}$ is normally accepted that corresponds to the stretching vibration mode of the NiO$_6$ octahedral (Kalyani et al. 2005). The band placed at 588 cm$^{-1}$ can be contemplated as the stretching vibration mode distorted octahedral coordination (NiO$_6$) or pentacoordinated (NiO$_5$) (Park et al. 2006). Both bands are resolved in two peaks by fitting each band (Table 3.02). To explain these peaks is important remember that during the synthesis process, H$_2$O$_2$ was added. Consequently, is very probable that some of the Ni$^{2+}$ was oxidized to Ni$^{3+}$, thereafter, in some of the octahedral and distorted octahedral sites Ni$^{3+}$ is placed. To justify the band at 588 cm$^{-1}$ was applied the Sanderson principle of equalization of the electronegativity (Sanderson 1976). This rule states that in a molecule composed of atoms with different electronegativity the electrons are restructured in such a way that they will be equally attracted to the nuclei in
Figure 3.04. Molecular structures of the Ni-DMF complex and the bis-bidentate, bridging-bis-bidentate oxalate ligands. 

A) Bridging-Bis-bidentate ligands, the nickel nodes have only five bonds linked to the oxalate ion, one of the bonds are unsaturated. B) Ni-DMF complex, the DMF molecules perpendicularly coordinated to the nickel. C) Bis-bidentate ligands, had six nodes linked to oxalate ion.
Figure 3.05. Raman spectrum of the as-synthesized Ni-Ox-MOF. A) Spectrum obtained from the as synthesized Ni-Ox-MOF in the RS. B) Shows the band placed at 588 cm\(^{-1}\) that can be contemplated as the stretching vibration mode of NiO\(_5\) in distorted octahedral coordination (NiO\(_6\)) or pentacoordinated (NiO\(_5\)).
the bond. Consequently, the molecule average electronegativity is postulated to be the geometric mean of the compound atoms of the molecule under consideration.

In the analyzed material, the decrease in the number of oxygen atoms from NiO$_6$ to NiO$_5$ induced a transfer of electronic density from the less electronegative atom, nickel, to the more electronegative, oxygen; subsequently, an increase in the bond strength accompanied by an increase in the wave number of the band was produced.

### 3.2.2. TGA test

To determine the guest molecules lost during heating and study other structural features, the TGA method was applied. The thermal gravimetric (TG) profile of the Ni-Ox-MOF is shown in Figure 3.06 a. It is evident that at relatively low temperatures, that is below 100 °C took place the release of H$_2$O, in two steps. This fact is confirmed in Figure 3.06 b where shown the derivative of the TG profiles of the material resolved in peaks. These peaks can be related, to the liberation of adsorbed (45 °C) and coordinated water (80 °C). Finally, also in two steps, 170 °C and 215 °C, DMF was released (Table 3.03). Finally, the material was decomposed at 300 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda^1$ [cm$^{-1}$]</th>
<th>$A_1$ [%]</th>
<th>$\lambda^2$ [cm$^{-1}$]</th>
<th>$A_2$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band at 535 cm$^{-1}$</td>
<td>522</td>
<td>0.32</td>
<td>534</td>
<td>0.31</td>
</tr>
<tr>
<td>Band at 585 cm$^{-1}$</td>
<td>583</td>
<td>0.18</td>
<td>592</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Table 3.03. Parameters calculated with the TG profile

<table>
<thead>
<tr>
<th>Sample</th>
<th>$W_{\text{TGA}}^{H_2O} , [cm^3/g]$</th>
<th>$T_1^{H_2O} , ^{[\circ C]}$</th>
<th>$T_2^{H_2O} , ^{[\circ C]}$</th>
<th>$T_1^{\text{DMF}} , ^{[\circ C]}$</th>
<th>$T_2^{\text{DMF}} , ^{[\circ C]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Ox-MOF</td>
<td>0.100</td>
<td>45</td>
<td>80</td>
<td>170</td>
<td>215</td>
</tr>
</tbody>
</table>

TGA was also applied as a method for the measurement of the pore volume in microporous materials, since the TG profile from 30 $^\circ$C to 150 $^\circ$C behaved merely as a water thermo desorption process (Roque-Malherbe et al. 2005). In this regard it was possible the calculation of the TGA micropore volume, with the TG data and the Gurvich rule (Roque-Malherbe, 2010).

