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Paramagnetic Silica Particles: Synthesis and Grafting of a Silane Coupling Agent Containing Nickel Ions onto Colloidal Silica Particles

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A method is presented for the preparation of stable model dispersions of paramagnetic silica particles. A specially designed silane coupling agent containing Ni^{2+} ions is grafted onto silica particles which are either commercially obtained or prepared by the Stöber synthesis. A wet process is described which avoids aggregation of ungrafted and grafted silica particles. The resulting magnetic silica particles have been characterized by dynamic light scattering, transmission electron microscopy, elemental analysis, and infrared spectroscopy. Preliminary magnetization measurements and magnetic relaxation (NMRD) experiments illustrate some of the possibilities for studying model silica colloids with a covalently bonded paramagnetic surface layer.

1. Introduction

Magnetic colloids are a subject of extensive study, with emphasis on the properties of dispersions of magnetite or maghemite particles as encountered in ferrofluids.^{1,2} Such iron oxide colloids have been used recently to provide silica spheres with a ferromagnetic moment. To achieve this, magnetic cores were surrounded by an amorphous silica shell.³ The resulting core-shell particles can be manipulated with a magnetic field (gradient), in contrast to "normal" silica colloids. In addition, the silica shell is very convenient for the covalent binding of organic (macro) molecules which stabilize the particles (i.e., prevent particle agglomeration) in organic solvents.³

We considered the question of whether it would be possible, in addition to "ferromagnetic silica", to prepare paramagnetic silica particles. One option is to modify the silica surface in some way with paramagnetic ions. The presence of paramagnetic ions such as Mn^{2+} as impurities in natural and commercial silica is quite common. However, the ions are usually *physically* adsorbed, with surface concentrations depending on pH and ionic strength. For a "model colloid" paramagnetic ions should be *covalently* bonded to the silica so that the paramagnetic properties of the colloids are well-defined and constant in time.

Such model colloids are of interest, for example, for nuclear magnetic relaxation dispersion (NMRD) studies on (silica) particles where the ill-defined nature and concentration of paramagnetic constituents present problems.⁴ (It is also conceivable that silica colloids loaded with metal ions are of interest for catalysis.⁵) Though in the present article some preliminary NMRD measurements are presented, our aim is in the first place to report

a synthesis procedure for the grafting of paramagnetic nickel-containing molecules onto silica spheres in stable organic dispersions.

Grafting procedures for silica particles using commercially available silane coupling agents are well established.^{6,7} To our knowledge, however, no commercial coupling agent is available for the binding of paramagnetic ions to a substrate. Therefore we have designed a silane coupling agent for grafting Ni^{2+} ions onto a silica core. We describe in section 2 the preparation of this silane coupling agent and a two-step surface modification of the silica particles. The first step is grafting of the coupling agent to the silica particle and the second step involves the reaction with a nickel complex whereby the nickel ions become bonded to the silane coupling agent attached to the particle. We also report a one-step surface modification of silica particles with a silane coupling agent that already contains bonded Ni^{2+} ions. Grafting reactions were performed with commercial silica particles (Ludox HS40, Dupont) and silica particles prepared by the Stöber method.^{8,9}

The resulting paramagnetic particles have been characterized using elemental analysis, infrared spectroscopy, electron microscopy, NMRD measurements, dynamic light scattering, and magnetization measurements. The various findings are discussed and compared in section 3. The conclusions with respect to the preparation route for paramagnetic silica colloids are summarized in section 4.

2. Experimental Section

2.1. Materials and Methods. Commercially available silica particles (Ludox HS 40, Dupont), ammonium hydroxide (25%, Merck), triethyl phosphate (99%, Janssen Chimica), and tetrahydrofuran (99% technical grade, Acros Chimica) were used as received. 5-Amino-2-bromo-1,3-bis[(dimethylamino)methyl]-benzene was prepared as reported in ref 10. (3-Isocyanatopropyl)-

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triethoxysilane 95% (ABCR GmbH & Co, Karlsruhe, Germany), ethanol (100%, technical grade), and tetraethoxysilane (Fluka, purum grade) were distilled before use. Tetrakis(triphenylphosphine)nickel was prepared according to a literature procedure.¹¹ Dilute dispersions were used for dynamic light scattering measurements; the equipment is described elsewhere.¹² Transmission electron micrographs were made with a Philips electron microscope CM 10. Specimens were prepared by dipping carbon-coated copper grids in dilute dispersions. After drying in air, the grid was placed in the electron microscope. Transmission electron microscopy (TEM) was also performed with a Philips CM 20 analytical electron microscope connected to an energy-dispersive X-ray detection system (EDAX). The presence of elements was checked qualitatively by EDAX and quantitatively by chemical analysis (Mikroanalysis Labor Pascher, Remagen, Germany). Particle sizes were determined with an interactive image analysis system. Fourier transform infrared spectra were recorded on a PE 2000 Perkin-Elmer FT-IR spectrometer equipped with a MIRTGS detector. The dried silica samples were ground to a particle size of about 2–4 μm , and the diffuse reflectance spectra were recorded against a KBr single-beam background spectrum. The silane coupling compound containing the nickel complex was mixed with KBr and pressed to a pellet under vacuum. The pellet was measured in transmission mode. All spectra were obtained with a resolution of 4 cm^{-1} .

