

In situ Diffraction Studies of Ni Nanostructure Growth using Microporous Materials as Supports

by

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ABSTRACT

Our objective is to study the growth mechanism of Ni nanostructures supported in microporous materials using X-ray diffraction. Since only the surface atoms of a catalyst are active, our aim is to find the optimum synthesis conditions for the formation of small Ni nanostructures. A state-of-the art XRD attachment called Reactor X was used to study the growth of the Ni nanostructures in situ. Our main focus was the study of the calcination and reduction of nickel acetate, as Ni metal precursor, impregnated into the one-dimensional channels of microporous VPI-8 and mordenite. Using the Reactor X we observed in the XRD diffraction patterns the appearance of nickel oxide (NiO) and Ni peaks during the calcination and reduction reactions, respectively. Among the most significant findings we found that the optimal reduction temperature that leads to the formation of metallic Ni crystals depends significantly on the metal loading and on the calcination.

RESUMEN

Nuestro objetivo es estudiar el crecimiento de nanoestructuras de Ni ancladas en materiales microporosos mediante difracción de rayos X. Debido que sólo aquellas partículas que se encuentran en la superficie de un catalizador son catalíticamente activas, queremos encontrar las condiciones óptimas que llevan a la formación de nanoestructuras de Ni pequeñas. El aditamento de XRD llamado Reactor X fue utilizado para estudiar el crecimiento de las nanoestructuras de Ni in situ. Nuestro objetivo principal era el estudio de la calcinación y reducción de acetato de níquel impregnado en canales unidimensionales de materiales microporos como VPI-8 y mordenita. De los difractogramas de XRD, observamos la aparición de los picos de óxido de níquel (NiO) y Ni durante la calcinación y reducción, respectivamente. Encontramos que la temperatura de reducción, que lleva a la formación de cristales metálicos de Ni depende significativamente de la cantidad de Ni que ha sido impregnada y de la calcinación.

To my “Bebe” ...

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1 INTRODUCTION

Metals are among the most important catalysts used for chemical processes such as hydrogenation [1], dehydrogenation [2], and petroleum refining [3]. Since only surface atoms are active in a catalyst, small metal clusters, defined as a group of two or more bonded metal atoms, are desired in order to maximize their efficiency.

The applications of transition metals for catalysis of several organic syntheses are being extensively studied due to their industrial importance. Among the transition metals, nickel (Ni) catalysts offer a wide range of catalytic application such as hydrogenation [1, 4-6], dehydrogenation [2], methanation [7-10], hydrogenolysis [11-13], and steam reforming [14, 15]. In addition, Ni has ferromagnetic properties and is relatively cheap in comparison with other catalysts used for similar applications.

In order to enhance and develop new catalytic properties, several studies of supported Ni catalysts are being conducted. Our main focus is to study the synthesis of Ni clusters inside the pore systems of zeolites which are used to constrain the cluster growth. The syntheses were carried out in an XRD attachment called Reactor X, which allows the study of the reactions as they proceed.

1.1 Zeolites

Zeolites are crystalline aluminosilicates with a three dimensional framework structure that forms uniformly sized channels of molecular dimensions [16]. Their framework consists of tetrahedrons of four oxygen anions coordinated to silicon or

aluminum ions. Each quadrivalent silicon ion is charge-balanced by the four tetrahedral oxygen atoms and the silica tetrahedra are therefore electrically neutral. Since aluminum is trivalent and it is coordinated to four oxygen atoms, each alumina tetrahedra has a residual charge of minus one (-1). Consequently, each alumina tetrahedron requires a charge of plus one (+1), which can be provided by a metal cation or a hydroxyl proton, in order to maintain electrical neutrality. Hydroxyl protons act as strong Brønsted acid sites, i.e., proton donors, and are located on oxygen bridges connecting the tetrahedrally coordinated silicon and aluminum, as shown in Figure 1-1 [16]. These cations can readily be replaced by ion exchange, which represents the most useful method for the alteration of zeolites properties.

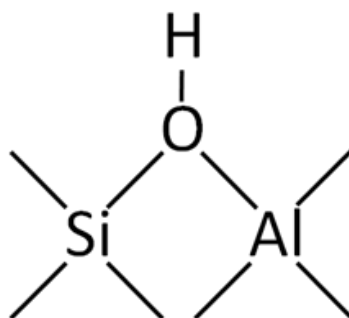


Figure 1-1 Schematic representation of structural OH-bridging groups.

Zeolites offer unique properties for studies of heterogeneous catalysis because of their ion exchange, catalytic and structural properties. Zeolites are used for several catalytic applications such as: hydrogenation [17] and cracking of hydrocarbons [18-20]. Zeolites are widely used in adsorption-related applications such as gas separation and

storage. Since 1960 silica-alumina catalysts used in the fluid catalytic cracking (FCC) of heavy petroleum fractions were replaced by acid zeolites of the faujasite type. Since then the use of zeolites has been widely successful in the industrial practice. Nowadays two zeolites are employed in most FCC units, namely ultrastable zeolite Y, which is used as the principal cracking component, and H-ZSM-5 which is used for the improvement of the octane number in the gasoline while enhancing the yield of propane as a by-product [16]. In addition to FCC, acid zeolite catalysts are used in several petrochemical processes such as catalytic dewaxing, isomerization of light gasoline, isomerization of xylenes, hydrocracking of heavy petroleum distillates, among others [21].

For many hydrocarbon reactions, zeolites have a higher activity and better selectivity than an amorphous catalyst. The higher selectivity could be attributed to the pore structure, which can limit the access of certain reactant molecules to the active sites of the zeolites.

Zeolites containing supported metals are often called bi-functional catalysts. This type of catalyst contains both strong acid and metal sites at the same time. Some researchers have studied possible applications for these bi-functional catalysts, such as in hydrocracking [22-24], dehydrogenation [25, 26], and hydroisomerization [27, 28] processes. In these types of applications, the zeolite promotes one part of the reaction and the metal promotes the other part. In the case of the hydrocracking reaction, mordenite does the cracking while Ni does the hydrogenation.

In the present work we have studied the growth mechanism of Ni clusters using two zeolites, mordenite and VPI-8, as support for the growth of Ni clusters. Zeolite mordenite (illustrated in Figure 1-2A) has a one-dimensional pore structure. It has two different sized main pores, one with a pore window containing 12 T-atoms (tetrahedral framework atoms) with dimensions of 6.5 Å x 7.0 Å and the other with 8 T-atoms with dimensions of 2.6 Å x 5.7 Å [29]. Similar to mordenite, VPI-8 (illustrated in Figure 1-2B) has a one-dimensional pore structure. It contains one sized main pore with a pore window containing 12 T-atoms with dimensions of 5.9 Å x 5.9 Å.

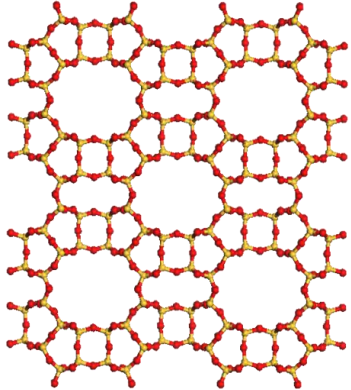
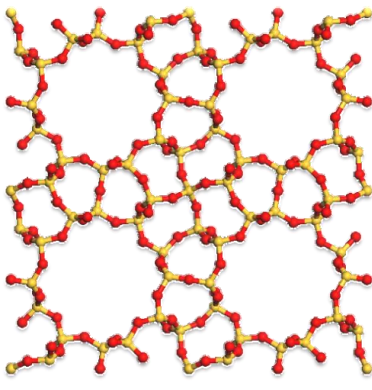
Properties	a) MOR	b) VPI-8
Chemical Composition	$\text{Na}^+_{6.4}(\text{H}_2\text{O})_{24}[\text{Al}_{6.4}\text{Si}_{41.6}\text{O}_{96}]$	$\text{Si}_{17}\text{O}_{34}$
Pore System	12-ring 6.5Å x 7.0Å	12-ring 5.9 Å x 5.9Å
		

Figure 1-2 Chemical composition and pore system characteristics of the supports studied: a) MOR and b) VPI-8.

1.2 Metal Incorporation Methods

Several metal incorporation methods are typically used to introduce metal atoms inside the zeolite pores. Among them, two of the most used are incipient wetness impregnation [30, 31] and ion exchange [32-35]. For incipient wetness impregnation, a salt solution is added dropwise to the zeolite. The amount of metal salt is calculated based on the final desired metal concentration. The salt is then diluted with deionized water and this solution is added dropwise to the zeolite until pore saturation is achieved, i.e. when the solution added equals the Pore Free Volume (PFV) of the zeolite. The sample is then dried to eliminate the excess water. If there is still solution left, it is added dropwise and then the sample is dried again. An advantage of this experimental method is that the amount of salt to be added is limited only by the free pore volume of the zeolite to be used. However, it has been reported that this method provides weak metal-support interactions that usually give path to large crystals [36].

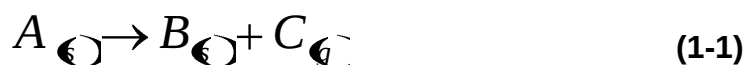
In the case of ion exchange, the cation balancing the negative charge associated to the aluminum atoms in the framework is exchanged with another cation. In this process, an aqueous salt solution is prepared with the desired amount of metal to be exchanged and then the zeolite is added under continuous stirring to enhance the cation exchange. This system is usually heated in order to speed up the ion exchange. This system is typically kept in solution for 24 hours and the zeolite is washed and filtered with deionized water. Sometimes, to enhance the ion exchange the process is repeated. This addresses possible diffusion problems since at a certain point the cation

exchange process will reach thermodynamic equilibrium, which will prevent the exchange process from continuing. The use of a new Ni salt solution will delay the thermodynamic equilibrium enhancing the cation exchange. The amount of metal to be incorporated to the zeolite will be limited by the cation exchange capacity (CEC) of the zeolite. According to the literature, ion exchange produces strong metal-support interactions, which diminish the mobility of the cation, avoiding the formation of large crystals [36].

1.3 Nucleation and Cluster Growth

1.3.1 Nucleation

In order to explain the nucleation concept, let's first consider the general reaction of the type,



At the beginning of the reaction, the first formed individual atoms (molecules, ions or crystallites) of B cannot be considered as a different and separate phase, instead they are expected to conform to the structure of, and retain their former position with reference to reactant phase A. As the accumulation of B increases, so the total deformation strain energy, leading to a transformation to the stable B structure. This could be explained as a change in free energy [37],

$$\Delta G = m\Delta G_B + \sigma\gamma \quad (1-2)$$

Where,

m = amount of molecules composing the particle B

ΔG_B = bulk free energy change per molecule

σ = shape factor, $4\pi r^2$ for spherical shape

γ = strain energy per unit area of interface

If we take v_m as the volume of product per molecule for a spherical nucleus then,

$$m = \frac{4\pi r^3}{3v_m} \quad (1-3)$$

Substituting Equation 1-3 into Equation 1-2 we get,

$$\Delta G = am^{2/3} - bm \quad (1-4)$$

Where,

a = proportional to the strain energy

b = the bulk free energy per molecule

Therefore, if the strain energy (γ) has a positive value, there has to be a critical size for which ΔG goes through a maximum,

$$m = m_c = \frac{32\pi\gamma^3 v_m^2}{3(\Delta G_B)^2} \quad (1-5)$$

Then, the nucleus and surroundings will be at equilibrium when,

$$\left(\frac{\partial \Delta G}{\partial m} \right)_m = m_c = 0 \quad (1-6)$$

Therefore, whenever the particle size of B is less than the critical size (m_c) nucleation will not proceed. In the case that the particle size is larger than m_c , then B will be stable and nucleation will proceed.

1.3.2 Crystal Growth

As soon as stable nuclei are formed (i.e., growth of B in section 1.3.1) they will grow into a crystal. Many mechanisms have been proposed to describe the growth behavior of crystals. They can generally be explained using surface energy and diffusion theories.

In 1878, Gibbs suggested that particles grow into crystals in such a way that the surface energy is at a minimum for a given volume, conforming then the most stable shape possible [38]. This could be described as,

$$\sum_{i=1}^n a_i g_i = \text{minimum} \quad 1-7$$

where a_i is the area of the i th face for a crystal containing n faces and g_i is the surface free energy per unit area of the i th face. In 1901, Wulff suggested that a crystal face will grow at rates proportional to its surface energy [38].

The growth rate of a crystal face and its surface energy should be inversely proportional to the lattice density of its lattice plane, meaning that faces containing lower lattice densities will growth faster than those having high lattice density. The velocity of crystal growth of a surface is measured by the outward rate of movement in a direction perpendicular to the face, as illustrated by the arrows in Figures 1-3a and 1-3b. Figure

1-3a represents a crystal where the geometry pattern is retained as it grows. Such a crystal is called invariant. In this figure, side A, the biggest, will grow at the slowest rate of the three, while side C, the smallest, will grow the fastest of the three. When a crystal does not retain its geometry pattern as it grows, as shown schematically in Figure 1-3b, such a growth is called overlapping. During this type of growth, the faster growing face (smallest) will gradually disappear.

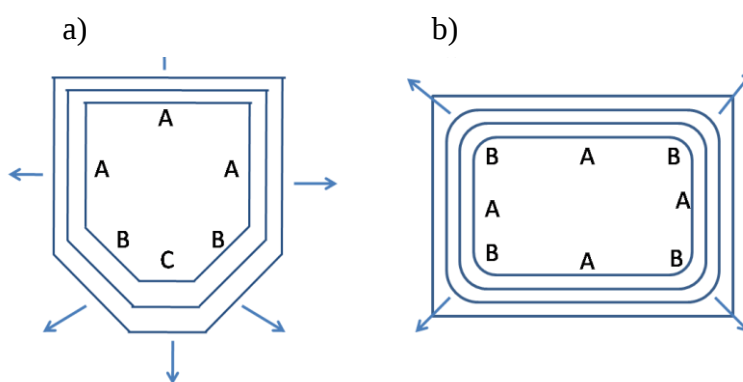


Figure 1-3 Crystal growth faces in an a) invariant crystal and b) overlapping crystal.

According to the Volmer – Gibbs theory, when particles (atoms, ions or molecules) reach the crystal surface they are not immediately added to the lattice, instead they are free to move through crystal face, forming a loosely adsorbed layer of atoms at the interface [38]. These particles will add to the crystal surface at points where the attractive forces are greatest and under ideal conditions the particles will continue to aggregate until the whole plane surface is completed. In order for the crystal face to continue to grow a “centre of crystallization” must be formed on the crystal surface.

In order to obtain accurate information about the crystalline structure, crystalline size, physical, and chemical compositions several characterization methods need to be used. The following sections describe some of the characterization methods most used for the study of solid materials.

1.4 Characterization Methods

1.4.1 XRD

1.4.1.1 Crystal Lattice and the Unit Cell

A solid substance is formed when electrostatic attractions between atoms, ions or molecules become so strong that translational freedom is significantly reduced. Even though atoms (ions or molecules) can be arranged in a randomly manner, it is more likely to find atoms arranged in an ordered and repetitive pattern, since it corresponds to a lower energy state in comparison with atoms distributed random in space. Such a material is said to have crystalline structure. Crystalline substances are known to have defects and impurities without losing their crystallinity. Their periodicity extends over a distance from 10^3 to 10^{20} atomic or molecular dimensions [39]. However, not all solids substances can be regarded as crystalline. Glass is a good example, since it is considered a solid substance but it has a highly disordered arrangement of atoms, and therefore, it is classified as being an amorphous material.

Let's consider the growth of a potassium chloride (KCl) crystal, which usually results in a cubic crystal. If this crystal is to be reproduced in space until the smallest

arrangement of atoms repeating in space is found, a single K and Cl pair in space would reproduce the whole KCl crystal. The smallest repeating unit is called a point group, which viewed in three-dimensional periodicity, could be reduced to a single representative point called a lattice point. The 3D array of points representing the whole crystal structure is known as the space lattice [21]. If lines are drawn between adjacent points a unit cell could be defined. The unit cell is defined as the smallest arrangement of atoms representative of the whole crystalline structure which contains all the chemical information and the atomic or molecular arrangement information of the whole crystal. It could be considered as the unit that could be propagated in space to make up the space lattice and consequently the macroscopic crystal could be constructed.

The three dimensional lattice or unit cell could be described using three non-coplanar vectors (a , b , c) as it is shown in Figure 1-4. These three vectors could be used to describe any point within the unit cell by determining vector q from equation 1-8, where x , y , and z are integer numbers.

$$q = xa + yb + zc \quad 1-8$$

In addition, a total of six scalar quantities, known as lattice parameters, could be used to fully describe the unit cell. These scalar quantities are shown schematically in Figure 1-4 as:

$$x, y, z, \alpha, \beta, \gamma$$

Where x , y , and z represents the length of the unit cell edges and α , β , and γ represents the angles formed between the edges a , b , and c .

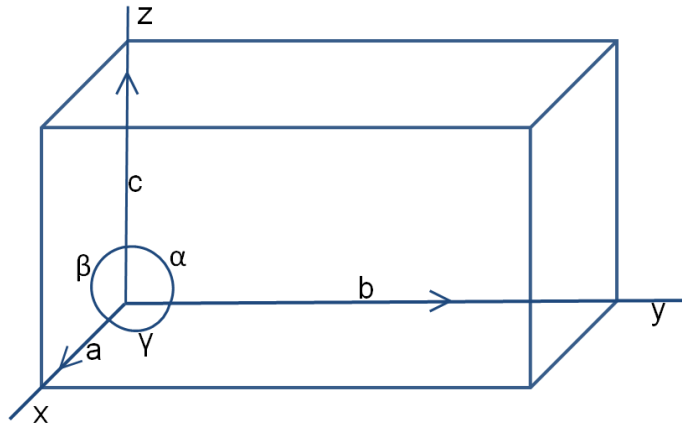


Figure 1-4 Representation of a unit cell with its lattice parameters.

1.4.1.2 Miller Indices and Crystallographic Planes

The unit cell, in addition to facilitate the characterization of the symmetry of a crystalline structure, also allows to specify crystallographic directions and interatomic distances [21, 40]. In order to describe crystallographic directions and distances it is necessary to imagine the unit cell being intersected from different places by crystallographic planes parallel to each other. These crystallographic planes could be described as a set of planes that intersect every lattice point. There are two important characteristics between planes corresponding to the same family: (1) the planes are parallel to each other and (2) they are equally spaced, separated by a distance d_{hkl} , known as the interplanar distance. In order to describe a family of crystallographic planes, integer indices h , k , and l , are used. These integer indices are known as Miller indices. Planes are identified using a set of three Miller indices enclosed in parenthesis as illustrated in Figure 1-5. These indices indicate that the set of crystallographic planes

that belong to the family $(h\ k\ l)$ divide the unit cell vectors a , b , and c , illustrated in Figure 1-4, into h , k and l parts, respectively. Miller indices are determined by taking the inverse of the fractional coordinates of the crystallographic axis intercepts. For example, if a plane intersects the lattice vector a at $1/4$, then the corresponding Miller index, h , will be 4.

When a plane is parallel to a crystallographic axis, it is assumed that it will intersect the axis at infinity resulting in a Miller index of 0 [40]. Figure 1-5, illustrates the Ni unit cell and the crystallographic plane $\langle 111 \rangle$, which means that it intersects the crystallographic vectors a , b , and c at 1.

