

Effect of thermal treatments on surface chemical distribution and catalyst activity in nickel on silica systems

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Abstract

The reducibility of several nickel on silica systems prepared by incipient wetness impregnation and precipitation–deposition has been studied using TPR and TG. The analysis of the results has allowed us to determine the minimum drying and reduction temperatures for both impregnation and precipitation catalysts. From an analysis of the obtained results, together with X-ray diffraction and the study of the reduction degree, dispersion and nickel particle size of catalysts activated at different reduction temperatures, conclusions on the nickel surface chemical distribution have been derived. An optimal reduction temperature for the catalysts has been determined from activity considerations in the hydrogenation of sunflower seed oil.

Keywords: Nickel/silica; Supported catalysts; Vegetable oil hydrogenation; Thermal treatments; Reduction

1. Introduction

Supported nickel catalysts are used in many industrial catalytic processes such as olefine hydrogenation, hydrogenolysis, reforming, gas shift conversion, etc. due to its easy availability, high activity and economics. Traditionally, nickel catalysts are those preferred for vegetable oils hydrogenation [1], a process of great importance in the edible oil and fat industry, since hydrogenation can modify the consistency and melting behavior of the products and contribute

to improvement of the oil stability. High metal loading, on silica, kieselguhr and alumina as the more common supports, is usual in commercial supported catalysts [2,3].

Silica-supported nickel catalysts are usually prepared using three different techniques: impregnation, ion-exchange and precipitation–deposition with different precipitating agents [4–9]. Although impregnation is the easiest catalyst preparation procedure, the catalyst performance can be improved by the use of ion-exchange or precipitation–deposition. Ion-exchange, as is restricted to the preparation of catalysts with very low metal contents, does not seem adequate to prepare catalysts for the hydrogenation of vegetable oils.

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The characteristics and distribution of surface nickel compounds on the silica depends on the preparation procedure and the activation conditions of the different precursors. This results in different extents of what is called 'interaction' between nickel and support and influences the general performance of the catalyst. The activation procedure becomes, then, of vital importance and its study particularly interesting for the researcher.

This paper constitutes part of a wider work in which the characteristics and structure of nickel catalyst are related to their activity in the hydrogenation of vegetable oils [10]. In this paper, several nickel on silica catalysts have been prepared using two silicas of very different textural characteristics and two preparation procedures: impregnation at incipient wetness and precipitation–deposition. The activation of the samples has been studied by temperature programmed reduction and thermogravimetric analysis, extracting conclusions on the minimum drying and reduction temperatures and on the surface chemical composition. These conclusions were supported with X-ray diffraction studies of the final catalysts and with the analysis of the surface nickel distribution in catalysts activated at different reduction temperatures. Conclusions on the optimal reduction temperature were derived from activity considerations.

2. Experimental

2.1. Catalyst preparation

Two silica supports were used for the preparation of the catalysts: CS-1030E, supplied by the PQ's Corporation, denoted as PSIL in this paper (porous silica) and Aerosil 200V, supplied by Degussa, denoted as ASIL (acrosil).

Four series of catalysts were prepared varying in: metallic content (from 0.58 up to 50.7 wt% Ni), support (either PSIL or ASIL) and preparation procedure (impregnation at incipient

wetness (I-catalysts) or precipitation–deposition (P-catalysts)).

The incipient wetness impregnation technique was carried out at 3 kPa and 308 K, from an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The catalytic precursor thus obtained was dried at 383 K for 14 h before activation.

P-catalysts were prepared following the method described by Van Dillen et al. [9], in which the thermal decomposition of urea was used to raise homogeneously the pH of an aqueous suspension of the support in nickel nitrate solution. The pH of the solution was initially adjusted to 3.5 by addition of diluted nitric acid and continuously stirred at 363 K and 1 h for the catalyst with 0.58 wt% Ni, 6 h for the catalysts with up to 20 wt% Ni and 20 h for the catalysts with higher nickel content. At the end of this time, the green precipitate obtained was filtered, washed with water at 363 K and dried at 383 K for 14 h before activation.

Precursors were activated as follows. I-precursors were first dried at 493 K for 1 h in a $25 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$ hydrogen flow. Afterwards, the temperature was raised up to the final reduction temperature at 4 K min^{-1} and after 4 h of treatment cooled down to room temperature. P-precursors were activated in a similar way, but the drying temperature was 423 K.

Due to the pyrophoric character of nickel, the activated catalysts had to be passivated for subsequent handling. This was realized immediately after activation, in 1% O_2/N_2 flow, at room temperature, and increasing progressively the oxygen concentration before exposing the catalyst to ambient conditions [7].

2.2. Catalyst characterization

Specific area, average pore radius and pore volume of the supports as well as the catalysts were determined by nitrogen adsorption–desorption isotherms at 77 K using the BET method in a Micromeritics Accusorb 2100E apparatus.