X-ray photoelectron spectroscopy (XPS) makes use of the electrons emitted from an atom by means of X-ray photoexcitation and is employed to determine elements present at the surface of a sample. X-ray photoelectron spectra from our samples were measured using a Vacuum Generators CLAM-2 system.¹³ The base pressure of the chamber was lower than 10^{-8} Pa. Measurements were performed at room temperature and at a fixed angle using nonmonochromatic Al K α (1486.6 eV) radiation. The analyzer was operated at a 50 eV pass energy, and the measuring spot was approximately 4 mm in diameter.

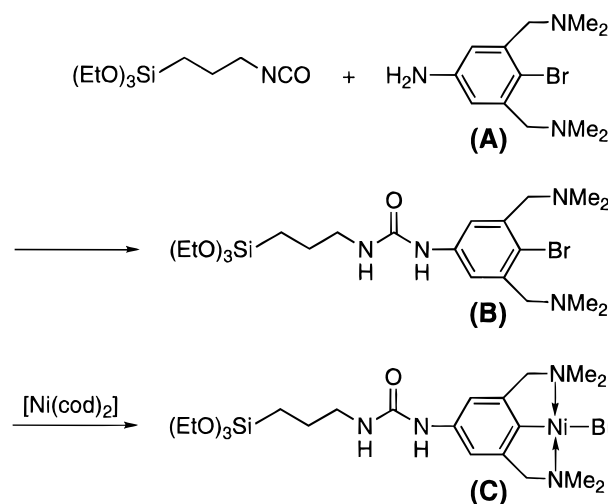
2.2. Magnetic Properties. Magnetic moments of paramagnetic silica particles were measured with a (Model 155 PAE) vibrating-sample magnetometer. When a sample is placed in a uniform magnetic field, a dipole moment proportional to the product of the sample susceptibility multiplied by the applied field is induced in the sample. The sample is made to undergo a sinusoidal motion, which induces an electric signal proportional to the magnetic moment. The apparatus was calibrated with a sample of 0.0895 g nickel at a saturation magnetization of 0.00495 A m^2 . The maximum applied magnetic field was 1.2 T. A cryostat was connected to the magnetometer and the temperature was varied using liquid helium. For the measurements, dried samples were used, which were weighed in the sample holder prior to the measurements. The magnetic moment of the samples was measured at 4.3 K with varying field strength B and also at constant B (1.0 T) with varying sample temperature. The magnetization M is given by eq 1¹⁴

$$M = BN\mu_B^2 P_e^2 / 3kT \quad (1)$$

where N is the number of individual moments in the measured sample, P_e is the effective number of Bohr magnetons, μ_B is the Bohr magneton, k is the Boltzmann constant, and T is the temperature in Kelvin. (The dependence of the magnetization of paramagnetic materials on T^{-1} is known as the Curie law.¹⁴) The magnetic field (and accordingly Larmor frequency) dependence of the solvent proton spin–lattice relaxation time T_1 , usually referred to as NMRD, was measured on the field cycling relaxation spectrometer of the Vrije Universiteit Brussel, as described in detail in ref 15.

2.3. Silane Coupling Agent B. The silane coupling agent, 1-(3-(triethoxysilyl)propyl)-3-[3,5-bis[(dimethylamino)methyl]-

Scheme 1



4-bromophenyl}urea, compound **B** in Scheme 1, was synthesized as follows. To a solution of 8.6 g (0.03 mol) of 5-amino-2-bromo-1,3-bis[(dimethylamino)methyl]benzene¹⁰ (**A** in Scheme 1) in 50 mL of dichloromethane was added 7.5 mL (0.03 mol) of (3-isocyanatopropyl)triethoxysilane. The reaction was carried out under an atmosphere of nitrogen and the reaction mixture was stirred for 4 h at room temperature. The solvent was removed *in vacuo* and the resulting yellow powder was washed successively three times with 20 mL of pentane and three times with 10 mL of diethyl ether. The resulting solid was dried *in vacuo* to afford the product as an off-white powder in a yield of 11.4 g (71%). The melting point of the product was 123–124 °C. The product formula $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHCONH}(\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2-2,6-\text{Br}-1)$ was determined by ^1H NMR, ^{13}C NMR, and IR spectroscopies. A similar type of reaction was reported recently for making metal complex catalysts.⁵

^1H NMR (CDCl_3 ; 300 MHz) δ (ppm): 0.57 (m, 2H, $\text{CH}_2\text{--Si}$); 1.43 (t, $^3J = 7$ Hz, 9H, $\text{CH}_3\text{--C}$); 1.56 (m, 2H, $\text{C--CH}_2\text{--C}$); 2.20 (s, 12H, NCH_3); 3.14 (m, 2H, $\text{C--CH}_2\text{--N}$); 3.39 (s, 4H, $\text{Ar--CH}_2\text{--N}$); 3.74 (q, $^3J = 7$ Hz, 6H, $\text{--CH}_2\text{O}$); 5.52 (t, $^3J = 5$ Hz, 1H, C--NH); 7.36 (s, 2H, ArH); 7.42 (s, 1H, Ar--NH).

