CHARACTERIZATION OF Ni/SiO$_2$ CATALYST PREPARED BY A MODIFIED IONIC EXCHANGE METHOD

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ABSTRACT

The preparation of nickel catalysts by a modified ionic exchange method results in the formation of two different types of layered nickel-hydrosilicates depending on the hydrothermal preparation condition employed. Thus, a non-stoichiometric superficial nickel hydrosilicate (like-Serpentine) is obtained when the samples are not hydrothermally treated but a well defined Talc structure is observed after an ammonium hydrothermal treatment. Both structures are distinguished by Temperature Programmed Reduction (TPR). It was found that the infrared spectroscopy (IR) in the hydroxile stretching frecuency range (4000-3000 cm^{-1}) is a very good technique to detect the different hydrosilicates formed. Pyridine (Py) chemisorption gives additional information about the acidic properties of the samples and about the density of the exposed nickel ions.

INTRODUCTION

Nickel catalysts are widely used in many important industrial processes such as methanation of synthesis gas, hydrogenation of fatty oils acids and benzene, steam reforming of hydrocarbons, selective hydrogenation of unsaturated aldehydes, hydrogenolysis of hydrocarbons and others (Thomas,1970).

These nickel catalysts can be prepared as unsupported material (by leaching nickel Raney or by organic salt decomposition) or as supported catalysts by employing semiconductor oxides such as Al$_2$O$_3$, SiO$_2$, MgO or TiO$_2$ as support (Uchiyama et al.,1989; Coenem,1984; Aguinaga et al. ,1989; Hoang et al.,1989).

These oxide supports play several roles both in the catalyst preparation as well as in the final catalyst behavior. Thus, they can either provide an adecuated pore structure where the precursor nickel oxide particles are dispersed, or acidic and basic sites on bifunctional catalysts or appropiate ligands where nickel ion complexes can be fixed on the surface. Of these oxides, silica was, by far, the most widely used and therefore the nickel-silica catalysts were the best characterized.

The properties of the Ni-SiO$_2$ system are very dependent on the precursors which emphasize the importance of the preparation technique employed. The impregnation method, the most simple procedure, results in relatively large particles with a weak support interaction and hence with a poor oxide particle dispersion; however, a more complex interaction between ions and support may occur simultaneously (Brunelle,1978). Therefore, both dry and wet impregnations lead to different precursors of nickel ions depending on the micromeritic characteristics of the silica employed. In this way, in the smallest pores (90 Å) the nickel precursor resembles the bulk nickel oxide while in the largest ones (150 - 300 Å) the nickel hydrosilicate behavior. The relative amounts of these precursors depend, very strongly, on the volume solution employed in the impregnation technique (dry vs. wet impregnation) (Mile et al.,1988).

On the other hand, pH controlled deposition-precipitation of nickel precursors on silica is recommended to obtain high and homogeneous dispersion with high metallic loading. A strong interaction between metal ions and silica can be obtained through a partial dissolution of the support by giving an adequated orientation of the sheets of hexagonal silica rings with the nickel hydroxide layers (two hydroxile groups of the nickel hydroxide are replaced by oxygen atoms from the two dimensional silica network at one side of the layer). With this technique it has been established the formation of a nickel serpentine (Nepouite structure, Ni$_3$Si$_2$O$_5$(OH)$_4$) by EXAFS (Clause et al.,1991,1992a).

The ionic exchange technique (Che and

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Bonneviot 1988; Clause et al. 1992b) leads to nickel complex ions fixed to the silica surface through silanol groups. In this case, the nickel ions interact with the silica surface giving up isolated nickel species or hydrosilicate-like structures depending on the chelating behaviour of the ligands or on the metal complex exchanged.This method produces high and homogeneous dispersion but has the disadvantage that the metal loading is controlled by the amount of silanol groups present on the silica surface at low pH or by the partial support dissolution at pH higher than 8.5.

To obtain higher nickel loadings, the authors modified the ion exchange method by preparing a nickel hydrosilicate from ammoniacal solutions of nickel hexaamin complex and ammonium silica-gel solutions.

The present paper reports results on Ni/SiO_2 materials prepared by this modified ionic exchange technique and on the resulting characteristics of the interaction between silica and nickel ions after different amonicum-thermal treatments.

The characterization is carried out by TPR, X-Ray spectroscopy, XPS, IR spectroscopy and pyridine (Py) chemisorption. A comparison with properties of catalysts prepared by other techniques (impregnation, ion exchange and controlled deposition-precipitation) is also presented.