A Malvern Mastersizer X, model MSX 14,

was used to measure the catalyst particle size distribution and thus determine the average catalyst particle size.

Temperature programmed reduction (TPR) measurements were carried out on samples of the precursors in order to determine the temperature at which the reduction process takes place, in an AMI-1 apparatus, equipped with a TCD, using a heating rate of 25 K min^{-1} . These measurements were combined with the thermogravimetric analysis of the samples, carried out in a Perkin Elmer TGS-2 thermobalance, in a reducing flow of H_2/N_2 and different heating rates, to determine the loss of weight that takes place during the reduction process.

The metallic content of the reduced catalysts was measured by atomic absorption spectrometry in a Perkin Elmer 1100B apparatus. The samples for analysis were previously dissolved in acidic medium.

Hydrogen chemisorption at 298 K was used for the measurement of nickel dispersion and metallic surface areas in the catalysts, in a Micromeritics Accusorb 2100E apparatus. Previous to the measurement, samples of the passivated catalysts were reduced in the equipment at 673 K and 27 kPa and subsequently degassed for 12 h at the same temperature and high vacuum. The monolayer adsorption capacity was determined by extrapolating down to zero pressure the linear regression of the equilibrium data obtained in the range 7 to 40 kPa hydrogen equilibrium pressure. The values obtained with this procedure are useful from a comparative point of view, although some discussion concerning its adequacy can be found in the literature [11].

The reduction degree of the catalysts, f , was determined by the procedure described by Bartholomew and Farrauto [12]. It was evaluated after hydrogen chemisorption by evacuating the sample at 673 K and then measuring the uptake of pure oxygen at that temperature. In these conditions, the oxidation of all metallic nickel to NiO can be assumed [13].

The validity of hydrogen chemisorption to

determine dispersion of P-catalysts, with low reduction degree, was checked by carrying out measurements under the same conditions on unreduced precursors. Hydrogen adsorption values obtained for the precursors were always below 5% of that adsorbed by the corresponding reduced catalysts, within the experimental error of the methodology. Thus, the total amount of hydrogen adsorbed has been used to determine nickel dispersion, nickel surface area and nickel particle size, without significant errors.

The metallic surface area was calculated with the following expression:

$$S_{\text{Ni}} = 1.358 \cdot 10^{-19} N_{\text{M}} \quad (1)$$

where N_{M} is the number of hydrogen molecules adsorbed in the monolayer per g of catalyst. Eq. (1) was derived considering the surface occupied per atom of nickel as $6.79 \cdot 10^{-2} \text{ nm}^2 \text{ atom}^{-1}$ and the adsorption stoichiometry as 0.5 hydrogen molecules per surface nickel atom.

Nickel dispersion on the catalyst was calculated with:

$$D = 1.95 \cdot 10^{-18} \frac{N_{\text{M}}}{C_{\text{Ni}} f} \quad (2)$$

where C_{Ni} is the nickel content of the catalyst, in wt% and f is the reduction degree in %. Eq. (2) was derived considering the atomic weight of nickel as 58.69 g mol^{-1} .

The average size of the nickel particles in the catalyst was calculated, for I-catalysts, assuming spherical shape, considering a nickel density of 8.90 g cm^{-3} and assuming a complete accessibility of the active phase, with:

$$d_{\text{Ni}} = \frac{0.967}{D} \quad (3)$$

A hemispherical shape is assumed for the nickel particles in P-catalysts [4]. Thus, the previous expression takes the form:

$$d_{\text{Ni}} = \frac{0.768}{D} \quad (4)$$

X-Ray diffraction patterns of samples of the passivated catalysts were obtained in a Philips

PW 1700 diffractometer using CuK_α radiation with a wavelength of 1.5417 Å, from 10 to 80° and a rate of 1° min⁻¹.

Catalyst activity has been tested in the sunflower seed oil hydrogenation carried out in a batch reactor, at constant temperature and pressure, keeping the catalyst slurred in the oil by mechanical stirring. A commercial refined sunflower oil (Coopsol) was used as reactant, with the following composition of fatty acid radicals (C:carbons/double bonds) in the triglycerides: 9.0% palmitic acid (C:16/0); 5.0% stearic acid (C:18/0); 29.0% oleic acid (C:18/1) and 57.0% linoleic acid (C:18/2).

As the catalysts had been passivated for characterization and handling, a reactivation was necessary before reaction. This reactivation consisted of reduction at 573 K for 30 min in a 100 cm³ min⁻¹ hydrogen flow. The active catalyst was immediately dropped over the oil at the reaction temperature to prevent reoxidation.

The course of the reaction was followed by analysis of liquid samples let out at intervals, determining: their refractive index at 333 K,

directly related to the concentration of double bonds in the samples and thus used to obtain a global reaction rate, and their composition by GLC.