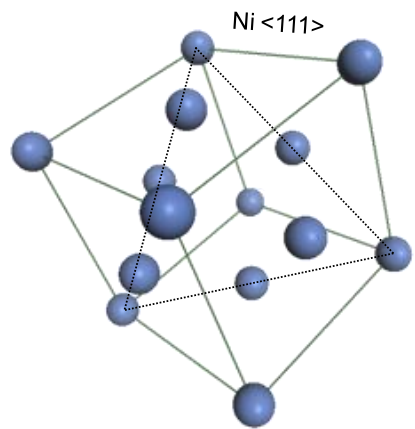


Figure 1-5 Ni unit cell with crystallographic plane $\langle 111 \rangle$ shown.

1.4.1.3 X-ray Production

X-rays are relatively short-wavelength high energy beams of electromagnetic radiation. X-rays tubes are usually used for the production of X-rays. [40] In it electrons emitted from a cathode, usually a negatively charged tungsten filament, are accelerated

by a high voltage to a positively charged metal (anode). If the energy of these accelerated electrons is greater than the electron's binding energy of the metal target, they can be knocked out of the shell of the metal target. This creates vacancies in the atomic shells of the metal, allowing electrons from higher energy levels to drop into these vacancies and in the process giving the excess energy in the form of X-rays. When an electron from the orbital L fills a vacancy in the orbital K, a K_{α} X-ray is produced. When the K orbital vacancy is filled with an electron from the orbital M, a K_{β} X-ray is produced. [41]

When X-rays propagate through a substance the excess energy is reradiated or scattered. When these scattered X-rays change in direction but do not experience losses in energy, the scattering is known as coherent or elastic. When coherent scattering occurs in a material made of atoms arranged in an orderly manner, and having a distance between each other in the order of the wavelength of radiation, then the phase relationships between the scattered waves will become periodic, leading to interference diffraction effects. When these waves are in phase, i.e., constructive interference, their amplitude is added as illustrated in Figure 1-6a. On the other hand, when the waves are completely out of phase, i.e., destructive interference, they will cancel each other, as shown in Figure 1-6b. The major peaks in a diffraction pattern are due to the constructive interferences while the smaller peaks are due to the superimposed waves, with different phases but that are not completely out of phase. [42]

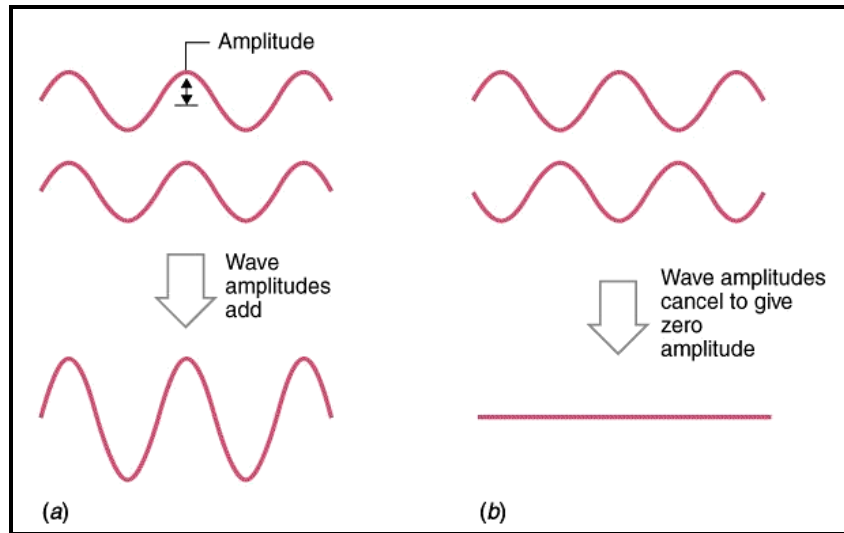


Figure 1-6. Illustration of (a) constructive and (b) destructive interference [43].

1.4.1.4 Particle Size Determination via Scherrer Equation

The particle size was determined using Scherrer's equation (1-9) using a particle shape factor of 0.9. This equation relates the wavelength of the metal used to produce the X-rays, the full width at half maximum (FWHM) of the particle peak, and the Bragg angle θ .

$$Thickness = \frac{0.9\lambda}{B \cos \theta} \quad \mathbf{1-9}$$

Where,

λ = wavelength of the metal used to produce the X-rays

B = FWHM or the width measured at the half intensity

θ = Bragg angle

1.4.1.5 Reactor X

The Reactor X (illustrated in Figure 1-7) is an XRD attachment available through Rigaku that allows the introduction of inert and reactive gases (i.e., H_2 and O_2) and also increases temperature from ambient to 1000°C using infrared technology. Since it uses infrared heating, the temperature could be increased using a very high rate ($50^\circ\text{C}/\text{min}$). It contains a Be window which allows the X-rays to enter and exit, which permit the user to follow reactions as it proceeds. Measurements can be conducted from 0 to 158° in 2θ angle. The sample plate is made of SiO_2 or black quartz. This sample plate contains a hole on one side where a thermocouple is connected. The temperature is controlled by means of a temperature controller.

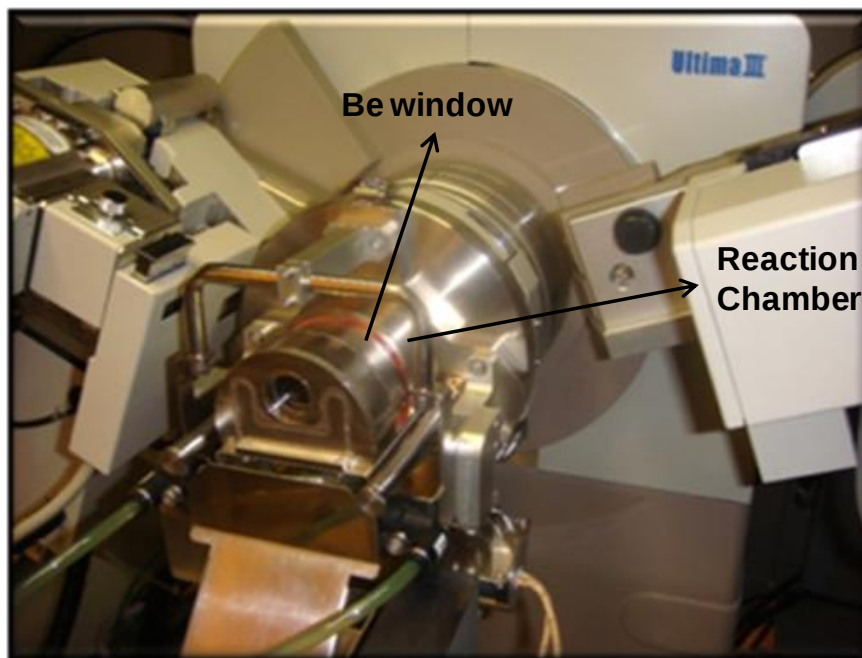


Figure 1-7. Reactor X attached to a Rigaku Ultima III XRD.

1.4.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is an analytical technique used to study the thermal stability of materials and their fractions of volatile components by monitoring the weight losses as the sample is heated. The measurement is usually conducted under air or an inert gas, such as helium, argon or nitrogen, while the weight losses are recorded as a function of increasing temperature or time [44]. TGA results are displayed as mass or percent mass against temperature or time. Complementary to this, the first derivative with respect to temperature or time could also be obtained and added to the TGA curve. This new curve is known as differential thermogravimetric (DTG) and illustrates the rate at which the mass changes with temperature.

Mass changes are illustrated in the TGA curve as steps or peaks in the DTG and occur for different reasons. Some of them are:

- Evaporation of volatile components
- Thermal decomposition
- Metal oxidation in air or oxygen reactive environments

1.4.3 FTIR

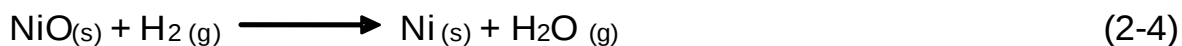
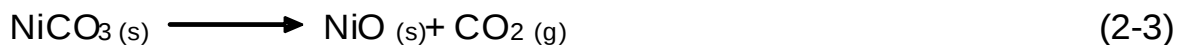
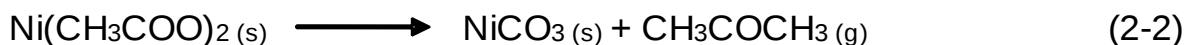
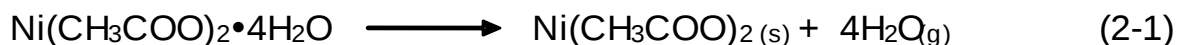
Fourier Transform Infrared Spectroscopy (FTIR) is a technique for the collection of infrared spectrum, which represents a fingerprint of a sample, containing the absorption peaks of the vibrational frequencies between the bonds of the atoms making up the material. During a FTIR measurement, the sample is exposed to a pulse of

radiation consisting of frequencies in a particular range. The resulting signal consists of a fast decaying combination of all possible frequencies. Resonant frequencies, which refers to specific frequencies at which molecules rotate or vibrate corresponding to discrete energy levels, will be dominant in the signal and by using Fourier transforms on the signal the frequency response, can be determined. [45]

Our aim in this study is to determine the thermal conditions that are the most suitable for the formation of small Ni clusters. In order to do this we used a state-of-the-art XRD attachment that allows the study of the crystallization of the metal particles in situ. This attachment, Reactor X, allows the sample to be heated under the flow of reactive gases while simultaneously allowing the recording of diffraction data. To achieve our objective, we studied the gas flow rate, role of the calcination, temperature ramp and reaction temperature effect on the NiO and metallic Ni crystal size.

2 Literature Review

Of the possible Ni precursors salts, the thermal decomposition mechanism of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ under different environments has been well studied [46-51]. De Jesus et al., reported that, under air, the first decomposition step is a dehydration reaction in which the four water molecules are removed from the molecule, which accounts for around 29% of the weight of the compound (reaction 2-1). According to him, after dehydration, nickel carbonate (NiCO_3) is formed (reaction 2-2), which spontaneously produces nickel oxide (NiO) (reaction 2-3) [46]. After the NiO has been formed, the calcined sample is exposed to hydrogen (H_2) and consequently a zero-valent Ni cluster is produced through the reaction proposed by Antoia and co-workers. [52] The overall mechanism for the formation of the Ni crystals can be described as:



Complimentary to this study, Hong et al. reported that decomposition of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ performed at a low heating rate leads to the formation of Ni_2O_3 , while higher heating rates lead to NiCO_3 . [49] Both of these structures could be reduced to form metallic Ni. Gadalla and co-workers [47] found that by increasing the gas flow rate during the thermal decomposition $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, all the thermal

decomposition reactions occurred at lower temperatures due to the enhanced removal of the reaction by-products by the increased gas flow.

In 1924, Benton and Emmett [53] studied the bulk NiO H₂ reduction. In order to produce NiO, they calcined hydrated nickel nitrate at high temperatures (360°C - 400°C) for several hours. During reduction, they measured water formation as an indication of the extent of reaction. Their work resulted in important observations regarding the NiO reduction as: (I) the NiO reduction is an auto-catalytic process; (II) it occurs at the interface of NiO and previously formed Ni; (III) there is an induction period that depends significantly on temperature and on the nature of the sample and (IV) added water reduces the reduction rate and increases the induction period. Rodriguez et al. [54] studied the Temperature Programmed Reduction (TPR) of NiO powders. For the reduction, they used a flow rate of 15 mL/min of a mixture of 5% H₂ in He and the temperature was increased from 25°C to 600°C at a 20°C/min, while XRD data were collected. They observed that a transformation from NiO to metallic Ni occurred at a temperature close to 260°C, after an induction period, without XRD diffraction features for an intermediate.

Biju et al., [55] studied the FTIR spectra of nanostructured NiO with average sizes ranging from 3 to 16 nm in the frequency range of 50 to 600 cm⁻¹. They found that, for every sample, a broad peak appeared in the region of 420 to 440 cm⁻¹. Furthermore, it was found that the peak became broader for the samples with a larger NiO particle size. Wang et al., [56] studied the FTIR absorption bands for bulk NiO and NiO nanoparticles. They found that the absorption band bulk NiO appeared at a

frequency of 482 cm^{-1} , while NiO nanoparticles exhibited an absorption band at 437 cm^{-1} .

Mohamed et al. [50] studied the thermal decomposition of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ using FTIR. He found that vibrations of COO^{-1} groups appeared within the frequency range of 1600 to 1400 cm^{-1} . In addition, they analyzed the products of a sample of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ heated to 400°C and found that the lattice vibrations of Ni-O appeared in an absorbance band close to 500 cm^{-1} .

Several studies have been published on the growth of supported Ni catalyst clusters. Canizares and co-workers [36] studied Ni clusters supported on H-mordenite using $\text{Ni}(\text{NO}_3)_2$ as Ni precursor. In order to incorporate the Ni particles, they used ion exchange and impregnation. After impregnation, the catalysts were calcined with air at 400°C for 4 hours. The reduction was performed using a H_2 flow rate of 190 mL/min while heating up to 460°C . The ion exchange was performed also using $\text{Ni}(\text{NO}_3)_2$. They reported that regardless of the incorporation method used, impregnation or ion exchange, large particles with an average size of $180\text{ \AA}$ were obtained. According to Canizares, such large particles should be localized outside the zeolite crystals. Tamagawa and coworkers [57] tried to control the Ni crystal size using SiO_2 as support. They concluded that the specific surface area of the particles decreased with increasing reduction temperature due to particle sintering, which suggest that the cluster aggregates at high temperatures. Richardson studied the hydrogen reduction of NiO on $\alpha\text{-Al}_2\text{O}_3$ by means of X-ray diffraction [58]. He found that the NiO crystals were quickly consumed once the reduction started but also that the samples contained NiO after the

reduction process was completed. Richardson also studied the H_2 reduction of bulk NiO using an in situ hot stage XRD [59]. He reported that NiO, under H_2 reduction, started to disappear at a temperature of 175°C while simultaneously metallic Ni started to appear. In addition, he found that the NiO $\langle 2\ 0\ 0 \rangle$ peak overlapped with the Ni $\langle 1\ 1\ 1 \rangle$ preventing an accurate estimate of the NiO crystal size. He also found that the NiO crystal size was decreased after reduction but it did not disappear completely. After reduction was completed the final metallic Ni $\langle 1\ 1\ 1 \rangle$ crystal size was bigger than the original NiO $\langle 2\ 0\ 0 \rangle$ crystal size.

Changlai et al. [60] conducted a FTIR analysis of mordenite. His results showed that the asymmetric stretching vibration of SiO_4 and AlO_4 tetrahedrons appeared close to 1100 cm^{-1} . In addition he also found that the deformation vibration band, corresponding to H-O-H, appears at a frequency close to 1640 cm^{-1} . Consequently, based on these results we designed a series of experiments to study the decomposition of nickel acetate mechanism inside the zeolite pores and the metallic Ni crystal growth in situ using X-ray diffraction.

3 Mordenite as a Support for Ni clusters

3.1 Materials

Mordenite with a Si/Al ratio of 6.5 was obtained from Zeolyst International. Nickel acetate hydrate (Alfa Aesar 99%) was used for the impregnation and ion exchange solutions.

3.2 Incipient Wetness Impregnation

In this work we incorporated nickel to mordenite and VPI-8 using incipient wetness impregnation. Due to its well studied decomposition mechanisms, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was used as Ni precursor. For the preparation of the samples by impregnation, the desired amount of nickel acetate was dissolved using a minimum volume of deionized water. These $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ solutions were impregnated into 1 g of mordenite, in a dropwise manner. After the impregnation was completed, the zeolite was dried to eliminate excess water. The process was repeated, if necessary, in order to achieve the desired Ni loading.

3.3 Ion Exchange

For ion exchange we first determined the cation exchange capacity (CEC) using nickel acetate as source of Ni^{+2} . Then we prepared 20 mL solutions containing 3-fold, 5-fold, and 7-fold CEC of the zeolite. For the preparation of the ion exchange sample 1 g

of mordenite was added to each salt solution. This solution was heated to 50°C, to enhance the cation exchange, and stirred for 24 hours. The sample was then washed with deionized water. To enhance the ion exchange, after the sample was washed, the ion exchange process was repeated.

3.4 Calcination and Reduction

As the crystalline NiO $\langle 2\ 0\ 0 \rangle$ peak appears at 43.3° and the metallic Ni $\langle 1\ 1\ 1 \rangle$ peak appears at 44.5°, the XRD patterns were obtained within the range of 40° to 50° in 2θ at a rate of 1°C/min. Each XRD pattern was gathered after a temperature step of 10°C. Initially, the samples were placed inside the Reactor X in a quartz sample plate. The calcination and reduction reactions were done using air and in 10% hydrogen in N₂ mixture, respectively. During calcination, the temperature was increased from room temperature (RT) to a target temperature using heating rates of 1°C/min and 5 °C/min. After the process was completed the sample was allowed to cool down naturally. During reduction the same heating and cooling down protocol was followed.

3.5 Characterization Techniques

3.5.1 XRD

The calcination and reduction processes were studied *in situ* using the Reactor X attached to a Rigaku Ultima III Powder Diffractometer using a Cu K-alpha radiation operated at 40 KV and 44 mA. Flow of reaction gases (air, containing 21.4% TRC <1.0 ppm and H₂ in a mixture with 90% N₂) and purge (N₂ high purity) gases was regulated

using Cole Palmer rotameters. Tubing and fittings used were made of stainless steel 316 and Swagelok fittings, including valves and quick connectors. The sample temperature was measured and controlled using a thermocouple, located inside the Reactor X, and a temperature controller, respectively

3.5.2 FT-IR Measurements

Fourier Transform Infrared spectrums were collected using a Thermo Nicolet 6700 FT-IR. The background, containing CO₂ and H₂O was subtracted. A resolution of 4 cm⁻¹ was used while 32 scans were accumulated for each spectrum.

3.5.3 Thermogravimetric Analyses

Thermogravimetric analyses were conducted using a Thermoanalytical TGA 2950. The sample was heated from RT to 350°C, under air, at a heating rate of 1°C/min and a hold time of 5 hours. The initial weight of the sample was 12.4 mg.

3.6 Results

3.6.1 XRD

We first studied the effect of the air and H₂ flow rates on the formation of the Ni clusters. We found that there were flow diffusion limitations inside the Reactor X chamber at low flow rates that resulted in inhomogeneous samples. After a careful flow

study it was determined that an air flow rate of 53.3mL and a H₂ flow rate of 56.2 mL/min was the minimum flow necessary for the reliable utilization of this method.

MOR-A is our reference sample which was impregnated with 16.7 wt% Ni. It was calcined in air with a heating rate of 1°C/min up to 350°C and a holding time at 350°C of 5 hours. The sample was then reduced in hydrogen using the same temperature protocol. These conditions are typical conditions for the synthesis of catalysts [36]. Figure 3-1 shows the results obtained from the calcination of this sample. As can be observed from this figure, the NiO <2 0 0> peak appears at a temperature close to 250°C and around $43.2^\circ = 2\theta$, indicating that NiO crystals have started to form. We refer to this temperature as the apparent calcination activation temperature (Calc T_{act}) from now on. As the reaction progresses this broad peak develops into a well defined peak suggesting that the particle has grown significantly. According to Scherrer's equation (Eq. 1.9) the particle size (PS) determined for the first defined peak was 39 Å. At the end of the calcination run the PS was found to be 86.0 Å.

