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Directing oxidation of cobalt nanoparticles with the capping ligand

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ABSTRACT

The oxidation of Co nanoparticles stabilized with various ligands has been studied in an autoclave. Tridodecylamine stabilized Co nanoparticles with different sizes (8 nm, 22 nm and 36 nm) were prepared by thermal decomposition of $Co_2(CO)_8$ in dodecane. The oxidation of the particles was studied by introducing oxygen into the autoclave and following the oxygen consumption with a pressure meter. Tridodecylamine capped particles were initially oxidized at a high rate, however, the oxidation layer quickly inhibited further oxidation. The thickness of the oxide layer estimated from the oxygen consumption was 0.8 nm for all three particle sizes showing that the oxidation is size independent in the studied particle size range. The tridodecylamine ligand was exchanged for various long chain carboxylic acids and the oxidation was studied. While the carboxylic acids give a slower initial oxidation rate, the formed oxide layer does not inhibit further oxidation as effectively as in the case of tridodecylamine. TEM studies show that tridodecylamine capping leads to particles with a metal core surrounded by an oxide layer, while particles capped with long chain carboxylic acids form hollow cobalt oxide shells.

1. Introduction

There are three elements which have ferromagnetic properties at room temperature: nickel, iron and cobalt [1]. Nanoparticles of these elements have attracted increasing interest among researchers of various fields due to their unique properties and possible applications in magnetic fluids, catalysis, biotechnology, magnetic resonance imaging (MRI) and data storage [2].

In the nanoscale the magnetic properties depend strongly on the size of the particles. Hence, monodisperse particles are desired when well defined magnetic properties are required [3]. The choice of synthesis method is critical since it determines size distribution, crystal structure and capping agents by interacting with the reactants already prior to nucleation [4]. Magnetic nanoparticles have been synthesized by many different types of methods. The most commonly used methods include synthesis in microemulsion [4,5], hot injection [6,7] and thermal decomposition of metal carbonyl compounds [8]. The influence of the capping ligands on the magnetic properties is not fully clarified yet [9].

In addition to control over magnetic properties, it is essential for many applications that the particles are stable over time. A major problem of transition metal particles is their high susceptibility towards oxidation. The magnetic properties may be drastically altered or completely lost when the nanoparticles are oxidized, e.g. Co nanoparticles are oxidized and lose their magnetic properties, when exposed to air [10]. There are numerous reports where oxidation has been observed, however, despite the importance of this matter only a few studies on the oxidation kinetics of nanoparticles have been carried out. Karmhag et al. [11] studied the oxidation of 10–150 nm nickel nanoparticles at 300–500 K using thermogravimetry. Linderoth et al. [12] studied the oxidation of 5 nm α-iron particles with Mössbauer spectroscopy. When the iron particles were exposed to air at room temperature, it was shown that the oxidation of the outer 1–2 nm layer proceeded very rapidly and further oxidation proceeded very slowly. The oxidation of the metallic iron particles seemed to follow the Cabrera–Mott model [12,13]. Chernavskii et al. [14] used magnetometry to study the initial stages of oxidation of cobalt particles supported at a carbon support. The particle size and width of the distribution varied with cobalt loading in the 1–20 nm range. Nakamura et al. [15] studied the oxidation of carbon supported Al, Cu, Zn and Pb particles with sizes varying between a few and 50 nm using transmission electron microscopy. One main conclusion was that the Cabrera–Mott model was operative for Al and Zn. The results were, however, complicated by the Kirkendal effect that leads to hollow particles.

In the Cabrera–Mott model it is assumed that electrons can rapidly tunnel through the oxide layer to ionize the oxygen at the outer surface. This ionization process creates a strong electric field across the oxide film. The electrical field drives the outward diffusion of the iron cation [16–18]. The rate limiting step is assumed to be the transport of ions through the film. The Cabrera–Mott model predicts that the oxidation is initially very fast but slows down significantly as the oxide layer grows thicker. The model is frequently applied to oxidation of metals, e.g. iron. According to an estimate made with the Cabrera–Mott model at room temperature, the

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formation of an oxide layer with thickness of 1 nm on an iron surface takes approximately 0.2 fs, 2 nm 40 s, 3 nm 40 weeks and 4 nm 600 years [12].

In the original derivation the macroscopic sample covered by a flat interface was considered. Zhdanov and Kasemo [19] modified the model to account for the high curvature characteristic for nanoparticles. The main conclusion of their work is that the oxidation rate should increase with decreasing size.

In this work, different sizes of Co nanoparticles were synthesized by decomposition of $Co_2(CO)_8$ at high temperature induced by a sudden drop of carbon monoxide pressure [20,21]. The particle size was adjusted to 8, 22, and 36 nm by adjusting the decomposition pressure. The particles have a multicrystalline core with fcc structure. After synthesis oxygen was introduced into the reactor and the consumption of oxygen was followed using a pressure meter. Ligand exchange of the tridodecylamine to various long chain carboxylic acids was also carried out prior to oxidation. The studied carboxylic acids were oleic acid and lauric acid. After ligand exchange the oxidation of the particles was studied. The comparison of particles capped by various ligands relies on the high reproducibility of the particle synthesis obtained for 8 nm particles.

