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Characterization of Nanosized Nickel Prepared by Surface Reactions of Ni-σ-organyl Complexes on Silica: An Electron Paramagnetic and Ferromagnetic Resonance Study

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Dispersed atomic nickel(0) is formed during the reaction of the nickel-σ-organyl complexes with silanol groups at temperatures below 373 K. That nickel is oxidized to Ni(I) by protons of the silanol groups in a consecutive step. The Ni(I) portion amounts to about 70% w/w of the Ni used. Six different Ni(I) species are detected by electron paramagnetic resonance. They are stabilized by interaction with the silica surface and the organic moieties; they act as anchor ions for the Ni(0) atoms. Ni(0) crystallites stabilized in this way are about 0.5 nm in diameter after a treatment at 373 K. The influence of the Ni(I) ions on the collective, magnetic properties of the clusters is revealed by calculation of ferromagnetic resonance (FMR) spectra using the independent-grain approach according to Schlömann and Kotyukov. A strain of about 10 GPa is brought about in the nickel crystallites by the interaction with Ni(I) ions. © **1998 John Wiley & Sons, Ltd.**

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INTRODUCTION

To prepare metal particles in a well controlled way, attempts have been made to deposit them on high-surface-area supports (1) by decomposition of metal carbonyls,[1] (2) by surface reactions of organometallic complexes,[2,3] (3) by adsorption of dispersed metal clusters,[4,5] (4) by metal vapour condensation techniques[6] and (5) by a two-step variant of the normal sequence of chemical operations to produce a metal/support catalyst, i.e. impregnation (precipitation, ion exchange), oxidation and reduction[7].

In this paper we report on the preparation of highly dispersed Ni clusters on silica formed by surface reactions of nickel-σ-organyl complexes, and the reaction of Ni(0) with silanol groups forming Ni(I) ions, which act as anchor atoms for the Ni crystallites.

EXPERIMENTAL

We used silica gel from Merck (Kieselgel 60, grain size 0.06–0.2 μm) as the support. Silica gel was treated for 4 h in vacuum at 673 K, cooled to room temperature and loaded in an argon atmosphere with a solution of nickel-σ-organyl complex in tetrahydrofuran (THF). For drying and for removal of the organic moieties the sample was heated in vacuum, Ar or H_2 at 373 K (labelled as Ni 100V, Ni 100Ar or Ni 100H, respectively) and sealed in glass tubes before electron paramagnetic (EPR) or ferromagnetic (FMR) resonance and electron microscopy measurements. The nickel loading is

 CCC 0268–2605/98/050321–05 $17.50

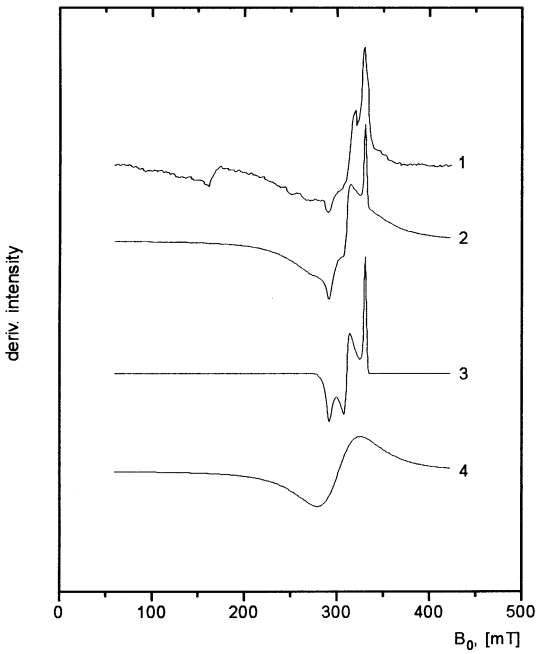


Figure 1 Experimental (1) and calculated (2) EPR powder spectrum of Ni 100 V. Curve 2 was calculated by superposition of 3 [Ni^+ ($\equiv$SiO) (O_2); $g_1^G = 2.28$, $\Delta B_1 = 4$ mT; $g_2^G = 2.14$, $\Delta B_2 = 3$ mT; $g_3^G = 2.01$, $\Delta B_3 = 0.5$ mT] and 4 [Ni(0) signal; for parameters see Table 3].