Gurvich rule is expressed as follows:

$$V_i = V^L n_a$$  \hspace{1cm} (1)

Where, $V_i$ = volume of the adsorption space; $n_a$ = the amount adsorbed; and $V^L$ = the molar volume of the liquid phase which conforms the adsorbed phase. The amount adsorbed (in mol/g.) is defined as follows (Roque-Malherbe, 2010):

$$n_a \approx \frac{n^a}{m_s}$$  \hspace{1cm} (2)

Where: $n^a \approx n^\tau$, and, $n^\tau$ is the surface excess amount. The mass of degassed adsorbent ($m_s$), measured in g. Thereafter,

$$m_s = 1 - WtL_{\text{PMM}}$$  \hspace{1cm} (3)

$$n^a = WtL_{\text{PMM}} / M_{H_2O}$$  \hspace{1cm} (4)

Where in the present case, $WtL_{\text{PMM}}$, was the weight lost at 100$^\circ$C in g/g; $M_{H_2O} = 18$ g/mol, is the molecular weight of water. Since, $V_{H_2O}^L = 18$ cm$^3$/mol. The micropore volume, $W_{\text{TGA}}^{H_2O}$,
the following relation was applied:

\[ W_{TGA}^{H_2O} = V_{H_2O}^{L} n_a = V_{H_2O}^{L} (WiL_{PMM} / M_{H_2O} n_a) = \frac{WiL_{PMM}}{1 - WiL_{PMM}} \]  

(5)

To calculate with our data the micropore volume the following relation was applied:

\[ W_{TGA}^{H_2O} = \frac{WiL_{PMM}}{1 - WiL_{PMM}} \text{ (cm}^3\text{/g)} \]  

(6)

Where, in the present case, \( WiL_{PMM} \), in g/g, was the weight lost at 100° C. The value for \( WiL_{PMM} = 0.09 \text{ g/g} \), consequently \( W_{TGA}^{H_2O} = 0.100 \text{ cm}^3\text{/g} \), for the tested Ni-Ox-MOF.

3.2.3. XRD structural analysis

The Figure 3.07 a showed the XRD profile of the as-synthesized Ni-Ox-MOF sample in the range between: 5-55 ° (2θ). After a deep analysis of the pattern displayed in Figure 3.07 a, was realized its resemblance with the profiles of layered compounds as the phyllosilicates (Plancon 2002; Ufer et al. 2004). Consequently, it was supposed that the Ni-Ox-MOF is formed by stacked layers. To justify the previous hypothesis, the powder pattern reported was resolved into separate Bragg components applying the whole-powder pattern decomposition (WPPD) the method proposed by Pawley (Pawley 1981), as shown in Figure 3.07 a. This method can refine the unit cell parameters and decompose the whole powder pattern into individual reflections. The concrete computer program applied to carry out the calculations was the Bruker DIFFRACplus TOPAS™ software. This is a graphics based, non-linear least squares profile analysis program that integrates between other features the WPPD Pawley method without reference to a crystal structure model. The XRD profile of the hydrated sample was fairly fitted (Figure 3.07 b) with the help of the Pawley decomposition method supposing that it crystallizes in the monoclinic \( P2_1 / m \) space group (Table 3.04).
Figure 3.06. Ni-Ox-PMM TG profile (a) and its derivative (b). The thermal gravimetric (TGA) profile of the Ni-Ox-MOF is showed in figure a, where took place the release of $H_2O$ and DMF. The figure b show the derivative of the TGA profiles of the material.
Figure 3.07. XRD profile of the as-synthesized Ni-Ox-MOF (a) and Pawley refinement of this profile (b). a) The pattern displayed as synthesized Ni-Ox-MOF 
b) Refinement of the XRD profiles to adjust it to a similar pre-studied crystalline profile.
Table 3.04. Cell parameters and space group.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ [Å]</th>
<th>$b$ [Å]</th>
<th>$c$ [Å]</th>
<th>$\beta$</th>
<th>$SG$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Ox-MOF</td>
<td>6.67</td>
<td>8.85</td>
<td>12.41</td>
<td>84.29</td>
<td>P2/m</td>
</tr>
</tbody>
</table>

To learn about the Ni-Ox-MOF stability, the material was degassed in vacuum at 75 °C and 200 °C in the Anton Paar XRD high temperature stage, and later were collected both profiles in vacuum at room temperature. The XRD profiles corresponding to both heat treatments are shown in Figure 3.08. By simple inspection it is evident that in the Ni-Ox-MOF after heating at 75 °C was preserved the layer structure; however, when heating at 200 °C, the structure collapsed.