When these results were compared to the results obtained by Richardson [59], who reported that the peaks changes were more subtle with temperature, suggest that the NiO crystal growth occurs quickly once the apparent calcination activation temperature is reached. This is evidenced by the initial crystal size, which is bigger than the pores of mordenite. As illustrated by Figure 3-2a, the NiO crystal size grew as the temperature increased suggesting that temperature promotes the NiO growth. Figure 3-2b shows that the NiO crystals continued to grow with time at 350°C until reaching a plateau after approximately 2.5 hours of hold time.

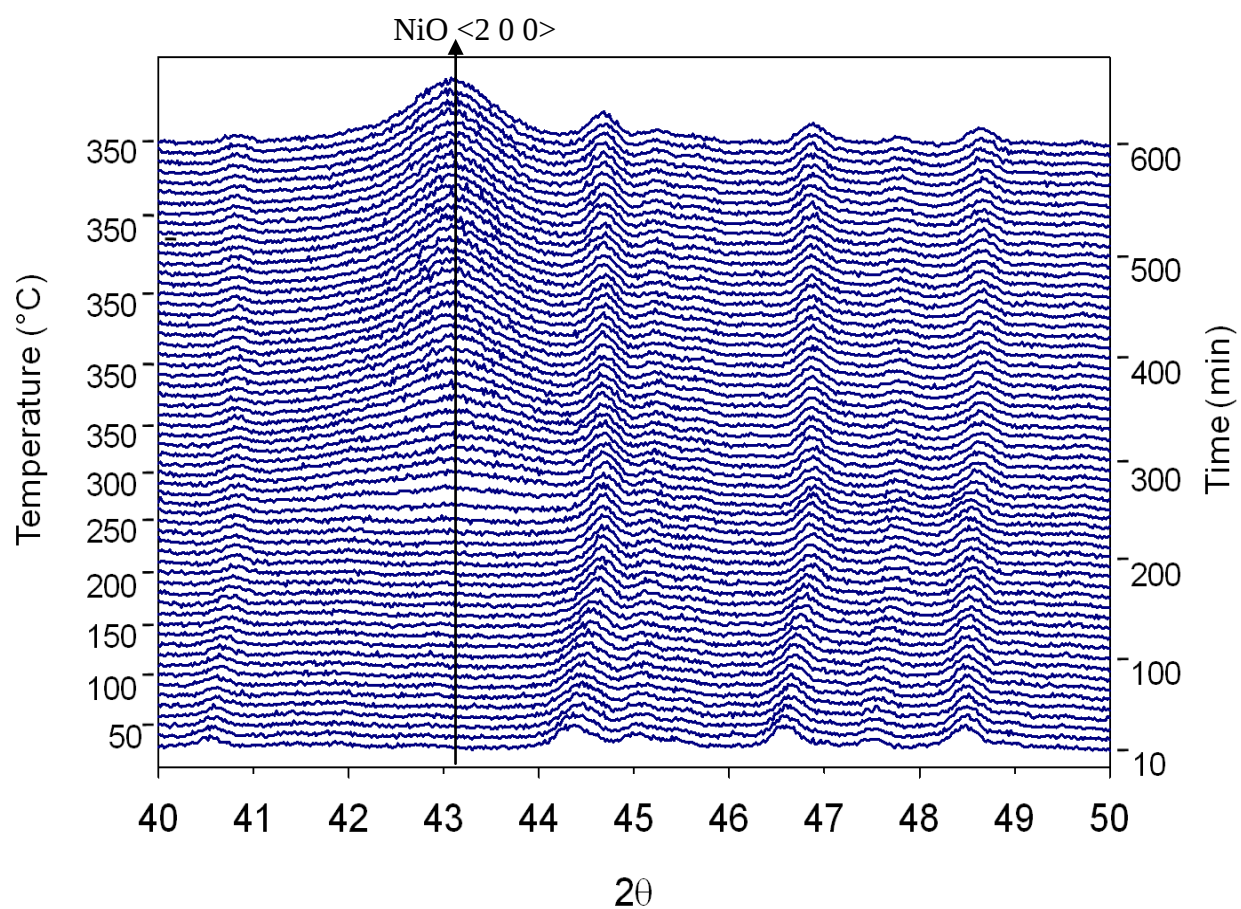


Figure 3-1 XRD patterns of mordenite of sample MOR-A impregnated with 16.7 wt% Ni during calcination at a heating rate of 1°C/min and using an air flow rate of 53.3 mL/min.

In order to have a better understanding of the Ni crystal growth behavior, the dependence of metallic Ni crystal size with temperature was also studied. For the sample described above the results are shown in Figures 3-3, 3-4a and 3-4b.

Figure 3-3, illustrates the XRD patterns taken during the reduction of this sample. As illustrated by this Figure, the NiO $\langle 2\ 0\ 0 \rangle$ peak begins to disappear with increasing T, while at a temperature close to 230°C a new peak starts to appear close to 44.5° corresponding to the crystalline Ni $\langle 1\ 1\ 1 \rangle$ peak. At this point, similar to Richardson [59], it can be observed that the NiO peak and Ni peak overlapped due to the small size of both particles. However, in disagreement with the results reported by Richardson [59], after 280°C, the NiO peak disappeared completely suggesting that NiO was entirely consumed. Also, the Ni peak appeared at a temperature close to 230°C, which is higher than the 175°C reduction temperature for bulk NiO reported by Richardson [59]. We refer to this temperature to as the apparent reduction activation temperature (Red T_{act}). The differences in temperature observed here vs. those in alumina are probably due to the increased H₂ diffusion limitation inside the zeolite pores.

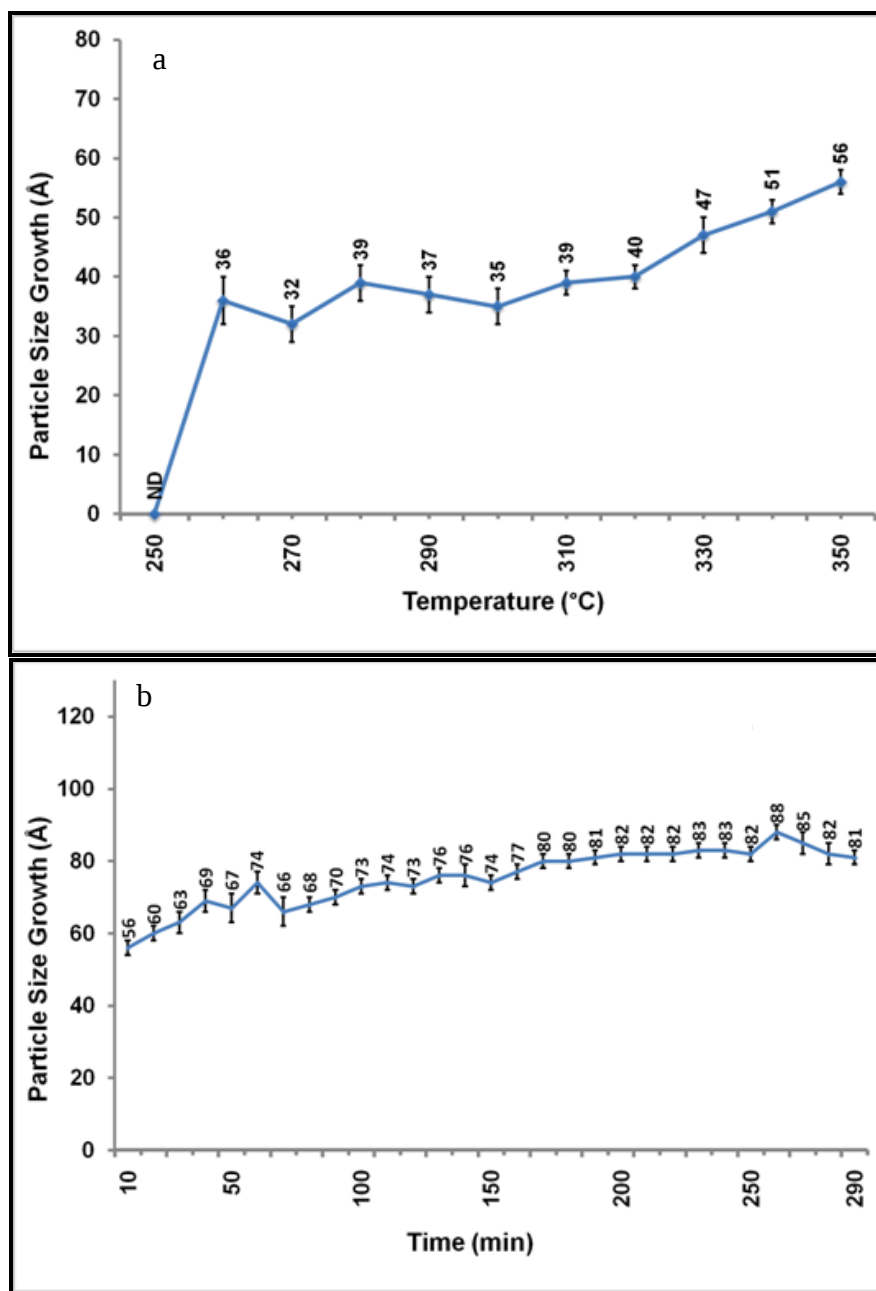


Figure 3-2 a) NiO particle size in sample MOR-A during calcination from RT to 350°C b) and during hold time at 350°C for 5hrs.

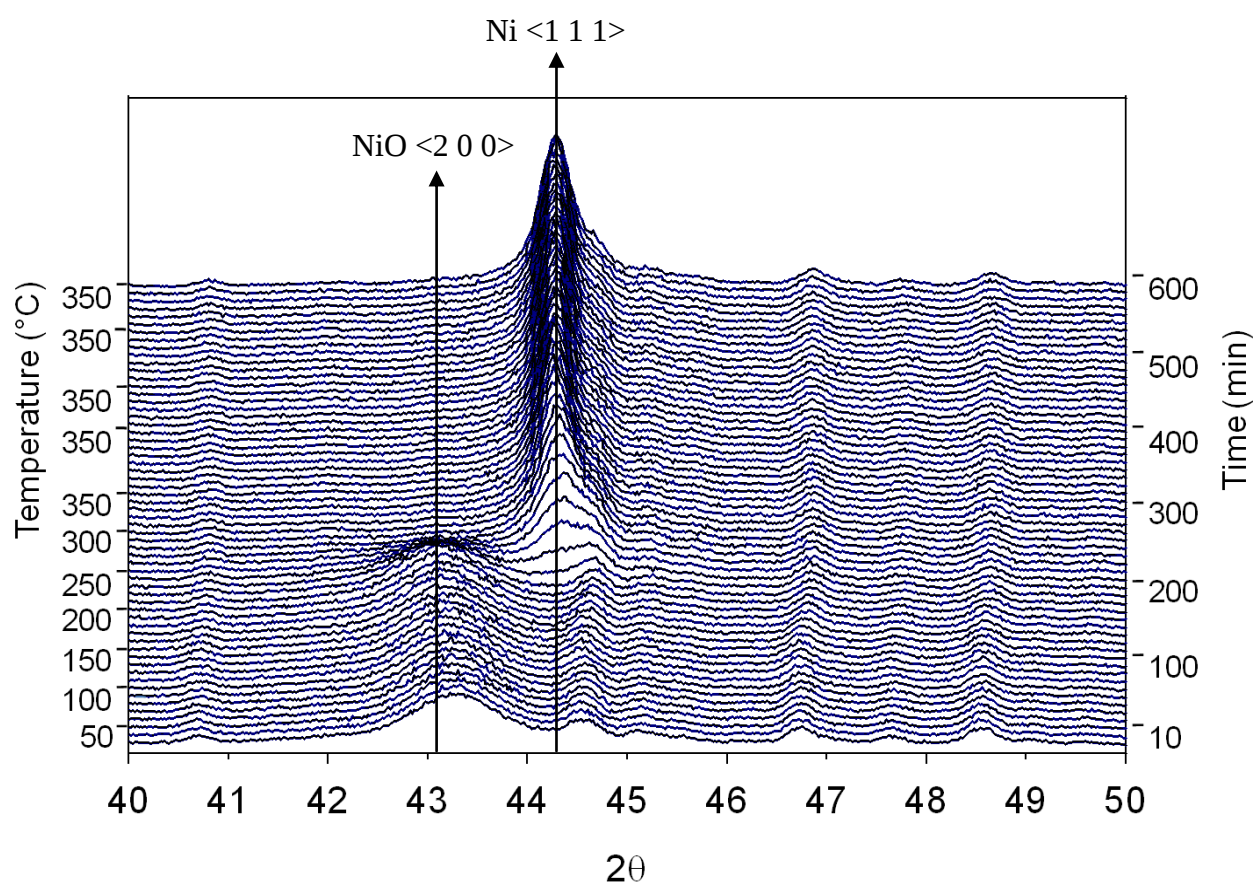


Figure 3-3 XRD patterns of sample MOR-A impregnated with 16.7 wt% Ni during reduction at a heating rate of $1^\circ\text{C}/\text{min}$ using a H_2 flow rate of $56.2\text{ mL}/\text{min}$.

The first quantifiable Ni crystal size was 101 Å (as observed in Figure 3-4a), which is larger than the pores of mordenite and to the final NiO crystal size, suggesting a much faster growth for Ni than NiO. At the end of the run the Ni crystal size was 256 Å as shown in Table 3-2. Since all the NiO was apparently consumed, according to the XRD, and the particle continued growing we have attributed this to coalescence effects. By comparing Figures 3-2a and 3-2b with 3-4a and 3-4b, it is evident that the Ni crystal growth with temperature is much faster than the NiO growth.

In order to verify that the crystalline structure of the zeolite was conserved after the calcination and reduction were completed, we ran an XRD pattern from a 2θ of 5° to 90° , as shown on Figure 3-5a. This figure illustrates three different XRD patterns, one for mordenite, another for MOR-A, and the theoretical peaks of Ni. Comparing these XRD patterns we can observe three differences between the XRD patterns for mordenite and that for the reduced sample. These three peaks were found to correspond to crystalline Ni crystal as it is on Figure 3-5. It is evident from this figure that the structure of the zeolite is not significantly altered during the reaction process and that the structure of the Ni clusters corresponds to that of the bulk.

Based on these results we decided to optimize the target temperature during calcination and reduction in order to control the metallic Ni final crystal size. Table 3-1 illustrates the conditions where the different experiments were conducted and Table 3-2 shows the corresponding results.

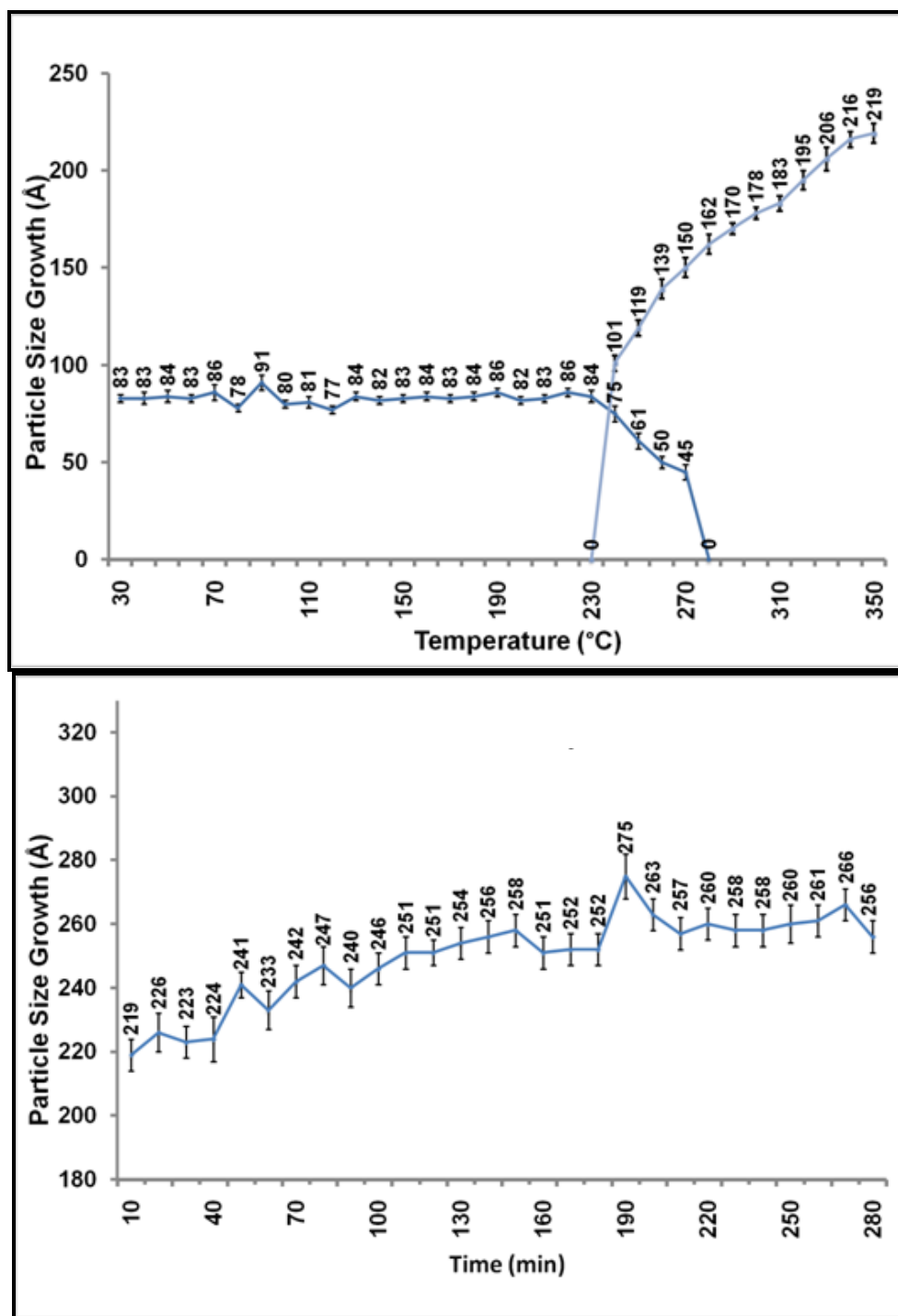


Figure 3-4 a) Ni growth behavior of in sample MOR-A during calcination from RT to 350°C and b) during hold time at 350°C for 5hrs.