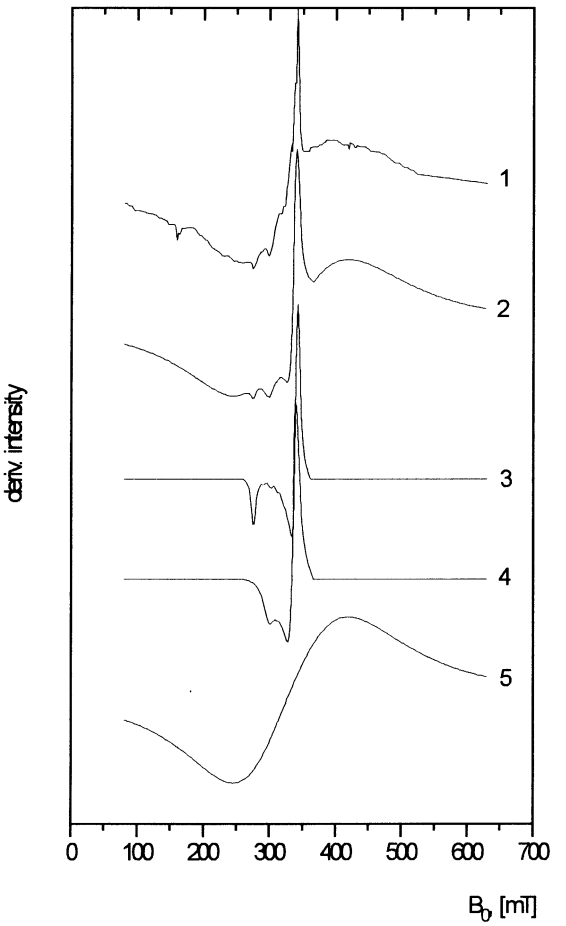


Figure 2 Experimental (1) and calculated (2) EPR powder spectrum of Ni 100 Ar. Curve (2) was calculated by superposition of 3 [Ni^+ ($\equiv$ SiO−)(DPE)Li_2; $g_{\|}^C = 2.41$, $\Delta B_{\|} = 4$ mT; $g_{\perp}^C = 1.95$, $\Delta B_{\perp} = 5$ mT], 4 [Ni^+ ($\equiv$ SiO−)$_2$ (DPE)Li_2; $g_{\|}^E = 2.22$, $\Delta B_{\|} = 11$ mT; $g_{\perp}^E = 1.97$, $\Delta B_{\perp} = 7$ mT] and 5 [an Ni(0) signal; for parameters see Table 3].

about 2% w/w. EPR investigations were performed at 123 K, using an X-band spectrometer (ERS 220, ZWG Berlin–Adlershof).

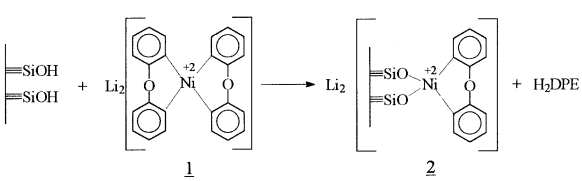
Transmission electron microscopy (TEM) was carried out with a JOEL 100C microscope. The synthesis of the nickel–σ-organyl complex ($Li_2[Ni(DPE)_2]\cdot 4THF$; DPE = 2,2′-dianion of the diphenyl ether) is reported in detail in Ref. 8.

RESULTS AND DISCUSSION

The hydrolysable nickel-σ-organyl complexes react with silanol groups forming Ni(0) (Eqn [1][2,3,8]

$$Li_2[NiR_4] + 2 \equiv SiOH \rightarrow 2 \equiv SiOLi + 2HR + R - R + Ni(0) \quad [1]$$

In the case of $Li_2[Ni(DPE)_2]\cdot 4THF$ (**1**), the results of the gas-chromatographic analysis[8] [diphenyl ether (H_2DPE) dibenzofuran (DBF) were estimated in both the expected quantities and in the ratio 1:1] point to the reactions represented by Eqns [2] and [3].