3.2.4. Proposed layer structure

The oxalate group main linkages are monodentate, bidentate, bis-bidentate and bridging bis-bidentate (Cotton et al. 1999). The layers could be formed by a two-dimensional (Figure 3.09) oxalate bis-bidentate and oxalate bridging bis-bidentate nickel coordination polymer (Wang et al. 2006). In these layers the nickel nodes have only five bonds linked to the oxalate ion (Figure 3.09); one of the bonds are unsaturated. On the other way, a layer shaped with bis-bidentate and bidentate ligands, had the six nodes linked to the oxalate ion, with no possibility to grow to a third dimension and form a porous material (Keene et al. 2009).

The DMF molecules could act as pillars, linking the remaining bond through the oxygen. In this research was proposed that the Ni-Ox-MOF could be shaped by the
Figure 3.08. Layers formed by oxalate bridging-bis-bidentate ligands and Ni-DMF Complex. The layers could be formed by a two dimensional oxalate bis-bidentate and Ni-DMF complex, as showed in this figure.
Figure 3.09. Layers formed by oxalate bridging-bis-bidentate ligands and Ni-DMF Complex. The layers could be formed by a two dimensional oxalate bis-bidentate and Ni-DMF complex, as showed in this figure.
oxalate bis-bidentate and oxalate bridging bis-bidentate layers (Figure 3.09) connected by DMF molecules perpendicularly coordinated to the nickel included in the layers. This is consistent with the Raman data.

3.3. Adsorption study

3.3.1. Ni-Ox-MOF adsorption space morphology characterization

A very good probe to test the adsorption space of microporous materials is the carbon dioxide molecule (Dunne et al. 1996; Cazorla-Amoros et al. 1998; Bacsik et al. 2010). As previously showed, the Ni-Ox-MOF is a material stable under heating up to about 100 °C. Also was proposed that this framework should be composed of micropores that pervade the crystal lattice as was suggested by the TGA data. Carbon dioxide adsorption could be applied to test the morphology of the adsorption space of the Ni-Ox-MOF.

The study of carbon dioxide adsorption was obtained in an upgraded Quantachrome Autosorb-1 automatic physisorption analyzer. The adsorption isotherms of CO₂ was at 273K, in samples degassed at 75°C (348K), during three hours in high vacuum (10⁻⁶ Torr). Was gathered the adsorption data in the relative pressure range, 0.00003 < P/P₀ < 0.03; where, the micropore filling takes normally place (Roque-Malherbe et al. 2010), since the carbon dioxide vapor pressure, P₀, at 0 °C (273 K), is very high, that is: P₀ = 26,141 Torr.

To calculate the micropore volume and the parameters characterizing the energy of adsorption, was applied the Dubinin-Radushkevitch (DR) adsorption isotherm equation; since, a vast amount of data indicates that the adsorption process in the micropore range is described by it (Roque-Malherbe et al. 2010; Roque-Malherbe 2010).

This adsorption isotherm equation can be represented as follows (Bering et al. 1972; Dubinin 1975; Roque-Malherbe 2000):
\[
\ln \frac{\alpha_n}{\alpha_n^0} = \ln \frac{\alpha_n}{\alpha_n^0} - \frac{RT}{E} \ln \frac{P_0}{P}^\gamma
\]  
(7)

Where, \( n_a \), is the amount adsorbed; \( P_0/P \), is the inverse of the relative pressure, \( P_0 = 26.141 \) Torr; \( E \), is a parameter named the characteristic energy of adsorption; and, \( N_a \) is the maximum amount adsorbed in the micropore volume.

