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From Al_2O_3-supported Ni(II)-ethylenediamine Complexes to CO Hydrogenation Catalysts: Importance of the Hydrogen Post-treatment Evidenced by XPS

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Abstract Ni (7 wt%)/Al_2O_3 catalysts prepared by decomposition of Ni(II)-ethylenediamine complexes in inert atmosphere initially contain a mixture of metallic and oxidized nickel. X-ray photoelectron spectroscopy shows that after a hydrogen treatment at 500 °C, the system contains more metallic nickel than catalysts prepared from the usual precursor, nickel nitrate. Carbonaceous species resulting from the partial oxidation of ethylenediamine are also eliminated. The catalyst post-treated in hydrogen exhibits a high metallic surface area accessible to reactants and is able to catalyze CO methanation.

Keywords Nickel · Alumina · X-ray photoelectron spectroscopy · Carbon · CO hydrogenation

1 Introduction

Ni/Al_2O_3 catalysts, often used in hydrogenation processes, are usually prepared by impregnation of alumina with nickel nitrate aqueous solutions. However, dispersed particles of metallic nickel (a few nm) are difficult to obtain by this method for two reasons: upon thermal activation, a fraction of nickel ions migrates into alumina to form an "aluminate" phase which cannot be reduced by hydrogen below 900 °C [1, 2]; when reduced at such temperatures, metallic nickel sinters and forms particles larger than 10 nm, with an associated low exposed metallic surface area [3]. Direct reduction in hydrogen of supported nickel nitrate has been reported to circumvent these problems, but metal sintering may nevertheless occur because of the exothermicity of nitrates reduction [4] and the absence of aluminate is not guaranteed [5].

Another route consists in changing the nickel precursor to salts containing nitrates and ligands such as ethylenediamine (en, NH_2–CH_2–CH_2–NH_2), and decomposing them in argon [3, 6, 7]. During heating, nitrates oxidize the en ligands but not completely. Organic residues release hydrogen soon afterwards. As a consequence, Ni(II) ions are reduced to the metallic state and their migration into alumina is prevented [6]. However, the dispersion of the metal particles is difficult to assess by TEM because of the lack of contrast between nickel and alumina [8] and upon exposure to air, magnetic measurements evidence oxidation of the metal [6], the extent of which is an unknown factor for low nickel contents. Moreover, the resulting system contains carbon which may perturb or even inhibit any catalytic activity. The purpose of this work is to investigate by X-ray photoelectron spectroscopy (XPS) Ni (7 wt%)/Al_2O_3 catalysts prepared by decomposition of Ni(II)-en complexes and submitted to a hydrogen post-treatment. We aim at comparing these novel materials to a catalyst prepared from Ni(II) nitrate and to check if the "en" route provides systems with satisfactory adsorptive properties. Preliminary catalytic results in CO hydrogenation are also presented.

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2 Experimental

2.1 Catalysts Preparation

The precursor salts $[Ni(en)_2(H_2O)_2](NO_3)_2$, and $[Ni(en)_3](NO_3)_2$ were synthesized as described in ref. [6, 7]. Catalysts were prepared by incipient wetness impregnation on a γ-alumina provided by the Institut Français du Pétrole (EC 1285, Ø = 150–250 µm, specific surface area = 200 m^2 g^{-1}, void volume determined by water impregnation = 0.68 cm^3 g^{-1}). Its void volume was filled with a 1.8 mol L^{-1} solution of precursor salt. The humid solid was then dried in air at 100 °C for 30 min. One gram of each sample was thermally treated in argon (flow rate = 100 mL min^{-1}) up to 500 °C (heating rate = 7.5 °C min^{-1}), and left 1 h at that temperature. Subsequent treatments are detailed in Sect. 3. Catalysts prepared from $[Ni(en)_2(H_2O)_2](NO_3)_2$ and $[Ni(en)_3](NO_3)_2$ will be named $Nien_2$ and $Nien_3$, respectively. The Ni weight content is 7% on both catalysts. A similar reference system was prepared from $[Ni(H_2O)_6](NO_3)_2$ following the procedure described in [6].