Activity has been expressed as global initial hydrogenation rate, $(-r_0)_{\text{H}_2}$, and also as global initial specific activity determined as turn-over frequency, TOF_{H_2} , defined as the number of hydrogen molecules (or double bonds) reacted per surface reduced nickel atom per second. It was calculated with:

$$\text{TOF}_{\text{H}_2} = \frac{163V(-r_0)_{\text{H}_2}}{WC_{\text{Ni}}fD} \quad (5)$$

where V is the reaction volume, in l and W is the catalyst weight, in g.

3. Results and discussion

Table 1 lists the characteristics of the supports and the prepared catalysts: their actual nickel content, support, preparation procedure,

Table 1
Characteristics of the prepared catalysts and the commercial supports

No.	C_{Ni} (wt%)	Sup	PP	T_{Red} (K)	S_{BET} (m ² /g)	V_{P} (cm ³ /g)	r_{P} (nm)	d_{p} (μm)	S_{Ni} (m ² /g)	f (%)	D	d_{Ni} (nm)
Support		PSIL			310	1.18	4.9	21				
1	0.58	PSIL	P	823	293	1.07	5.1	–	0.91	59	0.38	2.0
2	0.91	PSIL	P	823	–	–	–	22	1.06	57	0.29	2.6
3	5.6	PSIL	P	823	317	0.99	4.4	–	4.58	46	0.26	3.0
4	9.8	PSIL	P	823	332	0.91	3.9	17	8.08	46	0.26	3.0
5	14.7	PSIL	P	823	329	0.85	3.9	–	11.5	38	0.29	2.6
6	18.7	PSIL	P	823	383	0.86	3.2	22	12.9	38	0.26	2.9
7	29.3	PSIL	P	823	407	0.72	2.2	–	22.5	43	0.26	3.0
8	50.7	PSIL	P	823	325	0.35	2.0	–	35.7	71	0.14	5.4
9	4.6	PSIL	I	773	246	1.01	4.9	–	5.87	97	0.19	5.1
10	10	PSIL	I	773	293	1.04	5.0	28	12.7	101	0.18	5.4
11	9.5	PSIL	I	573	–	–	–	–	5.26	65	0.12	7.9
12	9.5	PSIL	I	673	–	–	–	–	11.2	91	0.19	5.2
13	9.5	PSIL	I	773	–	–	–	–	9.82	95	0.16	6.2
14	9.5	PSIL	I	873	–	–	–	–	11.0	100	0.17	5.8
15	18.3	PSIL	I	773	243	0.78	4.4	52	22.6	94	0.19	5.2
Support		ASIL			215	np	np	1.2e-2				
16	6.5	ASIL	P	823	206	1.21	7.0	32	5.20	42	0.27	2.8
17	5.6	ASIL	I	773	197	1.26	6.5	31	5.53	84	0.17	5.7
18	9.5	ASIL	I	773	197	1.01	5.7	37	9.63	90	0.16	6.0

np: non-porous support.

reduction temperature and their effect on specific surface area (BET), pore volume, average pore radius, catalyst particle size, nickel surface area, reduction degree, dispersion and particle size.

The two silicas used as catalytic supports were very different in structure as can be seen in Table 1. The original purpose of the non-porous (ASIL) silica was to try to prepare catalysts in which internal diffusion could be considered negligible, as the support presents no pores to which the reactants should enter. This objective was not fulfilled, as an assemblage of support particles took place during preparation (Table 1). Then, ASIL was used to check if the results could be extrapolated to other silica supports.

Preparation of I-precursors via incipient wetness is expected to produce mainly the precipitation of particles of $\text{Ni}(\text{NO}_3)_2$ on the silica surface.

During preparation of P-precursors, the chemical reaction of nickel species with the support can be analyzed following the evolution of pH with time. This evolution is shown in Fig. 1. Curve (a) represents the pH evolution during thermal hydrolysis of urea, NH_2CONH_2 , at 363 K and an initial pH of 3.5 adjusted with diluted nitric acid, to form CO_2 and NH_3 . Most of the CO_2 is dissolved as HCO_3^- and the ammonia increases pH up to a final value of 7.

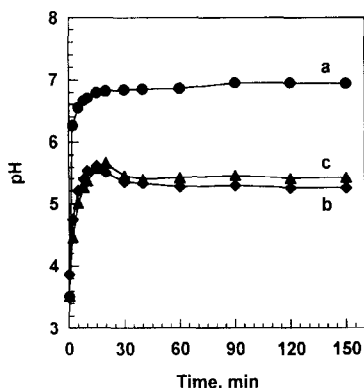


Fig. 1. Evolution of pH with time during thermal hydrolysis of urea at 363 K. (a) Urea + HNO_3 ; (b) urea + HNO_3 + $\text{Ni}(\text{NO}_3)_2$ + PSIL; (c) urea + HNO_3 + $\text{Ni}(\text{NO}_3)_2$ + ASIL.