1 2 [2]

First of all, the surface complex **2** is formed. This complex decays by homolysis of the remaining two

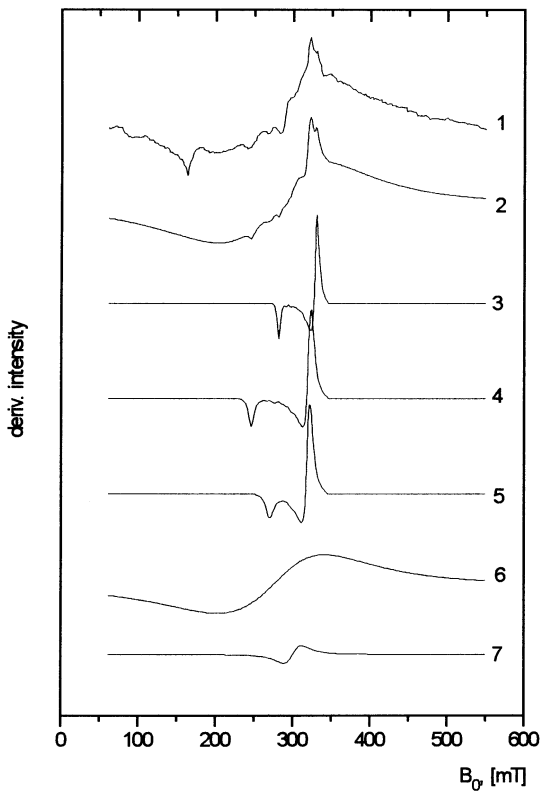
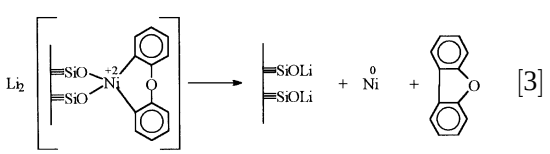


Figure 3 Experimental (1) and calculated (2) EPR powder spectrum of Ni 100 H. Curve 2 was calculated from 3 [Ni^{+} ($\equiv$SiO$-$)(THF)$_x$; $g_{\|}{}^{B} = 2.36$, $\Delta B_{\|} = 2$ mT; $g_{\perp}{}^{B} = 2.02$, $\Delta B_{\perp} = 4$ mT], 4 [Ni^{+} ($\equiv$SiO$-$)$_x$; $g_{\|}{}^{A} = 2.71$, $\Delta B_{\|} = 4$ mT; $g_{\perp}{}^{A} = 2.07$, $\Delta B_{\perp} = 6$ mT], 5 [Ni^{+} ($\equiv$SiO$-$)$_y$ (THF)$_x$; $g_{\|}{}^{D} = 2.46$, $\Delta B_{\|} = 6$ mT; $g_{\perp}{}^{D} = 2.08$, $\Delta B_{\perp} = 6$ mT], 6 [Ni(0); for parameters see Table 3] and 7 [a paramagnetic Ni(0) signal; $g = 2.22$, $\Delta B_{pp} = 20$ mT].

Ni–C bonds, forming DBF and dispersed atomic nickel.



[3]

Electron Paramagnetic resonance (EPR) measurements of the Ni 100 samples yield the spectra 1 in Figs 1–3. Inspection of these spectra revealed that they consist of both paramagnetic Ni(I) and superparamagnetic Ni(0) signals. This result points to the greater complexity of the surface reactions, and we have to take into consideration the Ni(I) formation reactions too.