2.2 Catalysts Characterization

Chemical analyses were performed by ICP (for Ni) or catharometry after fast calcination (for C) at the Vernaison Center of Chemical Analysis of the CNRS. X-ray diffraction (XRD) analyses were carried out on a Siemens D500 diffractometer, using Cu Kα radiation (1.5418 Å). A HPR20/DSMS mass spectrometer (MS) was used to analyze the gases produced upon thermal treatment in Ar. A 2 m capillary line connected to the reactor outlet was used to collect the gases at atmospheric pressure. The gases were analyzed after fragmentation in an ionic source. Temperature-programmed reduction (TPR) was performed under 5% H_2 in Ar (25 mL min^{-1}). The hydrogen consumption was measured by catharometry, from room temperature to 1,000 °C with a heating rate of 7.5 °C min^{-1}.

XPS were recorded with a VG ESCALAB 220 XL spectrometer using a monochromatized Al source (Al Kα = 1,486.6 eV). The analyzer was operated in a constant pass energy mode (E_{pass} = 30 eV) using the electromagnetic mode for the lens. The resolution measured on the Ag $3d_{5/2}$ line was 0.75 eV. Energy correction was made by reference to the Al 2p peak of alumina at 74.6 eV. Quantification of Ni^{2+} and Ni^0 was carried out by fitting the spectra with Gaussian functions, and by comparing experimental signals with linear combinations of reference spectra, recorded on Ni^0 and on the $Ni(II)/Al_2O_3$ sample prepared from nickel nitrate; similar results were obtained by both methods.

Samples $Nien_2$ and $Nien_3$ were characterized by XPS four times: after preparation in argon and subsequent exposure to air; after post-treatment in H_2 in the XPS chamber; after reexposure to air; after a new post-treatment in H_2 in the XPS chamber.

2.3 Dispersion and Catalytic Measurements

The chemisorptive properties of sample $Nien_2$ (200 mg) were measured by TPD of hydrogen [9, 10]. The post-treated catalyst sample was submitted to a temperature ramp in dilute H_2 up to 500 °C ($H_2/He/Ar$ = 36/20/44 vol%, total flow rate = 50 mL min^{-1}, heating rate = 10 °C min^{-1}), then brought back to room temperature under hydrogen flow. Gas flow was switched to argon (50 mL min^{-1}) and the temperature increased up to 500 °C (10 °C min^{-1}). H_2 desorption was monitored using a mass spectrometer (Pfeiffer Prisma 200) equipped with a two-stage pressure reduction device, allowing good linearity between ion currents versus partial pressure in the reactor line, argon acting as an internal calibration standard. CO hydrogenation was subsequently performed without reexposure of the sample to air. The sample was exposed to argon (flow rate = 50 mL min^{-1}) and heated to the temperature of reaction. After 10 min, the reactants mixture was let in ($H_2/CO/He/Ar$ = 12/4/76/8 vol%, total flow rate = 50 mL min^{-1}). Heating rate between two temperature plateaus was 3 °C min^{-1}. Conversions were measured by mass spectrometry (MS) after 30 min of reaction at each temperature in order to reach a stable value.

3 Results

3.1 Characterization of the As-prepared Catalysts

After impregnation and drying of the samples, XRD lines from the precursor salts (identified by comparison with the unsupported compounds) are clearly visible (Fig. 1). During heating in argon, the salts decompose, releasing first CO (m/z 28) and NO (m/z 30) at 260 °C, then H_2 (m/z = 2) at 350 °C (mass spectrometry). After thermal treatment, carbon contents of 2 and 3 wt% are measured on $Nien_2$ and $Nien_3$, respectively. These figures, higher than in a previous study [6], can be explained by the fact that the catalyst masses prepared here are more than five times higher than in ref. [6] for an argon flow kept constant.