Curves (b) and (c) correspond to the mixture of urea with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the silica support, PSIL and ASIL, respectively. A maximum can be observed in a short time, about 15 min, and subsequent stabilization at about pH 5.4. This maximum can be explained by two contradictory effects: the decomposition of urea increasing pH as in curve (a) and the precipitation of nickel hydroxide on the silica support, thus decreasing pH.

Activation of the precursors was carried out by thermal reduction in hydrogen. The purpose of activation is to reduce the nickel compounds present on the silica surface of the catalyst precursors to metallic nickel, in order to optimize the catalyst performance. This frequently implies maximize catalyst activity, related to catalyst reduction degree and dispersion.

The conditions in which activation is realized determine definitively the characteristics and performance of the final catalyst. Two aspects are known to be crucial: dryness of the precursor before reduction and the temperature at which reduction is carried out. In order to assure the first condition, all precursors were dried immediately before reduction. With respect to reduction temperature, its influence on the characteristics of the final catalyst has been carefully analyzed both for I- and P-precursors.

The reduction process was followed using the TPR technique. Fig. 2 shows some of the TPR diagrams obtained for the catalysts supported on PSIL (the corresponding ASIL catalysts showed a similar trend) as well as some nickel compounds: commercial $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NiO obtained by thermal decomposition of the former and $\text{Ni}(\text{OH})_2$ prepared by precipitation from a solution of nickel(II) nitrate with urea. Although neither NiO nor $\text{Ni}(\text{OH})_2$ obtained in this way are expected to be particularly pure, they were chosen because they are supposed to represent the nickel compounds that could be expected in the precursor probably better than any pure phase.

An analysis of the TPR curves obtained and its comparison with those for the nickel com-

pounds, gave us valuable information on how the nickel was deposited on the support during preparation. Thus, I-precursors consist mainly of nickel nitrate deposited on the silica surface, as expected, as their reduction produced one single, sharp peak with a maximum about 601 K (Fig. 2), in good agreement with that corresponding to $\text{Ni}(\text{NO}_3)_2$.

Fig. 2 shows, on the other hand, that P-precursors behavior with respect to TPR varied with the nickel content. For nickel contents below 30 wt% Ni, a very broad single reduction peak was obtained, with the maximum about 865 K. For higher nickel contents, 50 wt% Ni, a second reduction peak appeared, with a maximum about 718 K.

The peak at 718 K was attributed to $\text{Ni}(\text{OH})_2$, in agreement both with the reduction value obtained for this nickel compound and with the explanation provided for curve (b) in Fig. 1. The broad peak at 865 K, which denotes a

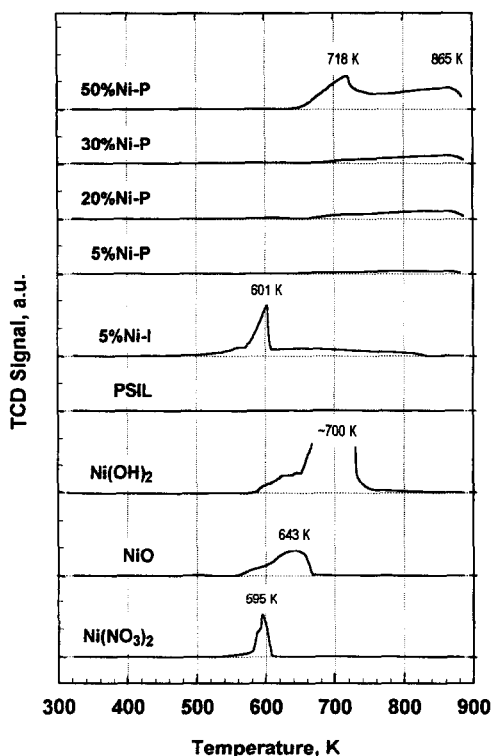


Fig. 2. TPR diagrams of several nickel compounds, PSIL and some of the prepared catalysts supported on PSIL.