EXPERIMENTAL.
Catalysts preparation

The Ni/SiO_2 materials have been prepared by a modified ionic exchange technique which is schematically described in Fig. 1.

20 g of sodium silicate (Riedel-de Haën, 63 % SiO_2, 18% Na_2O and 18% of weight loss at 800°C) were dissolved in hot distilled water (800 mL), cooled to room temperature (RT) and filtered. Then the silicic acid was precipitated by adding HCl (Conc.) (20 mL approximately) until the pH was 8-7. The SiO_2-gel obtained was aged 24 h, filtered and thoroughly washed first with distilled water and then with a $NH_4OH:H_2O$ (1:4) solution in order to eliminate the remanent Na^+ and Cl^- ions. The gel was dissolved in NH_4OH (34%) (800 mL) and filtered.

5 g of Nickel acetate.$4H_2O$ (Merck, analytical reagent grade) were dissolved in 50 mL of NH_4OH (Conc.) and this was slowly dropped with vigorous stirring into the ammonium hydrogel solution previously prepared. When all the hexaamin nickel complex was added (30 min. approx.) the stirring was continued for 30 min more and then the slurry was filtered. Different portions of the wet slurry were treated as follows:

* SN - 110°C: the gel was filtered, thoroughly washed with conc. NH_4OH in order to eliminate all the posible nickel hydroxide formed and then with $NH_4OH:H_2O$ (1:1) solution. The gel was dried at 110°C for 24 hs.

* SN - 450°C: a portion of SN - 110°C was calcined in air flow at 450°C for 5 hs.

* SN - R110°C: the gel was placed into a teflon vessel and heated in a closed reactor at 110°C; accordingly, the ammonium-water pressure rose to 6 atm approx. After 24 hs the material was cooled to RT, washed with NH_4OH (Conc.)
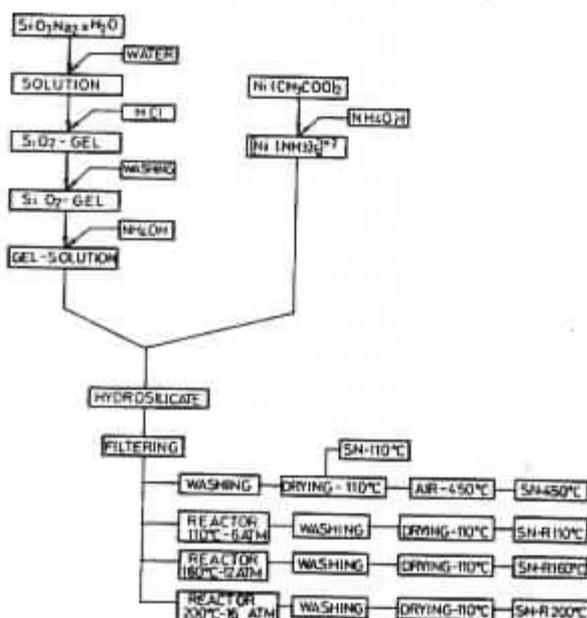

Fig.1: Schematic representation of the ion exchange method.

and NH_4OH-H_2O solution and dried 24 hs at 110°C.

* SN – R160°C: the same as SN – R110°C but the thermal treatment was at 160°C and the pressure into the reactor reached 12 atm approx.

* SN – R200°C: The same as the previous sample but treated at 200°C; the pressure reaches 16 atm approximately.

The support employed to prepare catalysts by impregnation (I), ionic exchange (IE) and precipitation-deposition (PD) was SiO_2 Davison type G-62 (B.E.T. area: 170 m^2/g and pore volume: 1.2 cc/g).

The PD catalyst was prepared by heterogeneous precipitation of nickel from an aqueous solution (2 L) of nickel acetate (13 g of $Ni(CH_3COO)_2 \cdot 4H_2O$, Mallinkcrodt, analytical reagent grade), slurried with silica (30 g). The precipitation was produced by the thermal decomposition of urea (10 g, Merck, analytical reagent). The slurry was stirred for 6 hs at 90°C and then the sample was filtered and dried at 110°C for 24 hs. A fraction was calcined in air flow for 5 hs at 450°C.

When catalysts were prepared by impregnation, the required amount of aqueous solution of $Ni(CH_3COO)_2$ was slowly added to the support (1.5 cc/g SiO_2), previously evacuated. The precursor was dried at 110°C for 24 hs and calcined 5 hs at 450°C. After this treatment the elimination of residual acetate groups was verified by infrared spectroscopy.