Carbon is characterized by XPS via the C_{1s} peak, present at 285.6 eV on both samples and accompanied by a shoulder at 289.5 eV (Fig. 2). The position of the main broad peak is intermediate between those of C engaged in C–H or C–C bonds (284.9 eV, contribution evaluated as 45% by fitting with Gaussians) and oxidized C of C–O type (286.5 eV, contribution = 35%), while the shoulder may

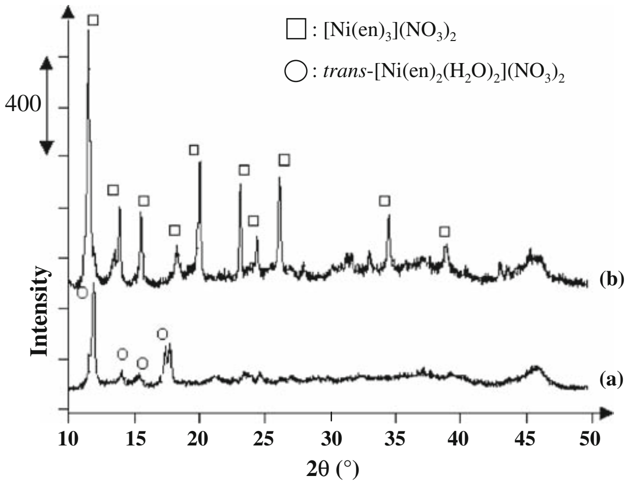

Fig. 1 X-ray diffractograms of catalysts Nien$_2$ (**a**) and Nien$_3$ (**b**) after drying

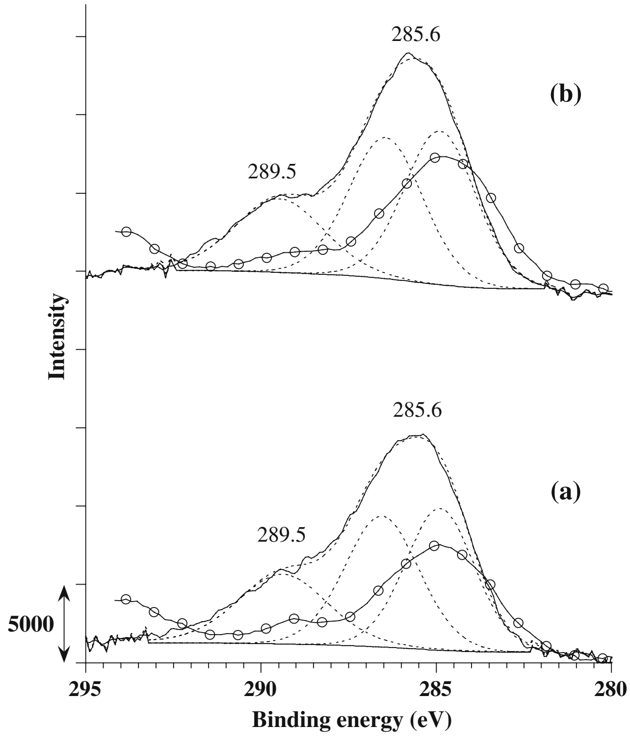

Fig. 2 C$_{1s}$ normalized XPS of Nien$_2$ (**a**) and Nien$_3$ (**b**) before (full line and dotted lines) and after hydrogen post-treatment (circles). Experimental signal and background: full lines. Individual components for fitting and global envelope: dotted lines

be due to C=O (contribution = 20%) [11]. The C$_{1s}$/Al$_{2p}$ ratio is twice higher on Nien$_3$ than on Nien$_2$ (0.2 compared with 0.1), in agreement with elemental analyses. A weak N$_{1s}$ peak, more than three times less intense than that of carbon, is also observed at 399.2 eV; it disappears upon further treatments.