Following oxidation by measuring oxygen consumption has the advantage that the measurements can be done in situ and at short time scales. The technique is also independent of the formation of a crystalline layer. Many other techniques, for example XRD, are difficult to implement directly in the reactor and require long times for data collection.

2. Materials and methods

2.1. Materials

Dicobaltoctacarbonyl ($Co_2(CO)_8$, 90–95%, Fluka), dodecane ($C_{12}H_{26}$, 98%, Fluka), tridodecylamine ($C_{36}H_{75}N$, 85%, Fluka), dodecanoic acid ($C_{12}H_{24}O_2$, 99%, Sigma), oleic acid ($C_{18}H_{34}O_2$, extra pure, Merck), ethanol (C_2H_5OH, 99,5%, Altia), carbon monoxide (CO, 99%, AGA) and oxygen (O_2, 99%, AGA) were used without further purification.

2.2. Synthesis of Co nanoparticles

The Co nanoparticles were synthesized using thermal decomposition of $Co_2(CO)_8$ in dodecane and tridodecylamine as a stabilizing agent. The synthesis was prepared by adding 40 ml of dodecane and 7.12 ml (11.2 mmol) of tridodecylamine into the reactor (Parr Item 4560, 100 ml), see Fig. 1. The mixture was bubbled with CO and 2 g (5.8 mmol) of $Co_2(CO)_8$ was added into the autoclave. The reactor was closed and pressurized with CO to 63 bar. The reactor was heated to 170 °C at rate of 3 °C/min. When 170 °C was reached the pressure (90 bar) was dropped rapidly down to 1–3 bar range by opening the gas release valves (valves 5 and 6). The pressure drop was achieved in less than 3 s. The release valve (5) was kept open for about 30 s and then closed. The temperature was kept for 30 min at 170 °C and then heated to 200 °C at a rate of 1 °C/min. When 200 °C was reached, the heating was turned off. When the temperature had cooled down to about 160 °C, the remaining CO gas was released from the autoclave and N_2 was bubbled through the reactor until the temperature cooled down to 30 °C.

2.3. Ligand exchange

Ligand exchange reactions were performed directly in the autoclave after synthesis by adding the new ligand into the reactor and stirring for 20 h. The molar ratio between the new ligand and tridodecylamine used in the particle synthesis was approximately 0.05.

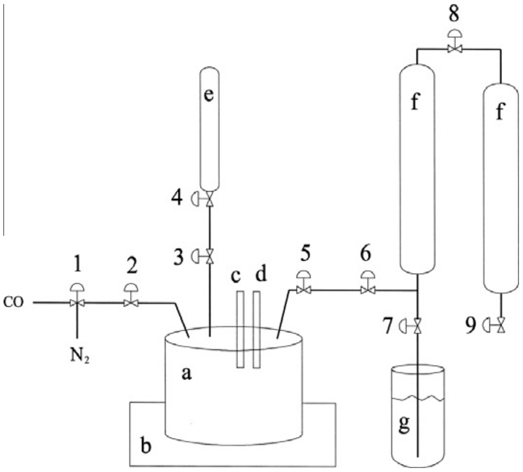

Fig. 1. The schematic of the autoclave system, which consists of: (a) the autoclave (100 ml, model Parr Item 4560), (b) heater, (c) temperature sensor, (d) pressure sensor, (e) burette of oxygen, (f) pressure releasing vessel (1 Gallon), and (g) bubbling vessel and 1–9 are valves.

2.4. Oxidation of Co nanoparticles

The oxidation of the Co nanoparticles was performed at a constant temperature of 30 °C by rapidly feeding oxygen into the autoclave until the pressure was approximately 5.5 bar after which the gas inlet valve was closed. The temperature and pressure of the system was recorded during oxidation and the amount of oxygen consumed was calculated assuming that the ideal gas law is applicable. All oxidation curves were corrected for dissolution of oxygen in the solvent system by subtracting blank experiments performed in absence of particles. This was important since a significant part of the apparent oxygen consumption stems from dissolution of oxygen.

The amount of cobalt was determined after oxidation by AAS using standard procedures. The volume ratio between cobalt and cobalt oxide after oxidation was calculated using the amount of oxygen consumed during the experiment yielding molar ratios between oxygen and cobalt. Additionally, the thickness of the oxide layers was estimated as a function of time. The densities used in the calculations were 8.8 g/cm^3 for cobalt and 6.4 g/cm^3 for CoO [22]. The volume ratio was calculated using the total amount of cobalt in the synthesis and the total amount of oxygen consumed during the experiments and does not consider the distribution of oxide.

2.5. Characterization

The sizes of the Co nanoparticles were examined by using transmission electron microscopy (TEM). The samples were prepared by placing drops of cobalt nanoparticle solution onto formvar/carbon-coated copper grids (Electron Microscopy Sciences, 400 meshes) and drying in air. The TEM measurements were done with a Tecnai 12 instrument operating at a 120 kV accelerating voltage. The size distributions were analysed by manually measuring particle diameters of approximately 150 particles for each sample.

The oxidation products were analyzed with XRD measurements performed with a Philips MPD 1880 diffractometer and Cu Kα radiation (λ = 0.15418 nm). The samples were prepared from the solutions by precipitating the nanoparticles with ethanol. The