Ionic exchange catalysts were prepared as follows: Silica-gel (5 g) was immersed in a $NH_4OH:H_2O$ (1:1) solution and stirred for 30 min. After that, 100 mL of hexaamin nickel complex solution prepared from nickel acetate salt, was slowly dropped (30 min) into the slurry. The amount of nickel salt used was determined in order to obtain catalyst with 1% w/w and 2% w/w of nickel. When all the nickel solution was added the stirring was maintained by 30 min more and then the slurry was filtered, washed with $NH_4OH:H_2O$ solution in order to eliminate the possible nickel hydroxide formation (Coenem and Linsen,1970; Coenem,1984), dried at 110°C for 24 hs and, finally, calcined in air flow at 450°C.

Catalyst characterization

The nickel contents were determined by atomic absorption spectroscopy. The loss of weight of the samples was determined by TGA in the range from RT to 800°C.

The total surface area of the catalysts was determined by a gravimetric technique using n-hexane adsorption at 50°C (Gonzo, 1982).

Powder X-ray diffraction analyses

were carried out with a Rigaku diffractometer using CuKα radiation.

Temperature programmed reduction (TPR) measurements were carried out in an apparatus similar to that described by Hurst et al. (1982). The weight of the samples was varied between 10 and 50 mg depending on the nickel loading. A mixture of 5% of hydrogen in nitrogen at a flow rate of 35 mL/min was employed. The temperature was ramped from RT up to 900°C at 10°C/min. The water produced during the reduction step was removed by a 5 Å molecular sieve trap which was cooled in ice and located before the thermal conductivity detector. The rate of hydrogen consumption was followed as a function of time and temperature.

The X-ray photoelectron spectroscopy measurements (XPS) were carried out with an ESCA 750 Shimatzu instrument. The Ni/Si atomic ratio was determined taking into account the photoionization cross section, the mean free path of the photoelectrons and the instrument factor. To determine the binding energy (BE) the Cls line (BE:284.6 eV) was used as internal standard reference. The same results were obtained when Si 2p was used as an internal reference. In such a way, the Si 2p BE adopted was 103.5 eV for impregnated and IE catalysts but 103.9 eV for the catalysts prepared by the modified ionic exchange technique.

The infrared spectroscopy (IR) measurements were carried out with a Perkin Elmer 683 spectrophotometer. The spectra were analysed by a Perkin Elmer data station. The samples were pressed at 4 ton/cm^2 at RT and the wafers (10 mm in diameter and 20 mg) were located into a cell that allows the vacuum and the heat treatments "in situ".

The Py chemisorption was performed at RT after the samples were pretreated in vacuum to the desired temperature. The physisorbed Py was eliminated by evacuating the system for 2 hr at R.T.

RESULTS AND DISCUSSION

Catalysts prepared by the modified ionic exchange technique:

In order to determine the effect of the amount of nickel complex added to the silica gel solution on the final nickel loading of the gel obtained after precipitation, two solutions with different amounts of nickel complex: one prepared with 5 g of nickel salt (Si/Ni atomic ratio = 12) and the other with 20 g of nickel salt (Si/Ni atomic ratio = 3) were used.

In the Table 1, it can be seen that the nickel loadings on these two resulting materials are similar and do not reflect the change on the Ni/Si ratio in the

starting solutions. Accordingly, the BET surface areas are very similar. This fact is congruent with the literature reports where both parameters (Ni loading and surface area) are generally correlated when superficial amorphous non-stoichiometric nickel hydrosilicates are formed (Coenem and Linsen,1970; Coenem,1984).

The surface composition of the obtained materials is shown in Table 2 and Fig.2. It can be seen that while the bulk composition gives a Ni/Si atomic ratio equal to 0.1, the XPS measurement gives a Ni/Si atomic ratio of 0.35 for the SN-110°C and SN-450°C suggesting that the exchange promoted a preferential enrich