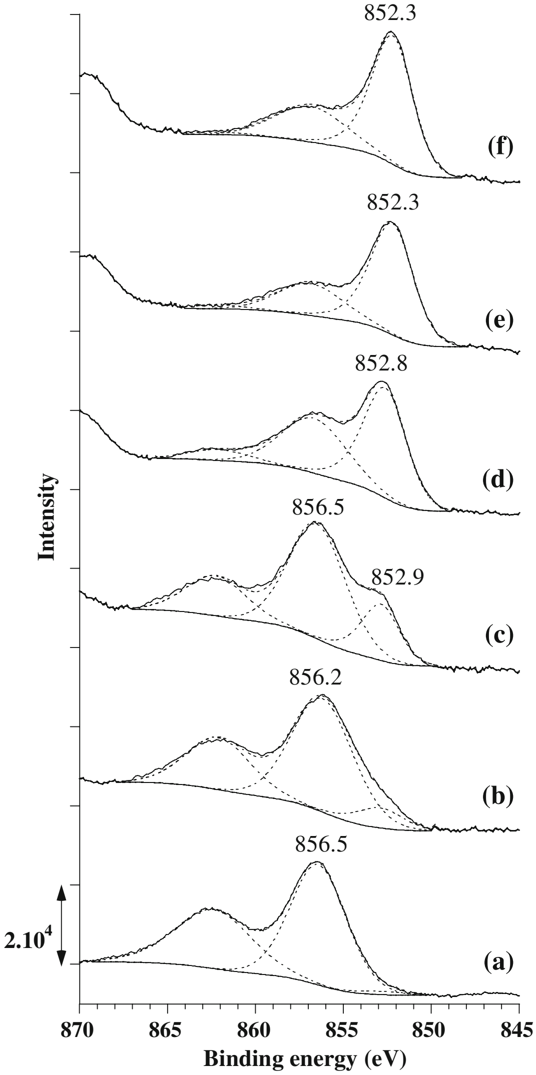

Fig. 3 Ni 2p$_{3/2}$ normalized XPS of: reference ex-nitrate sample (**a**), Nien$_2$ (**b**) and Nien$_3$ (**c**) before hydrogen post-treatment; reference ex-nitrate sample (**d**), Nien$_2$ (**e**) and Nien$_3$ (**f**) after hydrogen post-treatment. Experimental signal and background: full lines. Individual components for fitting and global envelope: dotted lines. The Ni^0 2p$_{1/2}$ peak is seen at 869.5 eV

Due to a lack of contrast with alumina, nickel particles, if present, are not clearly visible by TEM. Indeed, Ni^0 is detected on the as-prepared samples exposed to air (Ni 2p$_{3/2}$ contribution expected at 852.5 eV [12]), but the majority of nickel appear as Ni^{2+}, as evidenced by comparison with the reference sample prepared from nickel nitrate (Fig. 3a–c, Table 1). On Nien$_2$, the Ni 2p$_{3/2}$ signal is at 856.2 eV, with |ΔE| between the main peak (m) and its satellite (s) = 6 eV and an intensity ratio I$_s$/I$_m$ = 0.6, all parameters characteristic of ionic nickel as the major species [12] (Fig. 3b). The proportion of Ni^0 is higher on Nien$_3$: the shoulder above 852 eV is more visible (Fig. 3c). The amount of organic species was initially larger on that

Table 1 Characteristics of catalysts $Nien_2$ and $Nien_3$ as deduced from XPS

	Ni^{2+} (%)	Ni^0 (%)	Ni_{2p}/Al_{2p}
$Nien_2$			
As prepared	93	7	0.074
After post-treatment in H_2	34	66	0.058
After reexposure to air	77	23	0.064
After second treatment in H_2	28	72	0.058
$Nien_3$			
As prepared	79	21	0.085
After post-treatment in H_2	37	63	0.061
After reexposure to air	73	27	0.065
After second treatment in H_2	38	62	0.055

sample than on $Nien_2$: more hydrogen able to reduce Ni^{2+} was released during thermal treatment and more carbon may protect nickel particles from oxidation.

