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Nanostructures

Cobalt Nanocubes in Ionic Liquids: Synthesis and Properties**

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The magnetic, optical, and catalytic properties of soluble metal nanoparticles (MNPs) depend primarily on their size, shape, and type, and on the nature of the stabilizer.[1–6] The generation of MNPs of controlled size and shape has been achieved by using a variety of methods that are mainly based on the use of ligands.[7,8] Indeed, the vast majority of stable and soluble MNPs formed from transition metals have a ligand and/or oxide environment that has a substantial effect on the metal-surface properties of the nanoparticles.[7,9] The synthesis of stable, soluble, naked, and ligand-free MNPs of controlled size and shape still remains a challenge. Although these MNPs can be produced in organic solvents (e.g., alcohols or tetrahydrofuran) by the simple decomposition of organometallic precursors,[10] the properties of these nanoparticles cannot be investigated in solution because of their poor stability and the volatility of the solvents.[11] Since imidazolium ionic liquids (ILs) possess preorganized structures that can adapt or are adaptable to many species—as they provide hydrophobic or hydrophilic regions with high directionality—they are emerging as alternative liquid templates for the generation of a plethora of size- and shape-controlled nanostructures.[12–18] In particular, the size of "soluble" MNPs is apparently directly related to IL self-organization,[19] and can thus, in principle, be tuned by modulating the length of the *N*-alkyl imidazolium side chains,[20] reaction temperature,[21] anion volume,[22,23] or anion coordination ability.[24,25] Moreover, the advent of imidazolium ILs that possess very low vapor pressure[26,27] and high thermal stability has opened the way for the investigation of processes in solution using physical methods, for example, transmission electron microscopy (TEM)[28] and X-ray photoelectron spectroscopy,[29] which require special conditions such as high vacuum. We report herein that, with the proper combination of *N*-alkyl imidazolium side chain, anion, and reaction conditions, ligand-free cobalt MNPs with either cubic or spherical shapes can be prepared. Moreover, we present the magnetic and catalytic properties of these naked ligand-free MNPs in 1-alkyl-3-methylimidazolium ILs.

The in situ decomposition of $[Co_2(CO)_8]$ dispersed in 1-*n*-decyl-3-methylimidazolium *N*-bis(trifluoromethanesulfonyl)-imidate ([DMI][NTf$_2$]) at 150 °C over 1 h afforded a black solution containing $[Co^0]_n$ NPs with a cubic shape, together with MNPs with an irregular shape (Figure 1 and Figure S1 in the Supporting Information). These cobalt particles show a bimodal size distribution with a mean diameter of (79 ± 17) nm for the larger particles (cubic shape) and (11 ± 3) nm for the smaller particles (mainly spherical in shape; Figure 1). However, nanoparticles with an exclusively cubic shape ((53 ± 22) nm) were obtained by decomposition of $[Co_2(CO)_8]$ in 1-*n*-decyl-3-methylimidazolium trifluoro-tris-(pentafluoroethane) phosphate ([DMI][FAP]) after 5 min at 150 °C (Figure 2). Interestingly, MNPs with an irregular shape were obtained from reactions in 1-*n*-butyl-3-methylimidazolium (BMI) ILs associated with NTf_2^-, FAP^-, and BF_4^- ions under similar reaction conditions. Therefore, the formation of cubic-shaped cobalt MNPs is related to the IL self-organization that is, they are formed preferentially in the ILs that have more preorganized structures (with DMI^+ rather than BMI^+ and FAP^- rather than BF_4^- ions).[20,30] The cobalt MNPs were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) coupled with an electron dispersive spectroscopy (EDS) detector, and X-ray diffraction (XRD).

