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Colloidal nanometric particles of nickel deposited on γ-alumina: characteristics and catalytic properties

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The present paper deals with supported nanoparticles of metallic nickel prepared by impregnation of an organometallic colloidal precursor (NiRC complex) on γ-alumina. The obtained supported materials (NiRCS complex) were characterized by STEM, EELS, XRD and TGA and tested in the hydrogenation reaction of benzene and styrene both in the gas and liquid phases. EELS and STEM studies showed that the metallic nickel nanoparticles of the NiRC precursor were well dispersed (1–3 nm) on the support, without size variation during the impregnation step. However, particle growth in NiRCS was observed in samples used after reaction tests. On the other hand, TGA experiments showed that the nickel phase was inserted in an organic matrix which remained in the supported material after impregnation. This organic matrix should be partly removed or totally decomposed by washing with an appropriate solvent or thermal treatment above about 250 °C under N_2, H_2 or air atmosphere respectively. The supported nickel particles were active in the gas phase hydrogenation of benzene in the temperature range of 150–200 °C and their activity was enhanced by partial removal of the organic matrix with an organic solvent (e.g. ethanol) or by its total thermal decomposition. They were also found very active in the gas phase hydrogenation of styrene at room temperature. Finally, the supported nickel particles exhibited good hydrogen reservoir properties in organic solvent media. *© 1999 Kluwer Academic Publishers*

1. Introduction

Great attention has been paid in the past decade to the methods of preparation of metal nanoparticle powders and films due to their potential applications in both industrial and academic fields [1–9]. Among the various methods of preparation, the chemical route [10–24] has been intensively studied due to the better structure control at the microscopic level. These methods have generally involved the reduction of the relevant metal salt in the presence of a suitable surfactant which allows control of the growth of the metal particles.

The reason for such avid research arises from the drastic increase of the ratio of surface to volume to such an extent that the material properties are determined much more by the surface atoms than by the lattice atoms. Then the physical and chemical properties of the particles differ considerably from those of the compact solids. This behaviour is of particular interest in heterogeneous catalysis. Caubere *et al.* [21–24] have prepared metal clusters by reducing nickel salts in a mixture of alcaline hydride and alcaline alcoholate in refluxing organic solvent. These particles were found very active in the hydrogenation reaction of unsaturated molecules in organic solution [22–24].

In the present paper, we report results obtained on the structure and catalytic properties of colloidal nanoparticles of metallic nickel deposited on a γ-alumina support under inert atmosphere. The obtained solids were characterized by Scanning Transmission Electron Microscopy (STEM), Electron Energy Loss Spectroscopy (EELS), X-Ray Diffraction (XRD), Thermal Gravimetry Analysis, (TGA) and tested in the hydrogenation of benzene (to cyclohexane) or styrene (to ethylbenzene), both in an organic solvent medium or in the gas phase at atmospheric pressure.

2. Experimental

2.1. Catalysts preparation

2.1.1. Chemical processes

For a better understanding of the preparation procedure one must keep in mind the molecular process of

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formation of the reduced nickel phase in the organic medium and of their impregnation on the alumina support.

(i) The chemical process of formation of the colloidal reduced nickel complex (NiRC) can be summarized as follows [21]:

$$\begin{aligned}&4\mathrm{NaH} + 2t\text{-BuOH} + \mathrm{Ni(CH_3COO)_2}\\ &\rightarrow \underset{\text{(NiRC)}}{(\mathrm{Ni^0} + 2t\text{-BuONa})} + 2\mathrm{CH_3COONa} + 3\mathrm{H_2} \quad (1)\end{aligned}$$

When gaseous H_2 ($H_2/Ni = 3$) evolved the NiRC complex was produced. This complex was composed of metallic nickel colloidal particles inserted in the t-BuONa alcoholate species (t-BuONa/Ni = 2) playing the role of a stabilizing organic matrix [21, 25]. The colloidal solution also contained soluble Na-acetate ($CH_3COONa/Ni = 2$).

(ii) Impregnation of alumina with the NiRC complex colloidal solution led to a suspension of the supported reduced nickel complex (NiRCS):

$$\underset{\text{(NiRC)}}{\mathrm{Ni^0}/2t\text{-BuONa}} + \underset{\text{(support)}}{\mathrm{Al_2O_3}} \rightarrow \underset{\text{(NiRCS)}}{\mathrm{Ni^0}/t\text{-BuONa}/\mathrm{Al_2O_3}} \quad (2)$$

Filtering the above suspension led to powdered NiRCS composed of NiRC entities supported on alumina. The obtained powder is denoted “unwashed NiRCS”. Washing it with EtOH led to the partial removal of the organic matrix (see Results and Discussion) and was then denoted “washed NiRCS”.

2.1.2. Materials

Tetrahydrofuran (THF) was distilled from benzophenone-sodium adduct and stored over sodium wires. Tertiary butyl alcohol (t-BuOH) (Aldrich) was distilled from commercial sodium. Nickel acetate [$Ni(CH_3COO)_2$] (Fluka) was dried under vacuum (20 torr) at 110 °C during 16 h. Water content after drying was 0.1 mol %. Sodium hydride (NaH) (65% in mineral oil, Fluka) was used after three washings with 20 cm^3 of THF under N_2 atmosphere. The γ-alumina support (Degussa) was pre-treated 12 h in air at 500 °C and stored under N_2.

2.1.3. General procedure

The overall preparation procedure was performed under N_2 atmosphere. An excess of NaH can be used in order to ensure the complete reduction of the nickel salt precursor. This excess was in turn neutralized as t-BuONa salt by adding the equivalent amount of t-BuOH in the NiRC colloidal solution. Typical preparation was as follows.

The NiRC colloidal complex was prepared [21] by dropwise addition of 2×10^{-2} mol of t-BuOH to a mixture of 6×10^{-2} mol of NaH and 10^{-2} mol of anhydrous $Ni(CH_3COO)_2$ in 40 cm^3 of refluxing THF solvent. Gaseous H_2 evolved and a black colloidal solution was formed. 2×10^{-2} mol of t-BuOH was added to this solution. A 20 cm^3 sample was syringed, dropwise added to a suspension of 2.4 g γ-alumina in ethanol (EtOH) and the mixture was magnetically stirred for 3 h. A black suspension of the supported nickel complex (NiRCS) was formed. This suspension was then filtered. The filtered solution contained the excess t-BuONa. As to the solid filtrate it was washed several times with EtOH, dried and stored under N_2 atmosphere. The raw NiRC complex was also obtained as a metallic powder by evaporating the black colloidal solution then drying under reduced pressure [21].

2.2. Catalyst characterization

The nickel composition and specific area of the catalysts were determined on a Varian AA1275 atomic absorption spectrophotometer and Carlo Erba Sorptomatic 1900 equipment respectively.

The electron microscopy images were recorded with a Phillips CM20 STEM equipped with EELS instruments. The spectra were obtained by placing a drop of the nanoparticle suspension on the carbon coated copper grid. XRD patterns $I(\theta)$ were recorded at a classical $\theta/2\theta$ diffractometer using CuK_α radiation.

The TGA experiments were performed with a Sartorius 4102 balance. The catalyst samples (0.1 g) were heated in the quartz scale of the balance from room temperature to 500 °C (heating rate of 4 °C min^{-1}) under N_2, H_2 or air (>99.99%, Air Liquid) flow (3.6 l h^{-1}).

2.3. Catalytic testings

2.3.1. Gas phase hydrogenation

The gas phase hydrogenation reactions were carried out in a quartz fixed bed reactor with 0.2 g of catalyst sample. The catalytic activity experiments were done under atmospheric pressure and in the range of temperature and total rate flow of 150–200 °C and 3 l–12 l h^{-1} respectively. The reactant feed gas was obtained by flowing H_2 in liquid benzene or styrene placed in a saturator maintained at 8 and 15 °C, respectively. The reactant and product analyses were conducted on line using a Hewlett Packard 5730A FID gas chromatograph. Each reaction temperature was maintained constant until the corresponding steady-state was reached as indicated by gas chromatography analysis of the exit gases.

2.3.2. Hydrogenation in liquid medium

The hydrogenation reactions in ethanol solutions were conducted at constant atmospheric pressure with a classical hydrogenation vessel described elsewhere [22]. The reactor was first purged under H_2 flow before the solid complex sample then the hydrocarbon ethanol solution were introduced. The amount of H_2 consumed during the reaction was determined by measuring the volume variations. The hydrocarbons concentration variations were determined by gas chromatography using a Carlo Erba Fractovap G1 apparatus.

Definitions

$$\text{conversion (\%)} = \frac{\text{number of moles of reactant converted}}{\text{number of moles of reactant introduced}} \times 100$$

$$\text{selectivity (\%)} = \frac{\text{number of moles of product } i \text{ formed}}{\text{number of moles of reactant converted}} \times 100$$

specific rate [mol/h/g(Ni)] = number of moles of reactant converted per hour per gram of nickel.

3. Results and discussion

3.1. Nickel composition and BET surface area of the catalysts

The nickel composition and the BET specific areas of the solids are reported in Table I. Chemical analysis by atomic absorption showed that no notable loss of nickel occurred during the impregnation step. The TGA experiments (see below) roughly confirmed this result.

The surface area of the support (78.0 m^2 g^{-1}) was significantly decreased after impregnation with the NiRC complex as compared to that of the washed NiRCS catalyst (61.0 m^2 g^{-1}).

3.2. STEM, EELS and XRD studies

Fig. 1 shows the dark field STEM micrographs of powdered samples of the NiRC and NiRCS complexes. Amorphous and homogeneously dispersed nickel particles on the organic matrix or support can be observed for all samples. These particles were also similarly sized and the mean particle size was about 1–3 nm. The EELS technique confirmed this estimation and also the Ni^0 oxidation state of nickel. It thus appears that the particle size was not changed during the impregnation step nor when washing the supported complex with ethanol. On the other hand, close inspection of the micrographs showed that the nickel particles were highly ordered for the NiRC sample and the corresponding microcrystalline units seemed to have mainly a hcp structure and not the expected stable cfc structure [25]. In addition, it appeared that the observed structures were size dependent and changed by varying the concentration of the nickel salts or hydride and the time or temperature of reaction [25].

TABLE I Nickel composition and BET surface area of the used samples

Catalyst	(%) Ni (calculated)	(%) Ni (atomic abs.)	(%) Ni (TGA exper.)	BET area (m^2 g^{-1})
NiRC	11.7	11.5	10.6	—
NiRCS (unwashed)	5.5	5.4	7.7	—
NiRCS (washed)	—	7.2	—	61.0
γ-alumina	—	—	—	78.0

As to the supported NiRCS samples, they appeared less ordered and probably constituted of a mix of *hcp* and *cfc* structures.This apparent disorder was attributed to the effect of the support surface which probably interacted to some extent with the nickel particles. Investigations have been undertaken for a better determination of the morphology of the supported metal nickel clusters in the fresh NiRCS solid.

No diffraction pattern was observed for either NiRC or NiRCS samples when using the XRD technique, in good accordance of the amorphous character of the nickel phase. However, NiRCS samples used in the gas phase hydrogenation of benzene contained particles of larger size (>10 nm) after reaction. STEM and EELS studies confirmed these results.

3.3. Thermal gravimetry analysis of the catalysts

The stability of the catalysts under N_2, H_2 or air during redox cycles was studied by TGA. The obtained results are reported in Table I and Figs 2–5. In all experiments, the TGA peaks appearing at temperatures lower than 100 °C were attributed to the presence of residual solvent molecules in the analyzed sample. Blank experiments allowed us to identify the temperature peaks of t-BuONa and CH_3COONa species. No temperature peak was observed for the alumina support.

3.3.1. NiRC complex

In the temperature range studied, the thermogram of the solid raw NiRC complex under N_2 atmosphere exhibited a main temperature peak at 350 °C with a shoulder at about 270 °C (Fig. 2). These peaks were attributed to the thermal decomposition of the t-BuONa component of the complex more or less attached to the nickel phase; in good agreement, the weight loss was about 35%.

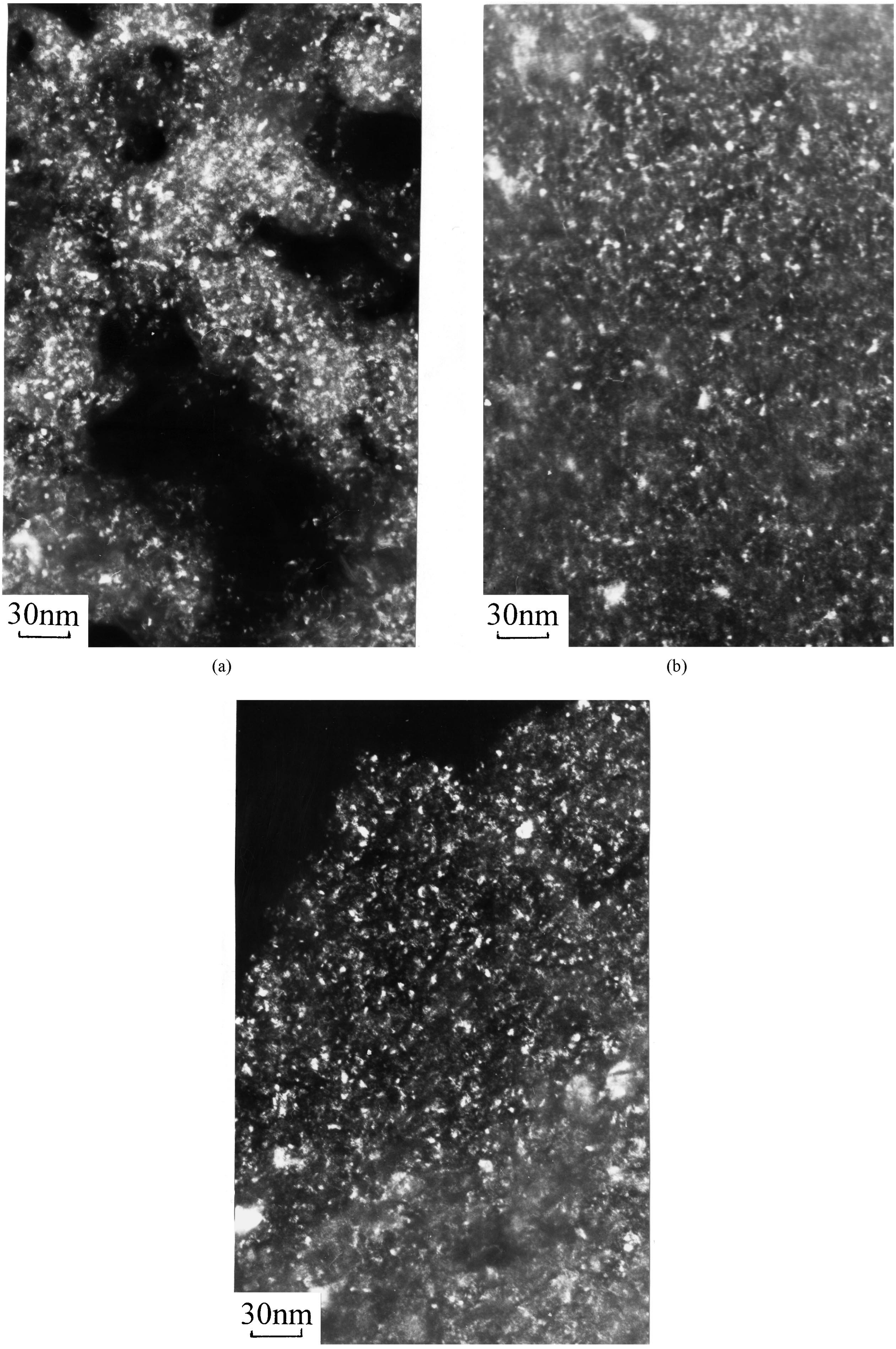
3.3.2. NiRCS complex

The thermogram under N_2 atmosphere of the unwashed NiRCS complex exhibited two peaks at 255 and 385 °C and the weight loss was about 10% (Fig. 3). These peaks were also attributed to the decomposition of the organic t-BuONa fragment. Weight loss calculations confirmed this assumption.

After washing the NiRCS complex with ethanol the peaks areas of temperature strikingly decreased, notably the peak appearing at 255 °C. Constant peak areas

TABLE II Gas phase hydrogenation of benzene. Catalyst: 200 mg, total flow rate: 50 ml min^{-1}, $P_{C_6H_6} = 42$ mbar, $C_6H_6/H_2 = 5.5\%$, $T = 200\,^{\circ}C$

Catalyst	Pre-treatment	Benzene conversion (%)	Cyclohexane selectivity (%)	Rate (mol/h/g(Ni))
NiRC	None	5	100	$1.4 \cdot 10^{-2}$
NiRCS unwashed	None	5	100	$3.4 \cdot 10^{-2}$
NiRCS washed	None	28.1	100	$14.2 \cdot 10^{-2}$
NiRCS washed	$H_2/350\,^{\circ}C/72$ h	42.9	100	$20.4 \cdot 10^{-2}$
NiRCS washed	air/300 °C/4 h + $H_2/350\,^{\circ}C/72$ h	50.5	100	$24.1 \cdot 10^{-2}$



(a)

(b)

(c)

Figure 1 Dark field TEM micrograph of the NiRC (a) and unwashed (b) and washed (c) NiRCS complexes.

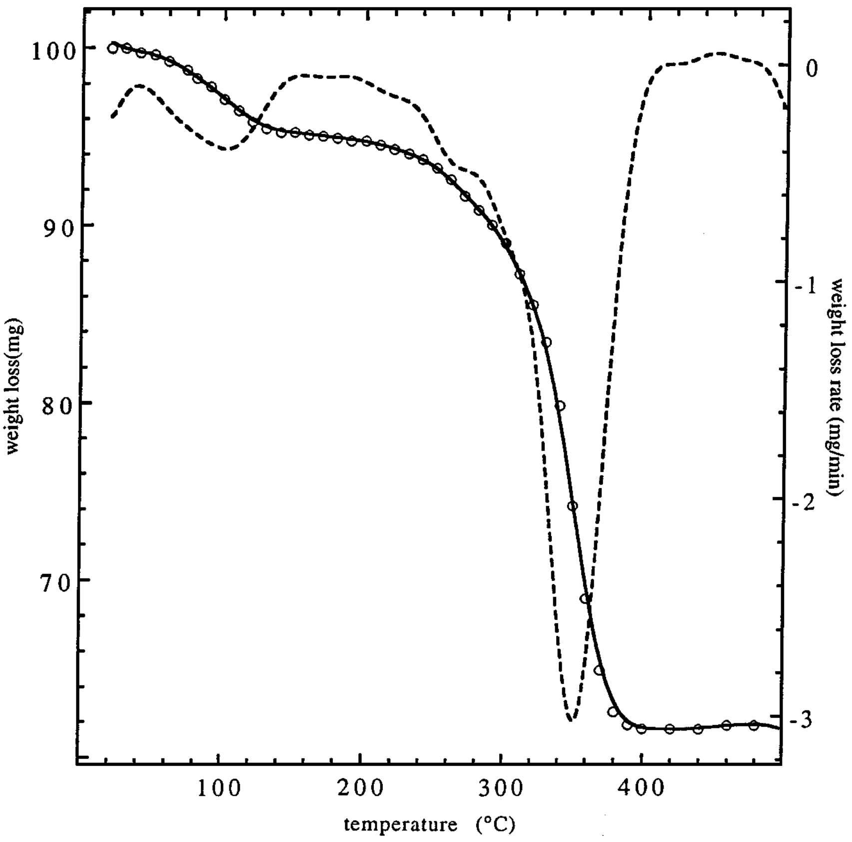


Figure 2 TGA profile under N_2 for the NiRC complex.

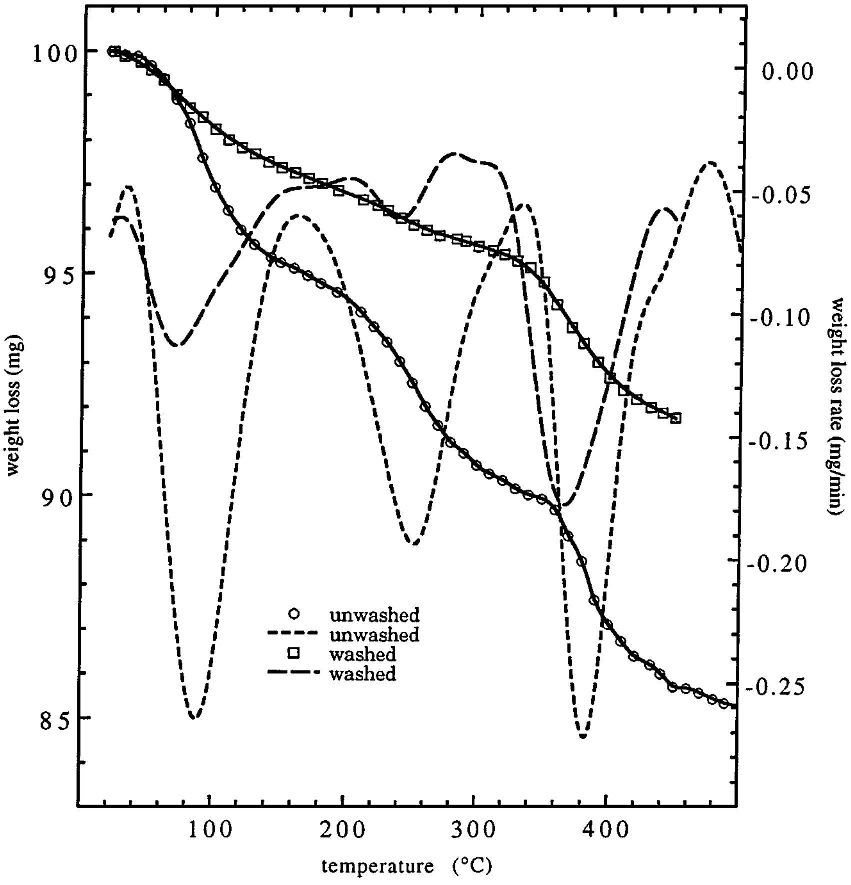


Figure 3 TGA profile under N_2 for the washed and unwashed NiRCS complex.

were observed after 3 washings (Fig. 3, washed NiRCS). The washing solutions were composed of *t*-BuONa entities. We thus conclude that the decrease in the peaks areas is due to the removal of part of the *t*-BuONa species by the ethanol solvent. Furthermore, the remaining species, less easily removed by the solvent, were probably those more tightly attached to the nickel particles and/or the support. Studies have been

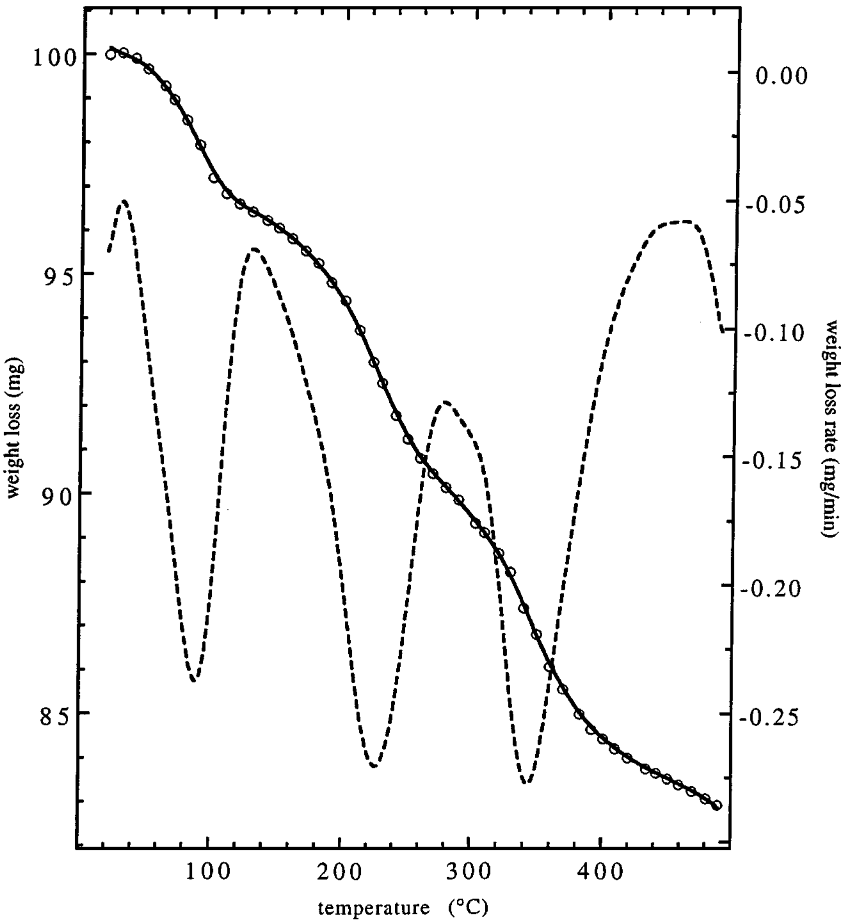


Figure 4 TGA profile under H_2 for the unwashed NiRCS complex.

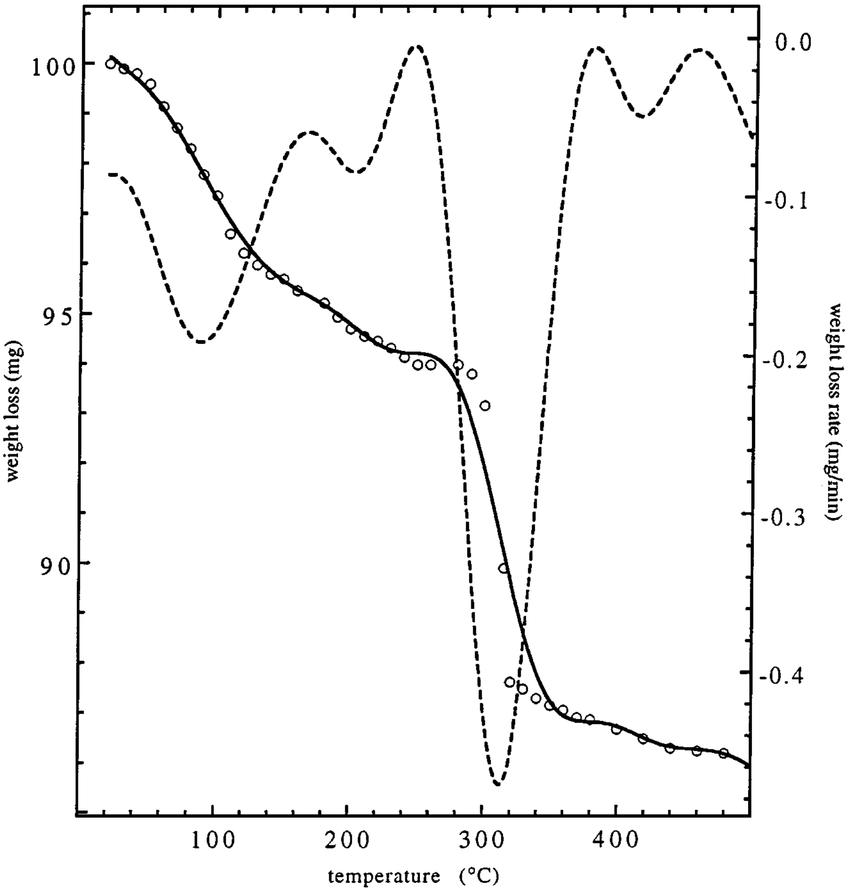


Figure 5 TGA profile under air for the unwashed NiRCS complex.

undertaken in order to obtain supplementary informations on these entities.

3.3.3. Thermal stability of the organo-nickel phase under reactive atmosphere

The thermal stability experiments under different atmospheres (N_2, H_2 or air) of the nickel particles were conducted with the unwashed NiRCS complex (Figs 4 and 5).

(i) Under H_2 atmosphere the thermogram of the NiRCS complex showed two peaks appearing at lower temperatures (225 and 345 °C, Fig. 4) than under N_2 atmosphere (255 and 385 °C respectively, Fig. 3). Then the thermal treatment under H_2 flow seemed to accelerate the removal of the organic matrix. The observed peaks were also attributed to the thermal decomposition of *t*-BuONa species in good accordance with weigt loss calculations.

On the other hand, when H_2 treatment was followed by air treatment, a weight gain was observed and calculations showed it corresponded to the oxidation of the nickel metal phase. The obtained value for the nickel composition (7.7%) was in good agreement with the atomic absorption measurements (Table I).

(ii) When the NiRCS solid was directly flowed under air the main temperature peak was observed at 305 °C (Fig. 5). This peak and the other smaller ones (210 and 410 °C) were attributed the decomposition of the *t*-BuONa organic matrix. Calculations showed that the observed weight loss corresponded to both the *t*-BuONa species decomposition and nickel phase oxidation.

When air treatment was followed by H_2 treatment, a weight loss was observed and calculations showed it corresponded to the reduction of the oxidized nickel phase. In this experiment also the value obtained for nickel composition (7.0%) was in good accordance with the atomic absorption measurements (Table I).

3.4. Catalytic activity

The NiRC and NiRCS complexes were used as catalysts in the hydrogenation reaction of styrene or benzene in the liquid or gas phase. These reactions served as selectivity [23] and activity [26–28] tests respectively. The obtained results are summarized in Tables II and III.

3.4.1. Gas phase hydrogenation

3.4.1.1. Benzene hydrogenation. The observed performances in the gas phase hydrogenation of benzene depended on the nature of the catalyst, its pretreatment and, also, on the reaction conditions (reaction temperature, partial pressures, rate flow). All samples were 100% selective to cyclohexane. The results obtained at 200 °C and atmospheric pressure are reported in Table II.

These results showed that the supported NiRCS catalyst was more reactive than the unsupported NiRC catalyst: the specific rate of the latter was about 2.5 times higher than that of the former. This result was attributed to a better dispersion of the active phase on the support for the NiRCS catalyst in which the number of surface sites was then higher.

The activity of the NiRCS catalyst was improved after washing it several times with ethanol (the specific rate was multiplied by 4.2). An additional improvement was also observed when the washed NiRCS complex was thermally pre-treated under H_2 flow or air then H_2 flow (the specific rate was multiplied by 6.0 and 7.1 respectively). This enhancement in catalytic activity was probably due to the removal of the organic matrix. Indeed, washing the NiRCS complex with the ethanol solvent removed the excess of organic matrix from the surface, as the TGA experiments showed (Fig. 3); then, probably, the access of the benzene molecule to the active nickel sites was improved and, as a consequence, the catalytic activity was enhanced (Table II). In the same way, a better access to the nickel phase was also probably achieved by the total decomposition of the organic matrix by thermal pre-treatment of NiRCS under H_2 or air then H_2 atmosphere (Figs 4 and 5), thus explaining the enhanced activity obtained (Table II).

3.4.1.2. Styrene hydrogenation. As expected [23] higher activities were observed for styrene hydrogenation than for benzene hydrogenation. Thus, the NiRCS complex was very active in the gas phase hydrogenation of styrene from room temperature. Indeed, when 0.2 g of a solid NiRC sample were flowed (200 ml min^{-1}) at room temperature and atmospheric pressure with a mixture of hydrogen and styrene ($P_{C_8H_8} = 4$ mbar) it was completely converted into ethylbenzene with a selectivity of 100%. This activity was constant for several hours. In the same conditions, benzene was not active at all and began to be transformed only above about 100 °C.

3.4.2. Liquid phase hydrogenation

In ethanol solution no benzene conversion to cyclohexane was observed at room temperature in the presence of NiRC or NiRCS. As for styrene hydrogenation in the same solvent the activity depended on the nature of the catalyst (Table III). Thus, styrene was hydrogenated totally (100% conversion) and very fastly (about 12 min) in the presence of the NiRC complex [23]. In contrast,

TABLE III Hydrogenation of styrene in ethanol solution. $[C_8H_8] = 10$ mmol/15 cm^3 EtOH, $P_{H_2} = 1$ bar, $T = 25$ °C

Catalyst	Ni amount mol × 10^3	Time of reaction	H_2 consumption (%)	Styrene conversion (%)	Ethylbenzene selectivity (%)
NiRC	0.25	12 min	100	100	100
NiRCS	1.0	45 h	176	100	100
	0.9	77 h	116	100	100

the unwashed NiRCS complex was almost inactive and total conversion to ethylbenzene was reached only after several tens of hours (up to 77 h), although the Ni content was four times higher (Table III). In addition, the experiments were not easily reproducible.

The excess H_2 consumption (116–176%) for the NiRCS complex during the hydrogenation of styrene but not for NiRC (100%) should be noted. We attributed this excess of H_2 consumption to the adsorption of part of the introduced gaseous H_2 by the supported nickel particles. Separate experiments showed indeed that a suspension of NiRCS in THF adsorbed H_2 up to $H_2/Ni = 6$ at room temperature. These results are in agreement with solid/gas interactions studies showing that nickel [29] and other transition metal [29–33] are good H_2 reservoirs, capable of large amounts of H_2 adsorption and storage ($H_2/Ni > 10$). Other experiments are planned for a better understanding of the mechanisms of both hydrogen storage and styrene hydrogenation in our catalytic conditions.

4. Conclusions

The present work shows that supported nanoparticles of metallic nickel can be obtained from an organic colloidal precursor. The nickel particle size in the organic precursor was not changed during the deposition step of the preparation. Part of the organic matrix of the precursor remained irreversibly attached to the final material, probably as structural moiety of the supported nickel particles, even after several washings with the ethanol solvent. Nevertheless, this organic matrix should be decomposed by thermal treatment above about 250 °C under N_2, H_2 or air atmosphere.

The supported nickel particles were active in the gas phase hydrogenation of benzene. The organic matrix seemed to inhibit the reaction since the activity was enhanced by its removal by washing with an appropriate solvent or its decomposition by thermal treatment under H_2 or air + H_2. In addition, these supported nickel particles were also excellent catalysts in the gas phase hydrogenation of styrene. They were capable to convert totally and selectively into ethyl-benzene at room temperature. Finally, they appeared to be good hydrogen reservoir in organic liquid media.

References

1. G. SCHMID, *Chem. Rev.* **92** (1992) 1709.
2. H. GLEITER, *Nanostruct. Mater.* **1** (1992) 1.
3. R. P. ANDRES, J. D. BIELEFIELD, J. I. HENDERSON, D. B. JANES, V. R. KOLAGUNTA, C. P. KUBIAC, W. J. MAHONEY and R. G. OSIFCHIN, *Science* **273** (1996) 1690.
4. C. SURYANARAYANA, D. MUKHOPADHYAY, N. PAVILAKARS and F. H. FROES, *J. Mater. Res.* **7** (1992) 8.
5. S. DAVIS and K. J. KLABUNDE, *Chem. Rev.* **82** (1982) 153.
6. M. JOSÉ-YACAMAN and R. F. MEHL, *Metall. Mater. Trans.* **29** (1998) 713.
7. H. WELLER, *Angew. Chem. Int. Ed. Engl.* **35** (1996) 1079.
8. C. ESTOURNES, T. LUTZ, J. HAPPICH, T. QUARABTA, P. WISSLER and J. L. GUILLE, *J. Magn. Mater.* **173** (1997) 83.
9. H. VAN SWYGENHOVEN and A. CARO, *Nanostruct. Mater.* **9** (1997) 669.
10. L. K. KURIHARA, G. M. CHOW and P. E. SHOEN, *ibid.* **5** (1995) 607.
11. T. D. XIAO, S. TORBAN, P. R. STRUT and B. H. KEAR, *ibid.* **7** (1996) 857.
12. J. H. FENDLER and F. C. MELDRUM, *Adv. Mater.* **7** (1991) 607.
13. F. FIVETR, F. FIEVET-VINCENT, J. P. LAGIER, B. DUMONT and M. FILGARZ, *J. Mater. Chem.* **3** (1993) 627.
14. R. D. RIEKE, *Acc. Chem. Res.* **10** (1997) 377.
15. *Idem.*, *Science* **246** (1989) 1260.
16. G. A. OZIN, *Adv. Mater.* **4** (1992) 612.
17. G. N. GLAVEE, *Inorg. Chem.* **32** (1993) 474.
18. H. BONNEMAIN, W. BRIJOUX and T. JOUSSEN, *Angew. Chem. Int. Ed. Engl.* **29** (1990) 273.
19. D. ZENG and M. J. HAMPTEN-SMITH, *Chem. Mater.* **5** (1993) 68.
20. K. VIJAYA SARATHY, G. U. KULKARNY and C. N. R. RAO, *Chem. Commun.* (1997) 537.
21. P. GALLÉZOT, C. LECLERCQ, Y. FORT and P. CAUBÈRE, *J. Mol. Cat.* **93** (1994) 79.
22. J. J. BRUNET, D. BESOZZI, A. COURTOIS and P. CAUBÈRE, *J. Amer. Chem. Soc.* **104** (1982) 7130.
23. J. J. BRUNET, P. GALLOIS and P. CAUBÈRE, *J. Org. Chem.* **45** (1980) 1937.
24. *Idem.*, *ibid.* **45** (1980) 1946.
25. S. ILLY, O. TILLEMENT, J. M. DUBOIS, Y. FORT and J. GHANBAJA, *Philo. Mag. A* (1998), in press.
26. P. N. RYLANDER, "Hydrogenation Methods" (Academic Press, 1985).
27. L. CERVENY (ed.), "Catalytic Hydrogenation," Stud. Surf. Sci. Catal., vol. 27 (Elsevier, Amsterdam, 1986).
28. M. A. KEANE, *J. Catal.* **166** (1997) 347.
29. M. P. SOHIER, G. WRÖBEL, J. P. BONNELLE and J. P. MARQ, *Appl. Catal. A* **84** (1992) 169.
30. L. JALOWIECKI, G. WROBEL, M. DAAGE and J. P. BONNELLE, *J. Catal.* **107** (1987) 375.
31. D. DUPREZ, J. BARBIER, Z. FERHAT-HAMIDA and M. M. BETTAHAR, *Appl. Catal.* **12** (1984) 219.
32. G. WROBEL, L. JALOWIECKI, J. P. BONNELLE, F. BALI and M. M. BETTAHAR, *New J. Chem.* **11** (1987) 715.
33. Z. MESBAH-BENYOUCEF, M. M. BETTAHAR, J. BARRAULT, A. TRANCHANT and R. MESSINA, *C1 Mol. Chem.* **2** (1987) 33.

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