3.2 Characterization of the Catalysts after Post-treatment in Hydrogen

The as-prepared catalysts are then treated in pure H_2 in the XPS chamber (flow rate = 100 mL min^{-1}, heating rate = 7.5 °C min^{-1}) up to 500 °C and kept for 1 h at that temperature. XPS spectra are recorded without intermediate exposure of the sample to air (Fig. 3d–f). On the catalysts prepared with ligands, reduction at 500 °C transforms two-thirds of nickel ions into the metallic state (Ni $2p_{3/2}$ signal is present at 852.3 eV) (Table 1). The reduction of the oxidic phase is confirmed in a parallel reduction experiment followed by mass spectrometry, during which water is detected between 200 and 300 °C. The remaining fraction of Ni^{2+} ions explains the intensity of the peak at 856.5 eV, higher than expected for the weak satellite of Ni^0 $2p_{3/2}$ (which has not been treated as a distinct peak in the fitting) [12].

A comparison can be made with the sample prepared from nickel nitrate, also treated in hydrogen (Fig. 3d). TPR shows that it contains equivalent amounts of Ni^0 and of Ni^{2+}-containing species (reduction peaks between 600 and 900 °C, assigned to small oxide particles and nickel aluminate [6]). After hydrogenation at 500 °C, the Ni $2p_{3/2}$ signal is still composed of two contributions, one at 852.8 eV due to Ni^0 and another one at higher energy, revealed by the intensity of the main satellite. The Ni^{2+}/Ni^0 ratio (51/49%) calculated from the fitting of XPS spectrum is consistent with that deduced from TPR.

The signal from carbon on $Nien_2$ and $Nien_3$ is smaller by 50–60% after post-treatment (Fig. 2), but it is still five to ten times more intense than that of contamination carbon detected on a sample prepared without organic ligand. The signal has shifted to 284.9 eV (C_x or C_xH_y species) and the shoulder at 289 eV has almost disappeared. Indeed, the parallel experiment of post-treatment followed by MS shows that methane (m/z 15) is produced between 350 and 500 °C. Moreover, the comparison of temperature-programmed oxidations monitored by MS before or after hydrogen post-treatment confirms that the release of CO_2 from adsorbed carbon decreases by 70% after post-treatment. The post-treatment at 500 °C thus acts both on the removal of adsorbed carbon and on the reduction of nickel. $Nien_2$ and $Nien_3$ exhibit close characteristics after post-treatment in hydrogen.

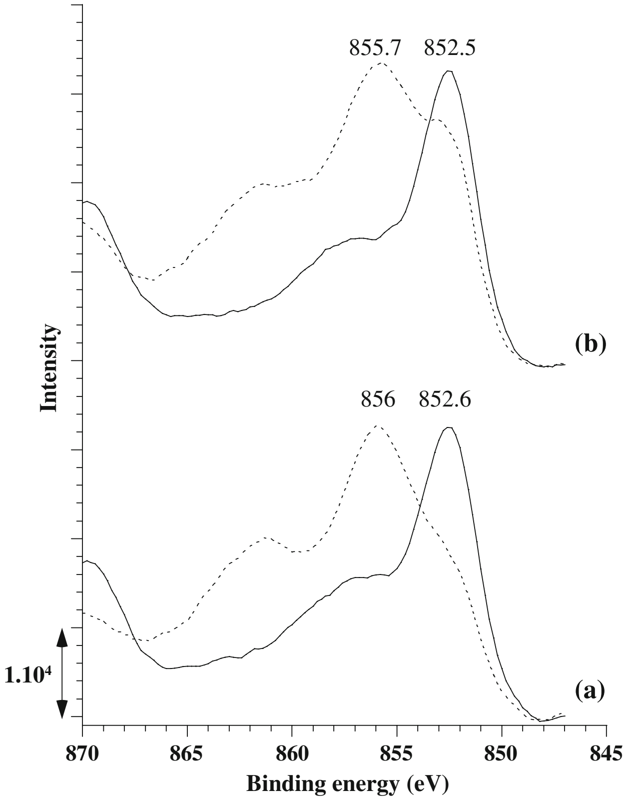

Fig. 4 Ni $2p_{3/2}$ normalized XPS of post-treated $Nien_2$ (**a**) and $Nien_3$ (**b**) after reexposure to air (dotted lines) and second step of reduction (full lines)

Upon reexposure to air, part of nickel is reoxidized, to a lesser extent though than it was after synthesis in argon. The Ni_{2p}/Al_{2p} signals ratio, which had decreased after post-treatment, increases (Table 1). It is checked that a new treatment in hydrogen brings nickel back to the metallic state, with characteristics similar to those before reoxidation (Fig. 4).