There are several paths to generation of Ni(I) species in the system under investigation:

(1) the nickel complex ($Li_2[Ni(DPE)_2]\cdot 4$ THF) can react with one or three silanol groups forming Ni(I) according to Eqns [4] and [5]:

$$Li_2[Ni(DPE)_2] + \equiv SiOH \rightarrow \equiv SiOLi + Li\,[Ni(DPE)] + HDPE\cdot \quad [4]$$

4

$$Li_2[Ni(DPE)_2] + 3 \equiv SiOH \rightarrow 2 \equiv SiOLi + H_2DPE + \equiv SiONi + HDPE\cdot \quad [5]$$

5

Accordingly radicals and Ni(I) species (**4** and **5**) should be generated to the same extent. However, from inspection of both the experimental spectra and the calculated spectra[9] (see Figs 1–3) it follows that in the Ni 100 samples the quantity of organic radicals can be neglected.

(2) Another possible explanation for the high Ni(I) content is the re-oxidation of the dispersed atomic Ni(0) by protons of the silanol groups (Eqn [6]).

$$Ni(0) + \equiv SiOH \rightarrow \equiv SiONi + H\cdot \quad [6]$$

Reaction [6] was observed on NiPd-containing zeolites at 773 K.[10] It is well known, however, that in the case of silver atoms in aqueous solutions[11] the analogous reaction takes place at room temperature. So we suppose that the majority of the Ni(I) is formed by reaction [6]. The hydrogen radicals are not stable; they recombine with each other or with the HDPE radicals.

The Ni(I) species **5** (species A in Table 1) have some vacancies in their coordination sphere. These vacancies are filled by interactions (1) with organic moieties[12–17] e.g. solvent molecules (species B in Table 1) or ligand molecules (species C in Table 1), (2) with both further silanol groups, analogously to Cu(II),[18,19] and further organic moieties (species D and E in Table 1), (3) with each other, pair formation resulting in a signal at half-field[20] (species F in Table 1), (4) with molecules captured from the atmosphere[12,21] (species G in Table 1) and (5) with Ni(0) atoms, giving a signal attributable to paramagnetic or superparamagnetic Ni clusters (see spectra 4,5 and 6,7 in Fig. 1, 2 and 3 respectively).

All interactions (1)-(5) occur in parallel under our experimental conditions. From this it follows

Table 1 Components of the g tensors for supported Ni^+ species

Species[a]	Code	$g_3/g_{\|\|}$	g_2	$g_1/g^{\perp}$	References
$Ni^+(\equiv SiO\text{-})_x$	A	2.71		2.07	12–14
$Ni^+ (\equiv SiO-)(THF)_x$	B	2.46		2.08	This work
$Ni^+ (\equiv SiO-)(DPE)Li_2$	C	2.41		1.95	This work
$Ni^+ (\equiv SiO-)_y(THF)_x$	D	2.36		2.02	This work
$Ni^+ (\equiv SiO-)_2(DPE)Li_2$	E	2.22		1.97	This work
$(\equiv SiO-Ni^+)_2$	F	—		4.3	20
$Ni^+ (\equiv SiO)(O_2)$	G	2.28	2.14	2.01	12, 21

[a] ($x \geq 1$; $y \geq 2$.

Table 2 Nickel particle size estimated by transmission electron microscopy

Sample	Size (nm)
Ni 100 H	< 1
Ni 100 V	< 1
Ni 100 Ar	< 1
Ni 300 V	< 1
Ni 300 Ar	2–4

that the best fit of the experimental spectra in the region $2.74 \geq g \geq 1.95$ is obtained by superposition of several Ni(I) signals. Only in the case of the sample Ni 100 V is one Ni(I) species sufficient to achieve a good fit.

The presence of a larger amount of Ni(I) is manifested by the small particle size of the Ni(0) species (see below), the high thermal stability of their dispersity (see Table 2) and the effect of Ni(I) on them, resulting from the spectrum calculation.[22–25] The collective magnetic components appear if the calculated Ni(I) signals are subtracted from the experimental spectra [see the signals of Ni(0) in Figs 1–3]. The signals of the collective magnetic Ni(0) components are nearly isotropic at a measurement temperature of 123 K. This low anisotropy agrees with the parameter sets used to calculate the spectra (Table 3).

