Chemical Synthesis of Magnetic Metal Nanoparticles

Bruno Chaudret

Laboratoire de Chimie de Coordination CNRS, 205, route de Narbonne, 31077 Toulouse Cédex 04, France.

TEL. : 33 (0)5 61 33 31 81 FAX : 33 (0)5 61 55 30 03. E-Mail : chaudret@lcc-toulouse.fr

The recent period has evidenced an ever increasing interest for chemical species of nanometric size.[1] This size corresponds to proteins, to organic macromolecules such as polymers or dendrimers or to relatively small molecules which self-organize into different sorts of objects such as micelles or vesicles. Inorganic molecular clusters[2] may also reach this size and display interesting physical properties[3]. Compared to this new approach of nanometric compounds, the inorganic particles in solution (colloids) may appear as outdated species. In fact, coloured solutions of noble metal, essentially gold, have been known for ages and the first rational synthesis of gold colloids has been described by Faraday in 1857.[4] Many methods to produce in solution particles of either pure metal or metal oxides, and more generally chalcogenides have been reported in the literature since then.[1] These species have recently attracted a renewed interest, mainly because of their real or expected physical properties resulting from their "quantum size". This concerns the fields of optics, electronics and magnetism.[5] This renewed interest in the properties of these objects has evidenced the need for the control of the particles monodispersity, of their size, their shape, their organization and the nature of the chemical species present at their surface. In this respect, the well-known reduction methods[6] display limitations due to their lack of variability. The use of reverse micelles as "nanoreactors" inside which salt reduction and particle growth occurs has allowed to obtain monodisperse nano-objects which may display a define shape (spheres,

rods, wires, ...) and which may self-assemble on various substrates.[7] In these processes, salt and water are always in contact with the surface of the particles thus passivating them, modifying their reactivity and, in some cases, leading to the production of oxides or hydroxides. The use of an organometallic precursor, able to decompose in mild conditions either spontaneously or in the presence of a reducing gas has appeared as a valuable alternative for the synthesis of nano-sized objects. Organometallic compounds have been used as material precursors in high temperature decomposition processes, for example in chemical vapour deposition.[8] They have also been deposited onto inorganic support to produce heterogeneous catalysts.[9] For example, metal carbonyls have been widely used as precursors of metals either in the gas phase (OMCVD for the deposition of films or nanoparticles) or in solution for the synthesis after thermal treatment,[10] UV irradiation or sonolysis[11, 12] of fine powders or metal nanoparticles. However, in order to be able to obtain a better control of the size and size distribution of the particles as well as to obtain clean surfaces for undertaking a reproducible chemistry, we have developed an approach based on the use of organometallic precursors able to decompose in mild conditions, generally using a reducing gas (scheme 1) [13-35]. The ideal precursor is an organometallic complex containing ligands, preferentially olefinic or polyolefinic, able either to be hydrogenated to give a bare metal atom which would condense in the reaction medium or to be substituted by CO to give an unstable intermediate. The second approach, using CO, had a few precedents[36] at the time we started this research whereas the first one, using a hydrogenation reaction, had none.

We will hereafter briefly review hereafter some preparation methods of magnetic metal nanoparticles.