3.3 Consequences on the Catalyst Chemisorptive Properties and Catalytic Activity

In order to test its chemisorptive and catalytic properties, sample $Nien_2$ freshly prepared in argon was submitted to a

Table 2 Activity of sample Nien$_2$ toward CO hydrogenation

T (°C)	Conversion (%)	Turnover rate (s^{-1}) × 10^3
163	2.7	0.5
185	5.4	1.0
207	10.7	1.8
227	22.1	3.8

post-treatment in hydrogen up to 500 °C. The catalyst was then cooled to room temperature under hydrogen and exposed to a flow of H_2 diluted in argon. A temperature ramp in argon monitored by MS followed, during which a H_2 desorption peak was evidenced between 20 and 400 °C, in line with earlier work [10, 13, 14]. Another peak was visible between 400 and 500 °C. Because it is absent from a TPD carried out on the ex-nickel nitrate catalyst, it is attributed to the decomposition of the remaining adsorbed C_xH_y carbonaceous species and is not taken into account to derive the dispersion.

From the H_2-desorption experiment, the fraction of metallic nickel exposed (FME) is evaluated to be 34% with respect to the total amount of Ni on the catalyst (assuming a stoichiometry of adsorption $H/Ni^0 = 1$ [5, 9]), a value higher than those given by Bartholomew et al. [15] for a 9 Ni wt% catalyst reduced at 75% (FME = 19%), or by Huang and Schwarz for 6–8 Ni wt% catalysts prepared by reduction of nickel nitrate and also characterized by hydrogen thermodesorption (FME ≤ 11%) [16, 17]. The application of the equation linking dispersion D and the average particles diameter Ø (D (%) = 97.1/Ø (nm) [9]) leads to a value of Ø comprised between 2 and 3 nm; the small size accounts for the high sensitivity of the catalysts to exposure to air. The metallic surface area exposed is 15 $m^2\ g_{cat}{}^{-1}$, assuming that one nickel atom occupies 6.3 Å^2 [18], to be compared with 2 $m^2\ g_{cat}^{-1}$ for the reference catalyst prepared without ligand.

Post-treated sample Nien$_2$ was able to catalyze CO hydrogenation, with methane as the only product (Table 2). Turnover rates are consistent with those reported earlier [15]. The activation energy calculated for conversions measured below 210 °C is 60 kJ mol^{-1}, a value close to that reported for the reaction on metallic nickel (51 kJ mol^{-1}) [19].

4 Discussion

In the post-treatment of catalysts prepared from the decomposition of Ni(II)-en complexes, the role of hydrogen is twofold. First, it ensures the reduction of oxidized nickel in the as-prepared sample. Oxidation is deeper than the mere passivation detected by magnetic measurements on catalysts prepared following the same procedure but containing twice more nickel [6]. Exposure to air certainly contributes to this oxidation, but it can be noted that once nickel particles have been reduced, the extent of their oxidation is lesser than before post-treatment. It is thus likely that an oxidic fraction is formed upon precursor decomposition, in line with the behaviour of the unsupported salts [20].

The presence of bulk NiO on Nien$_2$ and Nien$_3$ can be excluded for three reasons: the Ni 2p$_{3/2}$ signal would be expected near 854 eV [12, 21, 22]; a shoulder should be present at an energy higher by about 2 eV (interpreted as coming from Ni^{3+} impurities [23] or arising from screening by neighbouring [NiO_6] polyhedra [24]); |ΔE| should be higher (7 eV) [12]. According to ref. [25], the position of the Ni 2p$_{3/2}$ signal at 856.2 eV would rather correspond to ions present in an octahedral rather than in a tetrahedral oxidic environment (values in the range 857–858 eV for the latter [25–27]). Consequently, it does not correspond either to an aluminate phase resulting from a migration of nickel into alumina [25, 28].