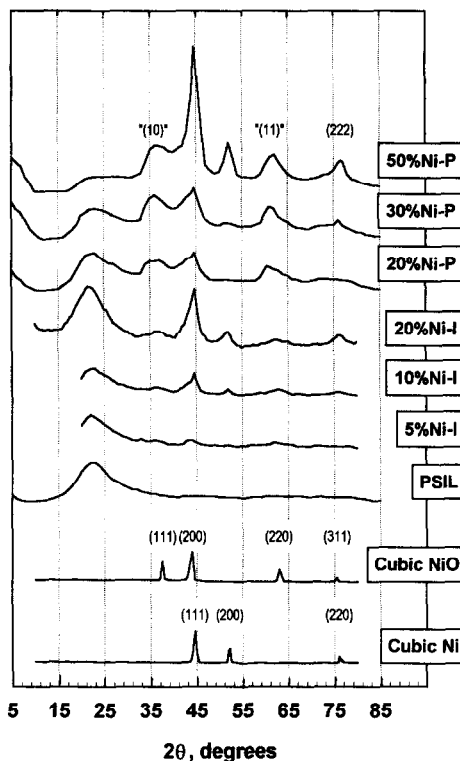


Fig. 3. X-ray diffractograms of some pure nickel phases, PSIL and some of the prepared catalysts supported on PSIL.

compound of difficult reducibility, can be explained if we consider that nickel hydroxide has been reported by a number of authors to react with the surface of the silica support forming nickel hydrosilicate, probably in an antigorite-like, $\text{Ni}_3(\text{OH})_3\text{Si}_2\text{O}_5(\text{OH})$, or talc-like structure, $\text{Ni}_3(\text{OH})_2(\text{Si}_2\text{O}_5)_2$, highly dispersed [4,5,14].

Thus, nickel hydroxide precipitating during urea hydrolysis in the preparation of P-catalysts on silica, reacts with the silica surface while free silica surface is still available, forming nickel hydrosilicate. For high nickel contents, above 30 wt% Ni, silica has been completely covered with a layer of nickel hydrosilicate and the remaining nickel precipitates as $\text{Ni}(\text{OH})_2$ on this layer.

Evidence of the formation of the nickel hydrosilicate layer is also found when X-ray diffractograms of the reduced and passivated catalysts are analyzed (Fig. 3).

Fig. 3 shows the X-ray diffractograms obtained for silica, pure nickel phases (Ni and NiO) passivated I-catalysts and passivated P-catalysts. The X-ray diffractogram of Ni(OH)₂ was not analyzed because catalysts had been reduced at temperatures above which reduction of Ni(OH)₂ takes place.

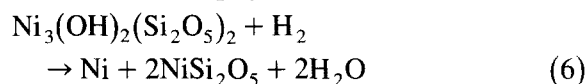
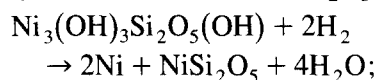
X-ray diffractograms of I-catalysts present the broad background peak associated to the amorphous silica support, constant in intensity with nickel content; peaks associated to metallic nickel (Ni (111), Ni (200) and Ni (220)) that increase with nickel content and small, broad peaks associated to NiO (NiO (111), NiO (200) appearing as a shoulder of Ni (111), NiO (220) and NiO (311) superimposed to Ni(220)) which denote small crystallite size or small crystallinity, associated to the layer of NiO formed on the catalytic surface during passivation of the catalysts.

P-catalysts present also the broad background peak associated to the silica support for relatively low nickel contents, but this peak decreases its intensity as the catalyst nickel content is increased, disappearing almost completely above 30 wt% Ni. This result is in accordance with the complete coverage of silica with a layer of nickel hydrosilicate above 30 wt% Ni that was postulated from the results of TPR in Fig. 2.

X-ray diffraction patterns of P-catalysts presented also the three peaks associated to Ni, although their intensity, compared to that of the corresponding I-catalysts for similar nickel contents, was about one half lower. Although peaks at angles corresponding to NiO were found as well and NiO was certainly present on the catalyst surface because of passivation, neither the relative intensity of the peaks nor their shape could be attributed only to NiO, but probably mainly to some nickel silicate formed by reduction of nickel hydrosilicate.

Nickel hydroxide consists of an hexagonally packed layer of nickel ions enclosed between two layers of hydroxide ions. Nickel hydrosilicate on the silica surface is formed by replace-

ment of two out of every three hydroxyl ions either in one side (antigorite-like structure) or in both sides (talc-like structure) with (Si₂O₅)⁻² [15]. These structures are characterized by a relatively weak bonding between the layers, forming a bidimensional structure [4]. Reduction of nickel hydrosilicate takes place with loss of water, to form metallic nickel together with some nickel silicate in the surface of the catalyst, probably mainly NiSi₂O₅, also laminar, by:



Thermogravimetric analysis (TGA) in a flow of a mixture 10% H₂/N₂ and a heating rate of 25 K min⁻¹ was carried out on both I- and P-precursors and their correspondence with TPR was established. The weight versus temperature diagrams obtained for some of the samples, together with their derivatives, are shown in Fig. 4.

A first loss of weight is observed for all precursors at low temperatures, associated to the wetness of the precursor and/or to the hydration degree of the adsorbed complex. This peak is not observed in TPR, as it does not imply hydrogen consumption and was used to determine the minimum temperatures at which the drying step before reduction should be performed.

