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Synthesis of Nanostructured Materials for Storing Hydrogen as an Alternative Source to Fossil Fuel Derivatives

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Additional information is available at the end of the chapter

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Abstract

The decline in global reserves of fossil fuels due to the increasing energy demand has caused the petrochemical industry to be interested in finding new energy sources. An alternative that should be considered is the technology based on hydrogen as it is friendly to the environment and its combustion is greenhouse.

The technology based on hydrogen considers the synthesis of metal-organic materials that have the ability to store, although this phenomenon (storage) is one of the biggest problems to overcome. For this reason, options synthesized for storing materials are provided in this chapter of Book Two. These materials are considered nanostructured systems with specific features in 2D and 3D. The synthesized materials are tetracyano-niquelates ($[M(H_2O)_2(Ni(CN)_4)(H_2O)_n]$ $M = \text{manganese, cobalt, and nickel}$) and hexacyano-cobaltates ($(M_3[Co(CN)_6] \cdot 2xH_2O)$; $M: \text{manganese, nickel, cobalt, zinc, cadmium, and copper}$), both systems with individual cavities that require study and characterization. Moreover, in this chapter, a thermogravimetric characterization is performed in order to establish the activation energy of the mobility of water molecules contained in the cavities, relevant information to establish the energy barrier to overcome in the storage of hydrogen.

Keywords: Fossil fuel, hydrogen, nanoporous, thermogravimetry, activation energy

1. Introduction

In recent years, micro-porous and nanocomposites have been wide, and there are special interests in specific areas in order to generate improved technological processes such as separation, gas adsorption, ion exchange, and heterogeneous catalysis, to mention some of them [1, 2].

Particularly in the separation and gas adsorption area in microporous and nanosystems, research has focused on hydrogen's adsorption and storage as an alternative energetic alternative resource since this element might become a long-term fossil fuel substitute because its caloric power is three times higher than gasoline (142 kJ/mol). It is noteworthy that when the hydrogen is at room temperature in its supercritical state ($T_c = 32.7^\circ \text{K}$), storage is difficult, hence the importance of finding new porous materials having cavities with the ability to store it safely. Similarly, once stored, it can be used in mobile systems (automotive), avoiding the production of greenhouse gas emissions [3].

Studies on porous media properties have focused mainly on inorganic materials such as zeolites or carbon-based materials such as activated carbons, the last one having a high porosity on one side and an irregular pore, while zeolites have opposite characteristics [4].

In order to generate a material having defined pores and specific physicochemical properties, the interest is held in the synthesis of new porous materials showing specific conditions from defined synthesis models, examples of these are as follows: (i) layered systems (2D), tetracyano-niquelates attached to a metal transition $[\text{M}(\text{H}_2\text{O})_2(\text{Ni}(\text{CN})_4)_n(\text{H}_2\text{O})]$, $\text{M} = \text{Co}, \text{Ni}, \text{Mn}$, known as Hoffmann-type compounds; and (ii) latticed porous materials, hexacyano-cobaltates bound to a transition metal $[\text{M}_3[\text{Co}(\text{CN})_6]_2 n\text{H}_2\text{O}]$, $\text{M} = \text{Co}, \text{Ni}, \text{Mn}, \text{Cd}, \text{Cu}, \text{Zn}$, known as Prussian blue analogue materials.

The importance of lamellar materials known as two-dimensional (2D) lies in the ability to include molecules in their interlamellar spaces known as guest molecules, with the sole purpose of generating pores or cavities with specific characteristics according to the same properties of the included molecule, generating a three-dimensional network, in addition, to be able to store various molecules such as H_2 and CO_2 in the pores obtained. The transformation of a layered structure in a porous structure throughout a molecular spacer insertion was first introduced into the clay mineral smectite to overcome the limitations of the size of the cavities in zeolites for the new materials obtained [5].

The proposed 2D systems have water molecules between the sheets, joined by the system for various attractive forces. There are two types of water molecules included in the material, some are called coordinated water molecules, which are forming bonds with transition metals present in the sheets and play the role of guest molecules to form the pillars of the final structure. Additionally, there are others known as zeolitic water, which are placed in the cavities or interlamellar region linked by hydrogen bond type interactions.

The water molecules (coordinated and zeolite) are also in the hexacyano-cobaltates, but the interaction with the system is weaker so the energy required to abandon the system is lower compared with the 2D systems.

Another important feature of layered systems is its ability to crystallize into three different phases known as L0, L1, and K [6, 7, 8]. All the structures contain water molecules between blades, and each phase has a different number of water molecules. The structural configuration that adopts the set of water molecules and its interaction with the crystal lattice is the cause of the three different phases.

Latticed porous materials are crystallized in a cubic cell (Fm-3m) and have between 10 and 13 water molecules (coordinated zeolite) per unit cell. In these structures, the transition metals (Co, Mn, Cd, Zn, Cu, and Ni) have the center of inversion, and Ni atoms are in a plane of symmetry [7]. Known latticed porous materials (hexacyano-cobaltates) as Prussian blue analogue materials are interesting to form windows and pore volumes suitable for the separation and storage of small molecular forms, as in the case of the hydrogen molecule [9, 10]. In both families, the main objective is to generate materials that provide these properties and specific characteristics such as pore size, shape of the window, pore volume of adsorption, etc., as this will dictate whether it is a functional material to be used as molecular sieve to catch species among its pores.

Once the structures of porous materials are defined, the property characterization of these is critical because it will determine whether the guest molecules may or may not remain in such pores. For this reason, special emphasis must be taken on the study of the interactions of the water molecules (coordinated and zeolitic water molecules) partially hosted on both materials and kinetic parameters involved in the dehydration process.

In the study of kinetics and their associated parameters, one of them is activation energy (E_a), which is the most relevant to study without leaving physicochemical aspects such as thermal stability and structural systems obtained from different aspects. There are several forms of useful characterization to define the structures and properties of materials under study. The use of thermal analysis is a fundamental technique, especially supported by high-resolution modulated thermogravimetric analysis (Hi/ResMTGA) supplemented with the technique of X-ray diffraction (XRD), which is the immediate basic characterization to provide relevant information and thus provide the monitoring structural changes during dehydration processes.

2. Porous systems

At the end of the 1990s, there were basically two types of porous materials: inorganic and carbon derivatives. In the case of the former, the two most important subclasses of materials with open structures are aluminosilicates (zeolites) and aluminophosphates (AlPO₄s); whose crystalline lattices offer permanent porosity to be stable before the removal of molecules of water of hydration. The market of zeolites is of several million tons per year, and it has success in a wide range of applications, especially in the petrochemical industry and the hydrocarbon separation, purification of gases and liquids, and the catalytic fragmentation of chain hydrocarbons long. Additionally, they have also been applied in ionexchange as detergent additives

and the separation of gases and solvents, for example, as "molecular sieves" to the dehydration of organic solvents.

In the case of activated carbons, they have large specific surface area as well as high porosity; however, they have a disordered structure. These materials are widely used in the processes of separation, catalytic converters, capacitors, storage of gas, and biomedical engineering applications [11].

2.1. Zeolites

Zeolites have been widely studied because of their H_2 storage capacity. For equal surface areas, there is a smaller capacity of absorption in the case of zeolites in comparison with the ones which are based on carbon structures.

Zeolites have structures mostly mesoporous, with volumes of relatively small microporous, which make them the least promising materials based on H_2 storage, as referred to in [12]. Their abilities range from 2% to 2.5% based on the weight of the lattice. Zeolites are crystalline aluminosilicates with a structure consisting of a three-dimensional combination of TO_4 -tetrahedra ($T = Si, Al$) linked together via oxygen atoms. The structural formula of zeolites can be expressed as [13] $M_{x/n} [(AlO_2)_x (SiO)_y] \cdot wH_2O$, where M is the exchangeable cation, n is the cation's valence, x and y are the total number of tetrahedra per unit cell, and w is the number of water molecules. The structure of zeolites presents channels and cavities of molecular dimensions, which are water molecules, adsorbates, and compensating cations' charge (negative charge created by the presence of AlO_4 structure). These channels and cavities give zeolites a porous structure, which allows these materials to have a very large internal surface compared to the external.

Some zeolitic materials pass through an intermediary laminating these precursors during their training, evidenced by their X-ray diffractogram. Zeolitic laminars are attractive candidates for pillarization processes, which could result in very interesting features such as microporous sheets and activity type zeolite, together with their properties such as mesoporous adsorbents.

Leonowicz et al. [14] proposed two sets of independent pores for the so-called zeolite MCM-22 type. One of the systems of pores is defined by sinusoidal and bidirectional channels; the other consists of large supercavities with a 7.1-Å free inner diameter A and an internal height of 18.2 Å. Figure 1 schematically illustrates the structure of MCM-22, where you can see the two systems of pores.