^{13}C NMR (CDCl_3 ; 300 MHz) δ (ppm): 7.6 ($\text{CH}_2\text{--Si}$); 18.2 ($\text{CH}_3\text{--C}$); 23.5 ($\text{C--CH}_2\text{--C}$); 42.7 ($\text{C--CH}_2\text{--N}$); 45.5 (NCH_3); 58.5 (CH_2O); 63.8 ($\text{Ar--CH}_2\text{--N}$); 119.8 ($\{\text{Ar}\}\text{C--Br}$); 120.9 ($\{\text{Ar}\}\text{--C--H}$); 138.1 ($\{\text{Ar}\}\text{C--N}$); 139.2 ($\{\text{Ar}\}\text{C--CH}_2\text{N}$); 160.0 (C=O).

IR (KBr; cm^{-1}): 3337 (N–H); 2887, 2818, 2768 (NCH_3); 1647 (C=O); 1562 (N–H).

2.4. Conversion of B to Silane Coupling Agent C Containing a Nickel(II) Center. The conversion of **B** to **C** (Scheme 1) was performed analogously to a literature procedure.¹⁰ A solution of 2.6 g (4.9 mmol) of **B** in 20 mL of THF was added in approximately 15 min to a solution of 1.34 g (4.9 mmol) of bis(1,5-cyclooctadiene)nickel,¹⁶ $[\text{Ni}(\text{cod})_2]$, in 20 mL of THF having a temperature of -70 °C. The temperature of the reaction mixture was allowed to rise to room temperature and the mixture was subsequently stirred for 2.5 h. During this time the yellow suspension turned into a clear orange-brown solution. The solvent was removed *in vacuo* and the residue was washed four times with pentane. After drying, the product was obtained as a red-brown foam with a yield of 2.6 g (90%).

^1H NMR (CD_3OD ; 200 MHz) δ (ppm): 0.70 (m, 2H, $\text{CH}_2\text{--Si}$); 1.28 (t, $^3J = 7$ Hz, 9H, $\text{CH}_3\text{--C}$); 1.65 (m, 2H, $\text{C--CH}_2\text{--C}$); 2.70 (s, 12H, NCH_3); 3.26 (m, 2H, $\text{C--CH}_2\text{--N}$); 3.73 (s, 4H, $\text{Ar--CH}_2\text{--N}$); 3.89 (q, $^3J = 7$ Hz, 6H, $\text{CH}_2\text{--O}$); 6.75 (s, 2H, Ar--H).

^{13}C NMR (CD_3OD ; 200 MHz) δ (ppm): 6.82 ($\text{CH}_2\text{--Si}$); 17.1 ($\text{CH}_3\text{--C}$); 23.0 ($\text{C--CH}_2\text{--C}$); 41.8 ($\text{C--CH}_2\text{N}$); 50.3 (NCH_3); 57.8 ($\text{C--CH}_2\text{--O}$); 72.4 ($\text{Ar--CH}_2\text{--N}$); 110.6 ($\{\text{Ar}\}\text{C--H}$); 136.8 ($\{\text{Ar}\}\text{C--N}$); 141.6 ($\{\text{Ar}\}\text{C--Ni}$); 146.7 ($\{\text{Ar}\}\text{C--CH}_2\text{N}$); 156.6 (C=O).

2.5. Preparation of Silica. The Ludox silica HS40 as received was an aqueous alkaline dispersion containing Na^+ and Cl^- ions. To remove these ions the HS40 dispersion was passed through a bed of Dowex anionic and cationic exchange resin as

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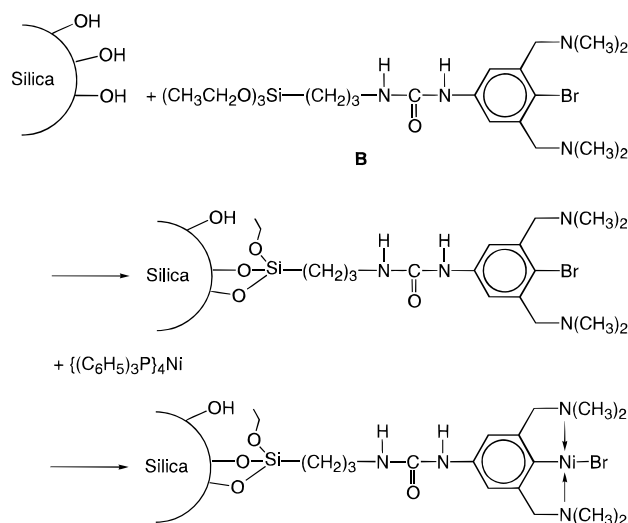
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Scheme 2



described in ref 17. The resulting dispersion had a pH of about 3. Ammonium hydroxide was added with stirring until the pH was 9, and the dispersion was then diluted with ethanol to about 5 vol % water. (This dilution is the first step to transfer the colloids to an organic solvent; see section 2.6.)