Thus the value of the magnetocrystalline anisotropy (K_0 = 0.0001 at 123 K, Table 3) deduced from the spectra calculation corresponds to a particle size smaller than 0.5 nm,[26] in agreement with the results of the TEM investigations. $K_{\sigma 1}$ and $K_{\sigma 1}$ are the isotropic and the anisotropic parts, respectively, of the magnetoelastic interaction, σ is an isotropic[24] strain or stress ($\sigma > 0$ or $\sigma < 0$). To estimate a rough measure of the resulting strain we used the isotropic part ($K_{\sigma 1}$) of the magnetoelastic interaction (see Table 3). The actual value of σ calculated from $K_{\sigma 1}$ is determined by the sum of three main factors of influence: (1) the differences in the thermal expansion of nickel and SiO_2 cause a strain,[25,27] (2) the surface tension of small particles is dependent on particle size and results in stress,[28] and (3) the presence of unreduced cations (Ni^+) in nickel crystallites causes a tension.[29] Both of the factors (1) and (2) are about 5×10^8 and -10^{10} Pa, respectively, and constant in our samples. The influence of the anchor atoms (Ni^+ ions) and the atmosphere results from the subtraction of these two values from σ estimated from $K_{\sigma 1}$. Thus the following sequence of σ was obtained: Ni 100 Ar, about 9.54×10^9 Pa; Ni 100 V, about 9.49×10^9 Pa; and Ni 100 H, about 9.3×10^9 Pa. The positive sign shows the dominant influence of unreduced Ni(I) in our samples. The positively charged Ni(I) ions withdraw electron density from the nickel atoms in the particle. This results in incompletely screened nickel atoms, which try to increase their equilibrium distance and cause a tensile stress within the particles.[29] The σ values given above reveal that differences in the pretreatment (Ar, H_2 and V, respectively) influence the resulting strain to a minor degree. Taking into

Table 3 Parameters of spectral simulations of the collective magnetic nickel clusters in Figs 1–3

Sample	g_0	W(mT)[a]	K_0	$K_{\sigma 1}$	$K_{\sigma 1}$	K_3	gf[b]
Ni 100 V	2.22	22.83	0.0001	0.0089	0.0012	−0.0100	0.0018
Ni 100 Ar	2.22	68.75	0.0001	−0.0296	−0.0042	−0.1196	0.0390
Ni 100 H	2.22	60.72	0.0001	0.1479	0.0207	−0.0813	0.0219

[a] W = half-width of the Lorentz line form function
[b] gf = goodness of the fit is given by the approximation error $[(I_{rel}^{exp} - I_{rel}^{cal})^2/(n-1)]^{1/2}$, where n is the number of data points.

consideration an uncertainty of about 30 MPa in the estimation of σ,[30] the influence of traces of oxygen (see Ni 100 V, Fig. 1) and that of an Ar atmosphere cannot be distinguished from the stress state of the Ni(0) particles in the presence of much Ni(I).

As expected from Eq. [6], the tensile constraints of Ni(I) are reduced in the case of Ni 100 H. The decrease in the tension, however, is small (9.5×10^9–$9.3 \times 10^9 = 2 \times 10^8$ Pa) because of a multitude of Ni(I) already existing in this sample (see Fig. 3).

However, the hydrogen atmosphere has an influence on the magnetization of the nickel particles too. This circumstance brings about an additional signal of paramagnetic Ni(0) (see Fig. 3 spectrum 7) compared with the samples Ni 100 V and Ni 100 Ar. The presence of paramagnetic Ni(0) is explained by the filling of the d-band hole of nickel with electron density from the hydrogen s-electron[31] during the adsorption. So the magnetic properties of the nickel particles change from ferromagnetic to paramagnetic with increasing amounts of adsorbed hydrogen. Taking into account the existence of a particle size distribution of the nickel crystallites, the smallest ones should behave paramagnetically. For this reason the paramagnetic nickel signal is observed in this sample.

K_3 describes the shape anisotropy of an ellipsoidal single-domain particle. $K_3 < 0$ corresponds to an oblate specimen.[32] The values of K_3 (see Table 3) are typical for nearly spherical particles.

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