TABLE 1

| | Ni/Si Atomic ratio | | % Ni w/w | Loss weight % w/w | B.E.T. m^2/g |
	Start Sol.	Bulk			
SN-110°C	0.08	---	8.5	-----	302
SN-450°C	0.08	---	8.0	-----	329
SN-110°C	0.33	0.107	7.01	23.7	285
SN-450°C	0.33	0.108	6.80	28.2	310
SN-R110°C	0.33	0.092	6.73	17.2	166
SN-R60°C	0.33	0.103	7.64	14.4	149
SN-R200°C	0.33	0.091	7.50	7.8	99
PD-110°C	0.11	---	8.3	-----	214
PD-450°C	0.11	---	7.9	-----	216
IE-1%	----	---	0.96	-----	182
I-1%	----	---	1.07	-----	160
SiO_2	----	---	----	-----	170

In aqueous basic solutions (NH_4OH), it is known (Greenwood and Earnshaw, 1984) that hydrated silica gels and colloidal suspensions are constituted by anions of "polysilicic acids" sols whose solubility is promoted by the existence of $SiO^- NH_4^+$ groups. The addition of nickel complex to such "solution" must cause the exchange of the ammonia groups by the hexaamin complexes (Che and Bonneviot, 1988) promoting the precipitation of the hydrogel with a Ni/Si ratio determined for the crosslinking degree of the polysilicics oligomers in the solution. In this case, it should be expected that the nickel must be preferentially located at the surface of the precipitated material.

ment of nickel at the surface. The increase in the Ni/Si atomic ratio observed with the XPS measurement on the ammonium thermal treated materials can be explained by a redissolution of the silica in order to develop a different hydrosilicate structure which will be discussed later.

By taking into account that we washed thoroughly the obtained hydrogel with ammonium solution, the presence of nickel hydroxide as a precursor on the wet material would be excluded. Accordingly, we found (Table 2) that the Ni $2p_{3/2}$ binding energy (857.8 eV) was in all cases very similar to that reported in the literature for materials where the nickel ions resemble an hydrosilicate structure (Uchiyama

TABLE 2

| | Ni/Si atomic ratio | Binding Energy (eV) | |
		Si 2p	Ni 2p3/2
SN-450°C	0.34	103.9	857.8
SN-110°C	0.35	103.9	857.8
SN-R110°C	0.36	103.9	857.8
SN-R160°C	0.44	103.9	857.8
SN-R200°C	0.59	103.9	858.0
PD(a)	-----	-----	857.9
IE-1%	0.013	103.5	857.0
I-1%	(*)	103.5	(*)
$Ni(OH)_2$ (b)	-----	-----	856.0-856.5
NiO (b)	-----	-----	853.5
Nickel Silicate	-----	-----	857.0-858.0

a) Van Stiphout et al. (1988)

b) Wagner et al. (1978)

(*) The nickel signal was not detected.

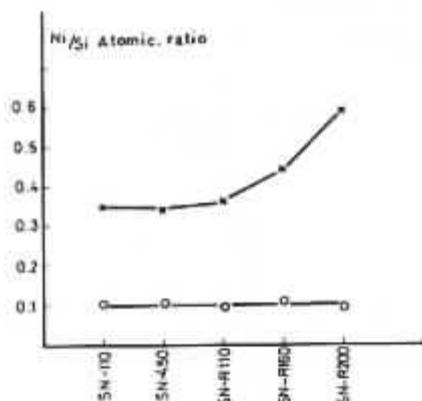et al., 1989; Houalla et al., 1980; Clause et al., 1991; Van Stiphout et al., 1988).

Fig. 2: Atomic ratio on Nickel-Silica catalysts. o Bulk composition determined by wet way method. * Surface composition determined by XPS.

On the other hand, the TPR experiences on the materials obtained without the hydrothermal treatment (SN-110°C and SN-450°C) showed the characteristic diagram of those catalysts with nickel in a high degree of interaction with silica (Fig.3).
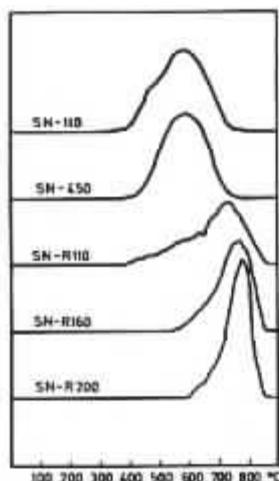

Fig. 3: TPR diagrams of catalysts prepared by the modified ionic exchange method.

