Synthesis of Nickel Nanoparticles. Influence of Aggregation Induced by Modification of Poly(vinylpyrrolidone) Chain Length on Their Magnetic Properties

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The physical properties of metal nanoparticles are attracting increasing interest, because they may differ significantly from the bulk properties as a result of surface or quantum size effects.[1] However, these properties are highly dependent on the size of the particles and the presence or not of interactions between their surface and ligands, contaminants or a support.[1] This therefore requires the need to control precisely the size distribution of the particles and their surface state. In this respect, the use of organometallic precursors has recently proven interesting since it leads to particles displaying a clean and controllable surface and, in some cases, an adjustable size.[2] For example, we have recently prepared 1.6 and 2 nm cobalt nanoparticles displaying a narrow size distribution[3] and demonstrated an enhancement of magnetization per cobalt atom[4] equal to that of particles of the same size measured in time of flight.[5] This is indicative of the absence of contamination of the particle surface since the oxidation or addition of ligands to the particles leads to a dramatic decrease of their magnetic properties.[3,6a] In contrast to cobalt, relatively few reports have been dealing with the synthesis and physical studies of nickel particles.[6,7] The particles are usually prepared by reduction methods or metal evaporation.[6] However, organometallic precursors such as $Ni(CO)_4$ and $Ni(Cp)_2$ have been used[7a] and a recent report by Bradley describes the synthesis and spectroscopic studies of nickel particles prepared by spontaneous decomposition of $Ni(COD)_2$ in CH_2Cl_2 in the presence of poly(vinylpyrrolidone).[7b] We have used the same precursor but decomposed it under H_2, a method previously successfully applied to prepare ruthenium particles from Ru(COD)(COT)[2a,2d] and cobalt particles from $Co(C_8H_{13})(COD)$,[3a] both displaying a clean surface state.

To prevent the particles from coalescing, polymers have been commonly used to sterically protect the particles.[2a] In the case of cobalt, it has furthermore been demonstrated that poly(vinylpyrrolidone) (PVP) would interact little with the surface of the particles and therefore would not modify the electronic and magnetic properties of the particles[3] which led us to choose this polymer in the case of nickel. Recently, much effort has been devoted to the organization of metal particles using various ligands[8] or an external constraint such as block copolymers[9] or mineral membranes for example.[10] However, no systematic study of the average molecular weight of the polymer and of its morphology in various

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solvents on the size, shape, and organization of the particles has to the best of our knowledge been reported.

We report in this communication the preparation of nickel particles of a clean surface state as deduced from magnetic studies and the influence of the polymer (PVP) molecular weight and conformation or flexibility in solvents on their aggregation.

Synthesis and Structural Characterization. The reaction of $Ni(COD)_2$ with H_2 (3 bar) in CH_2Cl_2 in the presence of poly(vinylpyrrolidone) (PVP) of medium molecular weight (K 30, $M = 40\,000$) leads rapidly at room temperature to a color change from yellow to black. Evaporation of the solvent leads to a black shiny powder (colloid **1**, 4 wt % Ni) which can be redissolved in CH_2Cl_2 or MeOH. Microanalysis and EDX studies indicate the absence of a significant amount of chlorine in the material and thus of possible contaminants such as $NiCl_2$[11] Bubbling CO into the solution leads to the observation of two bands at 2030 and 1915 cm^{-1}, corresponding respectively to terminal and bridging CO ligands coordinated to the surface of zerovalent nickel colloids as previously attributed.[10] A wide-angle X-ray scattering experiment (WAXS) evidences the presence of fcc particles displaying the same lattice parameters as bulk nickel and a coherence length larger than 3 nm. The high-resolution electron microscopy (HREM) images obtained after deposition onto a carbon grid of a drop of a CH_2Cl_2 solution of colloid **1** are, however, extremely surprising. They reveal the presence of regular agglomerates of size centered near 20−30 nm which form a monolayer on the carbon grid surface or, for more dilute preparations, which arrange into wires or rings as a result of magnetic interactions between agglomerates. Examples of such arrangements are shown on Figure 1. These agglomerates are composed of individual nickel nanoparticles of sizes centered near 3−4 nm as can be seen on a higher magnification of one agglomerate.

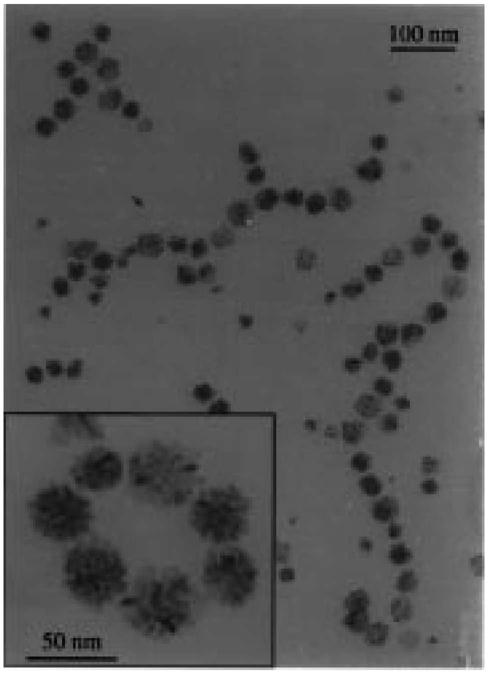

Figure 1. HREM micrograph of colloid **1** showing agglomerates of ≈30 nm displaying some superstructures.