I- Synthesis of Nanoparticles through reduction of metal salts

Reduction of transition metal salts is the oldest, easiest and still a widely used method for the preparation of metal nanoparticles. As far as magnetic metals are concerned, the most common reducing agents are borohydride derivatives, extensively studied by Klabunde et al. this method provides an easy route to nanoparticles of Fe, Co and Ni as well as to alloys such as Fe/Pd. The drawback of the method is however the incorporation of boron into the particles which leads to a modification of the magnetic properties of the particles. Cobalt particles were for example prepared with the microemulsion method in the binary system of DDAB (didodecyldimethylammonium bromide)/toluene by reduction of $CoCl_2$ with $NaBH_4$. The average particle size of the as-prepared samples could be varied from 1.8 to 4.4 nm by controlling the concentration of $CoCl_2$ in the soln. of DDAB in toluene. TEM studies showed that the particles were quite uniform and well isolated. The particle sizes determined from magnetic data were consistent with those measured by TEM. The coercivity of the particles at 10 K increased from 640 to 1250 Oe as particle size increased from 1.8 to 4.4 nm. The blocking temp. of the particles increased from 19 to 50 K for the same size range. The saturation magnetization at 2 K increased with decreasing particle size and reached a value of approximately 200 emu/g, 20% higher than the bulk value, for particles with average size of 1.8 nm, hence implying an enhancement of the magnetic moment per atom in the nanoparticle system.[37-39] Increasing the temperature led to the formation of clusters which display a higher blocking temperature.[40] A similar method could be used for the preparation of iron particles protected from oxidation by a passivating fluoride layer.[41] Fe/Co[42,43] and Fe/Pd[44] alloys were also obtained. Some of these particles gave rise to physical studies[44].

Bönnemann has developed a reduction method derived from the preceding one but involving alkyl ammonium borohydrides as both reducing agents and stabilizers for the growing particles.[45-47]

Pileni has synthesized cobalt nanoparticles through reduction of $CoCl_2$ by $NaBH_4$ in the presence of sodium [bis(2ethylhexyl)sulfosuccinate] (AOT). The particles spontaneously self-assemble into 2D super-structures[48] and can be processed into 3D super-lattices.[49,50]

II- Synthesis of Nanoparticles from Carbonyl Metal Complexes

Metal carbonyls are commercially available and easily handled precursors which have been used for a long time for the preparation of magnetic colloids of cobalt and iron and for the preparation of supported catalysts through various procedures.

One of the latest methods, sonolysis, has been developed by Suslick to decompose carbonyl metal complexes into nano-powders, nanostructured materials and nanoparticles in solution[51]. For example, superparamagnetic iron nanoparticles stabilized by PVP or oleic acid were obtained upon sonochemical decomposition of $Fe(CO)_5$[52]. Sonolysis was also used in our group to prepare iron nanoparticles stabilized by polydimethylphenylene oxide (PPO). The particles were found superparamagnetic and to adopt depending on their size the α (bcc) or the γ (fcc) structure.[12] It is however difficult with this method to control te particles size and impossible to control their shape.

A renewed interest for the use of such precursors has recently appeared with the search for self-assembled ferromagnetic nanomaterials usable in applications such as high density information storage. For this purpose, a number of groups have adapted procedures and reaction media previously used for the synthesis of III-V or II-VI quantum dots. Thermolysis of $Co_2(CO)_8$ in solution, in the presence of trioctyl phosphine oxide leads to cobalt nanoparticles adopting a new ε-cobalt phase.[53] Rapid thermolysis at high temperature (181 °C) of the same precursor in the presence of various organic molecules containing long alkyl chains and able to act as surfactants or ligands such as oleic acid, trioctyl phosphonic acid or TOPO allows the production of monodisperse spherical nanocrystals in the 3-17 nm range

adopting the same ε-cobalt[54]. When a mixture of surfactants/ligands is employed, namely oleic acid and TOPO, anisotropic nano-objects, initially thought to be nanorods form[55]. They were shown to consist of ferromagnetic nanodisks which self-assemble in 1 dimension.[56] Cobalt nanoparticles prepared in a very similar way from $Co_2(CO)_8$, oleic acid and trioctylphosphine in refluxing dioctylether were shown to be highly active catalysts for the Pauson-Khand reaction. Furthermore, the colloidal catalyst could be recycled five times without loss of activity.[57]

Thermolysis reactions can also be carried out in a block copolymer, PS_{25300}-*b*-MMA_{25900}, hence producing cobalt nanoparticles embedded in the poly(methylmetacrylate) block.[58]

Similarly, the decomposition of $Fe(CO)_5$ by thermolysis produces metal nanoparticles, the size and shape of which may be controlled by the surrounding medium. For example, a fairly complex procedure was employed for the fabrication of nanorods. Small iron nanospoheres are first prepared by thermolysis of $Fe(CO)_5$ in the presence of TOPO. Addition of this solution to excess $Fe(CO)_5$ in trioctylphosphine (TOP) at 320°C leads to the production of nanorods.[59]

This procedure has recently been extended to the preparation of bi- and even trimetallic nanoparticles. Thus, nanoparticles of FePt were synthesized through reduction of $Pt(acac)_2$ in the presence of 1,2 hexadecanediol, followed by addition of $Fe(CO)_5$ in the presence of oleic acid and oleic amine and reflux at 297°C. Exchange of ligands was performed on the as synthesized product to give nanocrystal super-lattices, which, after annealing at 560°C transformed into ferromagnetic nanocrystal assemblies on which recording studies could be carried out.[60] Similarly, colloidal $CoPt_3$ nanoparticles were prepared from $Co_2(CO)_8$ and $Pt(acac)_2$. The control of the reaction conditions allows the particles mean size to be varied from 1.5 to 7.2 nm. Alloy type and core-shell Co-Pt nanoparticles were obtained respectively upon mixing $Co_2(CO)_8$ and $Pt(hfacac)_2$ or upon decomposing first the cobalt precursor and

adding the nanoparticles to the platinum complex.[61] Finally Fe-Co-Pt nanoparticles were obtained from a procedure similar to that used for the synthesis of Fe-Pt nanoparticles but upon mixing an aditionnal cobalt precursor. Several compositions were obtained and the particles were shown to self-assemble upon removal of the solvent.[62]

III- Synthesis of Magnetic Metal Nanoparticles from Hydrocarbyl Complexes

Another organometallic approach has been developed in parallel for the past 10 years. It takes profit of the intrinsic reactivity of the metal complexes towards ligand displacement or ligand reduction. In this case, the reactions may take place in very mild conditions (room temperature or below) and a rigorous control of the surface species may be achieved. The ideal precursor is an organometallic complex containing an olefinic or polyolefinic ligand able to be hydrogenated to give a bare metal atom which would condense in the reaction medium. Prototypes of such complexes are $Co(C_8H_{13})(C_8H_{12})$ and $Ni(C_8H_{12})_2$ which decompose satisfactorily under dihydrogen in mild conditions.

Thus, $Co(C_8H_{13})(C_8H_{12})$ readily decomposes at room temperature in solution in the presence of a low pressure (generally 3 bars) of dihydrogen. When using PVP as a stabilizer, nanoparticles of 1.6 or 2.0 nm mean size were obtained as a function of the precursor concentration whereas with PPO larger particles (4 nm) form. The particles of small size (1.6 or 2 nm) adopt a non-periodic polytetrahedral structure whereas the larger ones (4 nm) adopt the hcp structure of bulk cobalt.[22]

Interestingly, and somewhat surprisingly, these particles were demonstrated to display the same magnetic properties as particles of same size prepared in ultra high vacuum in the gas phase by time-of-flight experiments.[14] Thus the particles are superparamagnetic with blocking temperatures near 10 K and display an enhanced magnetization at saturation per cobalt atom compared to bulk cobalt. Addition of O_2, pyridine, isocyanides or CO lead to a dramatic

decrease of the magnetic properties of the particles. This demonstrates i) the absence or low contamination of the as prepared particles and ii) the presence of a relation between the π-accepting properties of the ligand and the magnetic properties of the nanomaterials.