2.2. Structures of carbon-based materials

Materials with carbon-based structures offer potential to adsorb H_2 , values of relatively low density, appropriate chemical stability, and large pore structure, and they can be found in a wide variety of structural forms. These forms are closely related to the conditions of synthesis, carbonization, and activation, employed during its preparation [15]. Among the materials based on carbon are the so-called activated carbons (AC). In this type of material, the existence of a porous structure is determined by the spatial arrangement of the grapheme, which can be

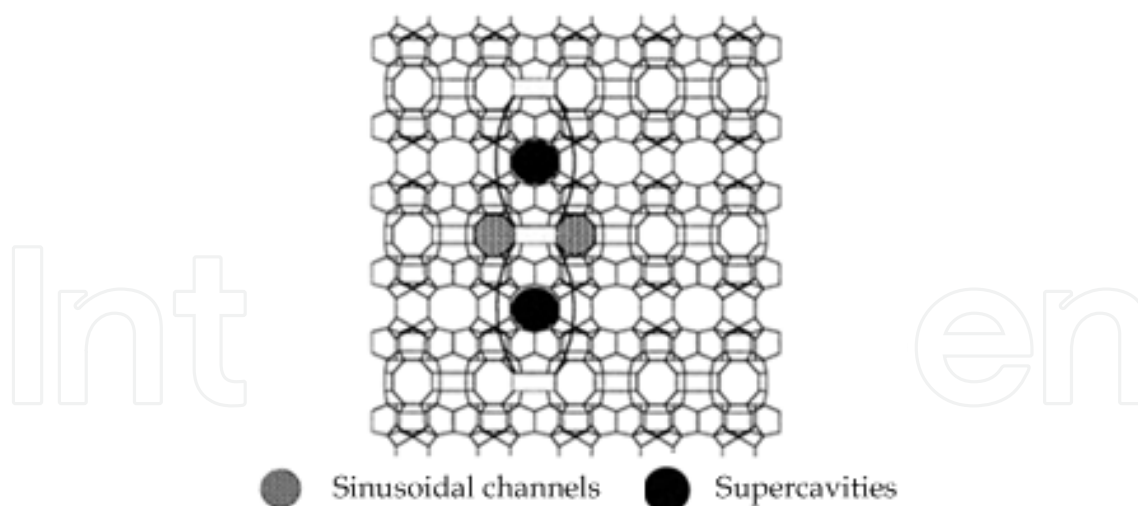


Figure 1. Diagram of the zeolite MCM-22 structure [1].

stacked to give place to the development of a porous structure relatively little polar. The adsorption/desorption processes of H_2 in such materials are characterized by a relatively rapid kinetics, and corresponding isotherms are hysteresis, in which results are attractive in systems that require a high-speed H_2 loading and unloading. However, the use of these materials is limited by highly dependent temperature and pressure adsorption capabilities [16, 17].

In materials based on structures of carbon, whose surface is not chemically modified, the physical adsorption of H_2 is only due to the existence of weak van der Waals adsorbent–adsorbate interactions. At environmental temperature, the energy corresponding to these interactions is similar to the energy of the thermal motion of the molecules of the gas, so by only decreasing the temperature, the adsorbent–adsorbate interaction energy becomes greater than the thermal movement, which decreases proportionally with the temperature [18, 19].

It has been reported that at low pressures, the amount of adsorbed H_2 increases with the increasing density in carbon nanostructures because the pores favor narrowing H_2 –surface interactions. At high pressures, the specific surface area available for the adsorption of H_2 is the determining factor, and the amount adsorbed increases by decreasing the material density [20].

2.3. Layered systems

Lamellar materials are solids with two-dimensional structures possessing atoms firmly linked together in two directions of space forming foil (planes), and they are weakly linked in the perpendicular direction among them. The region of weak interaction between the sheets is normally known as interlamellar region or gallery [21]. Many kinds of solid lamellar blades have electric charge due to substitutions of isomorphous ions of different network load. To reach the electrical neutrality of the structure, ions of opposite charge, normally solvated by water or other polar molecules, occupying the interlamellar region, are known as compensation ions. Layered solids have high surface areas between 100 and 1000 m^2/g . In many cases, the

interlamellar surface is accessible only to water and other small polar molecules that are capable of solvated ions of compensation.

The elimination of molecules of solvation by degassing at elevated temperatures results in a collapse of the interlamellar region, especially if interspersed compensating charge ions are small in relation to the occupied space; on the other hand, if the compensating charge ions are relatively large, they can have the role of pillars and prevent the collapse of the interlamellar regions when the middle of solvation is eliminated, resulting in solids called solid lamellar pillars. Figure 2 presents a system that shows some characteristics of layered solids.

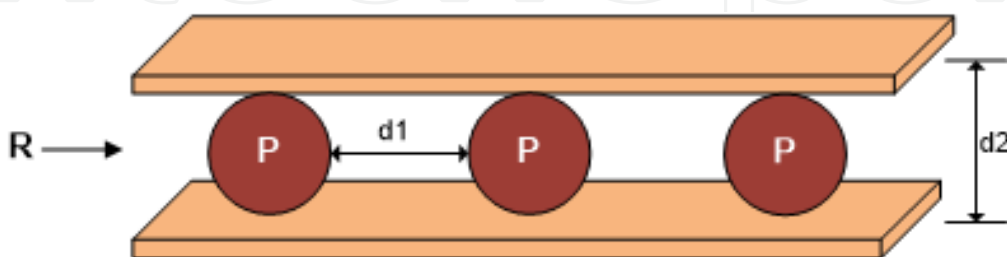


Figure 2. Representation of a layered solid pillared, wherein pores are defined by the height of the interlamellar space (d_2) and the lateral spacing (d_1) between the guest molecules or pillars (P). R denotes the interlamellar region.

Laminar solid pillars can be described as sandwich compounds serving three important criteria:

1. Interlamellar species must be sufficiently robust to promote the vertical expansion of the blades (d_2) and to prevent their collapse during any thermal process to which they are subjected.
2. The pillars must be sufficiently separated (d_1) to allow access to molecules. Simply expanding the blades to molecular size, collation of pillars, is not significant in relation to the properties of adsorption and catalytic behaviour of solid if the interlamellar region is fully occupied by pillars.
3. The blades must be rigid enough to maintain the separation desired between pillars. Otherwise, the flexibility of the blades could close gaps between pillar and pillar.

Lamellar surface area presented by solids (between 100 and 1000 m²/g) makes these materials an object of study important above all in the area of nanoscience and nanotechnology because they have been shown to generate opportunities in different fields of application, such as biomedical electronics, applications in the area of storage and energy conversion, and catalysis [22].

2.3.1. Host molecules (pillarization)

The basic function of the pillarization is to include molecules in the interlamellar region to obtain a three-dimensional porous system with well-defined and specific characteristics according to the material or molecules that are embedded as a result. The interaction host

species with active sites, which are normally present on the surface of the plates, is the driving force of the mechanism of formation of pillars in a structure laminating. These sites may be crystallographic positions or groups influenced by positive or negative charges, or sites with acid, basic, or polar character in general. The density of active sites on the surface on one side of the blade is expressed by the number of sites per cm^2 of surface layer.

The reciprocal value of the density of surface represents the average area per active site. This value, also called free area, is an important characteristic of a laminated solid. Knowing this, it is possible in many cases to predict whether the full collation of guest molecule stoichiometry is viable or not. In nature, the surface density and availability of the active sites is usually the same on both sides of the layers. However, in some cases, there are asymmetric blades.

The layout of the active sites in each side of the blade and its free area can be determined precisely when the blade structure is known.

In general, the pillarization process variables are as follows [23]:

1. Properties of the material, such as composition and location of the load on the blade
2. Nature of the agent formed with pillars
3. Ion exchange process
4. Subsequent treatments such as drying, cleaning, etc.

The most important parameters affecting the formation and the properties of the polynuclear cations as agent formed with pillars are as follows [24]:

- a. Metal ion concentration
- b. Basicity or degree of hydrolysis
- c. Preparation temperature
- d. Time and temperature aging
- e. Method of preparation

The water molecules in some materials tend to be regarded as pillars of the same due to interactions that generate with the transition metals present, and the study of these molecules provides information of the nature of the material.

Pillar materials include clay Al-montmorillonite and the Al-bentonite, which is used in gas-oil cracking and reactions of phenols hydroxylation reactions, respectively.

2.3.2. Tetracyano-metallates

In recent years, great efforts have been devoted to research directed toward the synthesis and characterization of multidimensional metal complexes with cyanide bridge groups [25]. The most common and controlled strategy at the time of preparing this type of system is in autoassembly specifically designed predecessors. They are normally used as a complex

cyanometallate that acts as a ligand and a complex of a metal transition coordination position for atoms of nitrogen from the groups free of cyanide (see Figure 3).

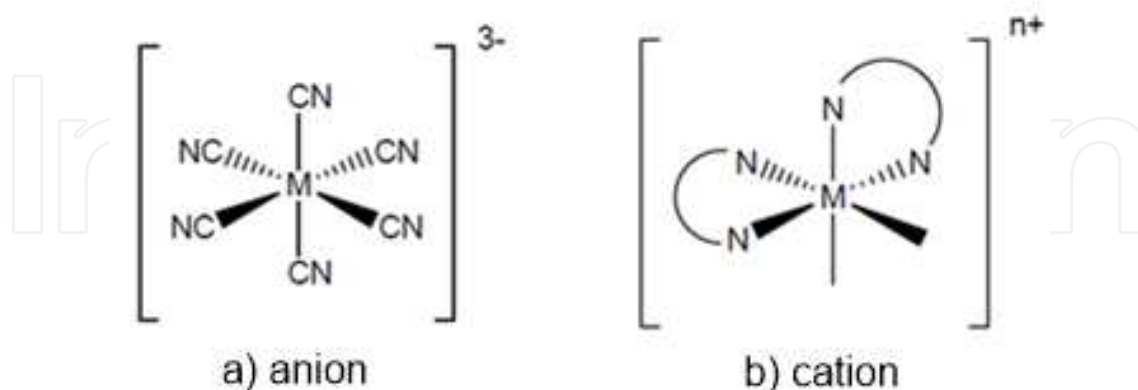


Figure 3. Assembly blocks of cyanometallate systems: (a) the anionic block $[M(CN)_6]^{3-}$, (b) the cationic block $[M'L_2]^{n+}$.

Tetracyano-metallates and hexacyano-metallates (Prussian blue analogues) are part of the materials with cyanide bridge group. Anion cyano (CN^-) is a functional group with the ability to be simultaneously coordinated by both atoms at different cations. This makes it an excellent molecular block to generate different lattices structural at 1, 2, and 3 dimensions. The chemical bond in the cyanometallate in networks is the linear bridge $M-CN-M$; M = metal, with a distance $M-M$ approximately 5 to 6 Å.