Thereafter, the \( \text{CO}_2 \) adsorption data was linearly fitted to equation “7” (Figure 3.10) and the calculation of \( N_a \) and \( E \) as the best fitting parameters. Then, the micropore volume was calculated applying the Gurvich rule, equation “6”. To better understanding, refer to the following description:

CO\(_2\) adsorption data was linearly fitted to DR adsorption isotherm equation:

\[
\ln \frac{\alpha_n}{\alpha_n^0} = \ln \frac{\alpha_n}{\alpha_n^0} - \frac{RT}{E} \ln \frac{P_0}{P}^\gamma
\]

\[ y = B + mx \]

The micropore volume was calculated applying Gurvich rule for \( \text{CO}_2 \) adsorption:

\[
W_{\text{MP}} = N_a V_L
\]  
(8)

Where \( V_L = 41.3 \) cm\(^3\)/g, is the molar volume of \( \text{CO}_2 \) at 273K. Solved the linear equation for \( B \), gives the \( \text{Ni-Ox-MOF} \) pore volume:

\[
W_{\text{MP}} = 0.08 \text{ cm}^3/\text{g}
\]

### 3.3.2. Isosteric heat of carbon dioxide adsorption on \( \text{Ni-Ox-MOF} \)

The parameters calculated with the DR adsorption isotherm equation are not only to evaluate the micropore volume of the sample, also describe the adsorption interaction between the adsorbate and the adsorbent. To evaluate this interaction was used the characteristic energy of adsorption (\( E \)), calculated by fitting equation “7”, to the data. The quantitative evaluation of the interaction of carbon dioxide was carried out with help of the isosteric heat of adsorption (\( q_{iso} \)), (Roque-Malherbe 2010). To calculate, \( q_{iso} \) is as follows
Figure 3.10. Dubinin-Radushkevich (DR) plot of the adsorption isotherm of CO$_2$ on Ni-Ox-MOF at 273K. The figure shows the CO$_2$ isotherm adsorption, with this data is possible determine the microporous volume.
(Bering et al. 1972; Roque-Malherbe et al. 2011):

\[
q_{iso}(\theta) = -\Delta G(\theta) + EF(T, \theta)
\]

(9)

Where: \( \theta = \frac{n_a}{N_a} \); \( E \), is the adsorption energy; \( n_a \), is the amount adsorbed; and \( N_a \), is the maximum amount adsorbed. Thereafter, was obtained that the \( q_{iso}(0.37) = 1.16E \).

The formerly described adsorption data indicated that the interaction of the carbon dioxide molecule with the Ni-Ox-MOF is not strong, but is accepted for the adsorption of carbon dioxide (Dunne et al. 1996; Roque-Malherbe et al. 2010; Roque-Malherbe, 2010; Bacsik et al. 2010; Roque-Malherbe et al. 2011). It is in general acknowledged that this physical adsorption process attach the carbon dioxide molecule inside the micropores, by the influence of the dispersive forces and the attraction of the quadrupole interaction (Dunne et al. 1996; Roque-Malherbe 2010).

3.3.3. DRIFTS study of the surface chemistry of the Ni-Ox-MOF applying carbon dioxide as test molecule

Another significant application of carbon dioxide adsorption as a means for the characterization of the surface chemistry of adsorbents is the study of the infrared spectra of adsorbed carbon dioxide; since, it is a small weakly interacting probe molecule very useful for the study of the acids and basics properties of solid surfaces (Lavalley et al. 1996; Zecchina et al. 1996; Knozinger et al. 1998; Bonelli et al. 2000).

The free carbon dioxide molecule show 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 et al. 1996; Zecchina et al. 1996; Knozinger, et al. 1998; Bonelli et al. 2000). The \( \nu_2 \) and \( \nu_3 \) modes are infrared active, whereas \( \nu_1 \) is only Raman active, in the free molecule (Bonelli et al. 2000).
However, when a carbon dioxide molecule interacts with a surface it is not more a free molecule, and its symmetry is lowered, as a result the \( \nu_1 \) mode becomes infrared active, and a small band is observed (Knozinger et al. 1998), whereas the other modes undergo moderate changes in wave number (Bonelli et al. 2000).