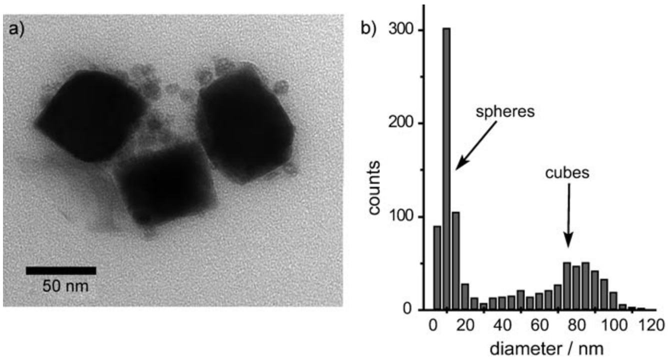

Figure 1. a) Selected TEM micrograph of the $[Co^0]_n$ particles prepared by decomposition of the $[Co_2(CO)_8]$ dispersed in [DMI][NTf$_2$] at 150 °C for 1 h and b) a histogram showing the size distribution.

The formation of the MNPs in ILs was followed by in situ TEM analysis of aliquots removed from the reaction mixture at different times (2, 5, 15, 40, 60, and 300 min). In the case of

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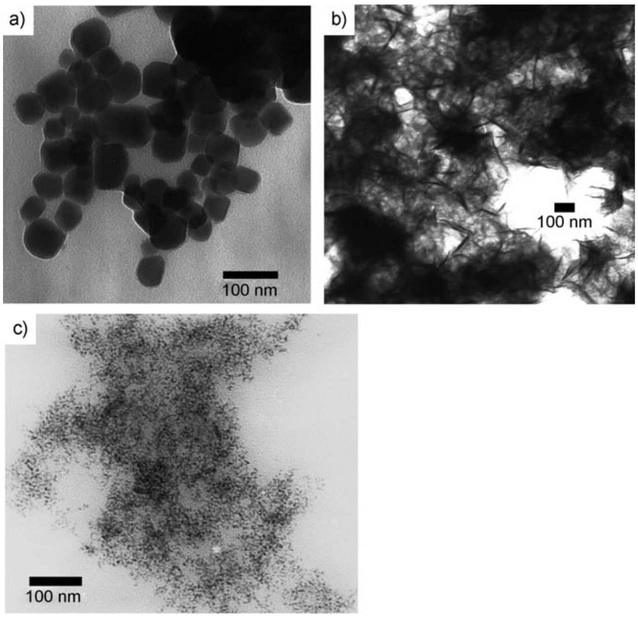

Figure 2. Selected TEM micrographs of the $[Co^0]_n$ particles prepared by decomposition of the $[Co_2(CO)_8]$ precursor dispersed in [DMI][FAP] at 150 °C after a) 5 min ((53 ± 22) nm), b) 15 min, and c) 300 min ((5.5 ± 1.1) nm).

the IL [DMI][NTf_2], both large cubic and small spherical particles were observed in all samples, except for the aliquot taken after 2 min, in which only irregular spherical particles were detected together with the organometallic cobalt precursor. TEM pictures of $[Co^0]_n$ NPs show that the mean diameter of the cubes decreases with longer reaction times (from about 88 nm at 15 min to 61 nm after 5 h), and the percentage of spherically shaped particles increases from about 25 % at the beginning of the decomposition to about 90 % after 5 h (see Figure S2 in the Supporting Information). These results indicate that the large cubic particles are gradually transformed into small spherical particles throughout the reaction.[31] Indeed, the cubic-shaped NPs obtained in [DMI][FAP] are completely transformed into irregular NPs ((5.5 ± 1.1) nm) after 5 h at 150 °C (Figure 2).

In addition, the reaction was also followed by XRD analysis of the $[Co^0]_n$ NPs embedded in the IL [DMI][NTf_2] (Figure 3). Only peaks corresponding to metallic cobalt were observed together to that of the IL (broad peaks below $2\theta = 30°$), and no cobalt oxide peaks were detected in the sample, indicating that the IL forms a protective layer around the metal surface and prevents its oxidation since the sample was air exposed for analysis. However, the pattern found does not correspond to either of the two most common structures of cobalt (hexagonal close packed and face-centered cubic). This phase was indexed as cubic with space group $P4_132$, which is defined as ε-cobalt. The Bragg reflections corresponding to crystalline cobalt MNPs were observed at $2\theta = 44.57°$, 47.12°, and 49.55°, which correspond to the indexed planes of ε-cobalt(0) crystals: (2 2 1), (3 1 0), and (3 1 1), respectively, with unit cell parameters of $a = (6.091 \pm 0.001)$ Å. The lattice parameters and the electron density obtained are quite similar to the values obtained by Bawendi et al.[32] It is

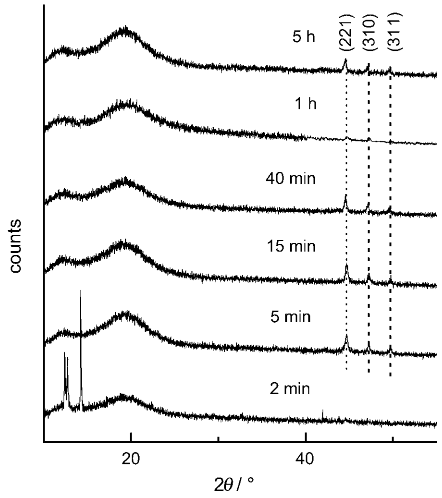

Figure 3. XRD analysis of the $[Co^0]_n$ particles prepared at different times during the decomposition reaction of $[Co_2(CO)_8]$ in the IL [DMI][NTf_2].

noteworthy the ε-cobalt phase was always observed, independent of reaction time (Figure 3). However, after a reaction time of 2 min, Bragg reflections at $2\theta = 12.37°$, 12.75°, and 14.28° were observed, which correspond to the intermediate $[Co_4(CO)_{12}]$;[33] this observation indicated that the reduction of the cobalt precursor was not complete after this time.[34] The material isolated from the IL was also analyzed by SEM/EDS, but in these cases oxygen was detected together with cobalt since the samples were exposed to air for analysis (Figure S3 in the Supporting Information).

Figure 4 shows the thermal magnetization curve of the cobalt sample prepared in [DMI][NTf_2] after a reaction time of 1 h. The zero field cooling (ZFC) curve shows two features, a clear maximum around 7 K, associated with the blocking temperature of the small spherical particles with a mean diameter of about 3 nm, and a broad shoulder around 150 K, associated with the blocking of larger particles with a diameter 10 nm (indicated by arrows in Figure 4).

The increase in the ZFC curve above 200 K corresponds to a reorientation of the magnetic easy axis, which results from the melting of [DMI][NTf_2]; this occurs in an analogous

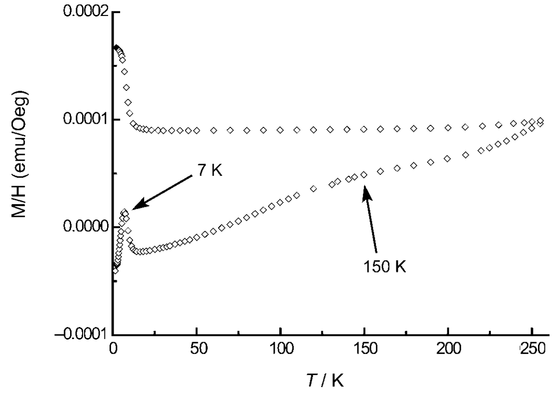

Figure 4. Thermal magnetization curve at 52 Oe of $[Co^0]_n$ NPs prepared in [DMI][NTf_2] at 150 °C for 1 h.

manner to that reported for [BMI][BF_4].[20] Assuming that the spherical particles are uni-axial and that only the ε-phase is present in the sample (according to X-ray measurements), the volume of this type of particle can be calculated using known values of the anisotropy constant.[35] The calculations give mean diameters of 3.3 and 9.7 nm, which correspond to the signals at temperatures of 7 and 150 K, respectively. These results corroborate the TEM analysis, in which spherical cobalt particles with diameters in the range 3-25 nm can be observed. Moreover, for the cubic particles ($\approx$79 nm by TEM analysis) it is difficult and perhaps impossible to estimate their volume from the magnetic measurements because the blocking temperature is above 300 K, and in addition they can be considered neither as monodomains nor as uni-axial.[36,37]

The magnetization curves saturate for applied fields around 1.0 T, showing that the sample is formed from ferromagnetic particles with a weak anisotropy embedded in the IL. At 200 K, small coercivity and remanence values of 0.042 T and 3.44×10^{-5} A m^2, respectively, are observed in the hysteresis curve. At 5 K, as expected for such a system, both the hysteresis and remanence increase to twice the values obtained at 200 K (see Figure S4 in the Supporting Information).