In the Stöber method the silica spheres are formed by hydrolysis of tetraethoxysilane in an alkaline ethanol–water mixture followed by a condensation polymerization reaction in which siloxane bridges are formed. The particle size is controlled by the initial concentration of ammonia, water, and tetraethoxysilane in ethanol.^{8,9,18} The thus prepared particles were coded SH1.

2.6. Grafting of Silica Colloids. In the grafting procedure triethyl phosphate (TEP) is used to help remove the water from the dispersion. It is also a suitable solvent for carrying out the reaction since both grafted and ungrafted charge particles are stable in it;¹⁹ TEP partly covers the silica surface, thereby promoting the stability. One possible drawback is a low grafting density of the coupling agent, because TEP may block “anchor sites” for the agent.²⁰

Grafting reactions were carried out as follows. To a two-necked 100 mL round-bottom flask containing 40 mL of TEP was added a 30 mL dispersion of silica HS40 in ethanol–water and ammonium hydroxide. The water was distilled off together with ammonia and ethanol. (The boiling point of TEP is 215 °C.) When the pH of the distillate was about 7, 0.5 g of silane coupling agent **B**, dissolved in ethanol (10 mL), was added to the dispersion and distillation was continued until all ethanol was removed. This procedure is summarized in Scheme 2. The dispersion was purified from unreacted **B** by sedimentation in a preparative ultracentrifuge at 25 000 rpm for 6 h. The particles (coded HS40Ni) were redispersed in tetrahydrofuran, and the sedimentation procedure was repeated three times. To this pale bluish white dispersion was added 0.181 g of tetrakis(triphenylphosphine)nickel dissolved in tetrahydrofuran under an atmosphere of nitrogen. The temperature was kept at 50 °C, and the mixture was well stirred for 4 h. The resulting off-white dispersions were cleaned by sedimentation at 25 000 rpm for 6 h, and sedimented particles were redispersed in tetrahydrofuran.

The whole grafting procedure was also performed for SH1 particles and the grafted particles were coded SH1Ni. The SH1Ni dispersion was cleaned by sedimentation in a table centrifuge at a speed of 3000 rpm. The results of elemental analysis are shown in Table 1. In ethanol, tetrahydrofuran, and chloroform the particles form stable dispersions without observable aggregation or settling of aggregates.

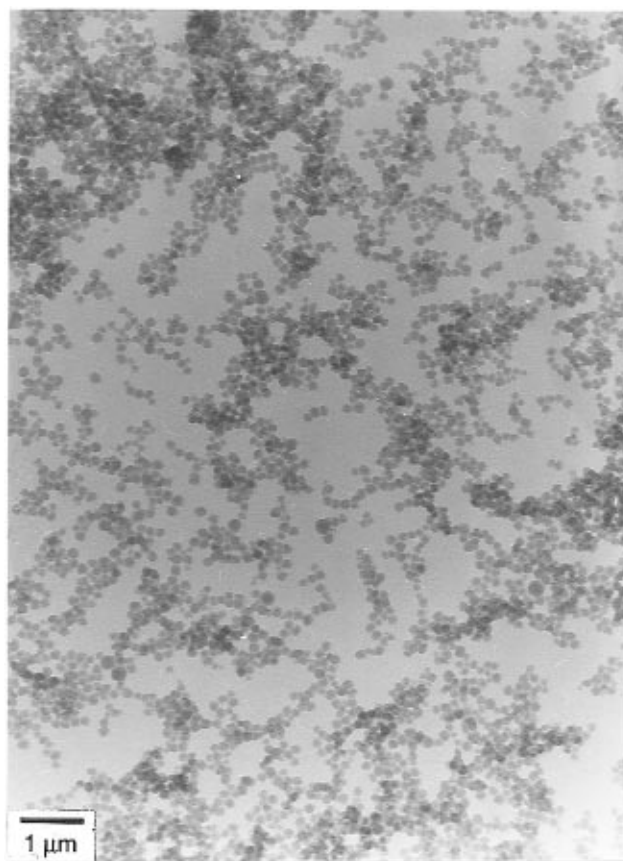


Figure 1. Transmission electron micrograph of HS40Ni silica particles.