When linear polyhedron $[Ag(CN)]$ acts as a binding between two centers of greater coordination, the others are connected to 2D or 3D networks [26]. In the union of blocks, the same metal center generates various structural patterns, showing the variability of crystal structures. There are other types of binders such as NH_3 and H_2O , which play an important role in the 3D structure stabilization and the volume of empty space that is occupied by species guests.

The initial structure of compounds including cyanometallate $[Ni(CN)_4]^{2-}$. The flat square is the clathrate of Hoffmann's formula $[Ni(NH_3)_2Ni(CN)_4]$, where a 2D network shares a corner in units of $[Ni(CN)_4]^{2-}$, separated by NH_3 binders. The resulting structure is in 2-dimensional (2D) structure, with the distance between blades occupied by the guest of benzene molecules that are perpendicular to the blades.

Materials with transition metals have been developed, which provide specific features to the two-dimensional network for the sole purpose of including pillars to further the creation of the same form, providing structures with defined pore and known dimensions. Such is the case of the tetracyano-niquelates. Although they are based on the principle of a structure-type Hoffmann, including transition metals such as Co, Mn, and Ni, the result is to have water molecules in the central part or interlamellar, which serve as pillars of the main structure.

The formation of tetracyano-niquelates involves square plane anion $[Ni(CN)_4]^{2-}$, with four sites attached to metal ions $M = Ni, Co, Mn$, via the nitrogen atoms of the cyano group. To have the octahedral geometry, the block has two further binders. For this particular case, those

additional ligands bind to water molecules to complete the coordination sphere as shown in Figure 4. The consecutive joining molecular building blocks of this two-dimensional space can build a two-dimensional structure.

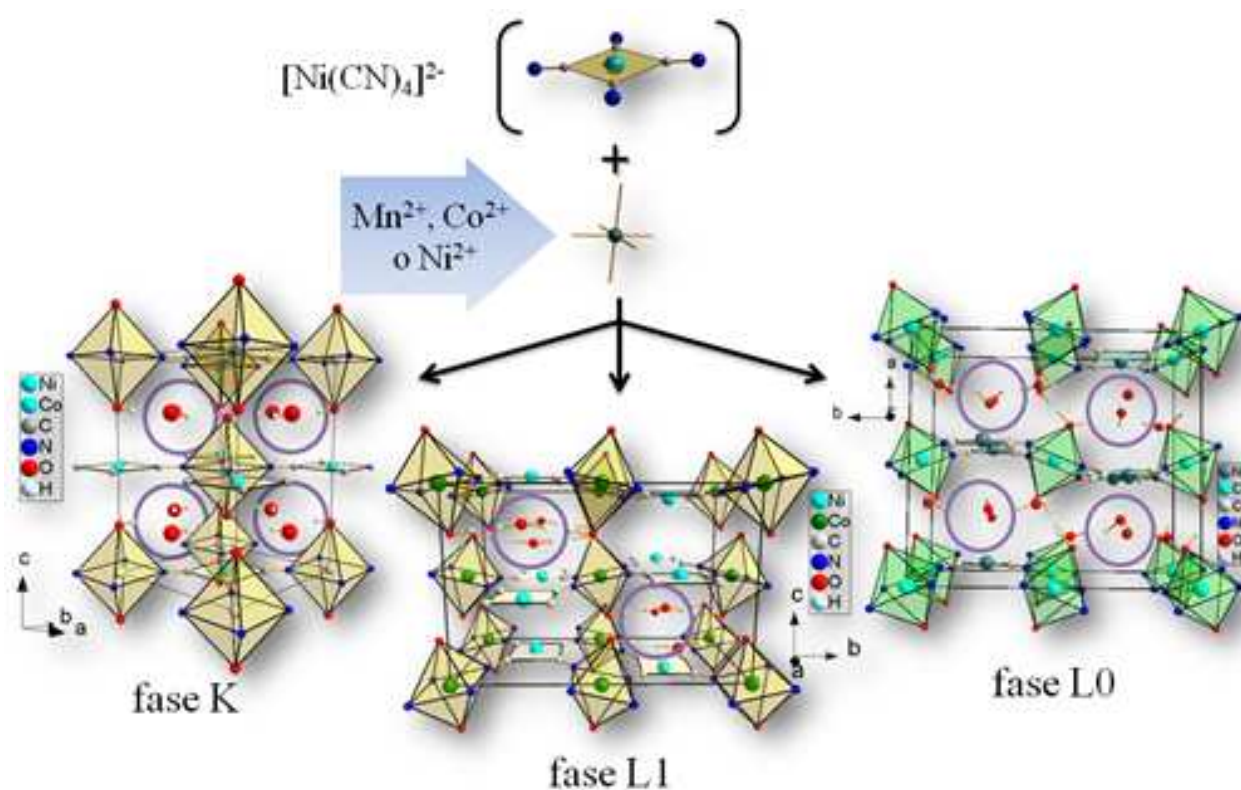


Figure 4. Schematic representation of the assembling process for obtaining K, L1, and L0 phases. The zeolite-like water molecules are highlighted with open circles in the interlayer region.

2.4. Prussian blue analogues

Historically, the “iron blue” is known as (ferric ferrocyanide) “soluble” Prussian blue and the blue is known as “insoluble” Turnbull (ferrous ferrocyanide); however, all recent studies conclude that both are identical. The formation of this pigment can be written as



Its low solubility evidence is the polymeric nature of the solid product. Due to the 4:3 ratio of Fe (III) and Fe (II), 25% of the sites of Fe (II) are vacant. The occurrence of more than one oxidation state of the same element in a particular compound is defined as a mixture of valence. Due to the partial relocation of electrons from valence, the Prussian blue is a semiconductor.

Depending on the properties desired in the product, many routes of preparation are known. Given its porous nature, it has a certain zeolitic character, which allows you to store small molecules in their cavities [27].

They have now developed materials under the same principle of formation of Prussian blue by changing the formation of anionic block metals. The hexacyano-cobaltates (of the family of the hexacyano-metallates) are an example of these materials considered as Prussian blue analogues.

2.4.1. Hexacyano-metallates

The hexacyano-metallates of the transition metals are microporous molecular family, whose structures are based on a three-dimensional arrangement of chains $M-C\equiv N-M$. Metal M (inner metal), linked to the carbon atom, is always forming octahedral molecular blocks $[M^{n+}(CN)_6]^{6-n}$ as the metal M (external metal) acts as an assembler of the octahedral blocks and possibly octahedral or tetrahedral coordination [28, 29].

The first studies of H_2 adsorption in this polymer-coordinated family were published in 2005, simultaneous with the reports of Long et al. [30] and Kepert et al. [31], who studied the formula of general Prussian blue analogues $M_3 [Co(CN)_6]_2$, known as hexacyano-cobaltates as the internal metal cobalt and being able to change the external metal; $M = Mn, Fe, Co, Ni, Cu, Zn$, and Cd .

Figure 5 shows the structure of a Prussian blue analogue in the cubic phase due to the octahedral coordination adopted by the external metal.

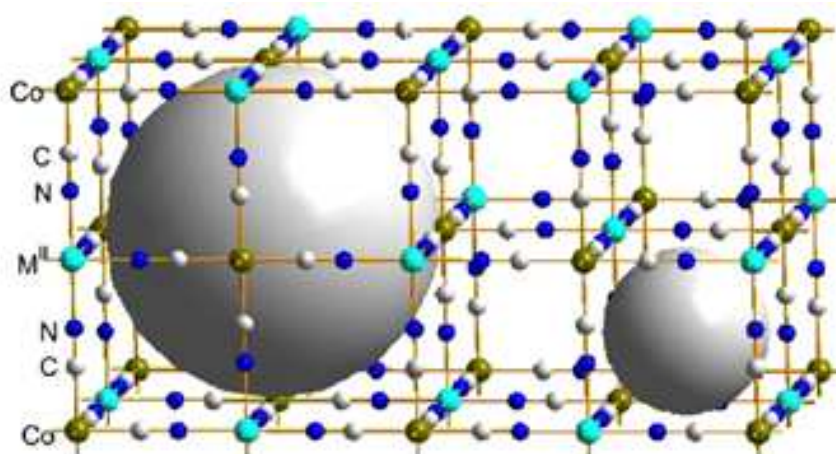


Figure 5. Porous framework for the cubic form, by a hexacyano-cobaltates and a transition metal [30].

2.5. Materials synthesis

Interest in synthesizing nanostructured materials has led to the study of families with specific characteristics. Here two families are addressed: (1) the family of tetracyano-niquelates (II) [with three different external metals, that is, (Co^{+2}) cobalt, nickel (Ni^{+2}) , and manganese $(Mn$

⁺²], which is synthesized in L1, K, and L0 phases for three metals, and (2) the hexacyano-cobaltates (III) [with six different external metals, that is, cobalt (Co⁺²), nickel (Ni⁺²), manganese (Mn⁺²), copper (Cu⁺²), (Zn⁺²) Zinc, and cadmium (Cd⁺²)]. X-ray diffraction (XRD) should be used to check the phases and structures of these materials.

Modulated thermogravimetry (MTG) is used for the kinetic analysis of dehydration, and scanning electronic microscopy (SEM) is used to analyze the morphology of the materials during the process of dehydration.

2.5.1. Tetracyano-niquelates synthesis (lamellar materials)

Figure 6 shows the procedure for the synthesis of materials $[M(H_2O)_2(Ni(CN)_4)(H_2O)_n]$: $M = Ni, Co, Mn, n = 1, 2, 4$], which are obtained by the method of precipitation.

