DOI: 10.1002/ejic.201100947

Ionic Additives and Weak Magnetic Fields in the Thermal Decomposition of Octacarbonyldicobalt – Tools To Control the Morphology of Cobalt Nanoparticles

Axel Dreyer,[a] Michael Peter,[b] Jochen Mattay,[b] Katrin Eckstädt,[c] Andreas Hütten,[c] and Peter Jutzi*[a]

Keywords: Cobalt / Nanoparticles / Synthetic methods / Surfactants / Magnetic properties

In the presence of ionic compounds, the thermal decomposition of octacarbonyldicobalt, $Co_2(CO)_8$, in an inert solvent leads exclusively to ε-Co nanocubes. The ionic species can be added directly or generated in situ by a chemical reaction between an additive and the precursor or between two additives. The additional presence of an inhomogeneous magnetic field leads to disc-shaped crystalline nanoparticles, which assemble to chains.

Introduction

Only very recently, we have investigated in detail the thermal decomposition of decamethylstannocene, $(Me_5C_5)_2Sn$, in organic solvents, which resulted in the formation of different morphologies of nanostructured β-tin particles. Surprisingly, the presence of ionic additives during the thermolysis led exclusively to the formation of cubes with controllable size.[1] In the context of our ongoing interest in the investigation of the magnetic properties of cobalt nanoparticles prepared from the thermal decomposition of octacarbonyldicobalt, $Co_2(CO)_8$, in organic solvents,[2–4] we now investigated the influence of ionic additives on the morphology of cobalt nanoparticles. The effect of ionic compounds as additives on the decomposition of $Co_2(CO)_8$ has not been described in the literature so far, though this synthetic strategy represents a classical procedure[5–7] for the preparation of Co nanoparticles,[8–16] together with the decomposition of other organometallic precursors[17] and with the reduction of cobalt salts.[18–22] Very recent studies have shown that changing the shape of cobalt nanoparticles from spherical to cubic can fundamentally change their magnetic behavior.[15,23–25] Here we describe our observation that the decomposition of $Co_2(CO)_8$ in the presence of ionic additives leads exclusively to Co nanocubes with average edge lengths between 35 and 95 nm, depending on the reaction conditions. For shape control, it is not important whether the ionic additive is present already from the beginning or formed only during the thermal decomposition.

The influence of an external magnetic field during the synthesis of cobalt nanoparticles[26–29] and the self-organization of cobalt nanoparticles under the influence of an external magnetic field[15,14] are documented in the literature. One-dimensional assemblies have been observed in all cases, and the resulting physical effects have been studied. To the best of our knowledge, the influence of an external magnetic field applied during the thermal decomposition of $Co_2(CO)_8$ has not been studied so far.[30] Here we describe the effect of an additional weak external field, which leads to a change in the shape of the cobalt nanoparticles from cubes to discs, which are self-organized to chains.

Results and Discussion

An overview of the performed experiments with a schematic representation of the particle shapes obtained together with a collection of TEM images is presented in Figure 1. The respective XRD patterns are collected in Figure 2. The magnetic properties of the Co nanoparticles correspond to those already described in the literature[11,15,20] and will not be discussed.[31]

The influence of the following additives has been investigated: (1) cetyltrimethylammonium bromide (CTAB), (2) benzylpyridine (BPy), and (3) mixtures of oleic acid (OS) and oleylamine (OA).

---

[a] Bielefeld University, Department of Chemistry, Institute of Inorganic Chemistry,
Universitätsstrasse 25, 33615 Bielefeld, Germany
Fax: +49-521-106 6026
E-mail: peter.jutzi@uni-bielefeld.de
[b] Bielefeld University, Department of Chemistry, Institute of Organic Chemistry,
Universitätsstrasse 25, 33615 Bielefeld, Germany
[c] Bielefeld University, Department of Physics, Institute of Thin Films & