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Structural and surface propperties of Ni-Cu nanoparticles supported on SiO_2

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Nickel (1%) and nickel (1%)-copper (0.2–0.75%) metal phases supported on silica have been prepared by aqueous hydrazine reduction of nickel acetate at 70°C. They were characterized by XRD, TEM, H_2-adsorption and TPD. The obtained results show that nickel is in a whisker-like shape or as a film of low density for the Ni/SiO_2 and $Ni\text{-}Cu/SiO_2$ systems respectively. The mean particle size is lower than 2 nm. Copper is in the shape of bigger facetted particles in the mono or bimetallic systems with a mean particle size of about 25 nm. The nickel phase dispersion, as determined by H_2-adsorption, decreased in the presence of copper, as probably a result of Ni-Cu interactions. All the solids were found to be good hydrogen reservoir through the formation of H-spiltover species. The amounts of hydrogen stored changed with the copper content due to changes in the Ni-Cu interactions. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

A great deal of attention has been paid to Ni-Cu bimetallic materials for several decades by a number of groups [1–9]. The reason is that addition of a second metal is a way to modify the structural and electronic properties of the first one. Alloying could affect both the number of metallic atoms involved in the active sites and their reactivity [1–9]. Generally speaking, the addition of copper to a nickel supported catalyst decreases the surface activity of the nickel phase.

Supported metals are usually prepared by *in situ* reduction of a metal salt or oxide. An alternative method used to obtain these materials with well-defined metal particles is the preparation *via* metal colloids [10–14]. We have undertaken a systematic study of nickel metal nanoparticles supported on silica of low surface area, prepared by reduction of nickel acetate by hydrazine in aqueous media [15–18]. The reduction led to metal crystallites of mean particle size increasing (from 3 to 20 nm) with increasing nickel loading (from 1 to 5%). The chemisorptive properties of the supported particles prepared have also been studied. A close examination of the materials prepared showed that, strikingly, a metal whisker-like phase is formed for low nickel loadings (<2%Ni), whereas various shapes, mainly spherical, are obtained for higher loadings [16]. The shape influenced the surface and catalytic properties of the metal nanoparticles.

In the present paper we report the results of a study of the effect of a metal copper additive on the structural and surface properties of silica supported nickel nanoparticles as prepared by the reduction of nickel acetate by hydrazine in aqueous media. They were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and H_2-adorption and H_2-desorption in programmed temperature (TPD). The chemical composition in the bimetallic system was 1% and 0.2%, 0.5% or 0.75% for the nickel and copper components respectively. The silica used was of low surface area (15 m^2 g^{-1}). A low metal content was expected to give rise to important metal-support interactions. Moreover, preliminary results showed that the Ni^{2+} ions are reduced by aqueous hydrazine on silica of low surface area and not on silica of high surface area [16]. Generally speaking, the chemical composition used is lower than that reported in the literature (>5%) for both nickel and copper [1–9]. In addition, silica supported nickel systems have been concerned with high surface area supports. Also the use of a very low nickel or copper loading as well as that of low surface area silica was expected to give rise to a significant contribution to the existing corpus of literature on $Ni\text{-}Cu/SiO_2$ systems.

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2. Experimental

2.1. Materials preparation

Thesilica support was supplied by Chempur (99.99%, 15 m^2 g^{-1}) pre-treated in air at 500°C then stored under argon before use. The impregnation was carried out at room temperature using a mixture of nickel acetate and copper nitrate ($\geq$99.0%, Fkuka) as precursors. The amount of the metal precursor was calculated in order to obtain the required Ni-Cu composition (Table I). A solution of the metal precursor is obtained after stirring in 25 mL of distilled water for 30 min. 5 g of silica is added to the solution and the obtained suspension is stirred for 16 h. After evaporating at 60°C under vacuum and filtering the impregnated precursor obtained is dried at 100°C for 16 h.

The preparation of the final materials was performed under argon atmosphere. A suspension of the impregnated precursor in 10 mL of water is stirred at room temperature for 20 min then gradually heated (4°C min^{-1}) to 70°C. 10 mL of 24–26% aqueous hydrazine in excess ($\geq$99.0%, Fkuka) are added then the reaction temperature is maintained for 2 h. The pH of the solution is 10–12 and remained constant during the reduction process. The black suspension formed is filtered, washed and dried at 60°C under vacuum. The Ni-Cu/SiO_2 bimetallic catalysts are denoted Cux where x is the Cu metal composition. The monometallic nickel and copper samples are denoted Ni and Cu respectively.

2.2. Materials characterization

Nickel composition and specific area of the materials were determined on a Varian AA1275 atomic absorption spectrophotometer and a Carlo Erba Sorptomatic 1900 equipment respectively. XRD patterns $I(\theta)$ and TEM images were recorded with a classical $\theta/2\theta$ diffractometer using Cu K_α radiation and the CM20 Philips microscope respectively. X-ray microanalysis chemical compositions were determined using energy dispersive X-ray spectroscopy (EDXS). EDX spectra were recorded by means of an EDAX spectrometer monted on the Philips microscope and equipped with an ultrathin window X-ray detector. The analysis were carried out in nanoprobe mode with a diameter of the probe of 10 nm. The K_{AB} factors were determined using standards.

TABLE I H_2-adsorption and desorption for the supported catalysts after a hydrogen pre-treatment at 300°C

Catalyst	Metal composition		H_2 adsorbed (μmol $g^{-1}{}_{\mathrm{Ni}}$)	H_2 desorbed (μmol $g^{-1}{}_{\mathrm{Ni}}$)		
	% Ni	% Cu		Type I	Type II	Total
Ni	1.0	–	937	521	1066	1587
Cu 0.2	1.0	0.20	837	681	872	1553
Cu 0.5	1.0	0.50	548	185	963	1148
Cu 0.75	1.0	0.75	518	216	1016	1232
Cu	–	1.0	190∗	–	1748*	1748*

*μmol $g^{-1}{}_{\mathrm{Cu.}}$

Chemisorption experiments were carried out with a sample of 100 mg on a pulse chromatographic microreactor equipped with the catharometric detector of a microchromatograph (AT M200, Hewlett Packard) fitted with molecular sieve columns and MTI software. The sample was pre-treated with pure H_2 with a flow rate of 50 mL min^{-1} for 2 h at 300°C, using a heating rate of 10°C min^{-1}. It was then purged under argon atmosphere for 2 h with a flow rate of 100 mL min^{-1} and cooled to room temperature. After that, gaseous hydrogen (100 ppm in argon) was injected in the reactor every 2 min untill saturation of the sample. The hydrogen saturated sample was purged at room temperature under argon for 2 h, a time after which no hydrogen (<2 ppm) was detected in the exit gas. It was subsequently submitted to a TPD by flowing with argon (50 mL min^{-1}) with a heating rate of 7.5°C min^{-1} to 700°C.

3. Results and discussion

3.1. Characterization

No nickel signal was observed in the XRD spectra of the Ni and Cux catalysts (Fig. 1). This could be ascribed to the sensitivity of the technique which does not allow to detect low metal contents ($\leq$1%) or small metal particles ($\leq$2 nm). Also the Ni mean particle size was estimated less than 2 nm. Small metal particles may be due to strong metal-support interactions. In contrast, the XRD spectra of the Cu or Cux samples exhibit the characteristic copper *fcc* structure (Fig. 1). The copper mean particle size, as estimated using the Debye-Sherrer equation, was around 25 nm for all these samples. The lower dispersion of copper as compared to nickel suggests a weaker metal-support interaction.

A previous TEM study showed that monometallic nickel is in a whisker-like shape in the fresh or thermally treated sample [16]. The present TEM study shows that monometallic copper is in the shape of facetted particles (Fig. 2). It also confirms the presence of nickel in all the bimetallic samples. In these systems, nickel and copper exhibit segregated metal phases (Fig. 3). Nickel is in the shape of a film of low density instead of a whisker-like morphology. This is ascribed to the influence of copper on the Ni° phase formation during the reduction process in the aqueous hydrazine media. As to copper, it remains in the shape of facetted particles with a bigger mean size (50 to 100 nm) than that determined by means of XRD. This may be due to the agglomeration of smaller copper crystallites.

No change is observed in the mono or bimetallic sample XRD spectra or TEM images after a hydrogen treatment at 300°C for 2 h.

The segregation of nickel and copper phases in Ni-Cu bimetallic systems is a well known process [1, 8], notably in case of films and powders [9]. Moreover, due to a lower surface energy of copper than nickel, it is generally found to segregate on the surfaces of the mixed Ni-Cu systems [8, 19]. Also it is suggested that the copper-rich alloy is

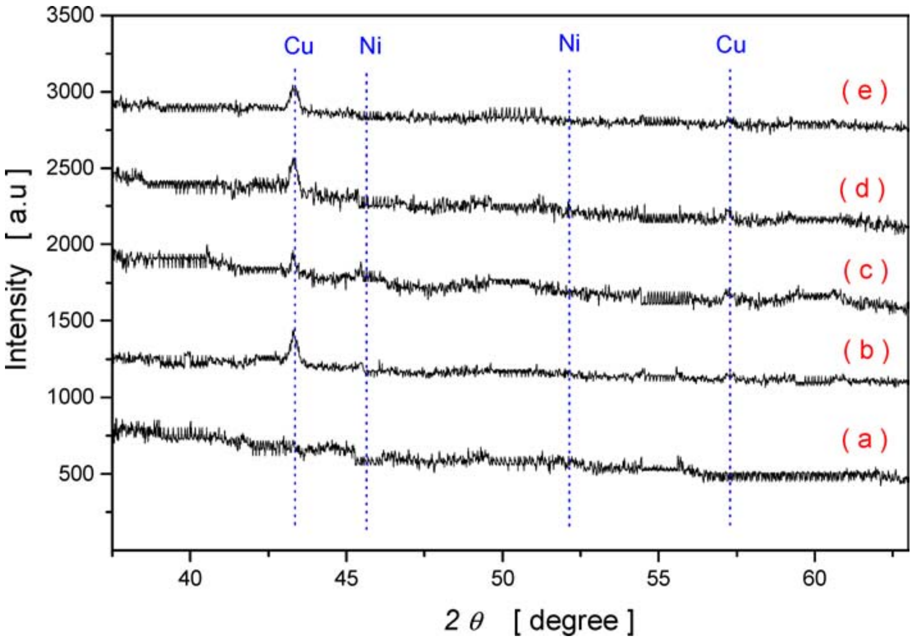

Figure 1 XRD spectra of the Ni and Cu*x* catalysts: (a) Ni; (b) Cu 0.2; (c) Cu 0.5; (d) Cu 0.75; (e) Cu.

located at the surface and the nickel-rich alloy below the surface. The structural properties of the phases formed depend on the chemical composition and thermal treatments of the catalysts [20, 21]. For unsupported bimetallic Ni-Cu materials, prepared by reduction of sulfate precursors by aqueous hydrazine, a pure monometallic or bimetallic phase or a mixture was found, depending on the Ni:Cu ratio [22].

In the present case, the absence of Ni-Cu bimetallic phase might be due to the very low metal content used (Ni or Cu<1%). Ni-Cu alloy could have been formed but in a too low concentration. However, it also could have been hidden by a pure copper phase so as it was not active under the electron beam. The chemisorption studies showed that, indeed, Ni-Cu interactions do exist in the bimetallic Ni-Cu/SiO_2 system.

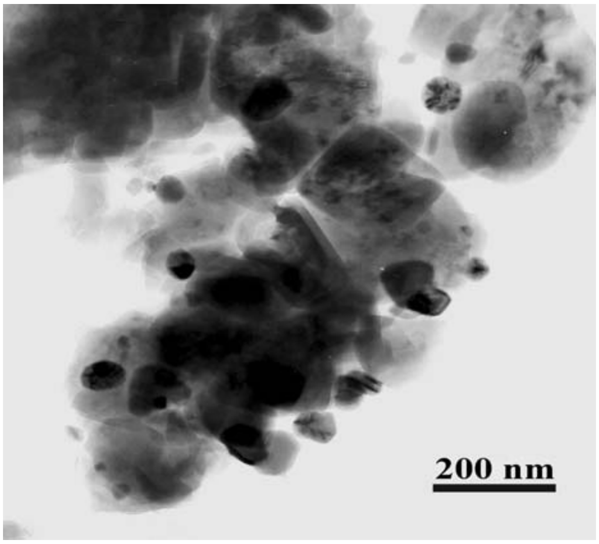

Figure 2 TEM micrograph of the Cu monometallic catalyst.

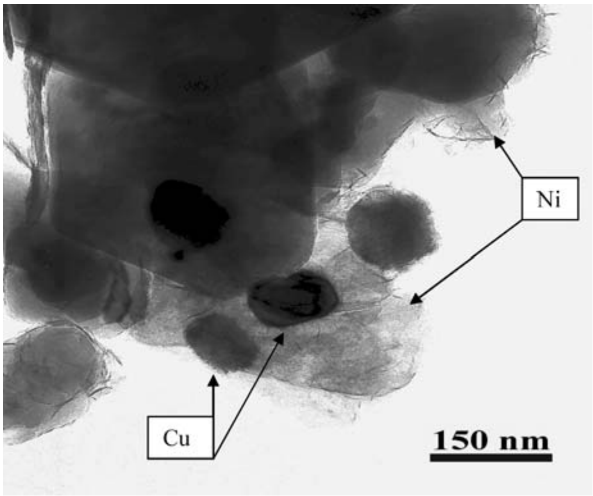

Figure 3 TEM micrograph of the Cu 0.5 bimetallic catalyst.

3.2. H_2 chemisorption studies

Hydrogen chemisorption is one of the most widely used method to probe the chemical surface properties of supported metals [17, 23–26]. The amount of adsorbed hydrogen is a good estimation of the metal dispersion [17, 23–27].

All the materials prepared were pre-treated under H_2/300°C before the chemisorption experiments. After purging under a helium flow, they adsorbed hydrogen in amounts depending on the copper content. They exhibited good H_2 reservoir properties as other transition metal materials [17, 23–26].

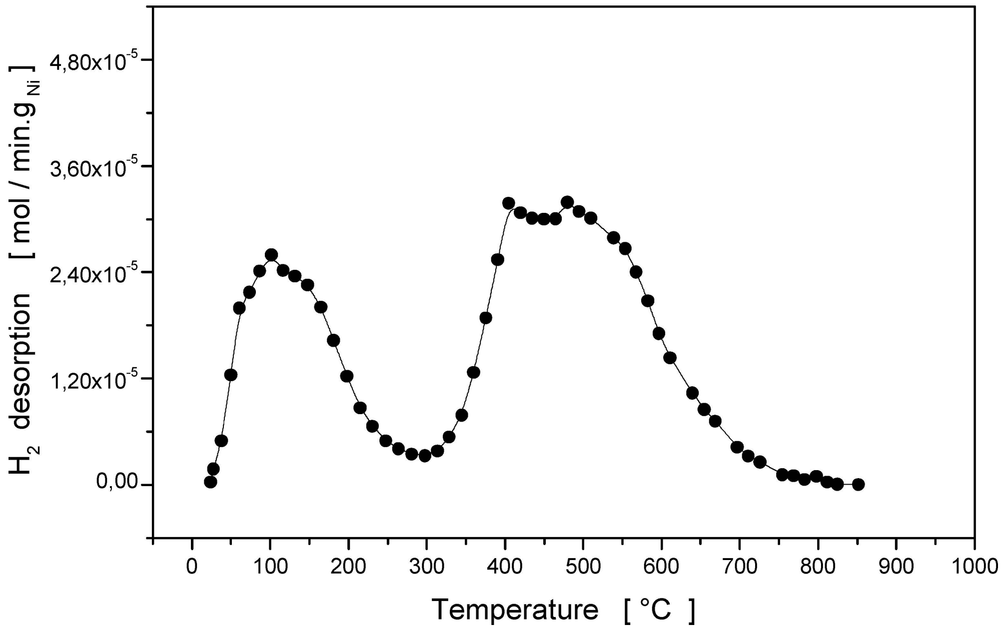

Figure 4 H_2-TPD profile of the Ni catalyst.

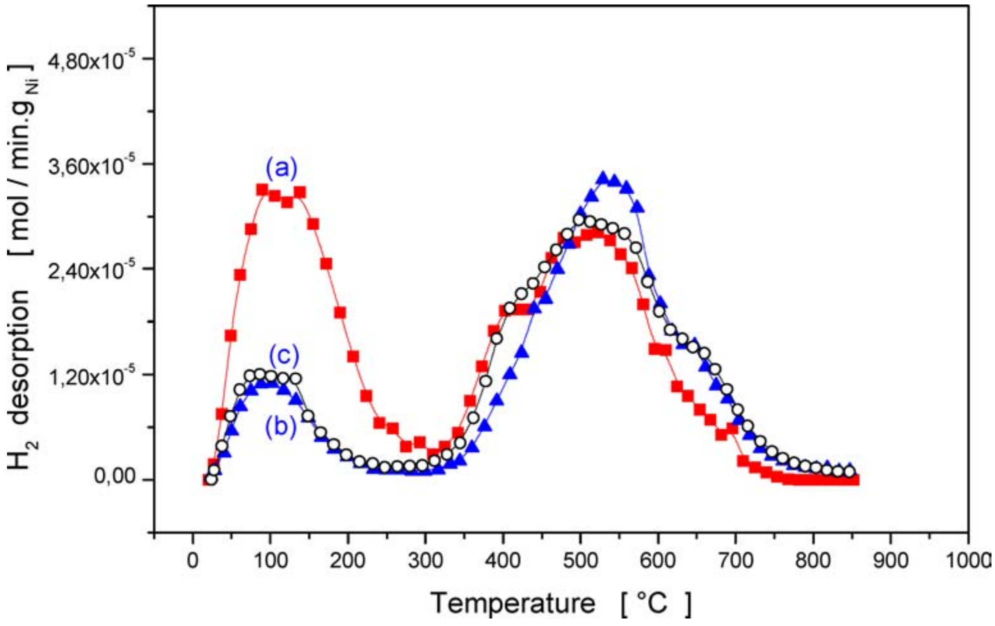

Figure 5 H_2-TPD profiles of the Ni-Cu catalysts: (a) Cu 0.2; (b) Cu 0.5; (c) Cu 0.75.

Monometallic nickel adsorbed the highest amount of hydrogen (937 μmol $g_{Ni}{}^{-1}$) and the monometallic copper the lowest (190 μmol $g_{Cu}{}^{-1}$) (Table I). In the bimetallic system the quantities of hydrogen adsorbed decreased with the copper content (Table I). This is a strong indication that part of the nickel surface is inaccessible to hydrogen molecules, may be through Ni-Cu interactions. It is worth recalling that copper has a positive or negative effect on nickel dispersion in copper bimetallic systems, according to the Ni:Cu ratio or temperature of pre-treatments [8, 9, 19, 20]. In the present case, low metal loadings (Ni, Cu$<$1%) and a relatively high Ni:Cu ratio (1.3–5.0) decrease the nickel dispersion.

The supported metals prepared desorbed more hydrogen than they adsorbed (Table I). The highest amounts are found with the monometallic catalysts, 1587 or 1748 μmol·$g^{-1}{}_{Ni}$ for Ni or Cu respectively. In the bimetallic system the quantity of hydrogen desorbed passed through a minimum as a function of the copper content (1148 μmol $g^{-1}{}_{Ni}$ at 0.5% of Cu). The nature of hydrogen desorbed is various as showed the H_2-TPD studies.

The H_2-TPD profiles under argon flow comprise several temperature peaks (Figs 4–6) as a result of the formation of several active sites [23, 27]. The broad width of these peaks confirms the presence of small metal particles. Two domains of temperature can be distinguished for the nickel

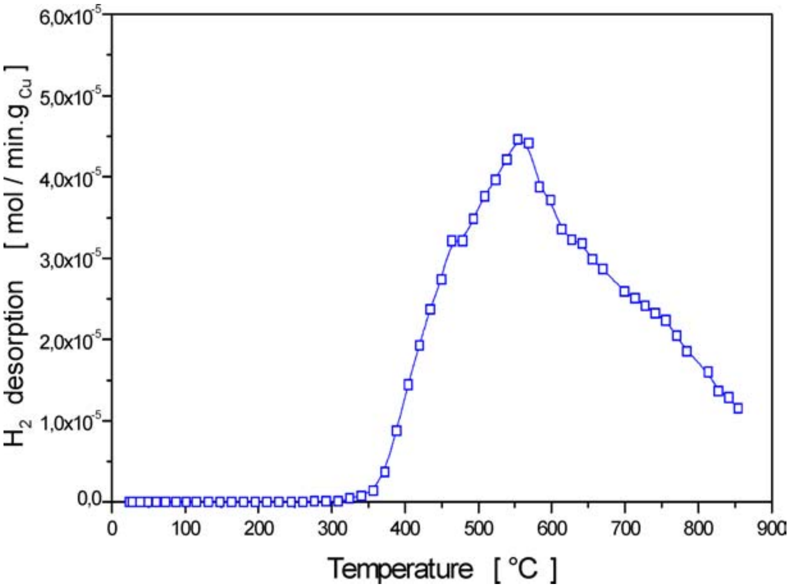

Figure 6 H_2-TPD profile of the Cu catalyst.

or nickel-copper phases and are denoted as type I (below 300°C) and type II (above 300°C). Each domain comprises one or several temperature peaks. These peaks are attributed to hydrogen adsorbed on surface active sites with a strength increasing with the desorption temperature. The amount of each type of hydrogen changes with the copper content. For the Cu0.2 composition this amount passes through a maximum for the first domain (681 μmol $g^{-1}{}_{Ni}$) and a minimum for the second domain (872 μmol $g^{-1}{}_{Ni}$). These changes suggests that copper changed the amount or/and strength of the adsorption sites through metal-metal or metal-support interactions. Indeed, as reported in the literature [22], several phases might have been formed depending on the Ni:Cu ratio. These various phases would have induced changes in the surface properties of the Ni-Cu/SiO_2 materials and, consequently, the hydrogen storage capability. The excess of the amounts of hydrogen desorbed as compared to that adsorbed (Table I) may be ascribed to a support effect, that is the formation of hydrogen species bonded to the support or to the metal-support interface. This would be due to the hydrogen spillover effect, namely the dissociation of H_2 on the nickel or copper sites then migration to the support of the hydrogen species formed from the metal [26, 28–31]. H-spiltover species desorb at high temperatures [26, 28–31], also part of the hydrogen of type II in our study may be ascribed to such species. Hydrogen of type I may be that species linked to nickel or nickel-copper active sites.

Monometallic copper exhibited the high temperature domain only (Fig. 6). Numerous studies have been devoted to hydrogen chemisorption on supported copper [24–26]. It was found that hydrogen is dissociatively adsorbed and associatively desorbed on the supported metal [26]. TPD studies showed two types of hydrogen: a low temperature peak (around 0°C) assigned to the H_2 desorption from the metallic Cu surface sites [26] and a more complex profile at higher temperatures (>250°C) attributed to spilt-over hydrogen [24–26]. In our case, the peak expected at 0°C is not observed because the beginning of the heating temperature was 25°C. The broad peak at higher temperatures is ascribed to hydrogen species adsorbed on the solid surface, probably partly bonded to the support or to the metal-support interface. The profile and surface area of this peak is different from that of monometallic nickel (Fig. 4) due to different metal-support interactions.

4. Conclusions

Our investigations show that nickel is in a whisker-like shape in monometallic Ni/SiO_2 and as a film of low density in bimetallic Ni-Cu/SiO_2. The Ni particle size is lower than 2 nm in both cases. The copper phase is in the shape of facetted particles in the mono or bimetallic systems with a mean particle size of about 25 nm. The metal dispersion was determined by hydrogen adsorption. It was found to decrease with the copper content as probably a result of Ni-Cu interactions. The H_2-TPD study showed that the solids stored hydrogen with amounts changing with the copper content. These changes are also ascribed to Ni-Cu interactions. The support participated to the hydrogen storage through the formation of H-spiltover species.

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