Table 1. Summary of Characterization Results of Silica Particles

	HS40Ni	SH1	SH1Ni	SH1Ni1
electron microscopy radius/nm	7.6		107.6	
hydrodynamic radius/nm		118.9	133.7	134.6
elemental analysis				
wt % C	5.04		4.25	
wt % H	1.06		1.20	
wt % N	1.03		0.45	0.45
wt % Ni	0.69		0.25	2.33
wt % Si	41.17		42.65	

An attempt was made to graft directly the nickel-complexed silane coupling agent **C** to the silica particle SH1 using the same procedure as described above for silane coupling agent **B** (Scheme 2). The resulting grafted particle-coded SH1Ni1 could be readily dispersed in ethanol, tetrahydrofuran, and chloroform.

The electron micrographs of HS40Ni and SH1Ni are shown in Figure 1 and Figure 2, respectively. The size of grafted particles is given in Table 1. The HS40Ni particles are partly aggregated due to sedimentation (sediments of small particles are difficult to redisperse), but the larger SH1 particles are almost without aggregates. The hydrodynamic radius of bare silica particles SH1 and the grafted particles (SH1Ni and SH1Ni1) is given in Table 1. The hydrodynamic radius determined with dynamic light scattering is larger than the radius determined from TEM. This difference is due to particle shrinkage in the electron microscope. The difference in hydrodynamic radius between grafted silica (SH1Ni, SH1Ni1) and SH1 is about 15 nm. This is probably due to multilayer formation of the silane coupling agent. Also any particle aggregates introduced by the grafting procedure will increase the size measured with light scattering.

3. Results and Discussion

3.0. Synthesis and Grafting Procedure. Scheme 1 summarizes the approach to synthesize coupling agent **C** designed for the grafting of Ni²⁺ ions to silica colloids. The NMR and IR results clearly confirm that this approach

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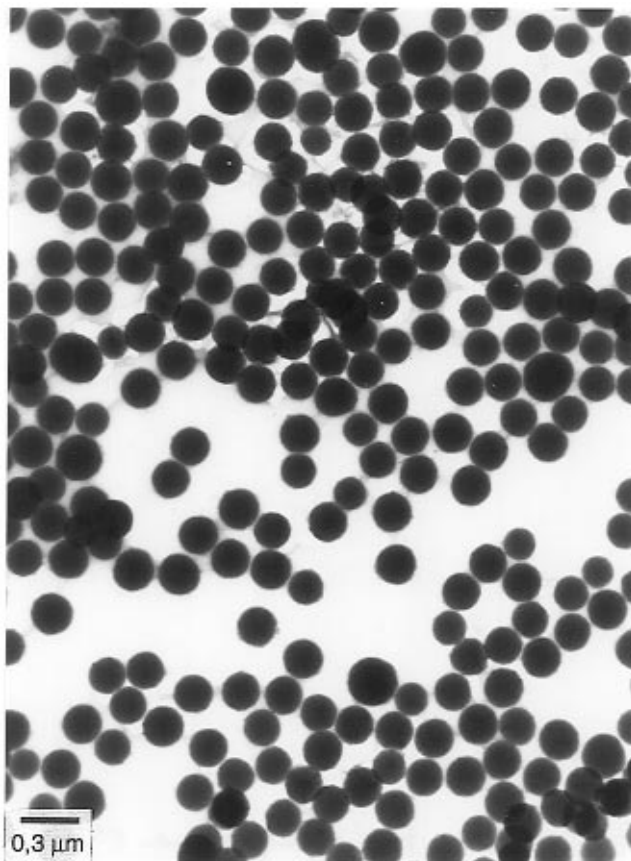


Figure 2. Transmission electron micrograph of SH1Ni silica particles.

yields the desired coupling agent. The grafting reaction itself comprises condensation of the (hydrolyzed) ethoxy groups of compound **C** (or **B**) with the silane surface silanol groups. The characterization results in the remainder of section 3 indeed show that a grafted layer is present on the silica colloids. (Note that any free coupling agent has been removed by the sedimentation procedures.) The grafting procedure works well for both commercial Ludox HS40 silica dispersions and silica spheres prepared by the Stöber method. Transfer of bare ungrafted silica particles from ethanol and/or water to triethyl phosphate and subsequent grafting does not lead to loss of colloidal stability, i.e., aggregation of particles. It should be noted that drying of particles, which favors formation of irreversible aggregates, is circumvented.

3.1. Elemental Analysis. The presence of nickel on the surface of grafted particles SH1Ni1 is clearly demonstrated by the XPS spectra (Figure 3). The characteristic nickel 2p peak in the XPS spectrum is observed only for SH1Ni1; for the other particles the concentration of nickel was apparently below the detection level. For the SH1Ni particles a characteristic nickel peak was detected with EDAX.