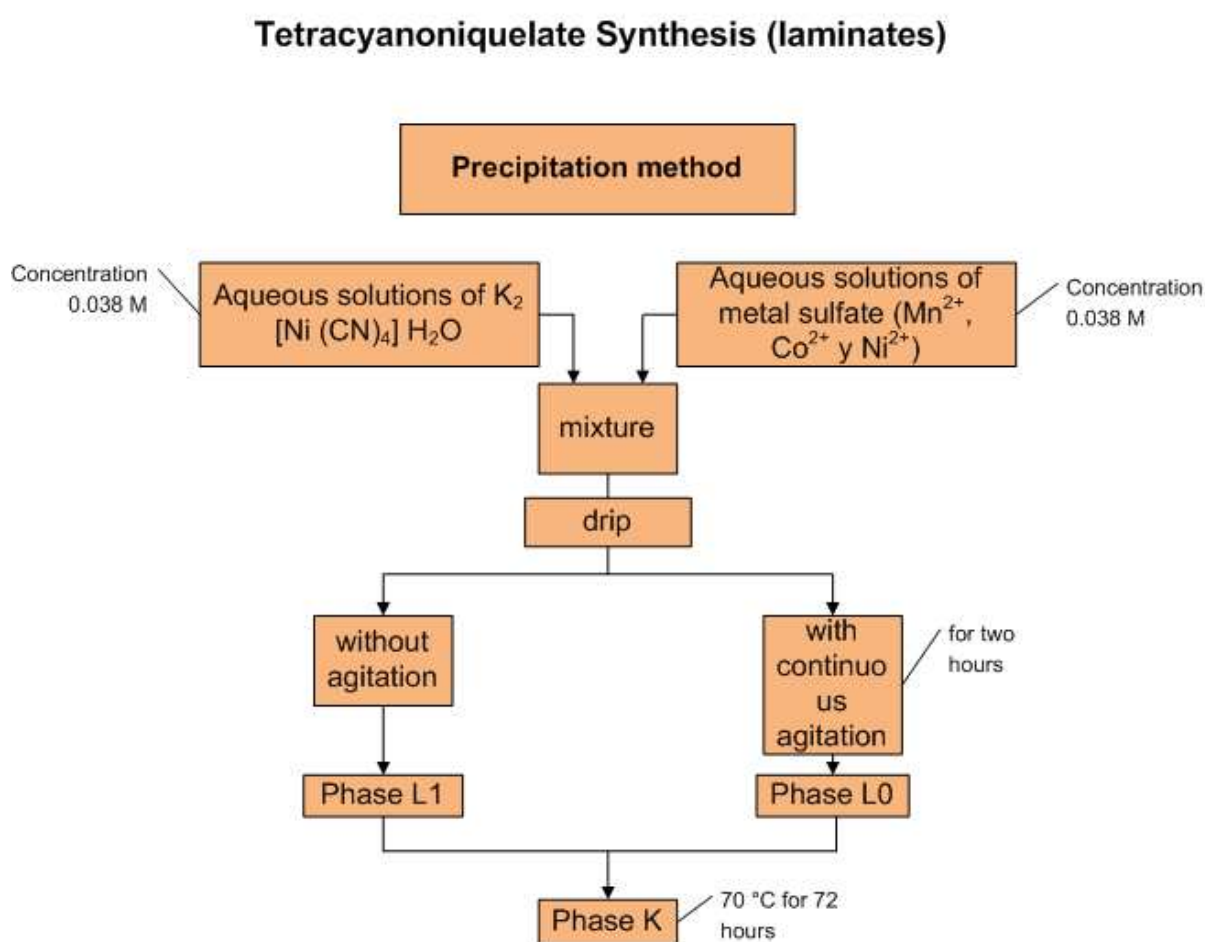


Figure 6. Materials synthesis $[M(H_2O)_2(Ni(CN)_4)n(H_2O)]$: $M = Ni, Co, Mn; n=1,2,4$].

Once the corresponding blends are obtained, the resulting precipitated solid is separated by centrifugation, and the solid fraction obtained is repeatedly washed with distilled water to remove the excess ions and then left at room temperature air-dried to constant weight.

2.5.2. Hexacyano-cobaltates synthesis (porous materials)

Figure 7 shows the hexacyano-cobaltates synthesis process.

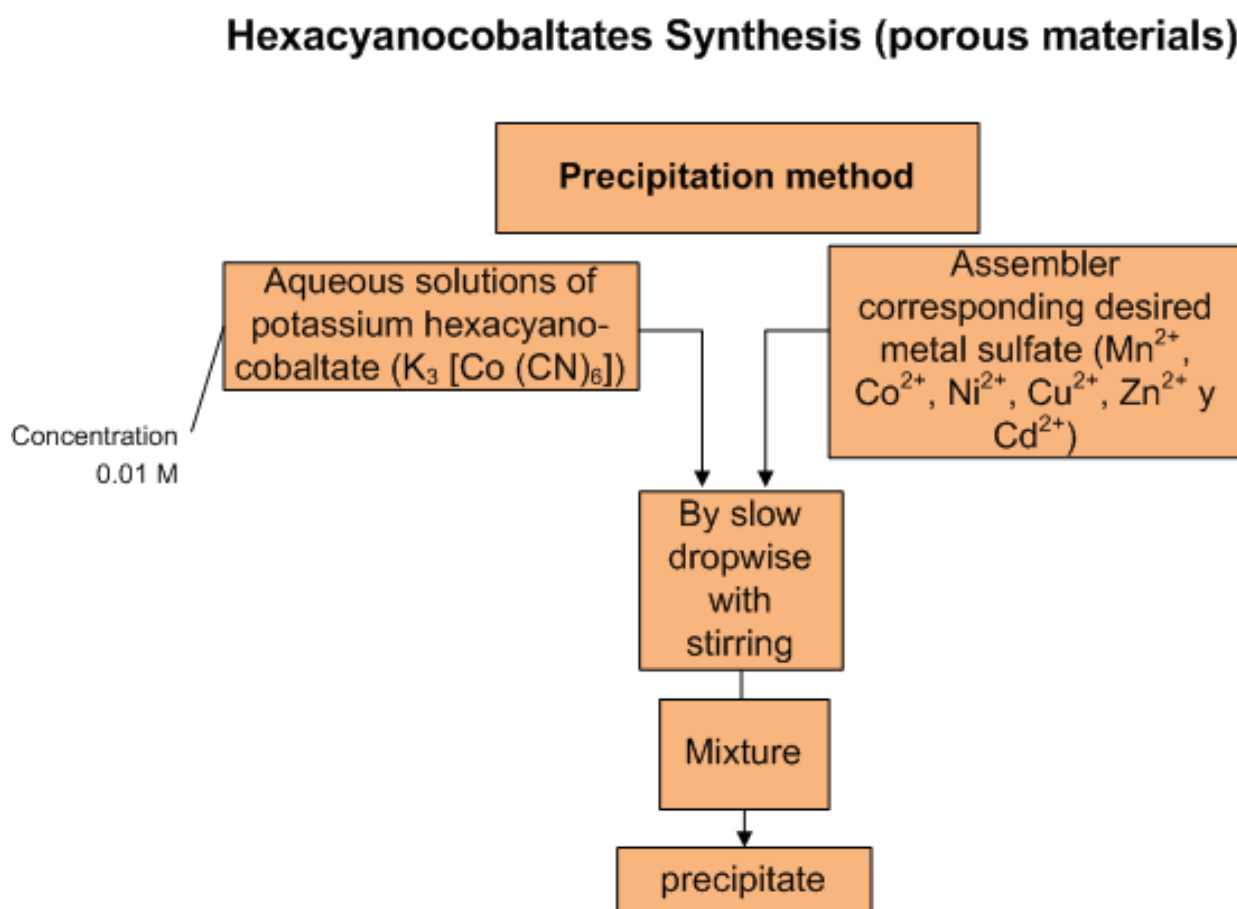


Figure 7. Hexacyano-cobaltates synthesis.

The amount in excess of the metals involved guarantees the formation of a single phase. The resulting precipitate remains for a week in the mixture. Then it is separated by centrifugation. The solid fraction is repeatedly washed with distilled water to remove the excess ions, and finally the material is air-dried to constant weight.

2.6. Characterization techniques

To ensure that the phases that have been obtained during the synthesis are correct, various techniques are used. This chapter will talk about three of them, which allude to the obtaining of the phases. One of them is X-ray diffraction (XRD), which is used under two aspects: to get the diffraction patterns of the synthesized material and to ensure that the crystalline phases of the structures meet the required specifications, which includes synthesis. On the other hand, this technique is used to perform a constant monitoring during the dehydration of materials and thus observe the structural change to drop out of the same water molecules present in the

system. Coupled with this technique, an SEM was used in order to follow up on the morphology of the material during the synthesis when dehydration was carried out. Finally, a thermal analysis to corroborate the number of molecules of water, in addition to providing information about the kinetic parameters, was involved during the dehydration of the study materials.

2.6.1. Systems lamellar characterizations

The family of tetracyano-niquelates ($M(H_2O)_2[Ni(CN)_4] \cdot xH_2O$); M : Mn, Co and Ni, $x = 1, 2$, and 4 has been studied recently due to its ability to store molecules such as H_2 , CO_2 , and N_2 . It is known that they crystallize in three different ways, that is, phase L1, phase K, and phase L0 [7]. The forms adopted due to the water molecules present in the structure and their interaction with metals assemblers. Figure 8 shows three phases reported.