The rest of the diagram is consistent with the results of TPR, presenting weight losses corresponding to each one of the reduction steps previously mentioned. The temperatures at which the peaks appear in the weight derivative and in the corresponding TPR for the same sample, however, do not always match e.g. the peak assigned to Ni(OH)₂ reduction in the sample 50% Ni-P (Figs. 2 and 4). This is not surprising if we consider that the processes measured in both analysis are very different and the maximum rate of weight loss is not necessarily the maximum rate of hydrogen consumption.

Although a heating rate of 25 K min^{-1} is necessary for the peaks of TPR to clearly appear in the diagram, it is too quick a rate for a precise determination of the temperatures at which the processes take place. This is clearly visualized when thermograms are carried out with a heating rate of 2 K min^{-1} (see also Fig. 4), where at least a 50 K shift of the weight losses to lower temperatures can be observed.

Thermograms carried out at 2 K min^{-1} provided then information on the temperature at which I- and P-precursors should be dried before reduction and the minimum temperature at which they should be reduced. Drying temperature was chosen as 493 K for I-precursors and 423 K for P-precursors [10].

The minimum reduction temperatures, determined from the maximum rate of weight loss in Fig. 4, should be thus 558 K for I-precursors and 720 K for P-precursors.

In order to select the optimal reduction temperature for I-precursors, an additional series of

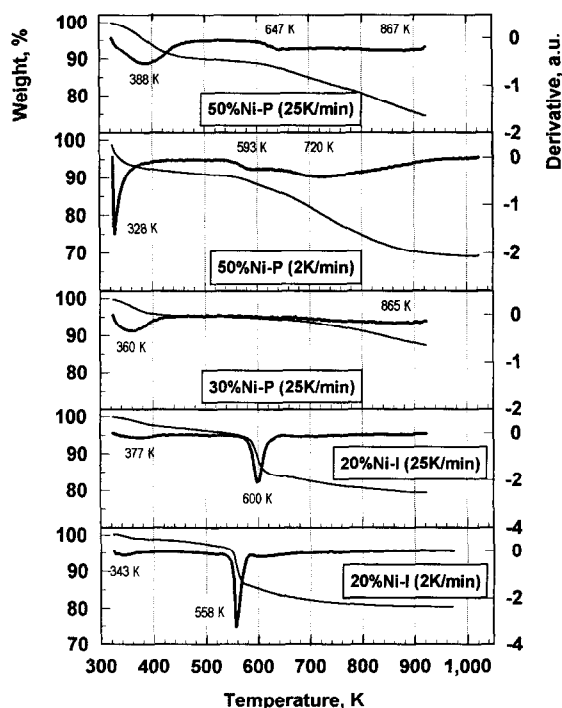


Fig. 4. TG diagrams and their corresponding derivatives of some of the prepared catalysts supported on PSiL.

Table 2

Surface chemical distribution and activity of I-catalysts about 10 wt% Ni, activated at different reduction temperatures

No.	T_{Red} (K)	S_{Ni} (m^2/g)	f (%)	D	d_{Ni} (nm)	$(-r_0)_{\text{H}_2}$ (mol/lh)	TOF_{H_2} (s^{-1})
10	773	12.67	101	0.18	5.4	2.53	1.26
11	573	5.26	65	0.12	7.9	1.40	2.18
12	673	11.21	91	0.19	5.2	1.79	1.16
13	773	9.82	95	0.16	6.2	2.45	1.80
14	873	10.98	100	0.17	5.8	2.22	1.43

Catalyst number corresponds to that in Table 1.

9.5 wt% Ni/PSiL-I catalysts was prepared by reduction of the corresponding I-precursor at 573, 673, 773 and 873 K, respectively (catalysts 11–14 in Table 1). Their characteristics, together with those of catalyst 10 in Table 1, as well as their activity in the sunflower seed oil hydrogenation were analyzed and are shown in Table 2.

Table 2 shows that from the point of view of reduction degree and nickel dispersion, a reduction temperature of 673 K produces the complete reduction of nickel, within experimental error, in agreement with thermogravimetric results and the maximum dispersion in the catalyst. However, when activity is analyzed, initial hydrogenation rate increase with reduction temperature, without significant variation of reduction degree and nickel dispersion. As no increment in activity is observed beyond 773 K, this temperature was chosen to reduce I-precursors. TOF_{H_2} is constant, within experimental error, for catalysts reduced above 673 K. This means that each reduced nickel atom in the surface (determined by hydrogen chemisorption) has the same activity. The fact that TOF_{H_2} obtained for catalysts reduced at 573 K is much higher than the rest, only indicates that hydrogen chemisorption is probably not adequate to evaluate dispersion for I-catalysts with a very low reduction degree [16–18].

With respect to P-precursors, due to the observed difficult reducibility of the samples, a temperature of 823 K was chosen for the reduction treatment well above the required 720 K and also above that of I-precursors.