Elemental analysis (Table 1) confirms the presence of nickel in all samples. From these elemental analysis results, it is also found that the molar ratio of nickel of nitrogen is about 0.5 to 0.6. This indicates that the reaction of nickel with the coupling agent is not complete in the two-step grafting reaction to obtain HS40Ni and SH1Ni. In the two-step procedure during the reaction with the tetrakis(triphenylphosphine)nickel, nickel is probably only attached to silane coupling groups on the outer layer of the surface coating, and as a result the concentration of nickel is low. For the sample SH1Ni1, the nickel concentration is about five times that of

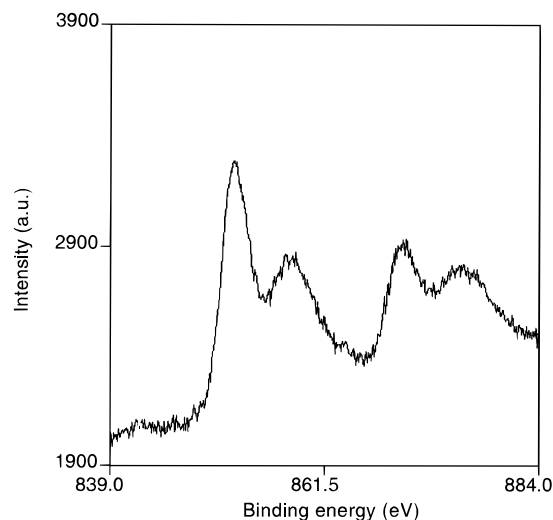


Figure 3. X-ray photoelectron spectra (XPS) of SH1Ni1 particles which confirm the presence of nickel because of its characteristic 2p peaks at 852.3 and 869.7 eV.

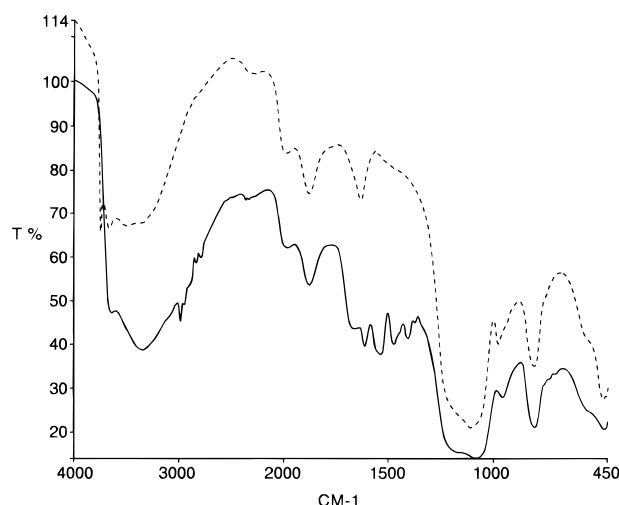


Figure 4. Diffuse reflectance infrared spectra showing that the coupling agent is grafted to silica: ---, HS40; dashed line, HS40Ni.

nitrogen. Since the σ -bonded complexed nickel is stable, it is not certain why the concentration is high. One possibility is that nickel ions covalently bonded to the coupling agent may have reacted with the acidic surface of silica.

3.2. FT-IR. Our hypothesis is that the nickel atoms which are σ -bonded and complexed by silane coupling agent **B** are, via this agent, covalently bonded to a silica particle. This is confirmed by the IR spectra for HS40Ni particles. The FT-IR spectra of samples HS40 and HS40Ni are displayed in Figure 4. Figure 5 shows the FT-IR spectrum of the silane coupling agent with nickel complex, **C**. In overlay of the FT-IR spectra the spectral differences can be recognized. The peak maximum observed and the assignment to specific organic functional groups are listed in Table 2. A decrease in the Si-O-H absorption peak at 3740 cm^{-1} indicates that the silane coupling agent has reacted with the surface OH groups of silica. In the region around 1550 cm^{-1} is the N-H bending vibration, which indicates the presence of N-H in the sample. The specific amide group absorptions, amide I, II, and III, in the region $1700\text{--}1200\text{ cm}^{-1}$ confirm the presence of a H-N-C-O unit. From analysis of the C-H stretching region it is clear that apart from aliphatic absorptions, $3000\text{--}2850\text{ cm}^{-1}$, also *N*-methyl groups are present at 2834 and 2789

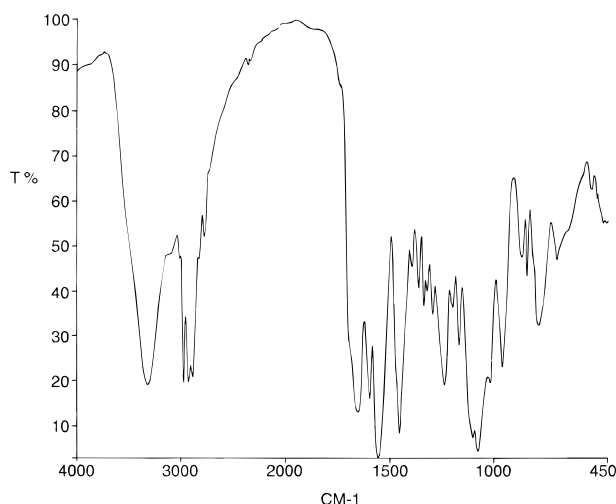


Figure 5. Infrared spectrum of silane coupling agent C.