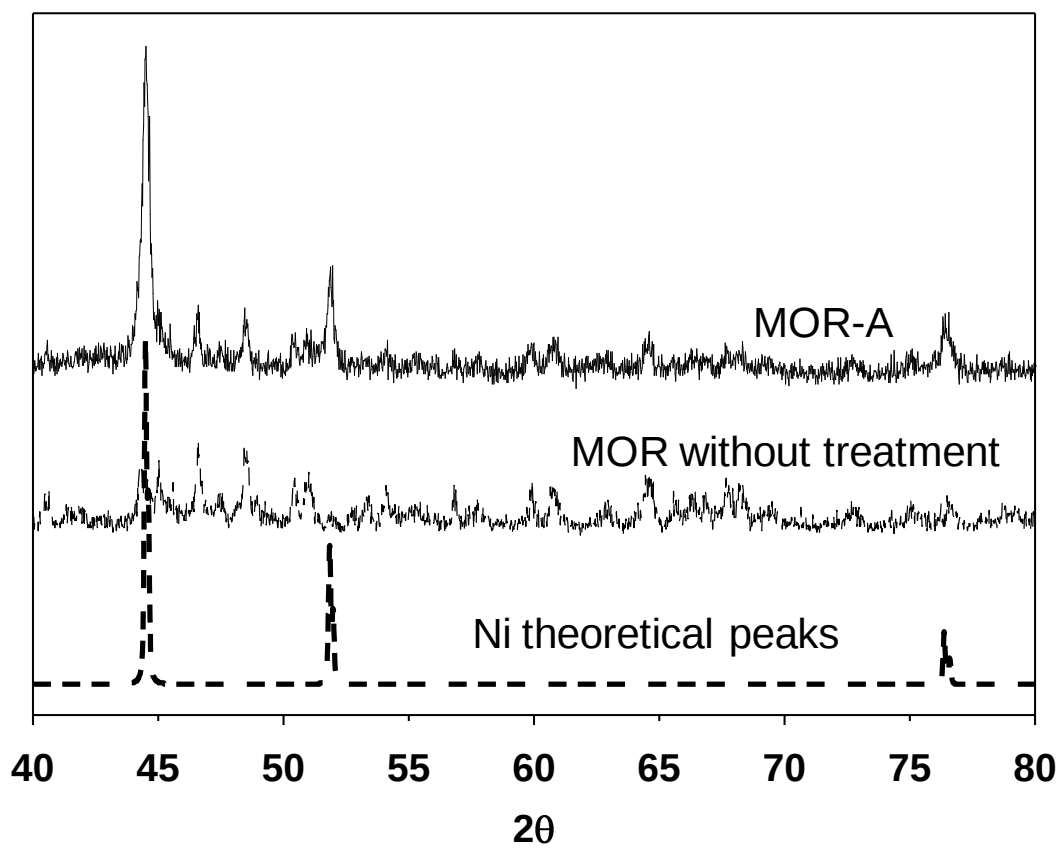


Figure 3-5 XRD pattern of mordenite, sample MOR-A, and the Ni theoretical peaks.

Table 3-1 Reaction conditions for the mordenite samples studied.

Sample	Ni loading (wt%)	Air Flow Rate (ml/min)	H ₂ Flow Rate (ml/min)	Analysis Description			
				Calcination	Hold Time (hrs)	Reduction	Hold Time (hrs)
MOR-A	16.7	53.3	56.2	RT to 350°C	5	RT to 350°C	5
MOR-B	16.7	53.3	56.2	Stopped at Calc T _{act} = 230°C	N/A	RT to 350°C	5
MOR-C	16.7	N/A	56.2	N/A	N/A	RT to 350°C	5
MOR-D	16.7	N/A	70.2	N/A	N/A	RT to 350°C	5
MOR-E	16.7	N/A	105.3	N/A	N/A	RT to 350°C	5
MOR-F	10.0	N/A	56.2	N/A	N/A	RT to 350°C	5
MOR-G	10.0	53.3	56.2	RT to 350°C	5	RT to 350°C	5
MOR-H	5.0	99.9	105.3	RT to 350°C	5	RT to 350°C	5
MOR-J	10.0	N/A	56.2	N/A	N/A	RT to 270°C	5
MOR-I ^a	10.0	N/A	105.3	N/A	N/A	RT to 350°C	5

*The calcination heating rate used for all samples but MOR-I was 1°C/min.

^a The reduction heating rate used was 5°C/min.

Oxi T_{act} = Apparent Calcination Activation Temperature

Table 3-2 XRD results for the samples described in Table 3-1.

Sample	NiO Apparent Activation Temperature (°C)	Initial NiO Size (Å)	Final NiO Size (Å)	Ni Apparent Activation Temperature (°C)	Initial Ni Size (Å)	Final Ni Size (Å)
MOR-A	250	39 ± 3	81 ± 1	230	101 ± 2	256 ± 4
MOR-B**	250	*	*	280	96 ± 2	187 ± 3
MOR-C ^a	T ₃	*	52 ± 2	270	109 ± 2	191 ± 4
MOR-D ^a	T ₃	*	55 ± 2	280	110 ± 1	186 ± 3
MOR-E ^b	T ₃	*	*	260	120 ± 2	191 ± 4
MOR-F ^b	T ₃	*	*	270	122 ± 3	113 ± 2
MOR-G ^a	230	*	51	230	*	145 ± 3
MOR-H	*	*	*	*	*	*
MOR-J ^{b,c}	*	*	*	270	137 ± 3	183 ± 3
MOR-I ^b	T ₃	*	*	245	118 ± 3	115 ± 3

* A quantifiable crystal size could not be obtained

**The calcination reaction for MOR-B was stopped at the NiO T_{act} while the reduction was allowed to run as normal.

^a NiO peak appeared during H₂ reduction.

^b NiO peak appeared during H₂ reduction but a quantifiable crystal size could not be obtained.

^cThe NiO T_{act} could be detected because the peak change was too smooth.

T₃ -The NiO T_{act} for these samples could be found in Table 3-3.

Table 3-3 NiO T_{act} for samples reduced without prior calcination.

Sample	NiO Apparent Activation Temperature (°C)
MOR-C	240
MOR-D	250
MOR-E	250
MOR-F	270
MOR-I	225

By comparing the results obtained from MOR-A and MOR-B, illustrated in Table 3-2, we can conclude that a sample exposed to a calcination environment for a longer period of time will result in larger metallic Ni crystals when reduced under a H₂ environment. This is probably due to the small NiO clusters present initially for the formation of Ni clusters. It can also be observed that the apparent reduction temperature for MOR-A is lower than the apparent reduction temperature for MOR-B. This could be due to the presence of undecomposed nickel acetate which under H₂ reduction atmosphere undergoes a different decomposition mechanism [49]. This is further confirmed with samples MOR-C, MOR-D, MOR-E, and MOR-F, which were not calcined prior to H₂ reduction.

By comparing MOR-A and MOR-C it can be observed that the final Ni crystal size is much smaller for MOR-C. The nickel acetate decomposition occurred faster for MOR-C suggesting that H₂ leads to a faster decomposition than air does. On the other hand the apparent reduction temperature was lower for MOR-A, which was previously calcined.

During this reaction it was found that nickel acetate decomposed under H_2 leads to metallic Ni $\langle 1\ 1\ 1 \rangle$. Samples MOR-C, MOR-D, and MOR-E were run with the purpose of determining the effect of calcination and the H_2 flow rate on the final Ni crystal size. These results show that there are no significant changes in the final Ni particle size when using different H_2 flow rates but a comparison with MOR-A shows that reduction without calcination in general leads to smaller Ni clusters. Even though MOR-C, MOR-D, and MOR-E were not calcined prior to H_2 reduction, it is evident from Figure 3-6 that both NiO $\langle 2\ 0\ 0 \rangle$ and metallic Ni $\langle 1\ 1\ 1 \rangle$ crystals were formed during the reduction reaction. This suggests that calcination is not needed for the formation of Ni clusters, if the precursor is reduced with H_2 .

The Ni loading was also studied. MOR-F and MOR-G were impregnated with 10.0 wt% Ni. A comparison between these two samples show that H_2 reduction without prior calcination (MOR-F) leads to smaller Ni cluster, as was found for samples impregnated with 16.7 wt% Ni. Results for MOR-F show higher activation temperatures for the appearing of both, NiO and Ni clusters. Similar to samples impregnated with 16.7 wt% Ni, this is probably due to the two decomposition steps taking place. Looking at the results for MOR-A and MOR-G, it can be observed that the Ni crystal size is much smaller for MOR-G suggesting that decreasing the Ni loading during impregnation, leads to smaller Ni clusters. The same is observed if the results for samples MOR-C and MOR-F are compared.

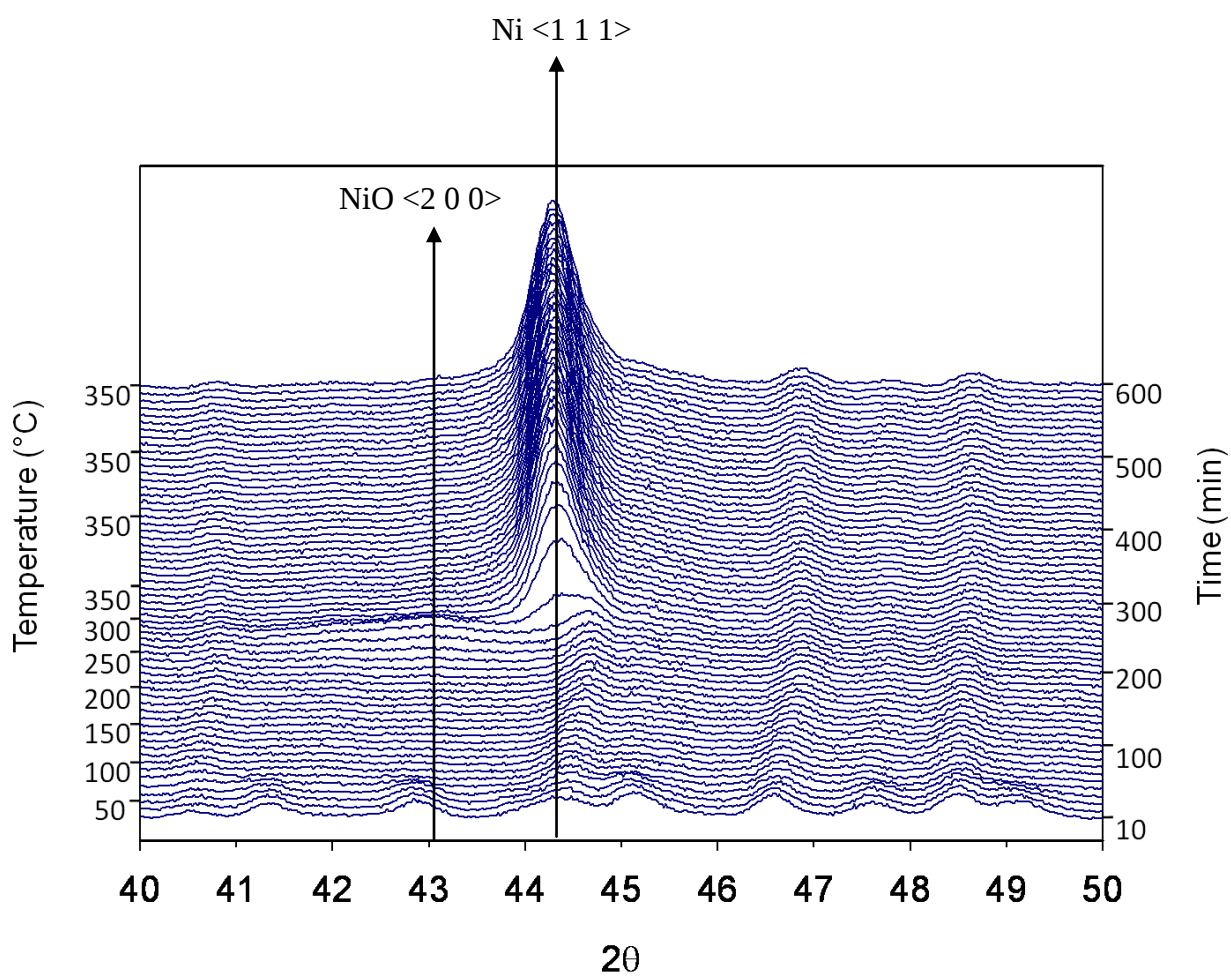


Figure 3-5 XRD patterns of sample MOR-C impregnated with 16.7 wt% Ni during reduction, without previous calcination, at 1°C/min using a H₂ flow rate of 56.2 mL/min.

After a Ni loading effect on the final Ni crystal size was evident, sample MOR-H was studied. Even though a quantifiable particle size couldn't be obtained from the XRD results, a TEM image (shown in Figure 3-7) showed that this sample contained small particles with an average Ni crystal size close to 70Å.

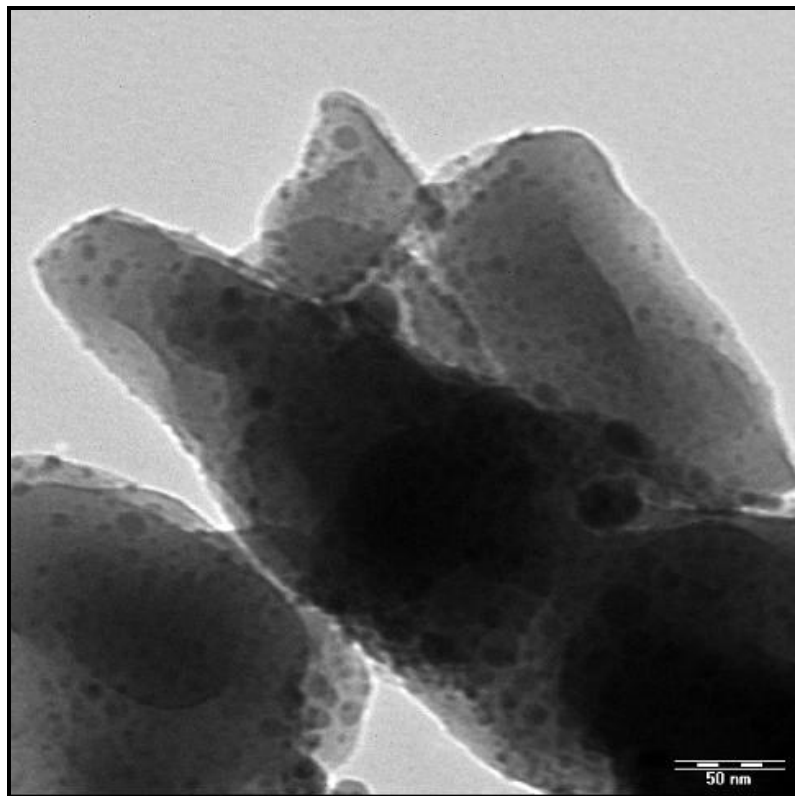


Figure 3-6 TEM image of sample MOR-H impregnated with 5 wt% Ni. The calcination and reduction were run from RT to 350°C at 1°C/min and held at 350°C for 5hrs. Air and H₂ flow rates used were 99.9 mL/min and 105.3 mL/min, respectively.

Sample MOR-I was reduced from RT to the T_{act} (270°C) and it was held at the T_{act} for 5 hours. A comparison with sample MOR-G shows that if the temperature is held at the T_{act} instead of a higher temperature, a larger metallic Ni crystal size is obtained. The heating rate was also studied. Sample MOR-J (illustrated in Figure 3-8) was reduced under H_2 , without prior calcination, at a heating rate of 5°C/min. A comparison with sample MOR-G shows that a higher heating rate doesn't affect significantly the final Ni crystal size but leads to faster decompositions. However, as illustrated in this Table 3-2, the initial Ni crystal size and the final Ni crystal size were almost identical, suggesting that as the heating rate increases, the agglomeration rate increases.

After a Ni loading effect on the final Ni crystal size was evident from sample MOR-H, we decided to run sample MOR-I. Even though a quantifiable particle size couldn't be obtained from the XRD results, a TEM image (shown in Figure 3-7) showed that this sample contained small particles with an average Ni crystal size close to 70Å.

The results obtained for the samples that were ion exchanged with $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ to determine the effect of this incorporation method were inconclusive as the particles appear to be too small to be detected by regular XRD.. This suggests that ion exchange yields smaller Ni clusters than impregnation and based on previous results, clusters smaller than 80 Å.

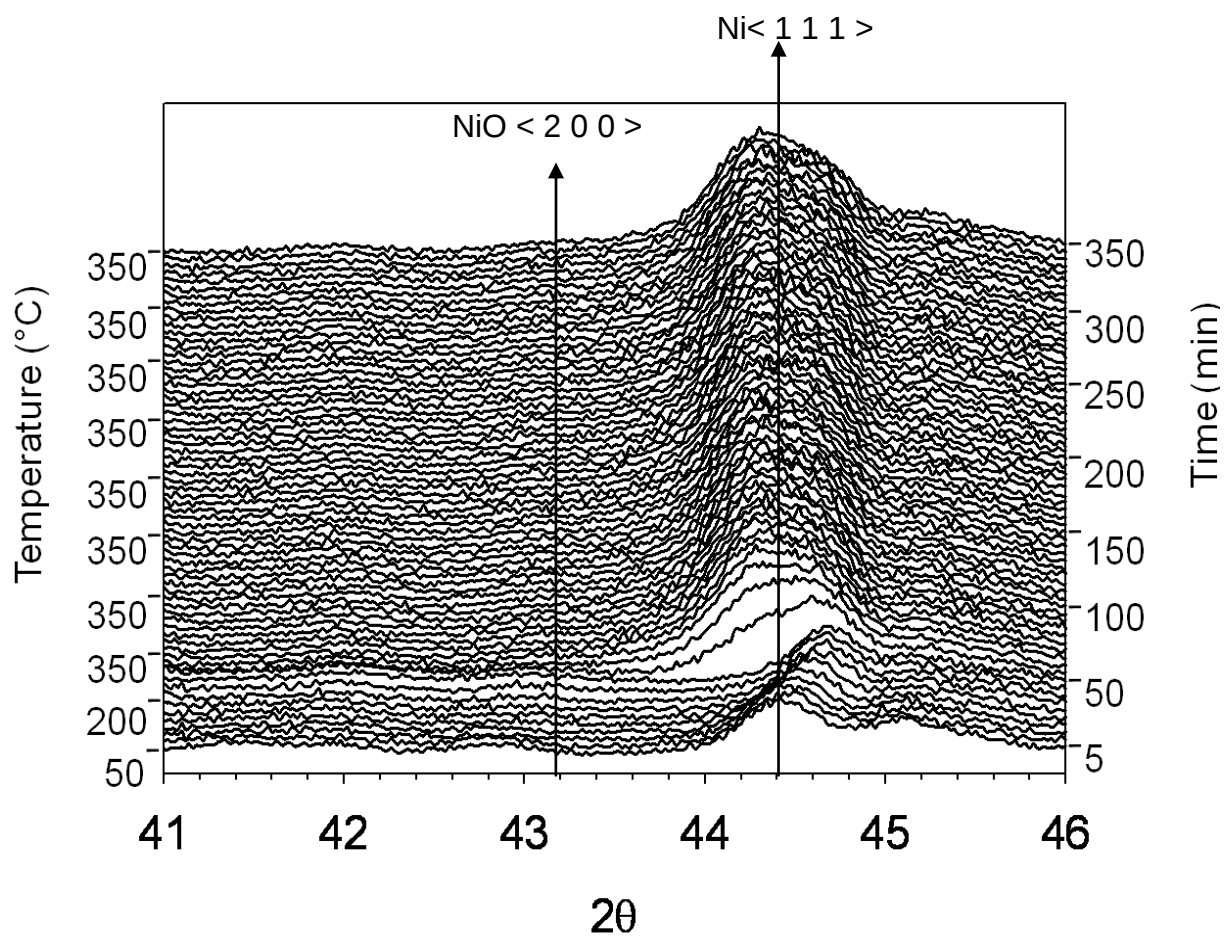


Figure 3-7 XRD patterns of sample MOR-I impregnated with 10.0 wt% Ni during reduction, without previous calcination, at 5°C/min using a H₂ flow rate of 105.3 mL/min.