It can be seen that their diagrams are very similar to that shown by IE catalyst (Fig.4) in which a "like-hydrosilicate" structure has been proposed (Houalla et al, 1980; Che and Bonneviot, 1988) and also similar to that obtained by Clause et al. (1991) with PD catalyst in which a nickel-Nepouite structure is developed. From these diagrams the inexistence of bulk NiO or nickel hydroxide as precursors is confirmed. The diagrams are different to that shown by impregnated catalyst (Fig. 4) in which bulk NiO is the predominant species with a reduction peak

at 330°C. This diagram is similar to that reported by Mile et al.(1988) for diffe rent catalysts prepared by impregnation. The higher temperature peak (500°C approx.) on this impregnation catalyst could be assigned both to a very small NiO crystallites and to a developed similar hydrosilicate structure (Houalla et al., 1980).

On the other hand, excepting the characteristic broad silica band, the XRD analysis showed the amorphous character of the samples by the total absence of diffraction bands. Only the SN-R200°C material presented two broad and low intensity bands centered approximately at 36 and 60 units of 2θ suggesting the incipient growing of an stratified hydrosilicate structure (Mendioroz and Munoz, 1990, Coenem and Linsen, 1970).

I.R. spectroscopy

The IR spectra, in the 1300-400 cm^{-1} region, is not useful to determine the structural characteristics of the samples without a hydrothermal treatment because of their extremely amorphous character, but it would gain importance for materials pretreated at different pressure-temperature conditions as will be discussed below.
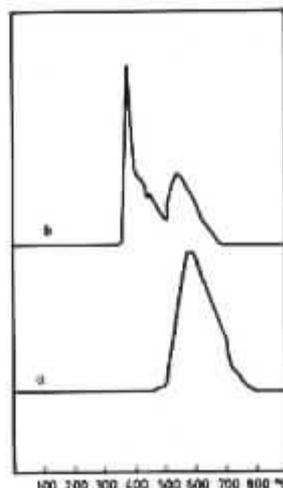

Fig. 4: TPR diagrams of catalysts prepared by: a) Ion exchange method. b) impregnation method.

Of more interest is the 4000-3000 cm^{-1} range where the oxygen-hydrogen stretching frecuency of silanol and hydroxile groups and their behavior against vacuum thermal treatment can be observed.

In Fig. 5, it can be seen that while an impregnation catalyst only shows, after evacuation at 500°C, a sharp band centered at 3734 cm^{-1}, the material with a suspected nickel hydrosilicate structure develops a broad band located at the lower frecuency side of this peak which is still

present after the vacuum treatment at 500°C. The IE catalyst (with only 1% of nickel) shows a small shoulder but the PD catalyst, with higher nickel loading, develops a broad band resistent to evacuation.
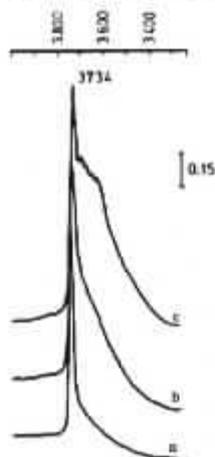

Fig. 5: I.R. spectrum of catalysts prepared by different methods after evacuation at 500°C. a) Impregnation catalysts b) Ion Exchanged catalysts c) P.D. catalyst.

On the other hand, the modified ionic exchange catalysts SN-110°C and SN-450°C show (Fig. 6) the 3734 cm^{-1} sharp band, the broad band at lower frecuency and a new one badly developed centered at 3623 cm^{-1}. This band is clearly seen in the IR spectra of the ammonium-thermal treated materials (Fig. 7).
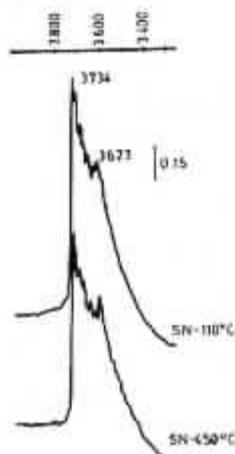

Fig. 6: I.R spectra of modified ionic exchanged catalysts whithout ammonium thermal treatment.

The absorption bands can be assigned by taking into account both, the frecuency and the thermal-vacuum resistance. So, the 3734 cm^{-1} band is assignable to the O-H bond stretching frecuency of free silanol groups at the silica surface (Peri, 1984; Boehm and Knözinger, 1983). The water present on the silica, interacting with

these groups, shows a broad band in the 3700–3200 cm^{-1} range but it disappears after vacuum treatment at 500°C as it can be observed on impregnation catalysts (Fig. 5).
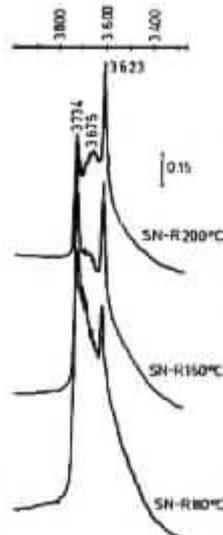

Fig. 7: I.R. spectra of modified ionic exchange catalyst with ammonium thermal treatment.