Nickel particles can be prepared in the same way from $Ni(C_8H_{12})_2$. They display a larger size (4-5 nm) and adopt the fcc structure of bulk nickel. These particles display the same magnetic properties as bulk nickel. Coordination studies at their surface confirm the strong magnetization decrease in the presence of CO but also demonstrate that coordination of a pure σ-donor such as amines has no effect on the magnetic properties of the particles.[63]

This synthetic method can also be adapted to the preparation of bimetallic nanoparticles. Thus Co-Ru, Co-Rh[32, 64] and Co-Pt particles[23] of various compositions have been prepared by co-decomposition of $Co(C_8H_{13})(C_8H_{12})$ with $Pt(dba)_2$, $Rh(acac)(C_8H_{12})$ or $Ru(C_8H_{10})(C_8H_{12})$. As a general rule, nanoparticles of size found between 1.5 and 2.5 nm were found whatever the metals and the compositions. Platinum metals rich nanoparticles adopt the structure of the corresponding metal, namely fcc, fcc and hcp whereas cobalt rich particles adopt the polytetrahedral structure of cobalt.[23, 64] For intermediate compositions, as yet unknown non-periodic structures are observed. The bimetallic nanoparticles display an enhanced coercivity as compared to cobalt in agreement with an enhanced anisotropy as also observed in bulk alloys.

The stabilization of magnetic nanoparticles can also be achieved by ligands. The decomposition of $Co(C_8H_{13})(C_8H_{12})$ in the presence of long chain acid and/or amine ligands yields nanoparticles of controllable size, shape and therefore magnetic properties. Thus, decomposition of $Co(C_8H_{13})(C_8H_{12})$ in the presence of a mixture of oleic amine and oleic acid affords at room temperature spherical nanoparticles of ca. 4 nm mean size. However at 150°C in the presence of dihydrogen, these particles convert into regular nanorods.[31] Changing the length of the hydrocarbyl chain of the amine surprisingly allows the control of the aspect ratio

of the rods from ca. 1.5 for octylamine to ca. 25 for hexadecylamine. Upon changing the shape and the aspect ratio of the nanoparticles, it is also possible to control the magnetic properties of the nano-objects from superparamagnetic to ferromagnetic at room temperature. In the presence of oleic acid only, very regular spherical nanoparticles are produced which form super-lattices in 2 or 3 dimensions upon deposition over a carbon grid[65] whereas a 2:1 mixture of oleic acid and oleyl amine leads to the formation of very long Co nanowires of 4 nm mean diameter and exhibiting the same hcp structure as the nanorods and bulk cobalt. These nanowires were demonstrated by magnetic holography to be monodomain. It has recently been possible using the electron holography technique to measure the magnetic properties of one such nanowire. [66] In all cases, the nano-objects display a magnetization at saturation per cobalt atom identical to that observed for bulk cobalt, hence demonstrating the absence of influence of pure σ-donor ligands such as amines and acids on their magnetic properties.

Similar reactions were carried out with nickel using $Ni(C_8H_{12})_2$ as a precursor but in the presence of amines only. It was found that the relative concentrations of amine and nickel is decisive as far as the aspect ratio of the particles is concerned. For a low concentration of amine spherical particles or double-arrow shaped particles were obtained whereas for 10 eq of amine relative to nickel very regular nanorods of ca 3 nm mean diameter were formed. Again, all these species display the same magnetization at saturation as bulk nickel. This contrasts with particles produced in the presence of TOPO (trioctyl phosphine oxide) as ligands which display a reduced magnetization which we attribute to the π-accepting properties of the ligand.[24]

Conclusion

In summary, chemical methods, and in particular methods derived from organometallic

chemistry may nowadays allow the synthesis of metal nanoparticles displaying physical properties identical or close to particles prepared by physical methods, e.g. in UHV. The nanoparticles can be assembled in ordered or disordered nanomaterials. In selected cases extended arrays of nanoparticles crystallized in 2 or 3 dimensions have been obtained. We have also reported the first 2D crystallization of cobalt nanorods identical in both length and diameter which could be usable in magnetic recording. These chemical methods are high yield, easily accessible and likely to experience a large development in the future to provide materials for research and applications ion physics.

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