3.6.2 FTIR

Each impregnated sample showed an absorbance band close to 1100cm^{-1} which corresponds to the asymmetric stretching vibration of SiO_4 and AlO_4 groups [60] as is expected for the zeolite support. Absorbance bands observed close to 3400 cm^{-1} could be attributed to the hydroxyl groups of mordenite. Each treated mordenite sample showed a band in a frequency close to 1650 cm^{-1} , which could be attributed to deformation vibrations of H-O-H [60].

The nickel acetate spectrum shows absorbance bands within the range of 1600 to 1400 cm^{-1} corresponding to the COO^- group [50]. This peak was not observed for the samples that were calcined prior to H_2 reduction neither for those that were reduced without prior calcination. This suggests that the nickel acetate was completely consumed in the treated samples under all studied synthesis conditions. The FTIR range and resolution of this instrument, however, was not enough to identify a NiO peak.

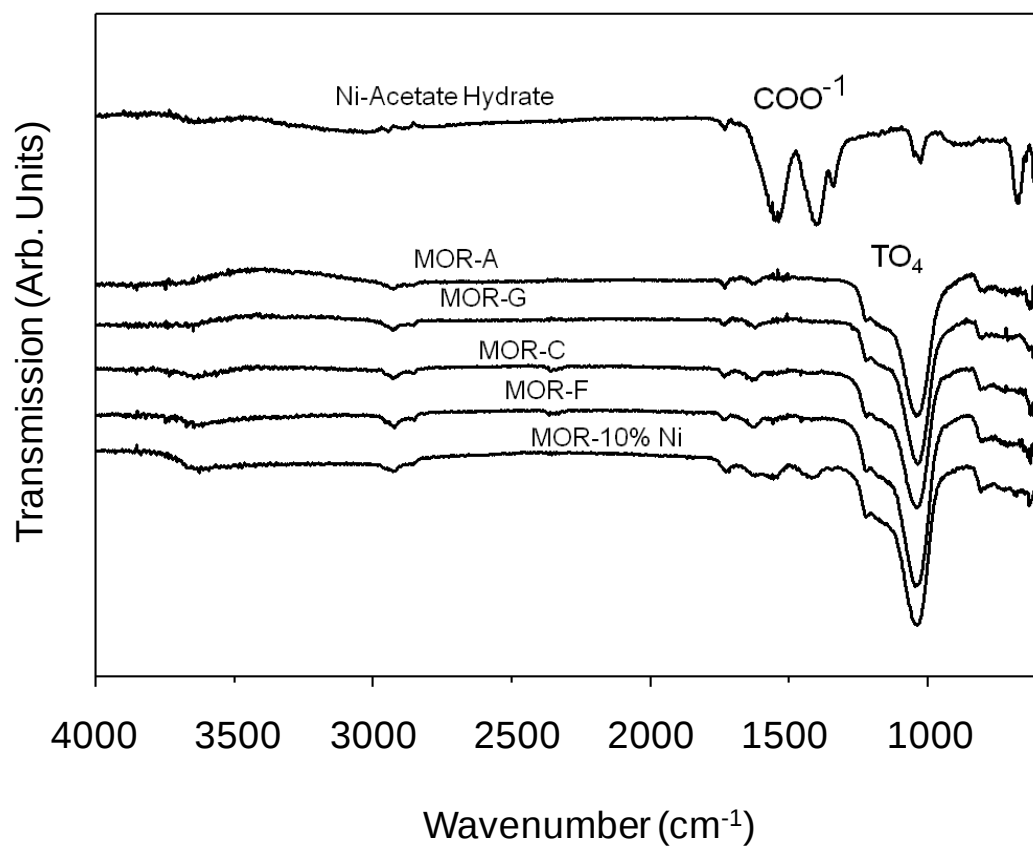


Figure 3-8 FTIR spectra of the samples studied, of an untreated 10 wt% Ni impregnated mordenite sample and of nickel acetate.

3.6.3 TGA Results

Figures 3-10, 3-11 and 3-12 show the thermogravimetric changes undergone by mordenite, hydrated nickel acetate, and nickel acetate impregnated mordenite, respectively. From Figure 3-10 it can be observed that mordenite loses weight rapidly when the temperature is increased from 25°C to 300°C. These losses could be attributed to the water molecules adsorbed at different sites in mordenite. After the temperature is increased from 300°C to 900°C, no significant changes are observed suggesting that the mordenite structure is very stable at high temperatures. As depicted in Figure 3-11, the dehydration of nickel acetate occurs from a temperature of 60 to 110°C. At this point a weight loss close to 33.2% was observed, which is significantly higher than the expected value for the release of one water molecule (9.2%). The difference between the expected and resulted mass loss for the dehydration process suggests that either a significant amount of precursor was converted to gas or that the precursor contained more crystalline water than specified. Then at around 220°C a new weight loss curve starts to develop. It has been reported that this curve is due to the overlapping of several thermal decomposition reactions that nickel acetate goes through to yield NiO [47].

According to our XRD results the decomposition of the Ni precursor (nickel acetate hydrated) under air leads to NiO and since the TGA results showed that the remained weight was 30.4% of the initial weight. It is probable that our Ni precursor contained four crystalline H₂O molecules instead of just one. In order for the nickel

acetate hydrated to produce NiO the remained weight should have been 38.4% of the initial weight, instead it was 30.4% which is in close agreement with the expected residual weight for the production of Ni (30.1%), but this would go against our XRD results. However, the formation of NiO from nickel acetate tetrahydrated is expected to result in a residual weight of 30.0% which is much more accurate considering our XRD results.

Figure 3-12 illustrates the thermal decomposition behavior of a mordenite sample impregnated with 10% by weight of Ni. From this figure it can be observed that the decomposition occurred through three different steps, contrary to that of Figure 3-10, which showed only a decomposition step. These two extra steps in Figure 3-12 could be attributed to the presence of nickel acetate, which thermally decompose through two steps as depicted in Figure 3-11. Therefore, the thermal behavior of nickel acetate remains almost identical to that of the bulk material. The decomposition temperature of impregnated nickel acetate agrees with that found from the Reactor X results.

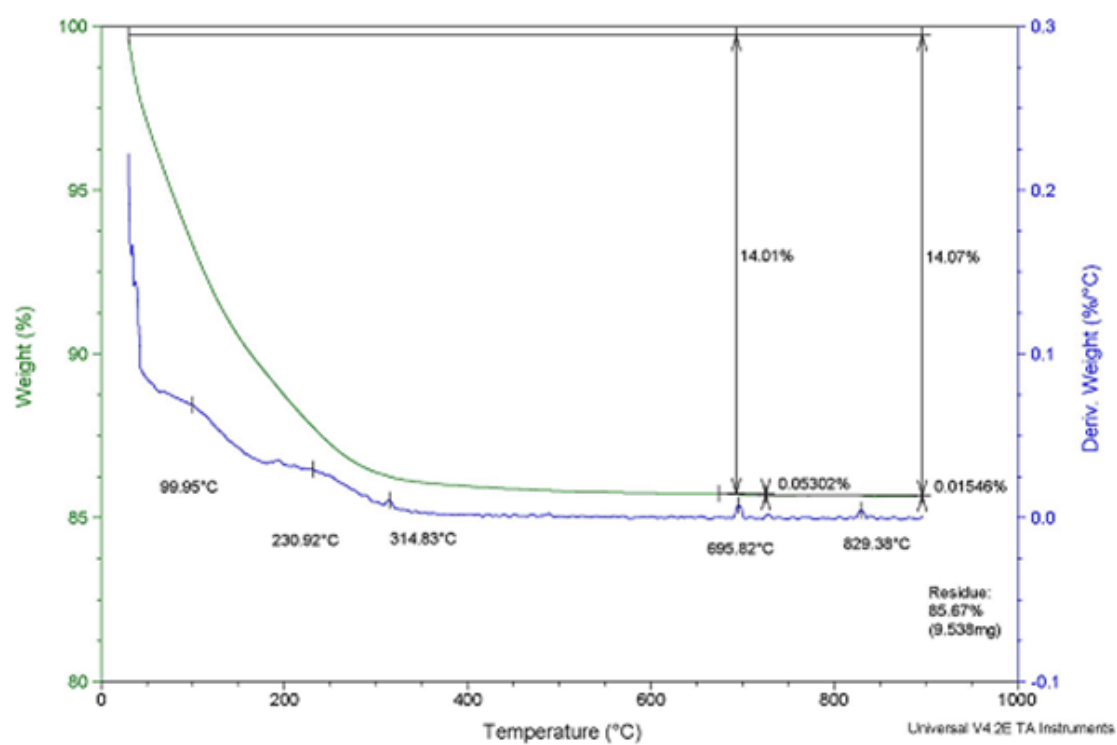


Figure 3-9 TGA curve of mordenite in air.

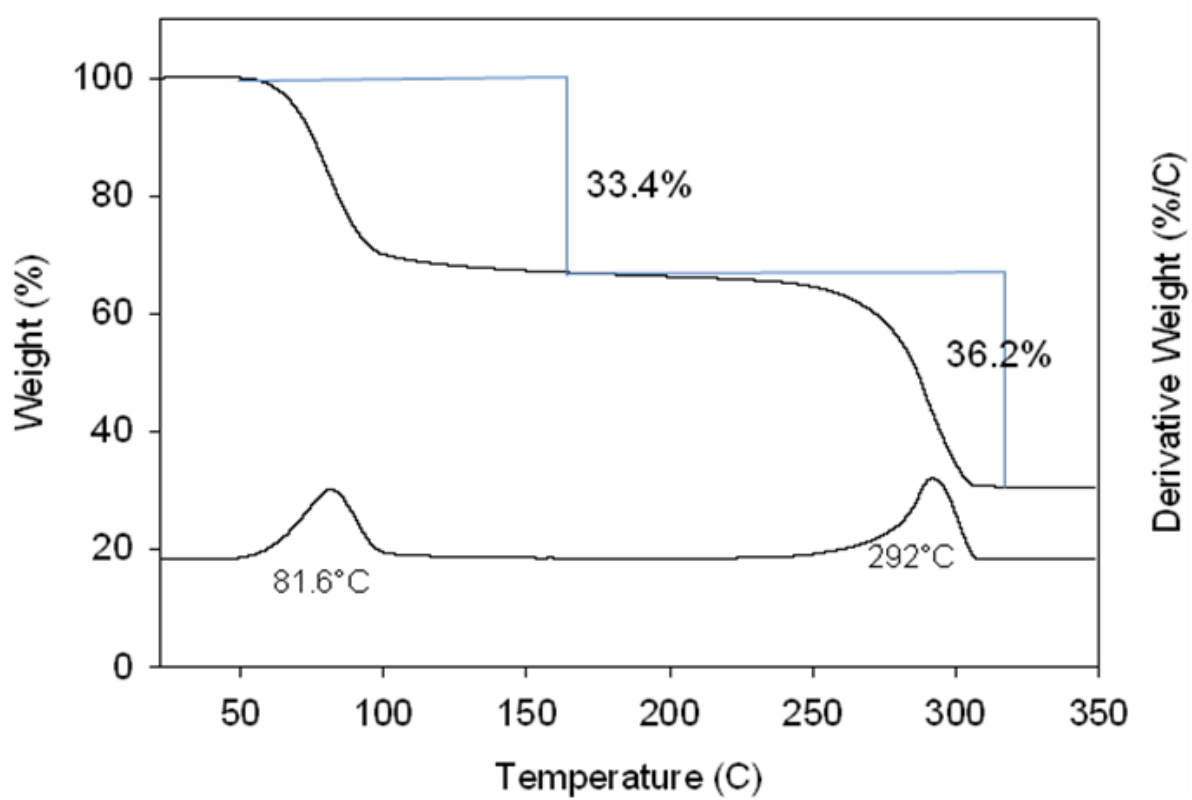


Figure 3-10 TGA curve of hydrated nickel acetate in air.

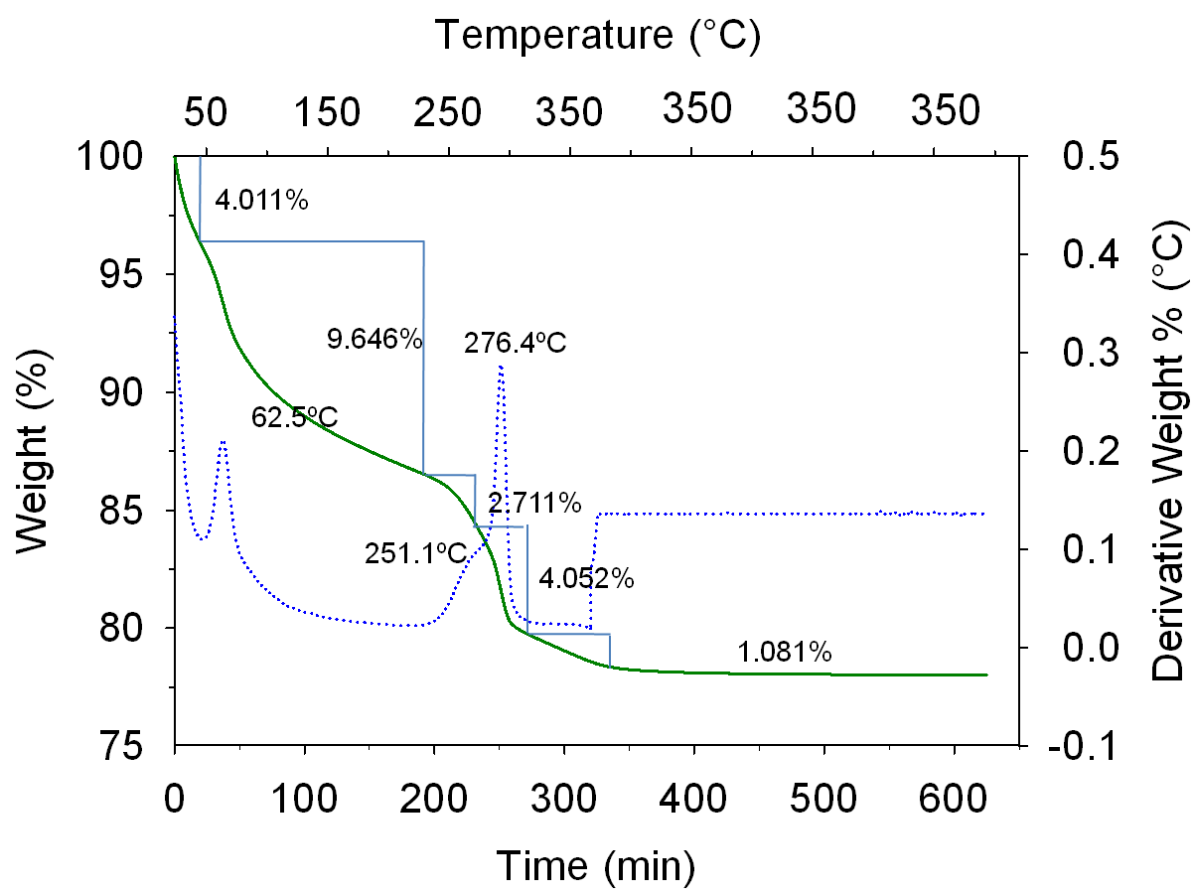


Figure 3-11 TGA curve of MOR dry impregnated with 10 wt% Ni in air.

3.7 Conclusions

It was found that H_2 reduction of samples previously calcined leads to bigger Ni clusters than samples reduced without prior calcination. During this process $NiO < 2 \ 0 \ 0 >$ is formed, which then decomposed to produce metallic Ni $< 1 \ 1 \ 1 >$. At the end of the reaction, the XRD results did not show residual NiO cluster, suggesting that the NiO clusters were completely reduced. From the metal growth behavior figures, 5-2a, 5-2b and 5-4, it can be observed that NiO grows much slower than metallic Ni, suggesting that Ni agglomeration is much faster. This could be due to some metal support interaction between the NiO and mordenite, which could be diminishing the movement of the NiO crystals consequently reducing the agglomeration.

In addition, it was found that the loading has significant effect in the final Ni crystal size. As the Ni impregnation loading was decreased the final Ni crystal size was significantly reduced. As the Ni impregnation loading increases, this could cause a decrease in the metal-support interactions, leading to an increase in Ni particle movement and consequently increasing the agglomeration of Ni particles. In general, it could be concluded that smaller Ni clusters could be obtained if a mordenite impregnated with low Ni loadings in reduced under H_2 without prior calcination.

The maximum Ni loading that could be achieved, taking into account the precursor dimensions, was determined using molecular simulations. It was found that the maximum Ni loading is close to 3.1 wt%. Since the loadings reported here are larger than this value, it is probable that a significant amount of the impregnated precursor was

located outside the pore system where agglomeration is most likely to occur, in comparison with particles contained within the pores, leading to large particles. Canizares et al [36] used $\text{Ni}(\text{NO}_3)_2$ as precursor to achieve Ni concentration of 2.5 wt% or less. Even though these Ni loadings were significantly smaller than the ones used in this study, they concluded that large Ni crystals were formed after reduction, reaching a crystal size of 180Å which is larger than some of the Ni crystal sizes reported in this study. This could be due to the differences in the treatment procedures. Canizares used air calcination at 400°C for 4 hrs. After calcination, they performed the reduction at 460 °C for 4 hrs. According to our results air calcination prior to reduction leads to larger Ni crystals than reduction without prior calcination. In addition the temperatures used by Canizares are higher than those reported here, which probably led to a faster Ni agglomeration and thus larger Ni crystals.

4 Studies of VPI-8 as a Support for Ni clusters

4.1 Materials

VPI-8 was synthesized by our group using a method described elsewhere [61]. The synthesis was carried out using Teflon-lined stainless steel autoclaves, heated in a convection oven. Several chemical reagents were used such as: tetraethylammonium hydroxide (TEAOH, 40 wt.% aqueous solution, Aldrich), LiOH (Fisher), colloidal silica (SiO_2), zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Fisher). After carrying the hydrothermal reaction following the directions given by Freyhardt et al., [61], the resulting product was filtered, washed using distilled water and dried at 80°C in a convection oven. Finally the dried product is calcined under air at high temperatures to remove the pore-filling organic tetraethylammonium cation (TEA^+).

4.2 Incipient Wetness Impregnation

In this work we incorporated nickel to VPI-8 using incipient wetness impregnation as previously described in Chapter 3 for mordenite.

4.3 Calcination and Reduction

In order to compare the effect of the support, the calcination and reduction conditions used for the VPI-8 samples are similar to those used for mordenite as discussed in Chapter 3.

4.4 Characterization Techniques

4.4.1 XRD

The calcination and reduction processes were studied *in situ* using the Reactor X using the methodology developed with zeolite mordenite described in Chapter 3.

4.4.2 FTIR

Fourier Transform Infrared spectrums were collected using a Thermo Nicolet 6700 FT-IR. The background, containing CO₂ and H₂O was subtracted. A resolution of 4 cm⁻¹ was used while 32 scans were accumulated for each spectrum.

4.4.3 Thermogravimetric Analysis

Thermogravimetric analyses were conducted using a TA Instrument TGA 2950. The sample was heated from RT to 350°C, under an air atmosphere, at a heating rate of 1°C/min and held there for 5 hours. The initial weight of the sample was close to 12.4mg.