As the amount of nickel interacting with silica increases, the broad band, resistent to evacuation at 500°C, also increases. By taking into account the TPR and XPS results, the presence of Ni(OH)$_2$ is excluded. Therefore, this band must be assigned to the development of a non-stoichiometric (probably like-serpentine) Nickel hydrosilicate formed by one side replacement of hydroxyl groups, from a hypothetical nickel hydroxide layer, by oxygen atoms from the silica structure in a similar way as it has been proposed by other authors (Clause et al.,1991; Geus,1985; Mendioroz and Munoz,1990) and detected by other techniques. This band is centered at 3675 cm^{-1} in the SN-R200°C material. Its position is congruent with the fact that in NiO the stretching frecuency of the O-H bond of the superficial hydroxide groups goes from 3730 cm^{-1} to 3630 cm^{-1} depending on the coordination number of this group to Ni atoms.

On the other hand, the 3623 cm^{-1} band observed in the modified ionic exchange catalysts must be assigned to the formation of a nickel-Talc structure (Farmer,1974) that is poorly developed in the SN-110°C and SN-450°C (Fig. 6) but it is clearly developed after these materials are hydrothermally treated (Fig. 7).

It is interesting to observe the TPR diagrams of the SN-R110°C, SN-R160°C and SN-R200°C samples (Fig. 3). These materials show a reduction peak centered at 750-780°C that increases and sharpens as

the amount of nickel Talc increases in the samples; accordingly the low temperature peak (500-600°C), corresponding to a like-nickel serpentine reduction, decreases.

In Fig. 2, it is shown that the Ni/Si atomic ratio of the samples increases with the ammonium thermal treatment. So, while the SN-110°C and SN-450°C materials have approximately the same atomic Ni/Si ratio (0.35) it increases to 0.59 for SN-R200°C. It should be noted that nickel Talc theoretical Ni/Si atomic ratio is 0.75.

The nickel Talc structure is very similar to that of the Serpentine (nepoui-te or antigorites). Thus, while the Serpentines consist of a superposition of sheets composed by one layer of silica ($Si_2O_5^=$ units) and one layer of nickel ions in octahedral coordination, the Talc structure is formed by superposition of "sandwiches" of nickel octahedrically coordinated between two layers of silica. The interaction of silica with the nickel hydroxide layer in both cases is done through the replacement of two of each three hydroxile groups at one side or two sides (serpentine or Talc respectively) of the nickel hydroxyde layer by oxygen atoms arising from the tetrahedra of silica groups present in the silica sheets. Because of these replacements, isolated hydroxile groups equidistants to three Ni^{+2} ions remain in the structure. These hydroxiles in the Talc structure are responsible for the 3623 cm^{-1} band but this is not the case of serpentine structures where it is not possible to distinguish between the absorption of inner and outer hydroxyls giving a much broader O-H stretching absorption band suggesting that the trioctahedral 1:1 minerals (serpentines) have a more complex and disordered structure (Farmer, 1974). As a consequence of this disordered structure, they must have a higher surface area. So, as shown in Table 1 and Fig. 7, those catalysts with a predominant like-nickel serpentine structure have a high surface area (300 m^2/g). However, as their structures change from a disordered like-serpentine to an ordered Talc, a clear decrease in the surface area is observed.

These hydroxyl groups are detected by IR spectroscopy because each group absorbs I.R. radiation almost independently of their neighbours although a long range ordered structure has not been developed . So, it can be seen that in the 1250-1000 cm^{-1} range only a broad band is observed instead of the expected sharp ones that must appear when ordered layer silicate structures are developed (Farmer, 1974).

Only an insinuation of these bands is observed, as a shoulder, at 1035 cm^{-1} in SN-R200°C in spite of the 3623 cm^{-1}

which is developed as the main hydroxyl band. It must be stressed that the I.R. absorption patterns allows the recognition of the hydrosilicate structures independently of the presence of the packets of layers required to give a distinctive X-Ray diffraction.