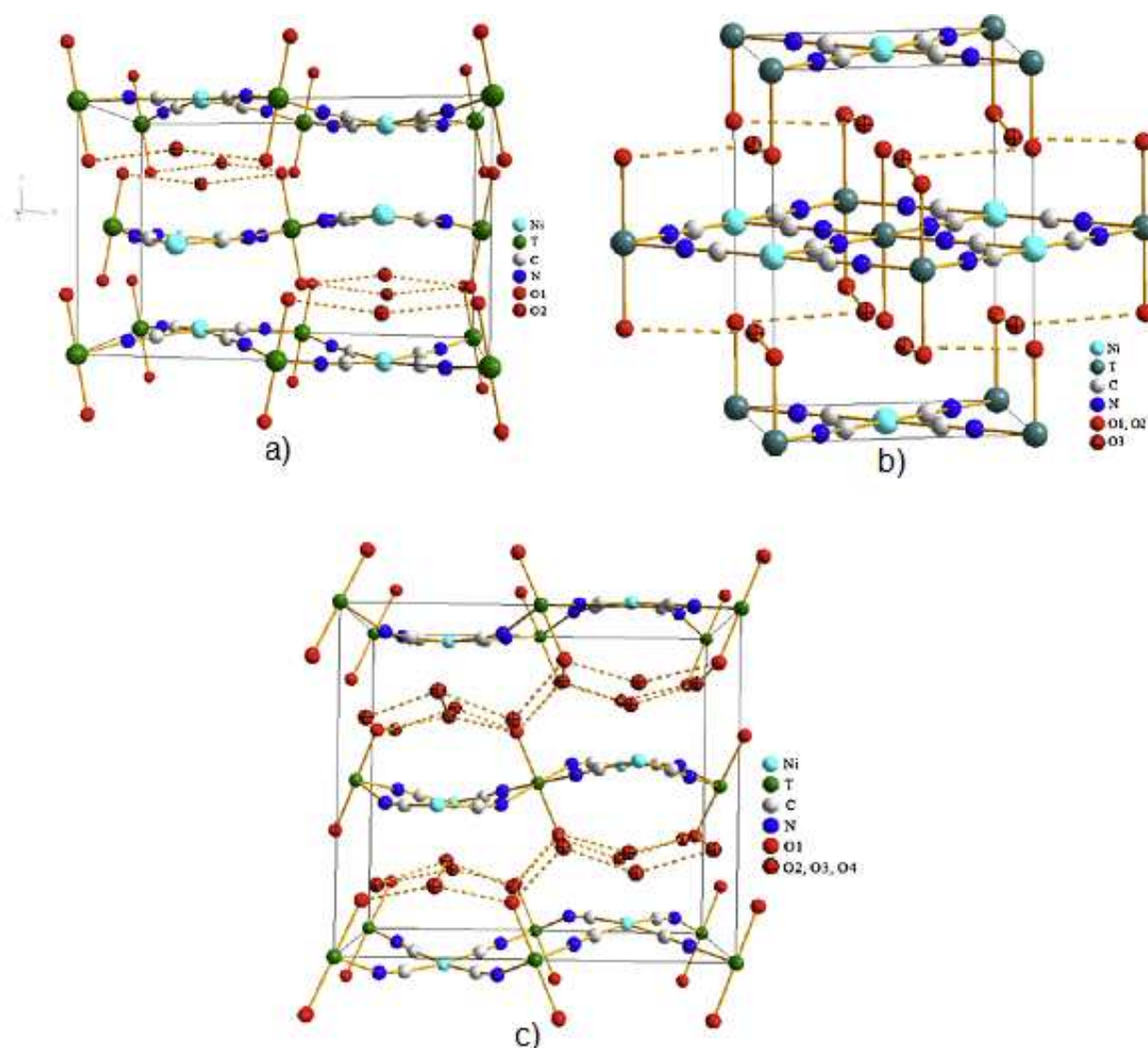


Figure 8. Framework for L1 (a), K (b), and L0 (c) phases. Coordinated water molecules from neighboring layers remains linked through aquo-bridges (hydrogen bonding interactions).

Thermal analysis is performed in four aspects: (i) analyze how to change kinetic parameters in a same phase for different metals of assembly, (ii) observe the influence of kinetic parameters over the same metal assembly on three different stages, (iii) analyze L0 to L1 phase change during the process of dehydration, and (iv) vary kinetic parameters as the partial pressure of water in the system is changed. All materials are needed to monitor the process of dehydration with the help of XRD to observe when there is a change in the structure or collapse once the material molecules are removed totally or partially.

2.6.1.1. Two-dimensional network of water molecules in the three phases interpretation

In order to understand how water molecules are found in the material and thus to make one website speedily of the kinetic parameters during the process of dehydration, two-dimensional networks of water molecules are presented in three different phases (see Figure 9). Note that the water molecules are organized along two-dimensional planes alternating the position between coordinated octahedral (defined by the position of the metal) sites and the position in the existing cavities between polyhedral.

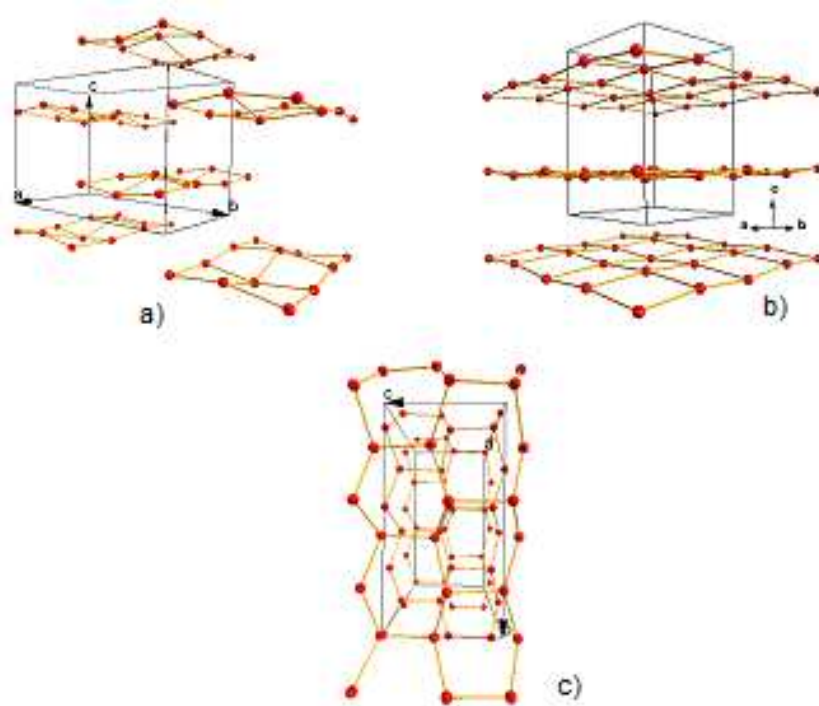


Figure 9. Two-dimensional representation of the network of water molecules in the different lamellar systems for (a) L1 phase, (b) K phase, and (c) L0 phase. Each red sphere is a water molecule without the hydrogen atoms.

2.6.1.2. Systems thermogravimetry lamellar characterization

Figure 10 shows samples of thermograms of the corresponding phase L1 as well as profiles of conventional or normal activation energy obtained from synthesized, likewise in gray color. The samples shown are the activation energy profiles obtained after dehydration of the

corresponding material in its phase L0. The difference between the profiles of activation energy is due to local variations of the chemical potential of water or kinetic disabilities in reversible reactions caused by the removal of part of the water when the temperature is increased in the same way.

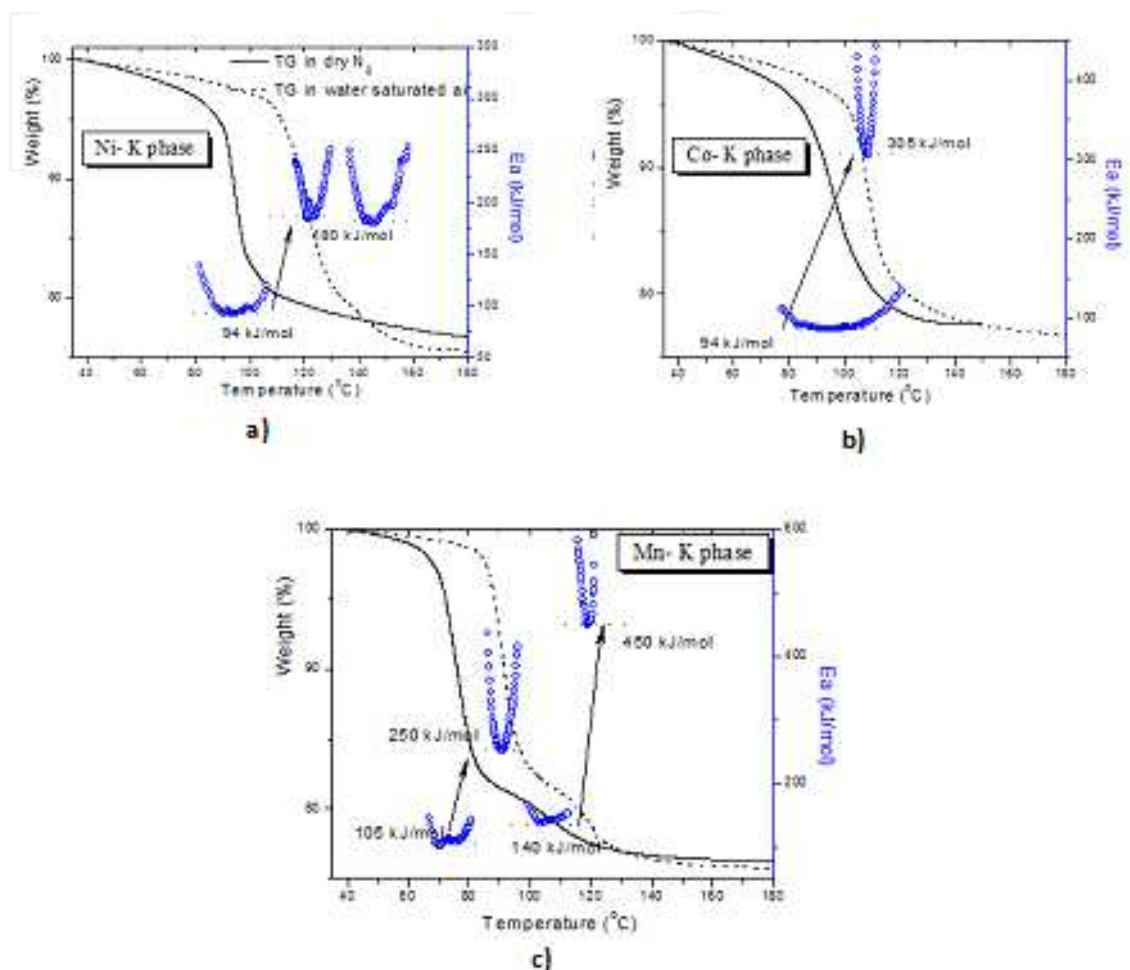


Figure 10. Thermogravimetric and activation energy profiles for K phase with the different transition metals: (a) Nickel (Ni^{2+}), (b) cobalt (Co^{2+}), and (c) manganese (Mn^{2+}). Blue points are activation energy profiles.