4.5 Results

4.5.1 XRD

We studied air flow rates up to 100 mL/min and H₂ flow rates up to 105.3 mL/min. It was found that low air and H₂ flow rates caused diffusion problems within the Reactor X chamber leading to a palpable inhomogeneous reduction throughout the sample. As

for mordenite, we determined that the minimum air and H₂ flow rates for the reliable utilization of this state of the art attachment were 53.3 mL/min and 42.1 mL/min, respectively.

As a reference sample we used sample VPI-8-A, which was impregnated with 16.7 wt% Ni. It was calcined in flowing air at 53.3 mL/min using a temperature ramp of 1°C/min up to 350 °C with a hold time of 5 hours. It was then reduced with a 10% hydrogen in nitrogen flow of 93.3 mL/min using the same temperature protocol. The XRD patterns obtained during the calcination of this sample is shown in Figure 4-1. As can be observed from this figure, the NiO [2 0 0] peak starts to appear at a temperature close to 270°C and around 43.2° in the 2θ axis. As for mordenite, we refer to this temperature as the apparent calcination activation temperature (Calc Tact) from now on. As explained before this rising peak indicates that NiO crystals have started to form. It can be observed that as soon as the NiO is detected, a large gap is observed between the pattern corresponding to the NiO Tact and the one before, suggesting that a very broad NiO <2 0 0> peak has been formed. When comparing these results with the ones reported in Chapter 3, where this large gap was not observed, it appears that this could be the result of very small NiO crystals. As the reaction progresses the NiO <2 0 0> peak definition increases, suggesting that the particle has grown significantly. According to Scherrer's equation (Eq. 1.9) the particle size (PS) determined for the first quantifiable peak was 38 Å. At the end of the calcination run the PS was found to be 56.0 Å.

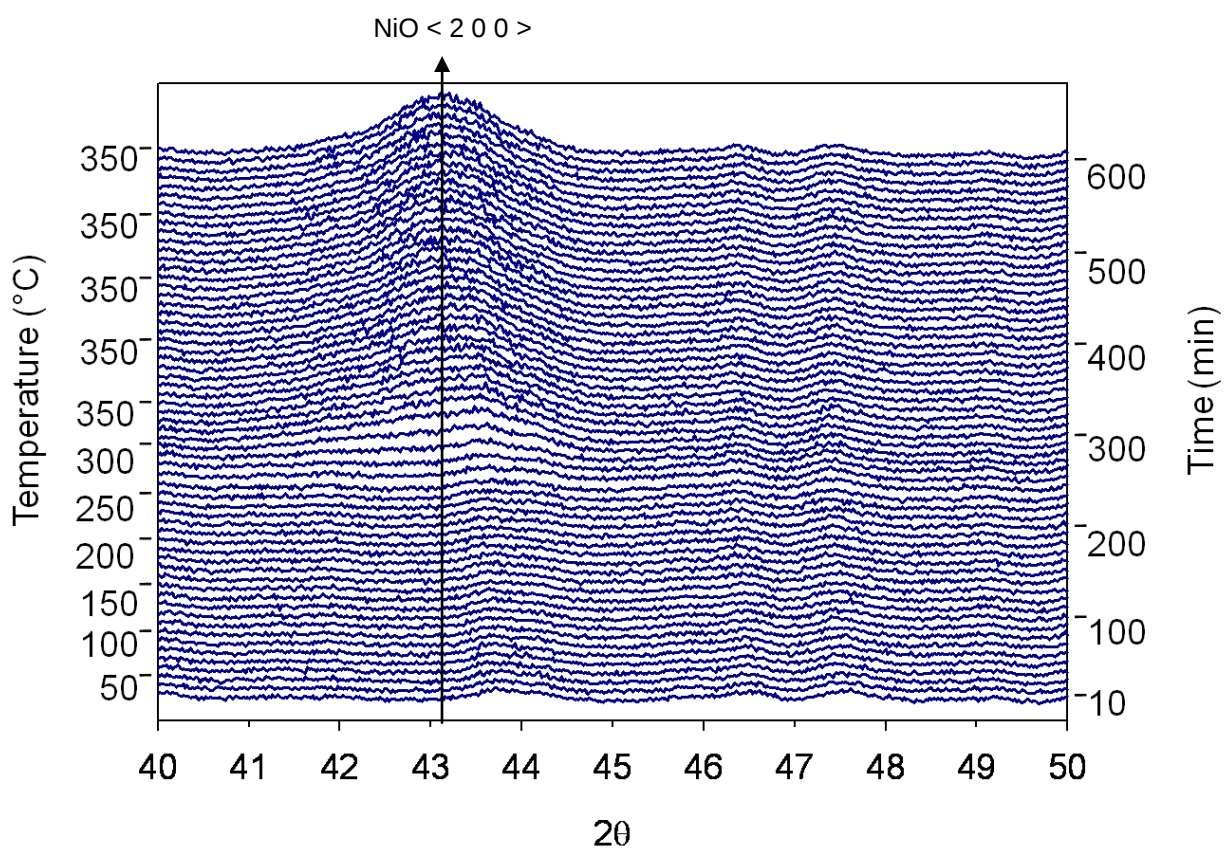


Figure 4-1 XRD patterns of VPI-8-A impregnated with 16.7 wt.% Ni during calcination at a heating rate of 1°C/min and using an air flow rate of 53.3 mL/min.

Table 4-1 Experimental conditions for the VPI-8 samples studied.

Sample	Ni loading (%)	Air Flow (ml/min)	H ₂ Flow (ml/min)	Analysis Description			
				Calcination	Hold Time (hrs)	Reduction	Hold Time (hrs)
VPI-8-A	16.7	53.3	98.3	RT - 350°C	5	RT - 350°C	5
VPI-8-B	16.7	53.3	56.2	RT - 350°C	5	RT - 350°C	5
VPI-8-C	16.7	53.3	42.1	RT - 350°C	5	RT - 350°C	7
VPI-8-D	16.7	53.3	42.1	RT - 350°C	5	RT - 350°C	2.5
VPI-8-E	16.7	N/A	105.3	N/A	N/A	RT - 350°C	5
VPI-8-F	16.7	N/A	56.2	N/A	N/A	RT - 270°C	5
VPI-8-G	10.0	53.3	56.2	RT - 350°C	5	RT - 350°C	5

*The calcination heating rate used for all samples was 1°C/min.

The hydrogen flow rate effect on the final Ni crystal size was also studied. From a comparison between samples VPI-8-A and VPI-8-B, it is evident that the particle size is within experimental error suggesting that we are working in a reaction limited regime. In order to have a better understanding of the Ni crystal growth behavior, the dependence of metallic Ni crystal size with temperature was also monitored. The growth behavior of NiO and Ni for the reference sample is illustrated in Figures 4-2a, 4-2b, and 4-4. As illustrated by Figure 4-2a, the NiO crystal size growth was invariant with temperature and only started to show particle growth with hold time reaching a steady state value of approximately 56 Å. This slow NiO growth compared to mordenite suggest that the NiO has a stronger interaction with VPI-8 that inhibits its diffusion and growth.

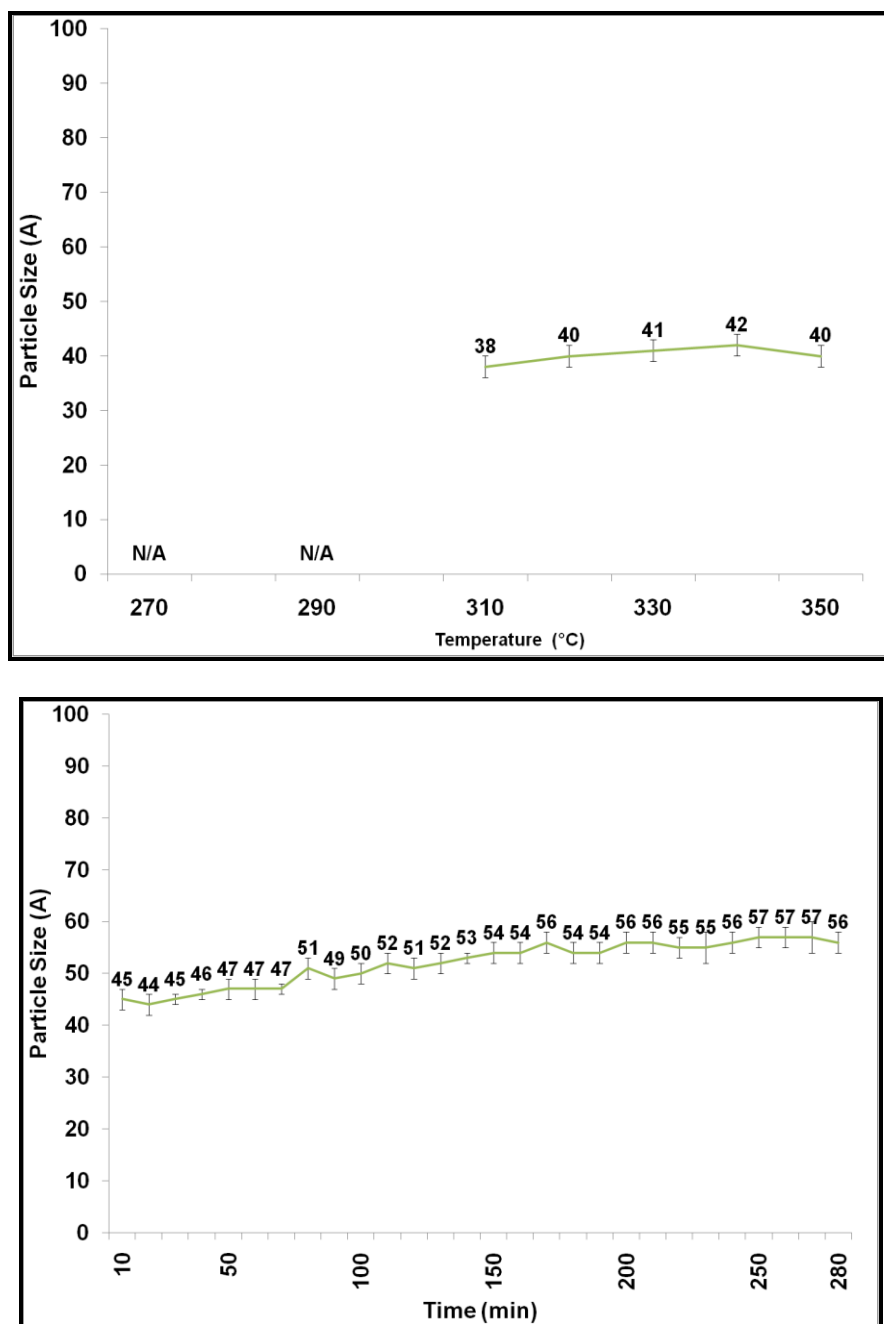


Figure 4-2 a) Growth behavior of NiO during calcination of sample VPI-8-A from RT to 350°C and b) at 350°C for 5hrs.

Figure 4-3, illustrates the XRD patterns taken during H₂ reduction of sample VPI-8-A, under the conditions listed in Table 4-1. It is evident that as the temperature

increases the NiO $\langle 2\ 0\ 0 \rangle$ peak starts to disappear at a temperature close to 250°C while a new peak starts to appear corresponding to the Ni $\langle 1\ 1\ 1 \rangle$ peak. As previously reported in Chapter 3, the NiO and Ni crystal peaks overlapped at the beginning of the reduction reaction. As the temperature increased the NiO peak continued to disappear while the Ni peak continued to grow, but contrary to what was found for mordenite, the NiO peak did not disappear completely, as is illustrated in Figure 4-4. This is in agreement with what Richardson reported [59].

It is evident that the holding time at a specified temperature leads to crystal growth until a stable particle size is obtained [36], therefore, we decided to study the effect of the hold time on the final Ni crystal size. Sample VPI-8-C and sample VPI-8-D were run using the same reaction conditions but sample VPI-8-C was held at 350°C for 4.5 hours more than sample VPI-8-D. The resulting final Ni crystal size for sample VPI-8-C was higher than that for sample VPI-8-D suggesting that the Ni crystals continued growing with time. Comparing the particle size of VPI-8-C and VPI-8-D with those of VPI-8-A and VPI-8-B it is evident that a hydrogen flow rate below 56.2 mL/min resulted in an increased particle size which is evidence of a diffusion limited regime.

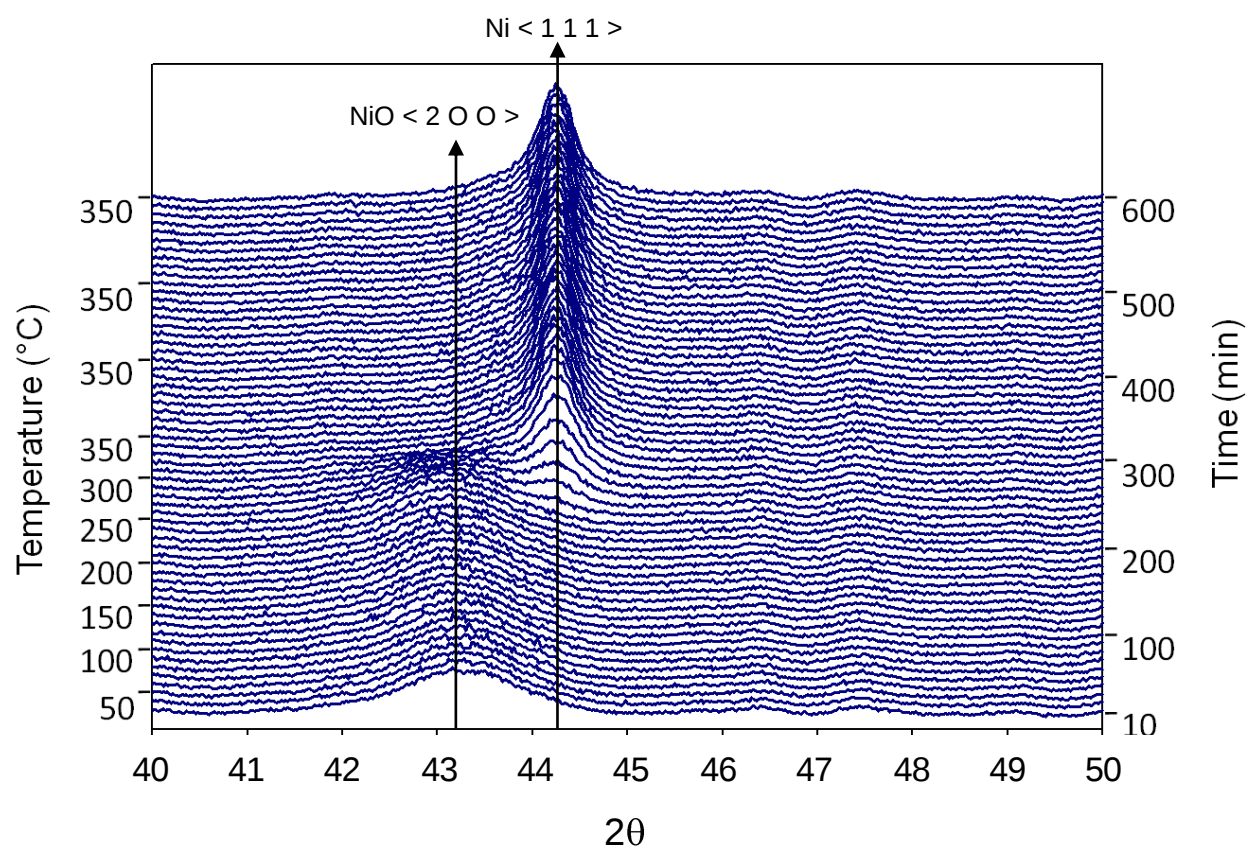


Figure 4-3 XRD patterns of a VPI-8 impregnated with 16.7wt% Ni during reduction at 1°C/min using a H₂ flow rate of 56.2 mL/min.

Table 4-2 XRD results of the samples described in Table 4-1.

Sample	NiO Apparent Activation Temperature (°C)	Initial NiO Size (Å)	Final NiO Size (Å)	Ni Apparent Activation Temperature (°C)	Initial Ni Size (Å)	Final Ni Size (Å)
VPI-8-A	290	39 ± 2	56 ± 2	260	98 ± 4	185 ± 5
VPI-8-B	240	34 ± 1	53 ± 1	250	106 ± 3	189 ± 4
VPI-8-C	270	41 ± 2	58 ± 2	260	88 ± 5	241 ± 6
VPI-8-D	270	54 ± 3	58 ± 2	260	83 ± 6	207 ± 5
VPI-8-E ^b	240	*	*	270	81 ± 2	118 ± 2
VPI-8-G	230	34 ± 1	37 ± 1	290	103 ± 5	156 ± 5
VPI-8-F	*	*	*	*	*	*

*A quantifiable crystal size could not be obtained

^b A NiO peak appeared during H₂ reduction but a quantifiable crystal size could not be obtained.

Table 4-3 NiO T_{act} for samples reduced without prior calcination.

Sample	NiO Apparent Activation Temperature (°C)
VPI-8-E	240
VPI-8-G	230

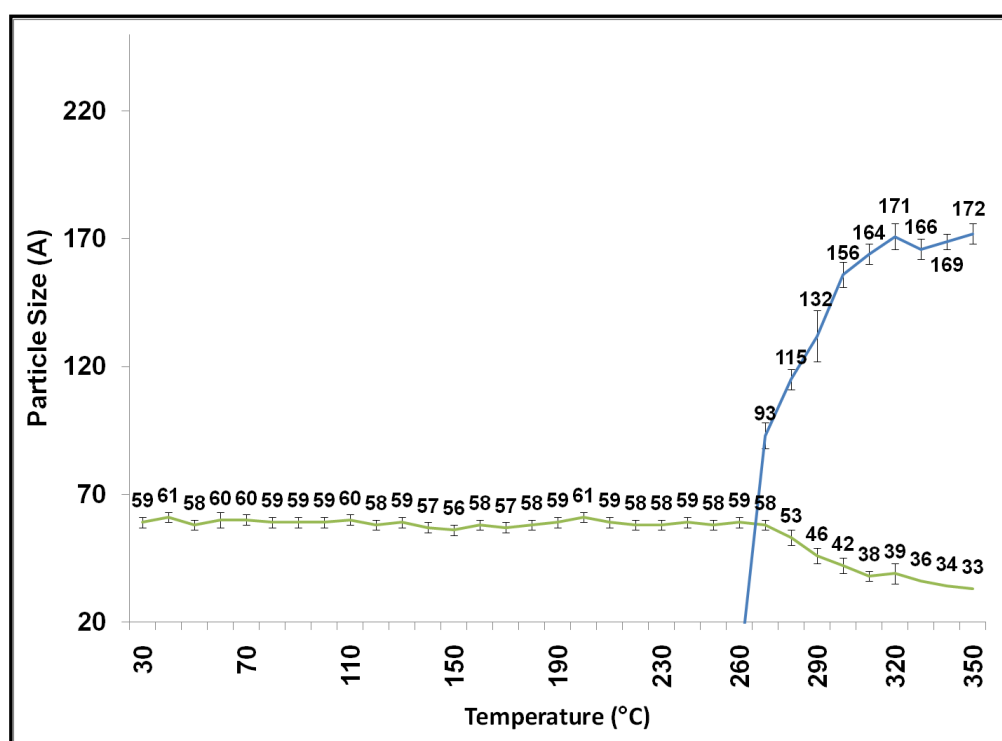


Figure 4-4 Left-hand curve describes the particle size of NiO and right-hand curve describes the particle size of Ni in sample VPI-8-A during reduction from RT to 350°C.