Table 2. Assignment of the FT-IR Absorption Bands of HS40, HS40Ni, and Coupling Agent C

HS40 (DRIFT)	HS40Ni (DRIFT)	coupling agent C (Transmission)	assignment
3740		3317	$\nu(\text{Si}-\text{O}-\text{H})$
	3340		$\nu(\text{N}-\text{H})$
3700–3000		3500–3000	$\nu(\text{H}_2\text{O})$
		3014	$\nu(\text{CH sat.})$
	2980	2973	$\nu(\text{CH}_3 \text{ asy.})$
		2923	$\nu(\text{CH}_2 \text{ asy.})$
		2886	$\nu(\text{CH}_3 \text{ sym.})$
	2833	2828	$\nu(\text{N}-\text{CH}_3 \text{ asy.})$
	2788	2778	$\nu(\text{N}-\text{CH}_3 \text{ sym.})$
2360–2340	2360–2340	2360–2340	CO_2
1628		≈ 1650	$\delta(\text{H}_2\text{O})$
	1609	1651	amide I
	1533	1553	amide II
	1472	1453	$\delta(\text{CH})$
	1400	1391	$\delta(\text{CH})$
	1369		$\delta(\text{CH})$
	1270–1230	1235	amide III
1250–1000		1200–1000	$\nu(\text{Si}-\text{O})$

cm^{-1} . The bands at 1400 and 1369 cm^{-1} might be assigned to CH-bending vibrations. Evidence for the presence of an aromatic ring is observed in the out-of-plane bending region; small peaks are observed at 725 and 695 cm^{-1} . The absorption peaks in the region 1400–1670 cm^{-1} are possibly due to the NH and CH vibration modes.

3.3. Magnetic Measurements. The results of the explorative NMRD measurements (discussed more extensively elsewhere^{21b}) of the samples HS40 and HS40Ni are shown in Figure 6. The particles were dispersed in a mixture of 90% ethanol and 10% water (v/v). The concentration of silica particles was 1.1% (w/w). The NMRD measurements were performed at 4.0 °C in the 0.01–25 MHz Larmor frequency range. It was reported earlier that the overall proton magnetization decay of colloidal silica suspended in ethanol exhibits a biexponential decay function.²¹ In Figure 6 the relaxation times were obtained from a monoexponential least-squares fitting, which introduces some uncertainty in the obtained relaxation times. Despite this uncertainty the NMRD relaxation curves provide a qualitative indication for the presence of paramagnetic ions such as Ni^{2+} and Mn^{2+} . The total proton NMRD curve is the sum of a diamagnetic relaxation dispersion inflecting at low frequencies and a contribution due to the presence of paramagnetic ions.

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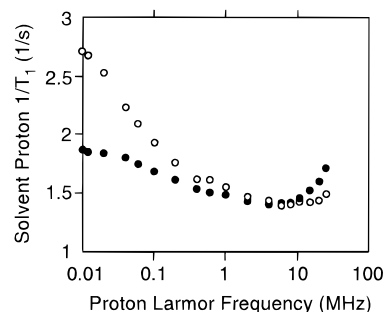


Figure 6. Proton NMRD curves of silicas HS40 (○) and HS40Ni (●), showing the solvent proton relaxation time as a function of Larmor frequency.

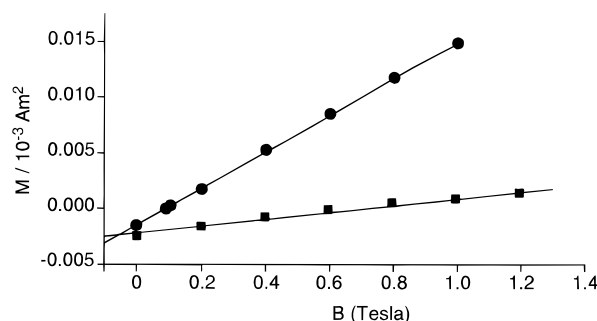


Figure 7. Magnetic moment versus magnetic field at 4 K for dried silica samples: HS40Ni (●) (0.0654 g) and SH1Ni (■) (0.0348 g).

From the low-frequency dispersions of Figure 6, it is inferred that the coated silica contributes to a larger extent to the proton relaxation than the uncoated sample. The increase of the relaxation rates ($1/T_1$) at high frequencies is typical for ions bound to a macromolecule.⁴ For the ungrafted sample HS40, this increase of the relaxation rates at high frequencies has been associated with the presence of trace amounts of Mn^{2+} as impurity.¹⁵ For the HS40Ni sample, this relaxation enhancement is attributed to the presence of the Ni^{2+} ions. The lower rate values near 10 MHz, compared to HS40, may indicate that the Mn^{2+} ions are shielded from the solvent by the silane coupling agent that is grafted to the core of the silica particle.