In Figures 11a and 11b, it can be observed that the morphology of the system once it passes from step L0 to L1 phase is maintained when three molecules of water are removed, showing only a change in the volume of material during the transition. The system presents forms as flakes, which is a laminar structure manifestation in these materials that crystallize. The L1 phase synthesized presents particle sizes smaller than that obtained by the transition.

In the characterization by SEM, the only sample that differs from the others is the phase L0 with nickel and external metal because this has very organized small flakes. Figure 12 shows that this structural arrangement explains why this material has low activation energies for the L1 phase derived from the corresponding L0.

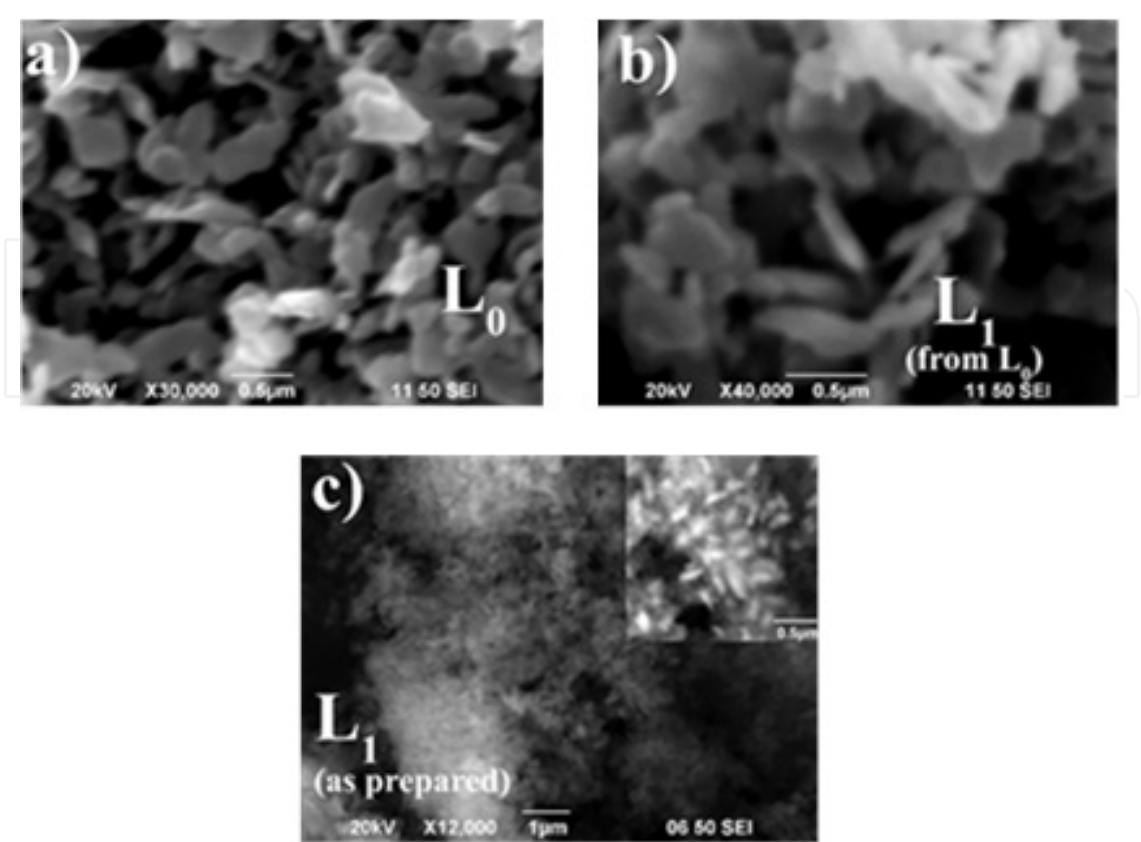


Figure 11. SEM micrographs of (a) as-prepared L₀ phase, (b) L₁ derived from L₀ after heating, and (c) as-prepared L₁ phase. The insets show a magnification of a selected area.

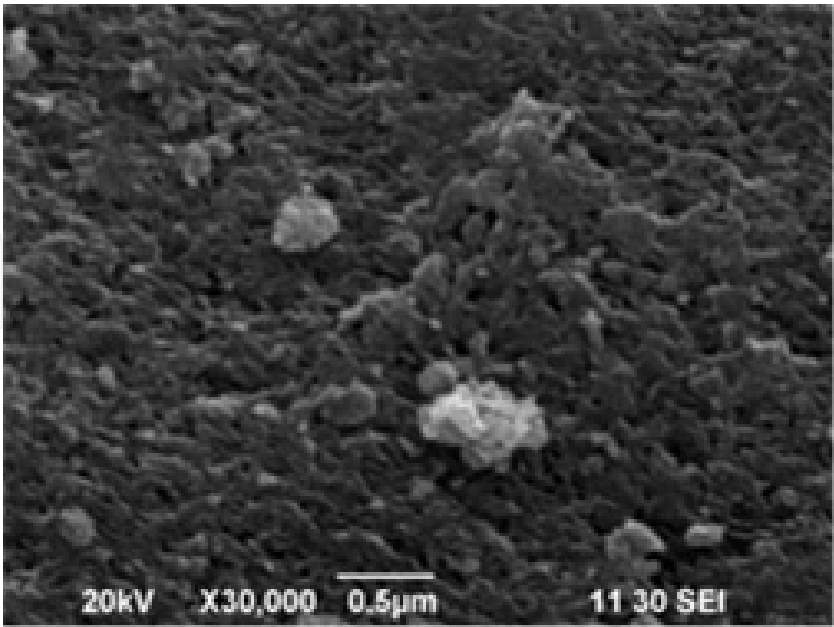


Figure 12. SEM micrograph of the as-prepared Ni-L₀ phase.

2.7. Porous molecular materials

The second family studied is similar to the Prussian blue materials. These materials are referred to as hexacyano-cobaltates ($M_3 [Co(CN)_6]_{2x}H_2O$; M: Mn, Ni, Co, Zn, Cd and Cu (see Figure 13). These materials form an interesting family with windows and pore volumes appropriate for the separation and storage of small molecules [32]. The synthesized material boasts of water molecules in pores formed, and these can be reversibly moved through the window without having some structural rearrangement in the material. The unitary formula specifies that six water molecules are coordinated to the material, and the remaining space is occupied by water molecules that are linked weakly by hydrogen bonds mainly.

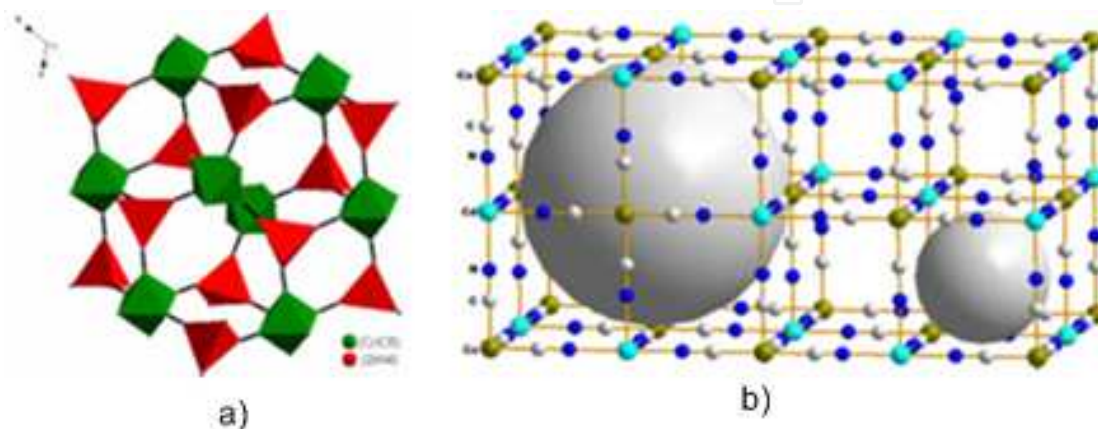


Figure 13. Lattice porous materials under study. (a) Representation of cavity Zinc cobalticyanide. (b) Porous lattice of the cubic phase in cadmium cobalticyanide.

The characterization in this family is carried out to evaluate the material according to its ability to remain at the same level and with the same crystal structure once the water molecules between the cavities are removed, as well as to obtain the corresponding activation energy profiles during dehydration as necessary energy values for the rupture of the interaction. Thus, this provides an idea of the power required for a molecule to be hosted inside the material.

2.7.1. Thermogravimetric molecular porous materials characterization

Materials under study lose the total number of molecules of water (both the coordinates and the zeolite) between 90°C and 180°C. The temperature dehydrated in a total way is highly linked with the polarizing power of the outer material, in addition to electrostatic forces with water molecules. Dehydration temperatures carry the following order: (117.54 °C) > Mn (106.57 °C) > Co (99.26 °C) > Cd (89.82 °C) > Cu > Zn (67.44 °C). This sequence of dehydration can be seen clearly in Figure 14, in addition to showing the corresponding graphics of the derivative for each sample. In the particular case of the material with Zinc as metal coordination, low temperatures of dehydration due to the tendency of this material to adopt a tetrahedral coordination by forming a rhombohedral phase, which tends to be anhydrous. In these materials, for all the samples, the water molecules, both the coordinates and that of the zeolitic type, leave the system through a virtually continuous and simple process, resulting in

dehydration cooperatively between the two types of water resulting in TG profiles without well-defined inflections, although at the beginning of all samples, a slight disturbance is recorded by the team (through the measurement of Ea).