The asymmetric stretching vibration, \( \nu_3 \), of the adsorbed carbon dioxide molecule is observed at 2338 cm\(^{-1}\) (Figure 3.11). This peak corresponds to carbon dioxide physically adsorbed inside the Ni-Ox-MOF (Roque-Malherbe et al. 2010). That is, the absorption band observed at around 2338 cm\(^{-1}\) (Table 3.05) is the result of the attachment of the carbon dioxide molecule by dispersive and electrostatic forces to the adsorption space defined by the Ni-Ox-MOF micropores. The band at about 2324 cm\(^{-1}\) (Table 3.05) is normally assigned to a combination band (Bonelli et al. 2000).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \lambda^1 ) [cm(^{-1})]</th>
<th>( A_1 ) [%]</th>
<th>( \lambda^2 ) [cm(^{-1})]</th>
<th>( A_2 ) [%]</th>
<th>( \lambda^3 ) [cm(^{-1})]</th>
<th>( A_3 ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Ox-MOF</td>
<td>2338 cm(^{-1})</td>
<td>24</td>
<td>2324</td>
<td>26</td>
<td>2362</td>
<td>50</td>
</tr>
</tbody>
</table>

3.4. Magnetic study

With the term magnetochemistry (Carlin 1986; Kahn 1993; Bertotti 1998; Miessler 1998; Orchard 2003) is designed the study of the magnetic properties of materials. One parameter that allows an assessment of the magnetic properties of materials is the effective magnetic moment, \((\mathbf{\mu})_{\text{eff}}\). This parameter measured in Bohr magnetrons \((\mu_B)\)
Figure 3.11. DRIFTS spectrum CO$_2$ adsorbed on Ni-Ox-MOF. A) The band is normally assigned to a combination band. B) The band characterizes the interaction of the carbon dioxide molecule with the Ni$^{2+}$ located in the framework of the Ni-Ox-MOF.
considering only the spin of the unpaired electrons of the magnetic centers present in the material under study, is given by (Carlin 1986):

\[ \mu_{\text{eff}} = 2.0023 S(S+1) \bar{\mu}_B \]  

(10)

Where \( \mu_{\text{eff}} \) is the effective magnetic moment; \( \mu_B \) Bohr magnetrons; and \( S = 1/2 \), for one unpaired electron, \( S = 1 \), for two unpaired electrons and so on. If was taking in count the spin and orbital angular momentum in the Russell-Saunders coupling approximation; then the effective magnetic moment \( \mu \), measured in Bohr magnetrons \( \mu_B \) is calculated with the following equation (Orchard 2003):

\[ \mu = \sqrt{4S(S+1) + L(L+1)} \bar{\mu}_B \]  

(11)

Where, \( S \), has the meaning previously stated and \( L \) is the total orbital angular momentum.

The magnetization curves of the Ni-Ox-MOF measured with the help of the VSM is reported in Figure 3.12. The calculation of the effective magnetic moment of the Ni-Ox-MOF is, \( \mu_{\text{eff}} = 4.9 \mu_B \).

The most significant structural characteristic in shaping the paramagnetic behavior of a material is the number of unpaired electrons in the compound. In the synthesized MOF, was found by Raman spectroscopy that nickel cations are coordinated in octahedral \( \text{(NiO}_6 \text{)} \) (Kalyani et al. 2005) and distorted octahedral or pentacoordinated \( \text{(NiO}_5 \text{)} \) (Park et al. 2006) in two valence states, specifically, \( \text{Ni}^{2+} \) and \( \text{Ni}^{3+} \). In practice \( \text{Ni}^{2+} \) in octahedral coordination, in complexes, showed the following effective magnetic moment range, \( 2.9 < \mu_{\text{eff}} < 3.4 \) (Chaudhary et al. 2010). That is a low value in comparison to data obtained in this research. If was considered the Russell-Saunders coupling (Lide 2002), with, \( S = 1 \), and \( L = 3 \), in this case the calculated effective magnetic moment yielded, \( \mu_{\text{eff}} = 4.47 \), a value approximate to those measured. However, this electronic configuration is highly improbable, since in solids, \( L \), is normally zero. Recently (Chaudhary et al. 2010), was
reported for a pentacoordinated Ni(II) complex a $\mu_{\text{eff}}$ value of $4.36\mu_b$. That is, an amount closer to those measured in this investigation. Finally, for Ni$^{3+}$, the electronic configuration is, [Ar] 3d$^7$; then, $S = 1.5$, then the spin only equation yields $\mu = 2.0023 \sqrt{1.5(1.5 + 1)} \mu_b = 3.87\mu_b$. Thereafter, the magnetic study is consistent with the Raman results.
Figure 3.12. Magnetization Curves of Ni-Ox-MOF. The figure shows the paramagnetic magnetization curves of the Ni-Ox-MOF. The magnetization curve, magnetization (M) versus field strength (H) was carried out at room temperature (300 K).
Chapter Four
Conclusions

In the present work were synthesized 35 materials applying the center and connection method. One of these materials the metal node was nickel and the organic linker oxalic acid. This material was very sensible to the preparation conditions. However, was obtained a consistently porous material. This material was thoroughly studied with DRIFTS, Raman, TGA, precise XRD measurements, CO$_2$ adsorption at 273 K and with a VSM.