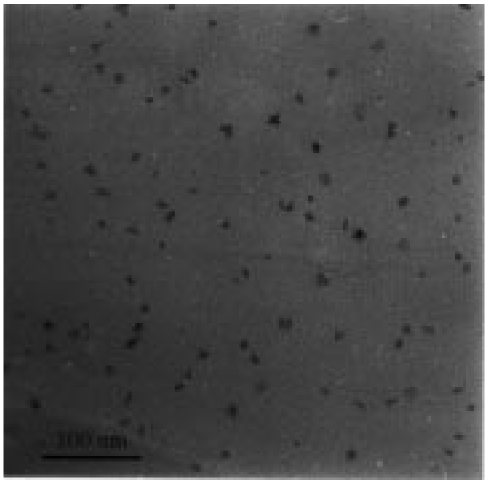

Figure 2. HREM micrograph of colloid **2**.

The existence of these regular agglomerates is puzzling. To find out their origin, we studied the influence of the polymer chain length and of the solvent. Using a lower molecular weight poly(vinylpyrrolidone) (K 15, $M = 10\,000$), the same result was obtained (i.e., nickel particles encapsulated into agglomerates of regular size centered near 20−30 nm). However, when the decomposition reaction was carried out in the same conditions as described here above but using PVP of a higher molecular weight (K 90, $M = 360\,000$), a similar black solution formed from which black films, soluble in CH_2Cl_2 and MeOH, could be obtained upon evaporation to dryness (colloid **2**, 3.7 wt % Ni). As for colloid **1**, this material adopts a fcc structure (WAXS experiments) and does not contain any significant amount of chlorine,[11] and bubbling CO into a solution of colloid **2** leads to the observation of two bands at 2030 and 1915 cm^{-1} corresponding to CO coordinated to zerovalent nickel. The high-resolution electron micrographs are, however, very different. They show well-dispersed crystalline (fcc) particles of mean size centered near 4 nm and displaying a relatively broad size distribution (see Figure 2). At high magnification, it is possible to demonstrate that these particles consist of mono- or polycrystals and are in some cases agglomerated.

When $Ni(COD)_2$ is decomposed by H_2 (3 bar) in anisole in the presence of low-molecular-weight PVP (K 30), a black shiny powder is again obtained after solvent evaporation (colloid **3**, 4 wt % Ni). Separate fcc particles of a relatively broad size dispersity centered near 4−5 nm and of morphology similar to that of colloid **2** are visible by HREM analysis together with the presence of some small agglomerates (size ≈10 nm).

The three reactions described here above were found reproducible.

Magnetic Studies. Magnetic studies were carried out on dried colloid samples, prepared in an argon

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(11) EDX: no Cl found. Microanalysis of colloid **1**, Cl = 0.37%, and colloid **2**, Cl = 0.19%. The chlorine observed in microanalysis might correspond to residual CH_2Cl_2 which is observed by ^1H NMR on the very samples sent to microanalysis and which could be evaporated in the high-vacuum conditions of the EDX experiments. The presence of significant amounts of paramagnetic impurities such as $NiCl_2$ is also ruled out by the observation of saturation of the magnetization for an applied field of 5 T.

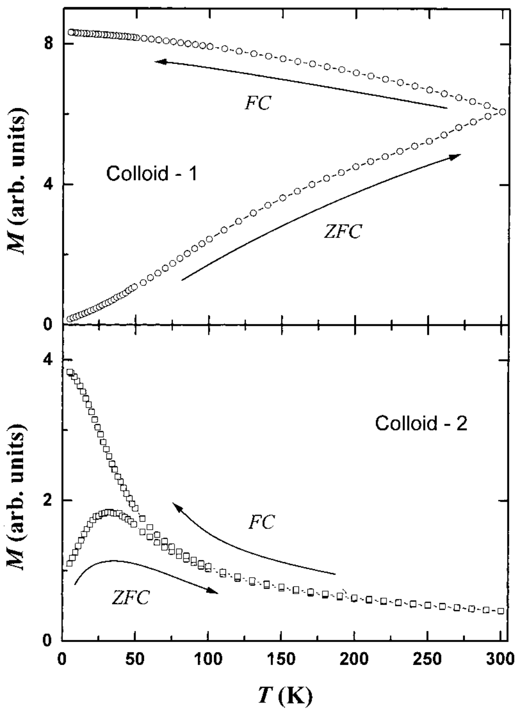

Figure 3. ZFC and FC magnetization versus temperature curves for colloids **1** (top) and **2** (bottom).