A general discussion on the influence of the support, preparation procedure and nickel content on the textural properties and surface chemical distribution of the activated and passivated catalysts has been presented elsewhere [19]. However, several aspects need to be commented in the light of what has been previously stated.

As to the textural properties of the catalysts (Table 1), it is interesting to note the increase of specific surface area with nickel content observed in P-catalysts. This increment can only be accounted for if a sufficiently porous surface compound of nickel and silica is formed. This again points to the presence of nickel silicate on the surface of these catalysts, supporting the evidence of TPR, TG and X-ray diffraction.

Table 1 shows that, from the point of view of nickel surface area, S_{Ni} , reduction degree, f , dispersion, D , and nickel particle diameter, d_{Ni} , the prepared catalysts can be studied in two groups: on the one hand P-catalysts and on the other hand I-catalysts; regardless of the silica support used in their preparation.

The reduction degree of the catalysts is a very interesting variable, as it is related to all which has been discussed during catalyst preparation and activation. I-catalysts present reduction degrees in the range 90–100%, for the standard reduction temperature, while the reduction degree of P-catalysts is much lower (Table 1). In agreement with TPR and TG results, the reduction degree of I-catalysts increases with reduction temperature (numbers 11 to 14 in Table 1) and is complete, within experimental error, above 673 K.

A minimum in the reduction degree with nickel content can be observed in Table 1 for P-catalysts. P-catalysts with a very low nickel content, below 1 wt% Ni (numbers 1 and 2 in Table 1) present reduction degrees of nearly 60%. This value decreases with nickel content until a minimum of 38% is measured for the catalysts with 14.7 and 18.7 wt% Ni (numbers 5 and 6), and gradually increases again up to 71% for the 50.7 wt% Ni/SIP-P catalyst (number 8).

If we assume that reduction of nickel hydro-

silicate takes place according to Eq. (6) and reduction of the laminar nickel silicate does not take place at least up to 1023 K (the maximum temperature used in TG) then reduction degree could be related to the ratio nickel–antigorite to nickel–talc present in the precursor surface, up to nickel contents of 30 wt% Ni and should be restricted to values between 33%, for a pure talc-like structure, and 67%, for a pure antigorite-like structure. Table 1 shows that this is the case for all P-catalysts. Of course, this is an oversimplified view of the system and some other facts such as the formation of other nickel silicates and the probable incomplete reduction of nickel hydrosilicate should be taken into account.

For higher nickel contents, as was already pointed out when the results of TPR and TG were discussed, nickel in excess precipitated during preparation as easily reducible $Ni(OH)_2$ (see Figs. 2 and 4) on the layer of nickel hydrosilicate on the precursor surface. The contribution of this compound to the total amount of nickel in the catalyst produces the observed increase in its reduction degree.

Summarizing all results obtained concerning reducibility of P-catalysts: TPR, TG, reduction degree and intensity of nickel peaks in DRX compared to those of I-catalysts for the same nickel content; point us to note that nickel in the form of nickel hydrosilicate is not reducible beyond 67% at least up to temperatures of 1023 K.

Considering the nickel species present on the catalyst surface that have been discussed up to now and its ‘interaction’ with the support, a spherical model was assumed for the nickel particles in I-catalysts, with low ‘interaction’, and a hemispherical model was assumed for P-catalysts, with high ‘interaction’. These assumptions mean that, for the same dispersion value, P-catalysts will have lower crystallite ‘diameter’ (equivalent length) than I-catalysts.

Analyzing then nickel particle size in Table 1, I-catalysts present an almost constant size, about 5.5 nm, in the range of nickel content

studied. P-catalysts present also practically constant particle size about 3 nm, one half the value observed for I-catalysts, except for the lowest nickel content catalyst, with slightly smaller particle size, and the highest nickel content catalyst, with particle size in the same range as I-catalysts. The high particle size obtained for the I-catalyst reduced at the lowest temperature, 573 K (number 11 in Table 1) should also be pointed out here. Considering its low reduction degree and high specific activity (Table 2), this should be attributed to the low reliability of hydrogen chemisorption to determine nickel dispersion of I-catalysts (easily reducible) with a low reduction degree.

4. Conclusions

Four series of supported nickel catalysts have been prepared using two silicas of very different structure: porous silica PSIL and non-porous silica ASIL and two preparation procedures: incipient wetness impregnation (I-catalysts) and precipitation–deposition (P-catalysts).

The behavior of the catalysts during reduction, studied by TPR and TG, has proved to be independent of the silica used as catalytic support and to depend only on the preparation procedure.