As a typical experiment to better evaluate the properties of the metallic surface, CO adsorption (20 atm at 25 °C for 20 h) was performed with the isolated cobalt MNPs (prepared in [DMI][NTf_2]) in a DRIFT cell (DRIFT = diffuse reflectance infrared Fourier transform; Figure S5 in the Supporting Information). Typical bands for CO adsorbed on the activated cobalt surface were observed around 2210–2050 cm^{-1} (terminal CO stretching), at 1732 cm^{-1} (CO adsorbed in a bridged mode),[38] 1367 cm^{-1}, and 1213 cm^{-1} (assigned to the CO group of carbonate),[39] while the band at 750 cm^{-1} is typical of a bridged CO carbonate.[39]

The isolated $[Co^0]_n$ NPs prepared in [DMI][NTf_2] were tested as catalysts in the Fischer–Tropsch synthesis (FTS). The reaction of syngas (20 atm, H_2/CO 2:1) over the isolated MNPs at 210 °C for 20 h afforded mainly hydrocarbons (8–26 carbon atoms) in the liquid phase (see Figure S6 in the Supporting Information). The chain-growth probability was estimated by using a modified Anderson–Shulz–Flory (ASF) equation,[40] to give an ASF growth factor (α) of about 0.75, which is similar to the values obtained for supported cobalt catalysts[41–43] (see Figure S7 in the Supporting Information).

The catalytic activity value of $0.2 \times 10^{-5}\,\mathrm{mol_{CO}\,g_{Co}^{-1}\,s^{-1}}$, based on the number of cobalt atoms exposed on the surface (considering only nanocubes), is of the same order of magnitude as the value observed for nanoparticles larger than 30 nm (see Figure S8 in the Supporting Information).[44] Interestingly, the hydrocarbons formed in the FTS with cobalt MNPs prepared in [DMI][NTf_2] showed a monomodal hydrocarbon distribution centered at C12, which is quite different from the bimodal distribution (centered at C12 and C21) obtained with cobalt nanoparticles prepared in [BMI][NTf_2].[45] It can be speculated that these differences are related not only to the different particle-size distribution, but also to the presence of different active sites, that is, the fcc phase for $[Co^0]_n$ in [BMI][NTf_2] and the ε phase for the $[Co^0]_n$ in [DMI][NTf_2].

In summary, we have demonstrated that the simple thermal decomposition of [$Co_2(CO)_8$] in ILs at 150 °C preferentially affords ligand-free $[Co^0]_n$ nanocubes or spherical MNPs, depending on the type of IL used and the reaction time. The mean diameter of the nanocubes was estimated to be (53 ± 22) nm and (79 ± 17) nm by TEM analysis for the samples prepared in [DMI][FAP] and [DMI][NTf_2], respectively. The shape of the "soluble" cobalt particles is apparently directly related to self-organization in the IL and thus can, in principle, be tuned by modulating the length of the *N*-alkyl imidazolium side chains, the anion type (volume or coordination ability), and the reaction conditions. Moreover, XRD measurements indicate the presence of ε-cobalt (a distorted cubic structure) for the $[Co^0]_n$ NPs prepared in [DMI][NTf_2] as well as the absence of cobalt oxide, which suggests that the IL produces a protective layer around the MNPs and prevents their oxidation. An adsorption experiment shows the typical carbonyl bands of CO adsorbed on an activated cobalt surface. In addition, these ε-cobalt MNPs demonstrate selectivity for the formation of diesel-like products in the FTS.

Experimental Section

A solution of [$Co_2(CO)_8$] (0.2 mmol in ca. 25 mL of hexane) was added in small portions under a stream of argon to a mechanically stirred system consisting of 1 mL of the IL[46] (preheated to 150 °C). After the addition of the precursor, the flow of argon was stopped and stirring (250 rpm) was maintained for the desired reaction time. The reaction mixture was cooled to room temperature and the black solution thus obtained was analyzed by TEM and XRD, and its magnetic properties were determined.

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