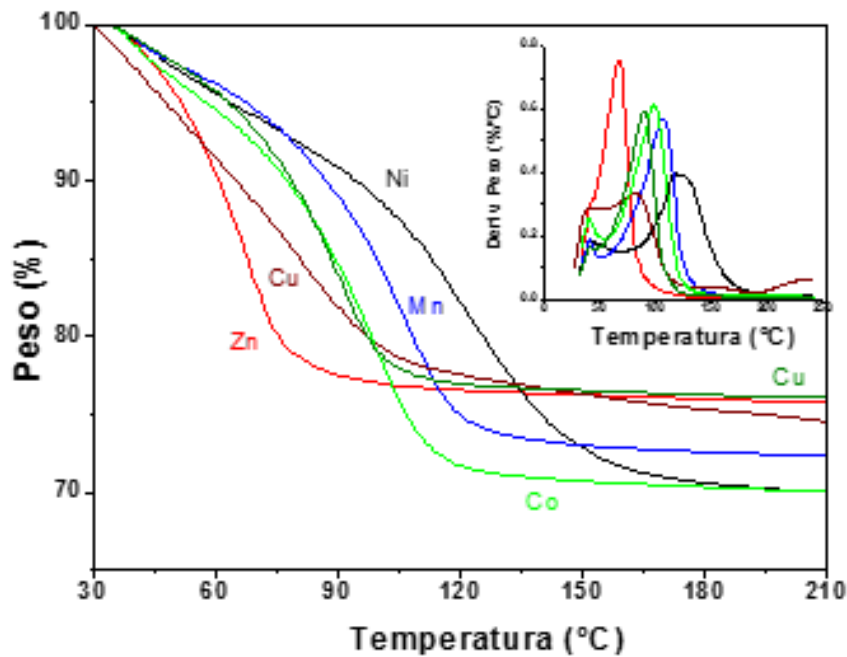


Figure 14. Thermogravimetric (TG) curves and the corresponding derivative (DTG) that expresses the progress of dehydration.

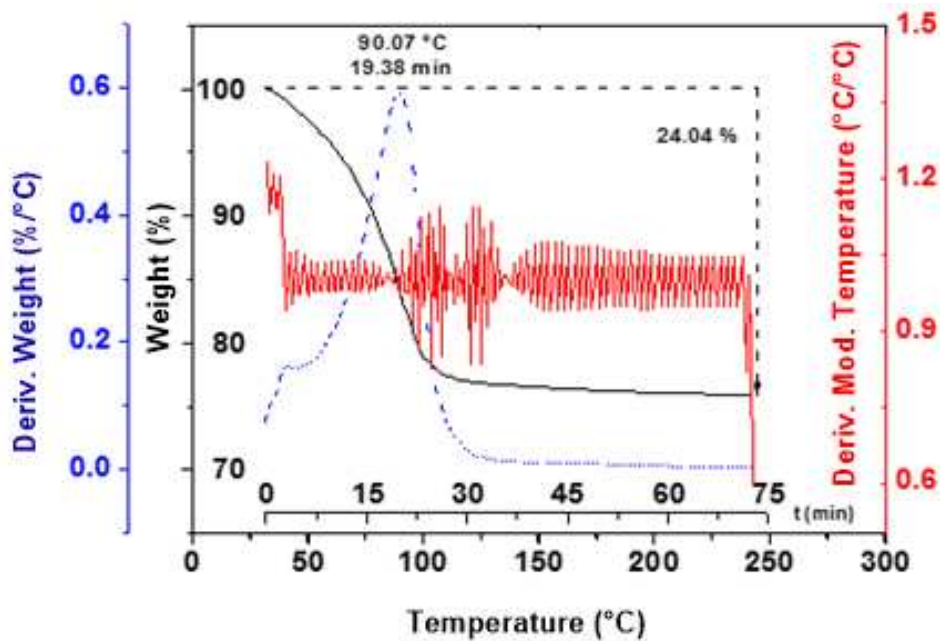


Figure 15. TG and DTG profile, modulation of temperature, and time set on a measure imposed on high resolution and modulated for material $\text{Co}_3 [\text{Co}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$.

As an example of a deeper analysis system, cadmium hexacyano-cobaltates are considered. In addition to being plotted and based on the weight loss derived from the corresponding weight, Figure 15 will also include the time of the process and the derivative of the temperature modulation time. The latter refers to the temperature disturbance along throughout the dehydration process, and the information provided is the resistance of the phenomenon, that is, as the modulation is increasing, the resistance of the water molecules evolves in the system. So, considering a constant disturbance implies that water molecules get out of the system without offering any more resistance. This agrees with what the E_a charts show.

2.7.2. Hexacyano-cobaltates activation energy

The activation energy profiles for these materials show that the E_a values are very close together, in a range between 60 and 90 kJ/mol with 60 kJ/mol in the case of Zinc as an external metal and 90 kJ/mol for nickel. Figure 16 shows the corresponding profiles mentioned. These two materials are considered because both ends are minimum and maximum in dehydration temperature.

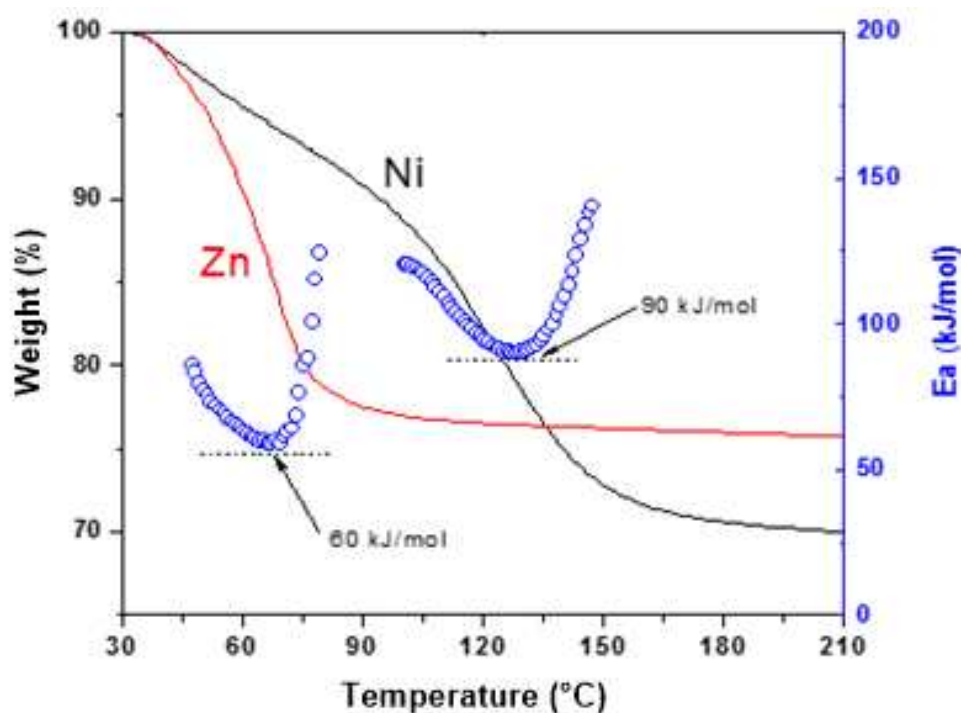


Figure 16. TG curves and profile of E_a for dewatering $M_3[Co(CN)_6]_2 \cdot xH_2O$, con $M = Ni^{2+}$ y Zn^{2+} .

3. Suggestions

In future research, we intend use a lattice Boltzmann method in order to copy the porous medium obtained experimentally and to make simulations. Figure 17 shows the simulation using the lattice Boltzmann method of randomly generated porous media [33].

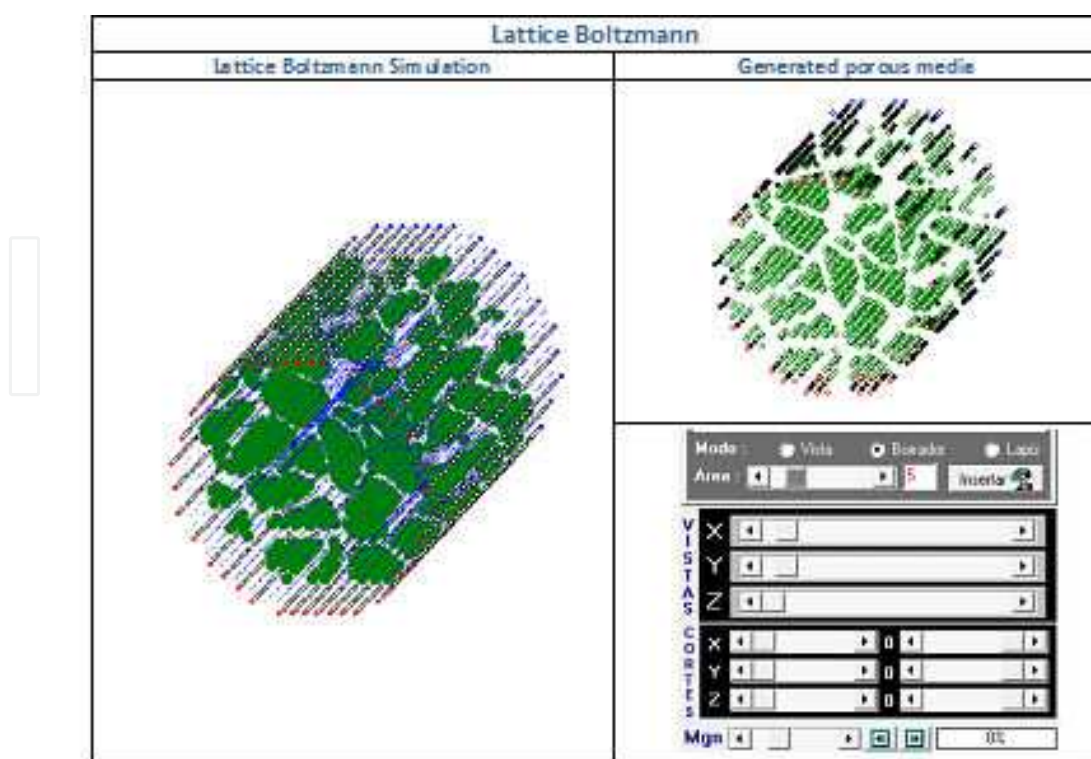


Figure 17. Lattice Boltzmann simulations through porous media.