The results of magnetic moment measurements with the vibrating sample magnetometer for particles HS40Si and SH1Ni are shown in Figure 7 and Figure 8. The graph (Figure 8) of magnetic moment versus reciprocal temperature is a straight line as expected from eq 1. Also the plot of magnetic moment versus magnetic field at 4.3 K (Figure 7) is a straight line. From the slope of the line and the amount of nickel calculated from the amount of silica used for the measurements and the percentage of nickel obtained from the element analysis, the value of P_e was calculated using eq 1. The values of 2.69 and 2.72 obtained for HS40Ni and SH1Ni confirm the presence of two unpaired electrons in the quenched state based on eq 2.¹⁴

$$P_e = 2\{S(S+1)\}^{1/2} \quad (2)$$

From eq 2 P_e has a value of 2.83 for spin quantum number $S=1$. Figures 9 and 10 show the results of the magnetic

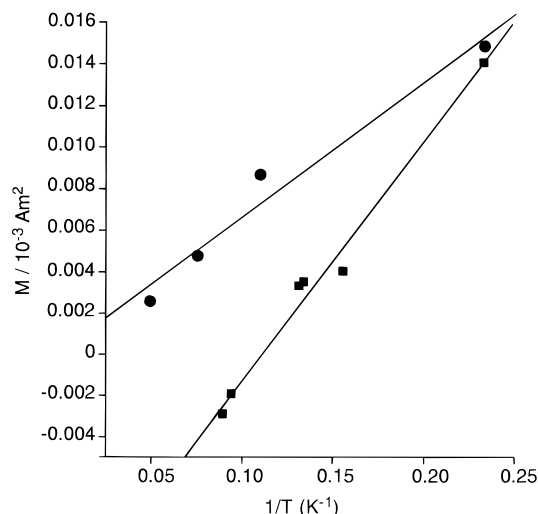


Figure 8. Magnetic moment versus inverse temperature at a magnetic field 1 T for dried silica samples HS40Ni (●) (0.0654 g) and SH1Ni (■) (0.0348 g).

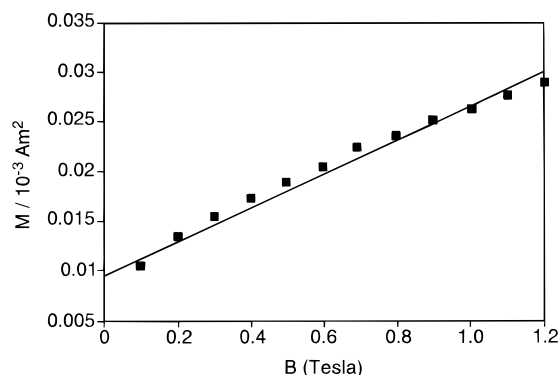


Figure 9. Magnetic moment versus magnetic field at 4 K for silica SH1Ni1 (0.03079 g).

moment measurements for sample SH1Ni1. Although we did not measure in the intermediate temperatures, nevertheless we performed a linear fit in Figure 10. The P_e value calculated from the experiment is 2.27, which is almost the theoretical value calculated for the quenched state. From previous studies on the organometallic Ni(II) aryl compounds, it is known that the square planar Ni^{2+} is diamagnetic.²² When Ni^{2+} was oxidized to Ni^{3+} state, it was reported²² that there was one unpaired electron resulting in paramagnetic properties. The value we obtain here for P_e corresponds to two unpaired electrons. The presence of a Ni^{2+} ion with a tetrahedral

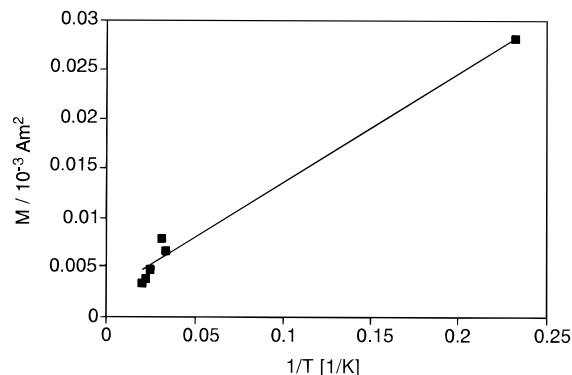


Figure 10. Magnetic moment versus inverse temperature at a magnetic field of 1.2 T for silica SH1Ni1 (0.03079 g).

or octahedral coordination sphere may account for the experimental observation of two unpaired electrons.²³

4. Conclusions

We have developed paramagnetic silica particles by the application of a silane coupling agent which is able to complex Ni^{2+} ions and can be grafted to silica particles. The grafted particles form stable dispersions in weakly polar solvents. For the Stöber silica particles (in this study with a radius of 100 nm), it is possible to prepare dispersions containing only minute amounts of aggregates. The preliminary NMRD dispersion and magnetization measurements indicate the usefulness of the paramagnetic silica for further studies as model systems. To avoid the influence of paramagnetic impurities such as Mn^{2+} , Stöber silica provides a more suitable core particle than commercial Ludox. It would be interesting to see whether the synthesis method presented in this article could be extended to ions such as Mn^{2+} and Fe^{3+} .

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