Production of water between 200 and 300 °C and comparison with the ex-nitrate reference sample (still containing small oxide particles after reduction at 500 °C) show that the fraction of ionic nickel that is reduced during post-treatment arises from an oxidic phase associated to the metal particles, as confirmed by the reversible oxidation/reduction cycles and the reproducible changes of the Ni_{2p}/Al_{2p} signals ratio. These variations, reported earlier [23], could be interpreted as the sign of a flattening of the particles over the support upon oxidation, while post-treatment in H_2 reduces their exposed surface area upon restoration of metal. The remaining, non-reduced third of nickel is probably present as small oxide particles strongly interacting with alumina [1, 2, 6].

The contrast between the size of the precursor salt crystals, as assessed from XRD (several tens nm), and the much smaller size of the metal particles has been noted previously [6] and attributed to the violent, exothermic decomposition of the precursor upon reaction between nitrates and en, leading to a release of gaseous molecules and to a splitting of the crystals. A parallel can be drawn with the synthesis of oxidic nanoparticles by reaction between metal nitrates and an organic additive [29–31]. Pyrolysis of supported precursors which do not contain oxidizing species, such as nickel glycinate, leads to larger metal particles (up to 40 nm) [32].

The second role of hydrogen is to eliminate carbon resulting from the decomposition of the precursor salts. The content of carbon is higher for Nien$_3$ than Nien$_2$, because the quantity of organic species is initially higher in the former (three equivalents of ligands instead of two) while the amount of oxidizing species able to destroy the ligands remains constant (two equivalents of nitrates). Carbonaceous deposits are initially present on the thermally treated catalysts not as purely graphitic, but also as oxidized species (possibly alkoxides and carboxylates). Nickel carbide Ni_3C is unlikely because of its temperature of decomposition (430 °C [33]); moreover the C_{1s} signal of carbides is expected to lie in the range 28–284 eV [34, 35]. These carbon deposits thus derive from the incomplete decomposition of ethylenediamine during the treatment in argon; they are probably adsorbed or grafted on the support, or they cover nickel species but do not associate chemically with the metal.

Adsorptive properties of the post-treated catalyst are consistent with results from the literature and poisoning by remaining carbon seems to be avoided. Despite its non negligible content in ionic nickel and the former oxidation of metal particles upon exposure to air, H_2-post-treated $Nien_2$ appears to challenge catalysts prepared without organic ligands in terms of metallic surface area exposed. In comparison, catalysts mentioned in the literature containing 6–9 Ni wt% and prepared from nickel nitrate exhibit metallic surface areas comprised between 2 and 9 $m^2\ g_{cat}^{-1}$ [5, 15–18]. Preliminary catalytic results show that systems prepared by decomposition of Ni(II)-en complexes are able to catalyze carbon monoxide hydrogenation and open the way to a more complete kinetic investigation.

5 Conclusion

When Ni (7 wt%)/Al_2O_3 catalysts are prepared by decomposition in argon of salts containing nickel, ethylenediamine and nitrates, a post-treatment in hydrogen at 500 °C is necessary both to remove carbonaceous deposits and to reduce nickel ions into the metallic state, so that the catalysts become active in CO hydrogenation. The metallic surface area developed by catalysts prepared from Ni(II)-en complexes appears to be higher than that of catalysts prepared from nickel nitrate and thermally treated at the same temperature. The number of ligands en initially added to Ni(II) influences only moderately the characteristics of the final catalyst, but a higher number of ligands leads to a system with a higher degree of reduction after treatment in argon. Post-treatment with H_2 should be carried out prior to any catalytic experiment, since cleaned metallic nickel particles reoxidize upon exposure to air due to their small size.

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