In spite that the nickel serpentines and nickel talc are structurally similar, from a chemical point of view, the differences in the stratification of the sheets of silica and nickel hydroxide cause some changes that can affect their catalytic activity. So, while in catalysts whith a disordered like-serpentine structure the nickel hydroxide layer is exposed to the surface, in the talc structure the nickel ions are between two silica sheets and hence not exposed to the surface. The sharpeness of the 3623 cm^{-1} band is due to the fact that the hydroxyl groups are isolated and "protected" by the structure. In such a case the nickel ions exposed are only those localized at the borders of the "sandwich" and they are interesting from a catalytic point of view because they are neighbouring to silanol groups in the border giving bifunctional properties, in a similar way as it happens in Mg talc or Mg serpentin structures. In that case it would be interesting to obtain particles as small as possible to increase the exposed area at the borders.

Py chemisorption.

Traditionally, Py was used as a probe molecule to characterize the acidic properties of the surfaces. So, the IR spectra of chemisorbed Py allow to distinguish between Py interacting with Lewis or Brönsted acid sites and hydrogen bonded Py (Parry, 1963; Boehm and Knözinger, 1983).
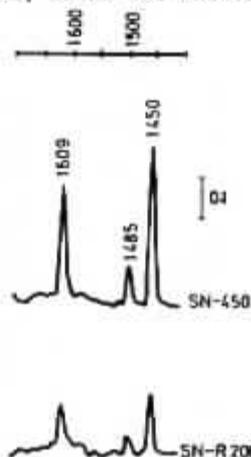

Fig. 8: Py chemisorption on catalysts prepared by modified ionic exchange method after 2 hr evacuation.

Prior Py chemisorption the catalysts were evacuated at different temperatures. In all cases, (Fig. 8), hydrogen bonded Py

and Lewis Py were observed, but never Py interacting with Brönsted acid sites. Because the hydrogen bonded Py was easily evacuated at RT the only species of Py that remain at the surface after two hours evacuation is Lewis Py characterized by three absorption bands at 1609 cm^{-1}, 1485 cm^{-1} and 1451 cm^{-1}.
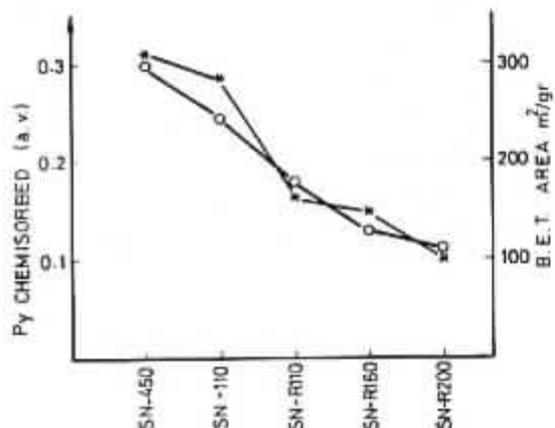

Fig. 9: BET surface area and Py chemi-sorption on Ni/SiO$_2$ catalysts prepared by modified ionic exchange method.

The ammount of Lewis Py was dependent on the previous vacuum-thermal treatment of the samples. Thus, the samples pretreated 1 hr at 500°C in vacuum showed more Lewis acid sites that those pretreated at lower temperature. The increase of the Lewis acidic sites is a consequence of a higher exposition of the nickel ions coordinatively unsaturated at the surface . The bands observed are assigned to Py molecules interacting with Ni^{+2} centers. Similar bands were observed by Vazquez et al.(1986) over NiO supported on Y-Zeolites after evacuation at 400°C.

The changes in the ammount of Py chemisorbed on Lewis acid sites and so on the exposed nickel ions observed with the materials previously evacuated at 500°C clearly agree with the changes in the BET surface area (Fig. 9). As a consequence, the nickel dispersion on the exposed surface is similar for all the samples.

On the other hand, from the XPS results it can be seen that there is a change in the Ni/Si atomic ratio which is coincident with a nickel talc formation detected both by IR and TPR. This fact can be explained by taking into account that the hydrosilicate initially formed (SN-110°C and SN-450°C) is a non stoichiome-tric surface compound (the nickel loading on these catalysts would be enough to cover only 20% of the surface if a monolayer of stoichiometric nickel antigo-rite structure were supposed). If we take into account that the mean free path of the photoelectrons is 30 Å approx. (Wagner et al., 1978) with XPS not only the sili-con atoms of the nickel rich layer will be seen but also silicon atoms from the internal structure of the silica. Therefo-re, as a result, a low value of the Ni/Si atomic ratio should be expected.