The most important inferences made through the examination of the DRIFTS and RS spectra were: the bis-bidentate oxalate ligand was found in the frameworks of the hydrated and dehydrated Ni-Ox-MOF; water was included in the pores of the as-synthesized Ni-Ox-MOF; and it was released during dehydration at 75 ºC; DMF was present in the as-synthesized and dehydrated Ni-Ox-MOF and the nickel cations were located in two coordination Ni$^{2+}$ and Ni$^{3+}$. The main issues that can be inferred from the analysis of the TG profile were: the synthesized Ni-Ox-MOF was porous; in the as-synthesized state the pores were filled by water and after water release DMF was liberated, and subsequent to DMF release the material was decomposed. The conclusions made with the help of the XRD data were: the Pawley decomposition of the XRD profile indicated that, with high probability, the Ni-Ox-MOF crystallized in the monoclinic P2$_1$/m space group, with a framework made of layers and the Ni-Ox-MOF dehydrated at 75 ºC preserved its structure.

The most important matters deduced with the help of the adsorption data were: it was confirmed that the synthesized Ni-Ox-MOF was porous after degassing; the estimated pore volume was, $W_{MP} = 0.08 \text{ cm}^3/\text{g}$; the Ni-Ox-MOF after heating at 75 ºC exhibited a
stable microscopic volume. That is, the tested material had a permanent porosity and the adsorption field corresponded to a physical adsorption process.

The study by DRIFTS of CO$_2$ adsorption demonstrated that: the Ni-Ox-MOF after heating at 75 °C had space to accommodate carbon dioxide molecules. The measurement of the sample effective magnetic moment confirmed that the Ni cations composing the layer of the Ni-Ox-MOF were located in octahedral and pentacoordinated sites. Finally a search in different databases confirms that the Ni-Ox-MOF is unique and none used in other investigations.

After the study, was submitted an article of this research in collaboration with Dr. Rolando Roque-Malherbe, Dr. Agustin Rios, Dr. Cesar Lozano, Dr. Luis Fuentes, Pedro Fierro and Geydi Garcia. Actually Pedro Fierro is using the Ni-Ox-MOF, to create sensors at University of Puerto Rico Mayaguez Campus, with a high chance of achieving patent the sensor.

This research develops a platform for further development of MOF materials with academic and industrial interests. The use of a cost effective carbon dioxide adsorption methodology, by using non expensive chemical materials in the synthesis of MOF’s may be attractive to industries and pharmaceuticals with high CO$_2$ emissions, especially if this porosity and magnetic framework could be used for industries as Sensor with electrostatic interaction on CO$_2$ molecules and the framework atoms.
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Appendix One

Instrumentation

A-1.01. X-Ray Diffraction (XRD). The equipment D8 Advance, Bruker AXS showed in this picture, report important information for characterize the sample.
A-1.02. Thermogravimetric Analysis (TGA). The TA Instrument, model TA, Q-500 is used for characterize the material, because it allows knowing of the weight loss of the sample, decomposition temperature and porosity of the material under studied.
A-1.03. Infrared Spectrometer (DRIFTS). The Diffuse reflectance infrared Fourier is a Thermo Scientific Nicolet iS10 FTIR Spectrometer used for. It was used to characterize the material.
A-1.04. RAMAN Spectometer (RS). The Renishaw Raman microspectrometer RM2000 system, is used for characterization.
A-1.05. The quantachrome Autosorb-1 (AS 1). The equipment showed in this picture was used to monitory the carbon dioxide adsorption and determine the pore volume.
A-1.06. Vibrating sample magnetometer (VSM). The equipment Lakeshore 7400 series, showed in this picture was used to determine magnetic properties of the sample.