I-precursors, prepared by incipient wetness impregnation from a nickel(II) nitrate solution, after the weight loss corresponding to drying observed in TG, presented one single reduction peak with a maximum reduction rate in excellent agreement with that of $\text{Ni}(\text{NO}_3)_2$, at relatively low temperature. Upon reduction and passivation, the X-ray diffractograms obtained showed the presence of both metallic nickel and NiO on the catalyst surface and also the peak corresponding to the silica support.

Thus, as expected, incipient wetness produced the precipitation of nickel(II) nitrate particles on the silica, with very little ‘interaction’ with the support. Reduction of these precursors took place at low temperature, that correspond-

ing to pure nickel(II) nitrate, to produce metallic nickel. After passivation, a layer of NiO was formed on the nickel particles.

Reduction of I-precursors at different temperatures showed that, although reduction was, within experimental error, complete at 673 K, a maximum of activity was found for catalysts reduced at slightly higher temperature, 773 K. Thus, 773 K was chosen as the optimal reduction temperature for I-precursors.

P-precursors, prepared by precipitation–deposition, presented also a weight loss at low temperatures corresponding to the drying step. With respect to reduction, the behavior depended on the nickel content of the samples. For relatively low nickel contents, below 30 wt% Ni, reduction took place very slowly and gradually with temperature and the reduction peak obtained was extremely wide and ill-defined, with a maximum at high temperatures. When the nickel content was above 30 wt% Ni, a new reduction peak appeared at lower temperature, in good agreement with that of $\text{Ni}(\text{OH})_2$ reduction.

X-ray diffractograms of the reduced and passivated catalysts showed also the presence of metallic nickel and NiO produced during passivation, but some of the peaks could not be attributed only to these compounds. Besides, the peak corresponding to the silica surface decreased with nickel content.

During preparation of P-catalysts, $\text{Ni}(\text{OH})_2$ precipitates on the silica surface. If no other process took place, the precursors would be expected to present a reduction temperature near that of $\text{Ni}(\text{OH})_2$ and upon reduction and passivation, the presence of nickel, NiO and the silica surface in X-ray diffractograms.

The real behavior of P-precursors can be explained if we consider that $\text{Ni}(\text{OH})_2$ is known to react with the silica surface to produce nickel hydrosilicates in the form of nickel–antigorite and/or nickel–talc. These nickel hydrosilicates, of difficult reducibility, would be responsible for the wide, ill-defined reduction peak at high temperatures. For very high nickel contents,

above 30 wt% Ni, all silica surface would be covered by the nickel hydrosilicates and the rest of Ni(OH)₂ formed would remain unreacted on the nickel hydrosilicate surface. This would explain the reduction peak at low temperature, in good agreement with the reduction temperature of Ni(OH)₂, found for the 50 wt% Ni–P sample.

Nickel has been found not to be completely reducible, at least up to the maximum reduction temperature of 1023 K used in this work: the hydrogen consumption in TPR, the maximum weight loss in TG, the height of nickel peaks in X-ray diffraction compared to those of I-catalysts, the reduction degree of the catalysts; all the parameters analyzed point to this. This behavior can also be very well explained considering that nickel hydrosilicates would form laminar nickel silicate during reduction. In this way, between 33 and 67% of the total nickel in the catalysts would remain unreduced. The reduction degree in Table 1 shows that this is the case for all P-catalysts except the 50 wt% Ni–P sample, in which the contribution of easily reducible Ni(OH)₂ increases the reduction degree.

Laminar nickel silicate on the catalyst surface accounts for the high ‘interaction’ in these catalysts. The presence of this compound is supposed to increase the affinity of the reduced nickel for the surface, maximizing the contact surface by forming hemispherical nickel particles and thus increasing the nickel stability in the catalyst.

5. Nomenclature

ASIL	Non-porous aerosil silica support.
C_{Ni}	Nickel content in the catalyst, in wt%.
D	Dispersion of nickel on the catalyst, in g of surface nickel per g of total nickel in the catalyst.
d_{Ni}	(Equivalent) diameter of nickel particle, in nm.
d_p	Catalyst particle diameter, in μm .
f	Reduction degree, in %.

I	Prepared by impregnation.
N_M	Number of hydrogen molecules adsorbed in the monolayer per g of catalyst.
P	Prepared by precipitation–deposition.
PP	Catalysts preparation procedure.
PSIL	Porous silica support.
$(-r_0)_{H_2}$	Global initial hydrogenation rate, in $\text{mol l}^{-1} \text{h}^{-1}$.
\bar{r}_p	Average pore radius of the catalyst particles, in nm.
S_{BET}	Specific surface area (BET), in m^2 per g of catalyst.
S_{Ni}	Nickel specific surface area, in m^2 of nickel per g of catalyst.
Sup	Support.
T_{Red}	Reduction temperature, in K.
TOF _{H₂}	Initial turn-over frequency for hydrogen, in s^{-1} .
V	Volume of oil, in l.
W	Catalyst weight, in g.

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