drybox to preserve from any uncontrolled oxidation, using a MPMS 5.5 Quantum Design (with a SQUID detector).[3] For each sample, hysteresis loops in fields up to 5 T and susceptibility in a field of 10^{-3} T according to the zero field cooling and field cooling processes (ZFC−FC) were measured for temperatures between 5 and 300 K. For all the samples, magnetization loops measured at 5 K present a hysteretic behavior and nearly saturate in a field of 5 T. The average magnetic moment per Ni atom determined at 5 K in a field of 5 T are found to be 0.62, 0.57, and 0.51($\pm$0.05)μ_B for colloids **1**, **2**, and **3** respectively. These values are in good agreement with those known for bulk nickel (0.606μ_B),[12] indicating the metallic character of these particles. Magnetization loops measured at 5 K after a field cooling at 5 T from 300 K give the same results. The lower magnetic moment per Ni atom determined for colloid **3** could result from partial oxidation or, more likely, from anisole coordination.[3]

Two different magnetic behaviors are observed on the susceptibilities and hysteresis loops versus temperature. Both colloids **2** and **3** display a superparamagnetic behavior above the blocking temperature (T_B) 32 and 30 K respectively, as expected for isolated nanoparticles (see Figure 3 for colloid **2**), the significant differences between the ZFC and FC susceptibilities up to 150 and 100 K for colloids **2** and **3**, respectively, evidencing a broadened size distribution. Indeed, the ZFC susceptibility increases with temperature as the volume fraction of particles which are blocked decreases, and then decreases according to a Curie law when the majority of the particles is superparamagnetic. In the FC process, as the temperature is reduced, the magnetic moment of each particle is blocked along the field leading to a continuous increase of the FC susceptibility. On the other hand, hysteresis loops of colloid **1** versus temperature remain hysterestic even at 300 K, and no blocking temperature in the ZFC−FC susceptibilities is observed below 300 K, hence revealing a ferromagnetic behavior (see Figure 3).[13] The majority of the particles are thus still blocked at room temperature. Dipolar magnetic interactions between the particles inside the agglomerates of colloid **1** could give rise to a ferromagnetic behavior in each agglomerate with a blocking temperature which rapidly increases with the size of the agglomerates.[14] These behaviors are in agreement with the particle dispersion in the polymer of each sample observed by HRTEM.

Discussion. This study first demonstrates the importance of using organometallic precursors for the synthesis of magnetic particles displaying a clean surface. In the present case well-dispersed superparamagnetic or agglomerated nickel particles can be easily prepared. The absence of contamination at the surface of **1** and **2** is visible in the present case through the IR spectrum displaying bands typical for zerovalent nickel and through the calculation of the magnetic moment per nickel atom which is similar to that observed for bulk nickel. This result is remarkable since the magnetic properties of nickel collapse with the presence of surface contaminants (oxides, ligands, etc.).[6a,15,16]

The most interesting result is, however, the demonstration of the modification of the magnetic properties of these particles induced by the agglomeration state which depends on the PVP chain length and the nature of the solvent (CH_2Cl_2 or anisole). The effect of the polymer molecular weight on the morphology of the sols can tentatively be rationalized. A chain of the high-molecular-weight polymer (PVP K 90) will interact with other chains and unable to condense on itself whereas for the low-molecular-weight polymers (PVP K 30 or K 15), the metal particles in strong magnetic interactions may be wrapped by the polymer chains. In the case of colloid **1**, the effect of this process is the formation of ≈30 nm spherical agglomerates displaying a ferromagnetic behavior. The individual particles of **1** trapped inside the agglomerates are similar to or smaller than those of **2** and **3** but the ferromagnetic behavior of colloid **1**, instead of the expected superparamagnetism, results from dipolar couplings between the particles inside the agglomerates as discussed in the preceding section. It is interesting to mention the air stability of colloid **1** which probably results from the perfect coating of the particles by the polymer. Finally, the formation of these agglomerates does not occur when the reaction is carried out in anisole which demonstrates the importance of the polymer conformation or flexibility in solution. It is noteworthy that with the same polymer chain length (K 30) well-separated superparamagnetic cobalt par-

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(13) The coercive field collapses with increasing temperature according to $B_c(T) = B_c(0)[1 - (T/T_B)^{2/3}]$ allowing us to extrapolate a blocking temperature $T_B \cong 325$ K.; see Pfeiffer, H. *Phys. Stat. Solid. (A)* **1990**, *122*, 377.

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ticles are obtained in THF. Our results therefore suggest that novel magnetic materials may be accessible in a simple way by choosing the right combination of solvent, polymer, and chain length. Preliminary results show that deposition of the agglomerates leads essentially to a monolayer.

In summary, the material here called colloid **1** is composed of individual spheres of regular size which are soluble in organic solvents, air-stable, which display a ferromagnetic behavior and which can be deposited as a monolayer. This is a potentially very interesting magnetic material, the properties of which are further studied in our group.

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