As the nickel talc is forming some silica must be redissolved to obtain the characteristic 2:1 trioctahedral mineral structure with a consequent change in the surface area. As the number of layers increases the XPS can only see these layers but not the silica structure on where they are supported. So, the observed Ni/Si atomic ratio must increase to a similar value to that theoretically expec-ted for the nickel talc (Ni/Si atomic ratio of 0.75).

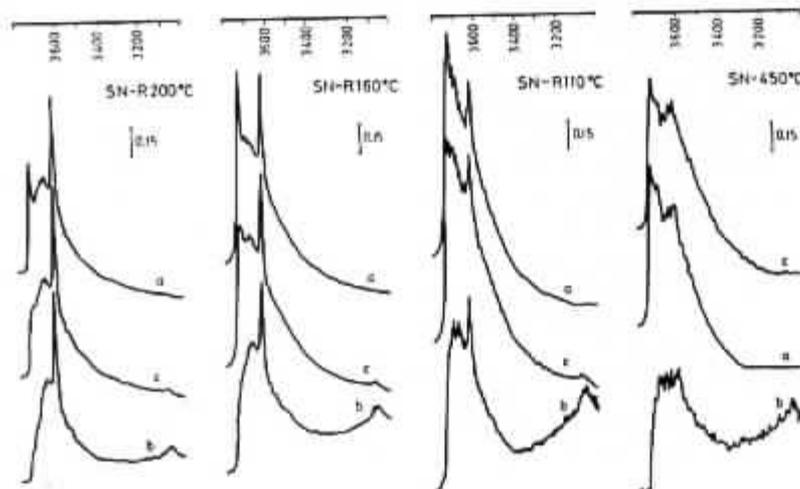Therefore, it can be concluded that the number of stratified layers of nickel

Fig. 10: Effect of the Py chemisorption on the hydroxyl stretching bands region a) Catalysts outgassed at 500°C previous to Py chemisorption. b) Catalysts whith 8 mmHg of Py. c) Catalysts after Py chemisorption and evacuated to R.T.

talc increases with more severe hydrothermal treatment (i.e. from SN-110°C to SN-R200). However, the exposed upper layer is mainly covered by an antigorite nickel-like structure.

Some additional structural information can be obtained by analyzing the behavior of the hydroxyl stretching bands when Py molecules interact with the samples. In Fig. 10 it can be seen that while the 3734 cm^{-1} band is shifted and transformed into a broad band, the 3623 cm^{-1} band, assigned to hydroxyl groups in the Talc structure, remains unaffected because they are occluded between two sheets of silica.

It can also be seen that the band assigned to free silanol groups is better developed while the broad band, corresponding to hydroxyl groups in the superficial serpentine-like structure, decreases. This is caused by the transformation into a more ordered and tridimentional 2:1 trioctahedral mineral.

On the other hand the evacuation of hydrogen bonded Py leaves only Lewis Py on the surface (Fig. 8) but it can be seen that in the SN-R200°C catalyst the free silanol groups are not restored in the spectrum. This behavior is more distinctive as the Talc structure becomes more evident.

Because neither Brönsted nor hydrogen bonded Py after 2 hr evacuation were detected, it can be assumed that the disappearance of the 3734 cm^{-1} band is a consequence of the interaction of free silanol groups with π electrons of the aromatic ring of Py chemisorbed molecules in neighbouring nickel centers.

Seeing, this behavior is more evident as the 3623 cm^{-1} band (talc structure) is better developed and because the formed talc crystallytes are so small that they can not be detected by X-Ray spectroscopy, these silanol groups would be related to the development of the Talc structure and probably they would be located on the borders of the incipient stratificated layers. Nevertheless, additional experiences must be programmed in order to obtain strong support on the last assumption.

CONCLUSIONS

The modified ionic exchange method allows to obtain Ni/SiO$_2$ materials with nickel predominantly at the surface and with a high degree of interaction with the support. Neither NiO nor nickel hydroxide were detected in the samples.

The TPR method in conjunction with IR spectroscopy in the 4000-3000 cm^{-1} range are suitable techniques to determine the structural characteristics of the obtained materials, although they do not have long range ordered structures that could be detected by XRD. With this preparation technique, the obtained material can be described as a non-stoichiometric layered hydrosilicate covering the surface when the samples are not ammonium-thermal treated but, when they are pretreated at different pressures and temperatures, this surface hydrosilicate is transformed into an ordered Talc structure.

Py chemisorption only shows Lewis acid sites present at the surface.

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