Prior thermal decomposition studies [46] found that the H_2 decomposition of nickel acetate leads to metallic Ni $\langle 1\ 1\ 1 \rangle$. This is in agreement with what we reported in Chapter 3 where the H_2 reduction of mordenite impregnated with nickel acetate yielded Ni crystals. Therefore, we also studied the H_2 reduction without prior calcination. A comparison between sample VPI-8-A and VPI-8-E shows that H_2 reduction without prior calcination leads to smaller Ni crystals than H_2 reduction after calcination. This suggests that Ni agglomerates faster when calcination is performed prior to reduction. Significant changes in decomposition temperature were not observed. As depicted in Figure 4-5, NiO appeared and was rapidly consumed to produce metallic Ni, suggesting that under H_2 reduction at least two different thermal decomposition reactions occur.

Sample VPI-8-F was run without calcination at a reduction T_{act} of 270°C . As can be seen from Figure 4-6 the NiO $\langle 2\ 0\ 0 \rangle$ peak grew significantly more and also lasted for a longer period of time than it did for sample VPI-8-E, resulting in a significantly larger particle size. This is probably due to the transition from a reaction limited regime to a diffusion limited regime with the reduction of temperature.

From these two figures, at the end of the reduction it can be observed that the NiO $\langle 2\ 0\ 0 \rangle$ and the Ni $\langle 1\ 1\ 1 \rangle$ peaks overlap suggesting that unreduced NiO crystals remained in the sample after H_2 reduction was conducted. However, overlapping NiO peak is larger in Figure 4-6 than in Figure 4-5, suggesting that the remaining NiO crystallites in sample VPI-8-F were larger than those for sample VPI-8-E. This could be due to the higher H_2 flow rate used for sample VPI-8-E, which could have enhanced the availability of H_2 molecules for the reduction of NiO crystals. Figure 4-6 shows a

disturbance in the whole pattern when the NiO peak starts to appear, which indicates that a very small NiO crystal has started to form. This disturbance actually leads to a very broad NiO crystal. The fact that this disturbance can be observed prior to a peak actually appears suggest that the growth of NiO is much slower in VPI-8 than in mordenite where no such behavior is apparent.

In mordenite it was observed that the metal impregnation loading affects the final metal crystal size probably do to a lack of metal-support interactions. Sample VPI-8-E was impregnated with 10.0 wt% of Ni and for this sample the final Ni crystal size for sample VPI-8-F was too small to obtain a quantifiable Ni crystal size, on the other hand the final Ni crystal size for sample VPI-8-A was large suggesting that as the Ni loading decreases, the final Ni crystal size decreases, as was previously observed in Chapter 3. The same was observed for mordenite but at a 5 wt% Ni loading suggesting that it is possible to obtain smaller Ni clusters in VPI-8 than in mordenite.

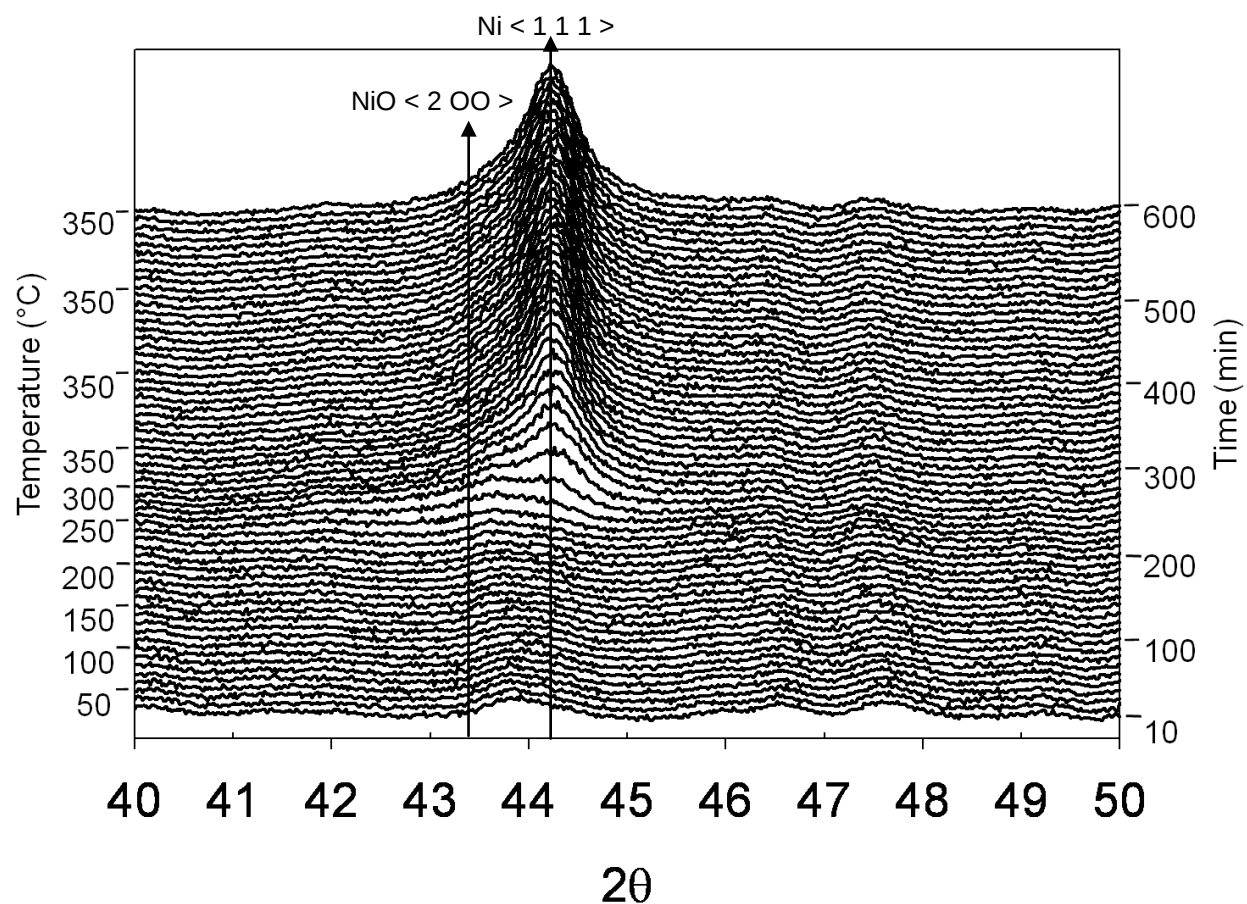


Figure 4-5 XRD patterns of sample VPI-8-E impregnated with 16.7 wt% Ni during reduction, without previous calcination, at 1°C/min using a H_2 flow rate of 56.2 mL/min .

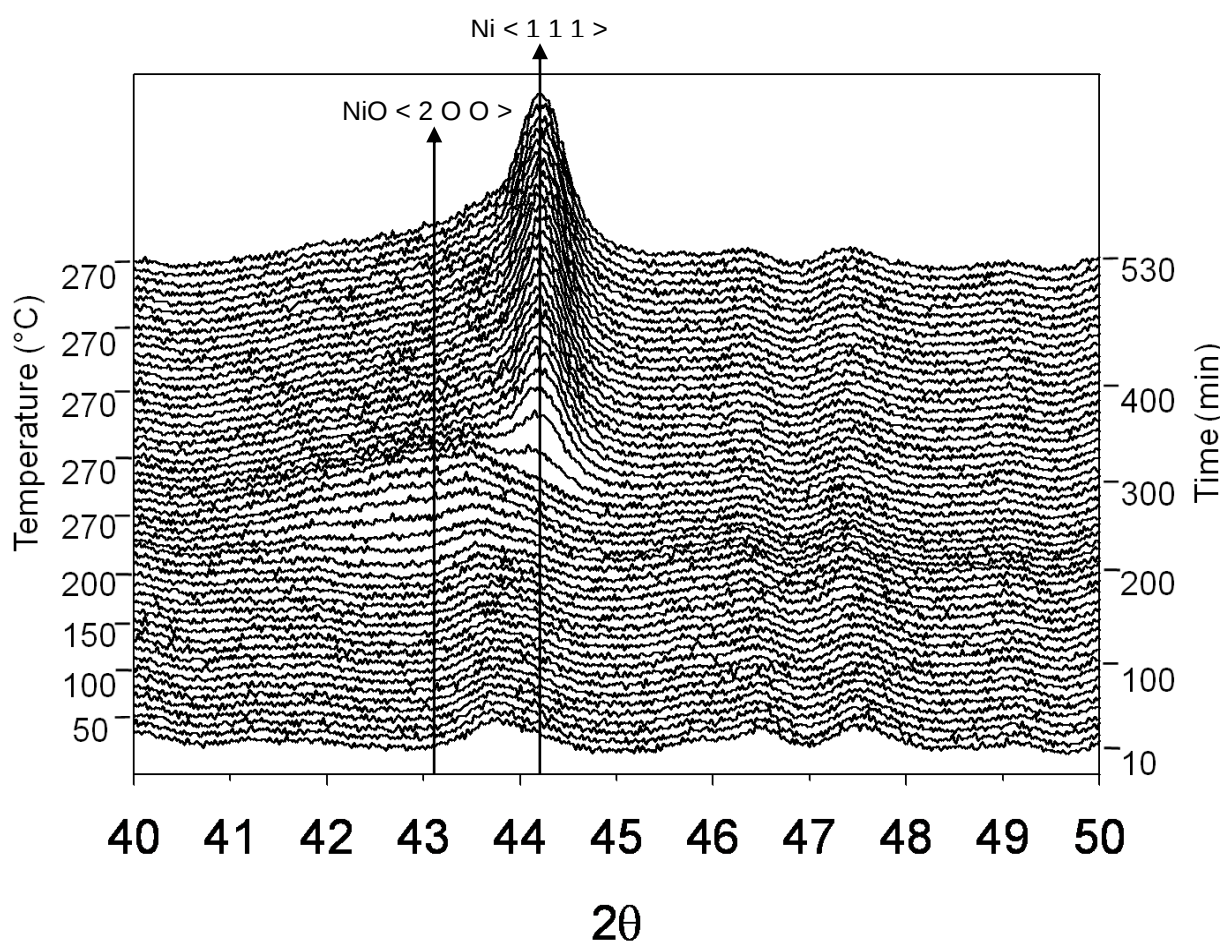


Figure 4-6 XRD patterns of sample VPI-8-F impregnated with 16.7 wt% Ni during H_2 reduction, without prior calcination, from RT to $270^{\circ}C$ at $1^{\circ}C/min$ using a H_2 flow rate of 56.2 mL/min .

4.5.2 FTIR

Figure 4-7 shows the FTIR spectra for some of the VPI-8 samples. Bands appearing close to 3400 cm^{-1} could be attributed to the hydroxyl groups of VPI-8. As can be observed, each treated VPI-8 sample showed a band close to 1650 cm^{-1} , which could be ascribed to the deformation vibrations of H-O-H [60]. According to Figure 4-7, at the end of each treatment, the nickel acetate appears to be completely thermally decomposed, as the band for COO^{-1} peaks that appears in the range of 1600 to 1400 cm^{-1} is not observed for the treated samples. Absorbance intensities appearing close to 550 cm^{-1} could be attributed to the Ni-O lattice vibrations of unreduced NiO [50].

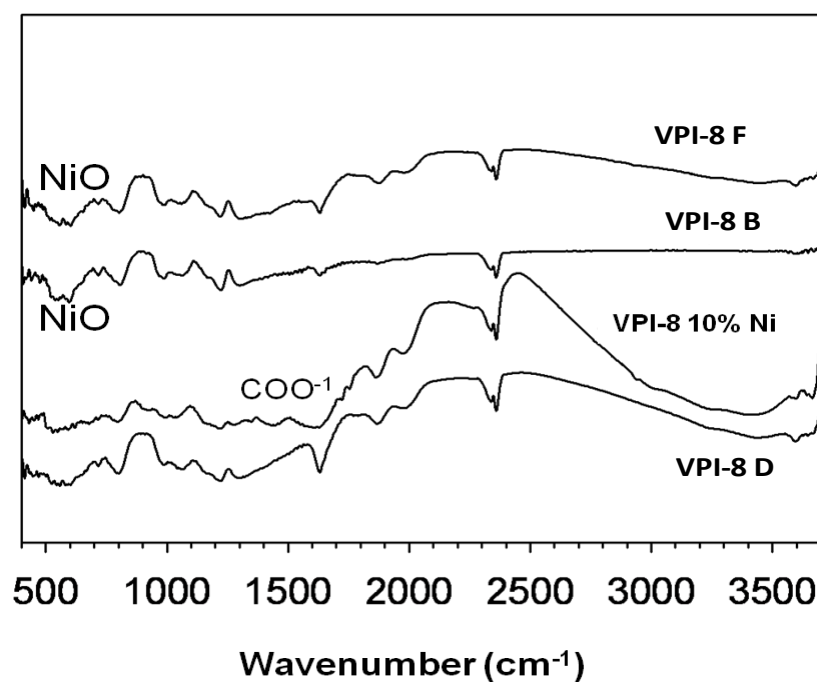


Figure 4-7 FTIR spectra of the VPI-8 samples compared to the FTIR spectrum of untreated VPI-8 impregnated with 10 wt% Ni.

4.5.3 TGA

From Figure 4-8 it could be observed that, similar to what was reported in Chapter 3, the thermal decomposition of the Ni impregnated VPI-8 sample occurred through three different steps. The first corresponds to the dehydration of VPI-8 which occurs close to 80°C. The second and third steps are due to the dehydration of the hydrated salt and the overlapping of the several decomposition reactions that take place in order to produce NiO. As concluded in Chapter 3, the decomposition behavior for nickel acetate was maintained supported in VPI-8.

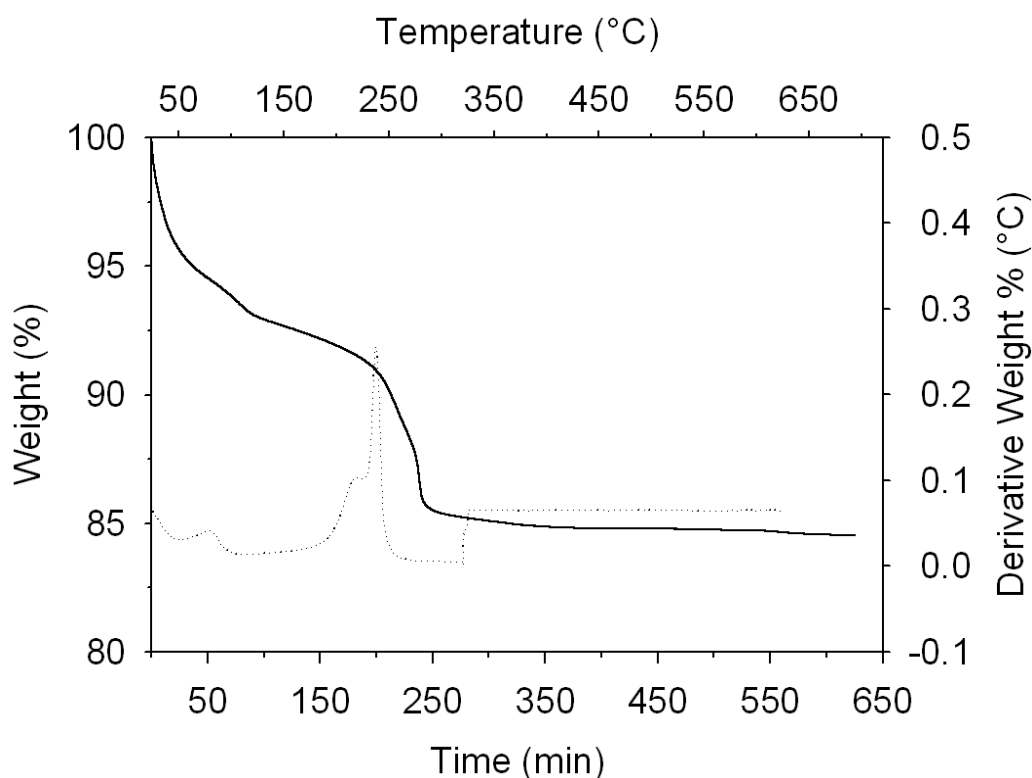


Figure 4-8 TGA of untreated VPI-8 impregnated with 10 wt% Ni in air.

4.6 Conclusions

It was found that H_2 reduction of samples previously calcined leads to bigger Ni clusters than samples reduced without prior calcination. However, the initial NiO growth seems to be much slower when calcination is performed prior to reduction, since XRD patterns, illustrated in Figure 4-1, showed a disturbance caused by the appearing of the NiO peak. This disturbance was not apparent in the results for samples reduced without calcination. It was also observed that the NiO growth is much slower than the Ni growth. At the end of the reduction reaction it was found that NiO remained unreduced, which was confirmed with the FTIR results, possibly due to H_2 diffusion problems due to the small size of the pore system of VPI-8.

As for mordenite, H_2 reduction without prior calcination leads to smaller Ni clusters. From the XRD results it is evident that H_2 reduction without prior calcination occurs through two different steps. First the nickel acetate hydrate is thermally decomposed to produce crystalline NiO $\langle 200 \rangle$, which then decompose to produce metallic Ni $\langle 111 \rangle$ clusters.

Similar to Chapter 3 it was found that a higher Ni loading leads to larger Ni crystals than lower Ni loadings, as it was clearly observed from the comparison of samples with a Ni loading of 16.7 wt% and that with 10.0 wt% Ni. Through simulations it was determined that the maximum Ni loading that could theoretically be achieved is close to 2.9 wt%. Since the loadings reported in this Chapter are much larger it is probable that a large amount of the impregnated precursor was located at the surface of

the support (VPI-8) leading to a faster growth and consequently to larger particles. Nevertheless it was apparent that very small particles could be obtained in VPI-8 in loadings as high as 10 wt% Ni which suggest that this zeolite could be used for applications that require small particles but at a higher loading. Also here it was evident that the H₂ flow rates lower than 56.2 mL/min and a temperature close to the apparent activation temperature were diffusion limited and resulted in larger particle size.

5 Comparison between mordenite and VPI-8 results

5.1 XRD

Results for both zeolites showed that the smaller Ni cluster were obtained when reduction was performed without prior calcination. However, a comparison of sample MOR-G from Table 3-1 and 3-2 with sample VPI-8-D in Tables 4-1 and 4-2 shows that when reduction without calcination is performed, the final Ni crystal size is much smaller in VPI-8. This could be attributed to the smaller pore size of VPI-8 which at the beginning of the Ni crystal growth process will prevent the agglomeration of large amounts of Ni, since the pore space available is less than that for MOR. It is also possible that the diffusion of particles inside the pores of VPI-8 is slower than the diffusion within the pores of MOR, leading to a more difficult agglomeration. It was observed that for VPI-8 a higher Ni loading is needed in order to obtain an X-ray diffractogram of NiO or Ni crystals than mordenite. For both zeolites it was observed that heating at constant activation temperature under H₂ leads to larger Ni crystals.