4. Conclusions

In general, the study of the relative stability of the tetracyano-niquelates and hexacyano-cobaltates processes of dehydration shows that this depends in the first instance of the interactions of the water molecule with the outside. A more polarizing power metal is the stability of the link $M-H_2O$ (for identical structures). Lamellar systems presented an energy barrier that must overcome the water molecules to begin to spread on the system. This barrier is the activation energy that lies in a range between 60 and 500 kJ/mol, depending on the type of water that comes out. In systems where the water molecules of subnetworks are homogeneous, water zeolite is indistinguishable from the coordinated water molecules.

To increase the partial pressure of water in laminar systems, there is an increase in the temperature of dehydration due to the increase in chemical potential of water in the system, and the immediate consequence is reflected in the increase in activation energy.

Studies by X-ray diffraction report the existence of a transition from L0 phase to L1 phase during the dehydration process, and during this transition, the phase change morphology of the material is maintained.

The process of dehydration in the hexacyano-cobaltates, which also presented the two types of water molecules (zeolite and coordinated), is carried out to lower activation energy values

(between 60 and 90 kJ/mol) compared to lamellar systems since coordinated molecules are linked weakly to assemble metal.

For molecular materials during dehydration, there was no structural collapse, even if there are changes in the material locally, which has a shrinkage of only 4% of the unit cell.

In future research, we aim to use the lattice Boltzmann method for the characterization of porous medium, which would help with different configurations of porous media.

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References

- [1] Knoblauch, K.: Pressure swing adsorption geared for small volume users. *Chem. Eng.* 1978;85(25):87.
- [2] Cheng C.D., Silvestri A.J.: The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts. *J. Catal.* 1997;47(2);249–259. doi: 10.1016/0021-9517(77)90172-5.
- [3] Schlapbach L., Züttel A.: Hydrogen-storage materials for mobile applications. *Nature.* 2001;414;353–358, doi:10.1038/35104634.
- [4] Kitagawa S., Kitaura R.: Pillared layer compounds based on metal complexes. Synthesis and properties towards porous materials. *Comments Mod. Chem. A. Comments Inorg. Chem.* 2002;23(2);101–126. doi:10.1080/02603590214512.
- [5] Mathey Y., Mazieres C.: Les phases cyanures de nickel(II) hydratés. *Can. J. Chem.* 1974;52(21):3637–3644. doi:10.1139/v74-544.
- [6] Barrer R.M., MacLeod D.M.: Activation of montmorillonite by ion exchange and sorption complexes of tetra-alkyl ammonium montmorillonites. *Trans. Faraday Soc.* 1995;51:1290–1300. doi:10.1039/TF9555101290.
- [7] Lemus-Santana A.A., Rodriguez-Hernandez J., del Castillo L.F., Basterrechea M., Reguera E.: Unique coordination of pyrazine in T [Ni(CN)₄]·2pyz with T = Mn, Zn, Cd. *J. Solid State Chem.* 2009;182(4):757–766. doi:10.1016/j.jssc.2008.12.028.
- [8] Rodriguez-Hernandez J., Lemus-Santana A.A., Cargas C.N., Reguera E.: Three structural modifications in the series of layered solids T(H₂O)₂ [Ni(CN)₄]·xH₂O with T =

- Mn, Co, Ni: their nature and crystal structures. *C. R. Chim.* 2012;15(4):350–355. doi: 10.1016/j.crci.2011.11.004.
- [9] Ferlay S., Mallah T., Ouahès R., Veillet P., Verdaguer M.: A room-temperature organometallic magnet based on Prussian blue. *Nature.* 1995;378;701–703. doi: 10.1038/378701a0.
- [10] Shin-ichi O., Ken-ichi A., Yusuke S., Kazuhito H.: Humidity-induced magnetization and magnetic pole inversion in a cyano-bridged metal assembly. *Nat. Mater.* 2004;3:857–861. doi:10.1038/nmat1260.
- [11] Lemus A.A.: Incorporación de pirazina y 4,4'-bipiridina en estructuras laminares de tetracianoniquelatos: síntesis, estructura, adsorción y separación de gases (Tesis), México, D.F., UNAM, 2010.
- [12] Nijkamp M. G., Raaymakers J. E. M. J., van Dillen A. J., and de Jong K.P.: Hydrogen storage using physisorption – materials demands. *Applied Physics A: Materials science and Processing*; 2001; 72(5): 619–623. doi: 10.1007/s003390100847.
- [13] Breck D.: *Zeolite Molecular Sieves: Structure, Chemistry and Use.* New York: J. Wiley; 1974. ISBN 0471099856, 9780471099857.
- [14] Leonowicz M.E., Lawton J.A., Lawton S.L., Rubin M.K.: MCM-22: a molecular sieve with two independent multidimensional channel systems. *Science.* 1994;264(5167): 1910–1913. doi:10.1126/science.264.5167.1910.
- [15] Thomas K.M.: Hydrogen adsorption and storage on porous materials. *J. Catal. Today.* 2007;120(3–4);389–398. doi:10.1016/j.cattod.2006.09.015.
- [16] Zhao X.B., Xiao B., Fletcher A.J., Thomas K.M.: Hydrogen adsorption on functionalized nanoporous activated carbons. *J. Phys. Chem. B.* 2005;109(18);8880–8888. doi: 10.1021/jp050080z.
- [17] Zhao X., Villar R., Fletcher A.J., Thomas K.M.: Kinetic isotope effect for H₂ and D₂ quantum molecular sieving in adsorption/desorption on porous carbon materials. *J. Phys. Chem. B.* 2006;110(20):9947–9955. doi:10.1021/jp060748p.
- [18] Panella B., Hirscher M., Roth S.: Hydrogen adsorption in different carbon nanostructures. *Carbon*, 2005;43(10):2209–2214. doi:10.1016/j.carbon.2005.03.037.
- [19] Züttel A., Sudan P., Mauron P., and Wenger P.: Model for the hydrogen adsorption on carbon nanostructures. *Appl. Phys. A. Mater. Sci. Process.* 2004;78(7);941–946, 2004. doi:10.1007/s00339-003-2412-1.
- [20] Lachance P., Benard P.: Specific surface effects on the storage of hydrogen on carbon nanostructures. *Int. J. Green Energy.* 2007;4(4):377–384. doi: 10.1080/15435070701337434.
- [21] Pinnavaia T.J.: Nanoporous layered materials. *ACS Adv. Chem. Ser.* 1995;245:283–300 doi:10.1021/ba-1995-0245.ix001.

- [22] Bizeto M.A., Shiguihara A.L., Constantino V.R.L.: Layered niobate nanosheets: building blocks for advanced materials assembly. *J. Mater. Chem.* 2009;19(17):2512–2525. doi:10.1039/B821435B.
- [23] Vieira P. and Santos C.A.C.: Propriedades catalíticas dos argilominerais (Parte II): Argilominerais intercalados e pilarizados. *Boletín Técnico de Petrobras.* 1988;31(2):143–157.
- [24] Sterte J.: Hydrothermal treatment of hydroxylation precursor solutions. *Catal. Today.* 1988;2(2):219–231. doi:10.1016/0920-5861(88)85005-3.
- [25] Dunbar K.R., Heintz R.A.: Chemistry of transition metal cyanide compounds: modern perspectives. *Prog. Inorg. Chem.* 1997;45:295–296. doi:10.1002/9780470166468.ch4.
- [26] Iwamoto T., Nishikiori S.-I., Kitazawa Y.H.: Dalton transactions. *J. Chem. Soc.* 1997;22:4127–4136. doi:10.1039/A702539D.
- [27] Ludi A.: Prussian blue, an inorganic evergreen. *J. Chem. Educ.* 1981;58:1013. doi:10.1021/ed058p1013.
- [28] Ludi A., Gudel H.U.: Structural chemistry of polynuclear transition metal cyanides. *J. Inorg. Chem.* 1973;14:1–21 doi:10.1007/BFb0016869.
- [29] Roque J., Reguera E., Balmaseda J., Rodriguez H.J., Reguera L., del castillo L.F.: Porous hexacyanocobaltates(III): role of the metal on the framework properties. *Microporous Mesoporous Mater.* 2007;103:57–71. doi:10.1016/j.micromeso.2007.01.030.
- [30] Kaye S.S., Long J.R.: Hydrogen storage in the dehydrated Prussian blue analogues M₃ [Co(CN)₆]₂ (M = Mn, Fe, Co, Ni, Cu, Zn). *J. Am. Chem. Soc.* 2005;127:6506–6507. doi:10.1021/ja051168t.
- [31] Chapman K.W., Southon P.D., Weeks C.L., Kepert C.J.: Reversible hydrogen gas uptake in nanoporous Prussian Blue analogues. *J. Chem. Commun.* 2005;26:3322–3324. doi:10.1039/B502850G
- [32] Boxhoorn G., Moolhuysen J., Coolegem J.G.F., van Santen S.R.: Cyanometallates: an underestimated class of molecular sieves. *J. Chem. Soc., Chem. Commun.* 1985;19:1305. doi:10.1039/C39850001305.
- [33] Romo S.R., Ortega J.L.V. Simulation of non-Newtonian fluids through porous media. Chapter 5. In Patel V (ed.), *Petrochemicals*. Rijeka, Croatia: Intech; 2012:75–100. doi:10.5772/2069. ISBN 978-953-51-0411-7.