5.2 FTIR

The Fourier Transform Infrared spectrums showed similarities between the results for mordenite and those for VPI-8. Both results showed that the COO⁻ group, which appears at absorbance bands within the range of 1600 to 1400 cm⁻¹ [50], disappeared after the H₂ reduction was conducted. Both supports showed an absorbance band close to 1100cm⁻¹ which corresponds to the asymmetric stretching

vibration of SiO_4 and AlO_4 groups [60]. In addition, samples from both supports showed absorbance bands close to 3400 cm^{-1} , which were attributed to the hydroxyl groups that make up the support's frameworks. Every support-metal sample displayed a wavelength band close to 1650 cm^{-1} , which was attributed to deformation vibrations of H-O-H [60]. However, it was found that VPI-8 treated samples displayed a band close to 550 cm^{-1} , which was attributed to Ni-O lattice vibrations [50] of unreduced NiO. This is in agreement with the results obtained from the Reactor X.

5.3 TGA

Thermogravimetric analyses conducted to both impregnated supports showed new decomposition steps which were attributed to the dehydration of nickel acetate and the thermodecomposition of this precursor to produce NiO, respectively. These results are in agreement with the results obtained using the Reactor X. As was expected, both supports showed stability at high temperatures which make them suitable supports for the synthesis of metal nanostructures at high temperatures.

6 Conclusions and Future Work

6.1 Conclusions

It was found that the apparent reduction activation temperature decreases when a sample is calcined for a longer period of time. The higher activation temperature without calcination was probably due to remaining nickel acetate in the sample, which leads to two different thermal decomposition reactions during reduction. It was found that this two step decomposition mechanism leads to smaller particle size. In addition to the reaction mechanism several parameters were found to influence the particle size: flow rate, Ni loading and temperature. In general it was found that when the flow rates were low and the temperature was close to the apparent activation temperature the reactions were diffusion limited and resulted in larger particle sizes.

The smaller final Ni crystals obtained at lower Ni loadings can be explained by the relative isolation of the Ni grains, as compared to higher loadings, that might make them resistant to agglomeration. Nevertheless, the large Ni particle sizes obtained in general in these experiments, which are an order of magnitude larger than the zeolite pore size, evidences that the particles are either growing at the surface of the zeolite or breaking the pore as they grow. From the techniques used it is not possible to establish definitely which of the mechanisms is occurring but TEM images presented suggest that the nanostructures are forming inside the zeolite.

According to the XRD results, the NiO is completely consumed after the H₂ reduction is completed. This was in contrast with what was reported by Richardson et al

[59], who found that the NiO crystal size decreased after reduction but was still present when reducing bulk NiO. This might be due to a hydrogen diffusion limitation inside bulk NiO particles that is not evident in smaller NiO crystals.

The heating rate effect in the final Ni crystal size was also studied. The results obtained suggest that the heating rate do not appear to have any effect on the final Ni crystal size. It was found, nevertheless, that the initial Ni crystal size and the final Ni crystal size were almost identical at faster heating rates, suggesting that the Ni agglomeration occurs much faster.

VPI-8 results showed that, contrary to mordenite, unreduced NiO remained in the pores after reduction. This suggests that the smaller pores of VPI-8 hinder the H₂ diffusion leading to a slower NiO reduction. This slower reduction explains the slower Ni growth and the presence of a large gap observed in this zeolite, the latter which was attributed to the formation of very small NiO crystal particles. This slow reduction and presence of smaller NiO influenced the growth mechanism leading to the smaller particles sizes in VPI-8 samples when compared to mordenite samples studied under comparable synthesis conditions. It is thus concluded that zeolites with smaller pores like VPI-8 are more suitable for the controlled growth of Ni crystals.

Another possible explanation for the smaller particle sizes obtained in VPI-8 could be attributed to the local stability of the framework with the synthesis conditions. The presence of alumina tetrahedra in the structure of mordenite makes it vulnerable to the local breakage of the structure during synthesis conditions possibly forming extra framework octahedral alumina, not so for VPI-8 which does not contain aluminum atoms

in its structure. This local breakage would not be evident in an XRD pattern but would allow more room for the Ni nanostructure growth decreasing, thus, its growth constrictive capabilities. This suggests that for applications where no Brønsted acidity from the zeolite is needed an all silica zeolite should be preferred over an alumina containing one as support for small sized nanostructures.

The loading also had a clear influence in the diffusion limitation of the reaction. For mordenite samples with a loading higher than 5 wt% Ni showed Ni $\langle 111 \rangle$ peaks in the XRD pattern corresponding to particle sizes larger than 80 Å. For VPI-8 this limit was at 10 wt% Ni which was significantly higher than mordenite.

Our observation also suggested that the NiO formed during the decomposition reaction had a stronger interaction with VPI-8 than with mordenite resulting in a slower NiO particle growth which influences the fact that smaller Ni particles could be obtained with this zeolite. This could also explain why there was still unreduced NiO in this zeolite.

Finally it was concluded that the Reactor X is a versatile attachment that allows the study of the growth of nanostructures once a critical size of at least 35 Å is reached.

6.2 Future Work

Among the several applications that these bifunctional catalysts may have, one of the most important is catalysis. As discussed in Chapter 1, Ni supported in mordenite could be used for several catalysis applications in the petrochemical industry. Therefore, we are proposing to study the catalytic properties that this system may

provide. Among several studies that could be conducted, we propose to study the effects that the crystal size, dispersion, distribution and reduction temperature may have on the conversion and selectivity of the catalytic reactions.

We have already studied some of the effects that impregnation has on the final Ni crystal size. However, there are several other integration methods that could be used in an attempt to obtain smaller crystal sizes. In addition we also propose the study of the chemical state of the Ni particles before and after reduction in order to study the degree of reduction from Ni (II) to Ni⁰, using X-ray Photoelectron Spectroscopy (XPS).

In addition we propose the use of Nuclear magnetic resonance spectroscopy (NMR) for the study of the possible local breakage of the support's pore system. This could help in the understanding of how the particles are growing larger than the pores.

7 References

1. Goodman, D.W., et al., *Kinetics of the Hydrogenation of Co over a Single-Crystal Nickel-Catalyst*. Journal of Catalysis, 1980. **63**(1): p. 226-234.
2. Tsai, M.C., et al., *Dehydrogenation Processes on Nickel and Platinum Surfaces - Conversion of Cyclohexane, Cyclohexene, and Cyclohexadiene to Benzene*. Journal of the American Chemical Society, 1982. **104**(9): p. 2539-2543.
3. Reynolds, J.G., *Nickel in Petroleum Refining*. Petroleum Science and Technology, 2001. **19**(7): p. 979 - 1007
4. Agnelli, M., et al., *CO hydrogenation on a nickel catalyst - II. A mechanistic study by transient kinetics and infrared spectroscopy*. Journal of Catalysis, 1998. **175**(1): p. 117-128.
5. Lee, S.P. and Y.W. Chen, *Selective hydrogenation of furfural on Ni-P, Ni-B, and Ni-P-B ultrafine materials*. Industrial & Engineering Chemistry Research, 1999. **38**(7): p. 2548-2556.
6. Li, H., Q.F. Zhao, and H.X. Li, *Selective hydrogenation of p-chloronitrobenzene over Ni-P-B amorphous catalyst and synergistic promoting effects of B and P*. Journal of Molecular Catalysis a-Chemical, 2008. **285**(1-2): p. 29-35.
7. Alstrup, I., *On the Kinetics of Co Methanation on Nickel Surfaces*. Journal of Catalysis, 1995. **151**(1): p. 216-225.
8. Fujita, S.I. and N. Takezawa, *Difference in the selectivity of CO and CO₂ methanation reactions*. Chemical Engineering Journal, 1997. **68**(1): p. 63-68.
9. Lee, G.D., et al., *Raney Ni catalysts derived from different alloy precursors Part II. CO and CO₂ methanation activity*. Korean Journal of Chemical Engineering, 2005. **22**(4): p. 541-546.
10. Takenaka, S., T. Shimizu, and K. Otsuka, *Complete removal of carbon monoxide in hydrogen-rich gas stream through methanation over supported metal catalysts*. International Journal of Hydrogen Energy, 2004. **29**(10): p. 1065-1073.

11. Huang, S.X., D.A. Fischer, and J.L. Gland, *Aniline Hydrogenolysis on Nickel - Effects of Surface Hydrogen and Surface-Structure*. Catalysis Letters, 1995. **34**(3-4): p. 365-374.
12. Jackson, S.D., G.J. Kelly, and G. Webb, *Supported nickel catalysts: Hydrogenolysis of ethane, propane, n-butane and iso-butane over alumina-, molybdena-, and silica-supported nickel catalysts*. Physical Chemistry Chemical Physics, 1999. **1**(10): p. 2581-2587.
13. Carter, J.L., J.A. Cusumano, and J.H. Sinfelt, *Catalysis over Supported Metals .V. Effect of Crystallite Size on Catalytic Activity of Nickel*. Journal of Physical Chemistry, 1966. **70**(7): p. 2257-&.
14. Adhikari, S., et al., *Conversion of glycerol to hydrogen via a steam reforming process over nickel catalysts*. Energy & Fuels, 2008. **22**(2): p. 1220-1226.
15. Borowiecki, T., A. Golebiowski, and B. Stasinska, *Effects of small MoO₃ additions on the properties of nickel catalysts for the steam reforming of hydrocarbons*. Applied Catalysis a-General, 1997. **153**(1-2): p. 141-156.
16. Maesen, T., *The Zeolite Scene - An Overview*, in *Introduction to Zeolite Science and Practice*, H.v.B. Jirí Cejka, Avelino Corma, Ferdi Schüth, Editor. 2007, Elsevier Science: Amsterdam. p. 1 - 12.
17. Castano, P., et al., *The role of zeolite acidity in coupled toluene hydrogenation and ring opening in one and two steps*. Industrial & Engineering Chemistry Research, 2008. **47**(3): p. 665-671.
18. Li, L., H.F. Pan, and W.B. Li, *Study on application of beta zeolite in cracking catalyst*. Chinese Journal of Catalysis, 2002. **23**(1): p. 65-68.
19. Babitz, S.M., et al., *Monomolecular cracking of n-hexane on Y, MOR, and ZSM-5 zeolites*. Applied Catalysis a-General, 1999. **179**(1-2): p. 71-86.
20. Liu, B.J., et al., *Catalytic Performance of ZSM-5/MOR Composite Zeolite Catalyst for Conversion of Mixed C-4 Hydrocarbons*. Chinese Journal of Catalysis, 2008. **29**(9): p. 940-944.

21. Jens Weitkamp, M.H., *Acid and Base Catalysis on Zeolites*, in *Introduction to Zeolite Science and Practice*, H.v.B. Jirí Cejka, Avelino Corma, Ferdi Schüth, Editor. 2007, Elsevier Science: Amsterdam. p. 787-836.
22. Cesana, A., et al., *Conversion of heavy aromatic hydrocarbons to valuable synthetic feed for steamcrackers*. Oil Gas-European Magazine, 2008. **34**(2): p. 89-94.
23. Vazquez, M.I., A. Escardino, and A. Corma, *Activity and Selectivity of Ni-Mo/Hy Ultrastable Zeolites for Hydroisomerization and Hydrocracking of Alkanes*. Industrial & Engineering Chemistry Research, 1987. **26**(8): p. 1495-1500.
24. Isoda, T., et al., *Hydrocracking of pyrenes over a nickel-supported Y-zeolite catalyst and an assessment of the reaction mechanism based on MD calculations*. Energy & Fuels, 1999. **13**(3): p. 617-623.
25. Pidko, E.A., E.J.M. Hensen, and R.A. van Santen, *Dehydrogenation of light alkanes over isolated gallyl ions in Ga/ZSM-5 zeolites*. Journal of Physical Chemistry C, 2007. **111**(35): p. 13068-13075.
26. Cortright, R.D. and J.A. Dumesic, *L-Zeolite-Supported Platinum and Platinum-Tin Catalysts for Isobutane Dehydrogenation*. Applied Catalysis a-General, 1995. **129**(1): p. 101-115.
27. Funez, A., et al., *Hydroisomerization in liquid phase of a refinery naphtha stream over Pt-Ni/H-beta zeolite catalysts*. Chemical Engineering Journal, 2008. **136**(2-3): p. 267-275.
28. Canizares, P., et al., *n-butane hydroisomerization over Pd/HZSM-5 catalysts. 1. Palladium loaded by impregnation*. Industrial & Engineering Chemistry Research, 1998. **37**(7): p. 2592-2600.
29. Meier, W.M., *The crystal structure of mordenite (ptilolite)*. Zeitschrift Fur Kristallographie, 1961. **115**: p. 439-450
30. Bowker, M., A. Nuhu, and J. Soares. *High activity supported gold catalysts by incipient wetness impregnation*. 2007: Elsevier Science Bv.

31. Lebedeva, O.E., W.A. Chiou, and W.M.H. Sachtler, *Metal migration from zeolites onto iron oxide: An alternative to hydrogen spillover*. Journal of Catalysis, 1999. **188**(2): p. 365-374.
32. Barrer, R.M. and R.P. Townsend, *Transition-Metal Ion-Exchange in Zeolites .1. Thermodynamics of Exchange of Hydrated Mn-2+, Co-2+, Ni-2+, Cu-2+ and Zn-2+ Ions in Ammonium Mordenite*. Journal of the Chemical Society-Faraday Transactions I, 1976. **72**: p. 661-673.
33. Inglezakis, V.J., *The concept of "capacity" in zeolite ion-exchange systems*. Journal of Colloid and Interface Science, 2005. **281**(1): p. 68-79.
34. Kuronen, M., R. Harjula, and J. Lehto, *Comparison of techniques for measuring ion exchange selectivities in zeolites*. Radiochimica Acta, 2005. **93**(2): p. 119-123.
35. Mondale, K.D., R.M. Carland, and F.F. Aplan, *The Comparative Ion-Exchange Capacities of Natural Sedimentary and Synthetic Zeolites*. Minerals Engineering, 1995. **8**(4-5): p. 535-548.
36. Canizares, P., et al., *Characterization of Ni and Pd supported on H-mordenite catalysts: Influence of the metal loading method*. Applied Catalysis a-General, 1998. **169**(1): p. 137-150.
37. W.E. Brown, D.D., A.K. Galwey, *Theory of Solid State Reactions Kinetics*, in *Reactions in the Solid State*, C.F.H.T. C.H. Bamford, Editor. 1980, Elsevier Scientific Publishing Company: Amsterdam. p. 41 - 72.
38. Mullin, J.W., *Crystallization*. 2001, Oxford: Reed Educational and Professional Publishing Ltd.
39. Vitalij K.Pecharsky, P.Y.Z., *Fundamentals of Powder Diffraction and Structural Characterization of Materials*. 2nd ed. 2008, New York: Springer Science.
40. Ron Jenkins, R.S., *Introduction to X-Ray Powder Diffractometry*. 1996, New York: John Wiley and Son.
41. Zhang, Y., N. Kohler, and M. Zhang, *Surface modification of superparamagnetic magnetite nanoparticles and their intracellular uptake*. Biomaterials, 2002. **23**(7): p. 1553-1561.

42. Rodriguez-Carvajal, R.B.V.D.a.J., *The Intensity of a Bragg Reflection*, in *Powder Diffraction: Theory and Practice*, S.J.L.B. R.E. Dinnebier, Editor. 2008, The Royal Society of Chemistry. p. 58 - 86.
43. John Wiley and Sons, I., *Constructive and Destructive Interferences of Light Waves*, in <http://web.sbu.edu/chemistry/wier/electrons/interference.jpg>. 1998.
44. Bottom, R., *Thermogravimetric Analysis*, in *Principles and Applications of Thermal Analysis*, P. Gabbott, Editor. 2007, Wiley-Blackwell p. 87-118.
45. Niemantsverdriet, W., *Spectroscopy in Catalysis*. 3rd ed. 2007, Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA.
46. De Jesus, J.C., et al. *Thermal decomposition of nickel acetate tetrahydrate: an integrated study by TGA, QMS and XPS techniques*. 2005.
47. Gadalla, A.M. and H.F. Yu, *Thermal-Behavior of Some Ni-2 and Fe-3 Salts*. *Thermochimica Acta*, 1990. **164**: p. 21-36.
48. Galwey, A.K., et al., *A Kinetic and Mechanistic Study of the Thermal-Decomposition of Nickel Acetate*. *Reactivity of Solids*, 1988. **6**(2-3): p. 173-186.
49. Hong, J.H., G.H. Guo, and K.L. Zhang, *Kinetics and mechanism of non-isothermal dehydration of nickel acetate tetrahydrate in air*. *Journal of Analytical and Applied Pyrolysis*, 2006. **77**(2): p. 111-115.
50. Mohamed, M.A., S.A. Halawy, and M.M. Ebrahim, *Nonisothermal Decomposition of Nickel Acetate Tetrahydrate*. *Journal of Analytical and Applied Pyrolysis*, 1993. **27**(2): p. 109-118.
51. Baraldi, P., *Thermal-Behavior of Metal Carboxylates .3. Metal Acetates*. *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy*, 1982. **38**(1): p. 51-55.
52. O. Antoia, L.H.a.P.P., *Miner. Proc. Extr. Metal. Rev.*, 1995. **15**: p. 169.
53. Benton, A.F. and P.H. Emmett., *The Reduction of Nickelous and Ferric Oxides by Hydrogen*. *J. Am. Chem. Soc.*, 1924. **46**: p. 2728.

54. Rodriguez, J.A., et al., *Experimental and theoretical studies on the reaction of H₂ with NiO: Role of O vacancies and mechanism for oxide reduction*. Journal of the American Chemical Society, 2002. **124**(2): p. 346-354.
55. Biju, V. and M.A. Khadar, *Fourier transform infrared spectroscopy study of nanostructured nickel oxide*. Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 2003. **59**(1): p. 121-134.
56. Wang, Y.P., et al., *Preparation of NiO nanoparticles and their catalytic activity in the thermal decomposition of ammonium perchlorate*. Thermochemica Acta, 2005. **437**(1-2): p. 106-109.
57. Tamagawa, H., et al., *Control of Ni Metal-Particle Size in Ni/SiO₂ Catalysts by Calcination and Reduction Temperatures*. Journal of the Chemical Society-Faraday Transactions I, 1987. **83**: p. 3189-3197.
58. Richardson, J.T., R.M. Scates, and M.V. Twigg, *X-ray diffraction study of the hydrogen reduction of, NiO/alpha-Al₂O₃ steam reforming catalysts*. Applied Catalysis a-General, 2004. **267**(1-2): p. 35-46.
59. Richardson, J.T., R. Scates, and M.V. Twigg, *X-ray diffraction study of nickel oxide reduction by hydrogen*. Applied Catalysis a-General, 2003. **246**(1): p. 137-150.
60. Hu, C.L., et al., *Development of novel mordenite-filled chitosan-poly(acrylic acid) polyelectrolyte complex membranes for pervaporation dehydration of ethylene glycol aqueous solution*. Journal of Membrane Science, 2007. **293**(1-2): p. 142-150.
61. Freyhardt, C.C., et al., *VPI-8: A high-silica molecular sieve with a novel "pinwheel" building unit and its implications for the synthesis of extra-large pore molecular sieves*. Journal of the American Chemical Society, 1996. **118**(31): p. 7299-7310.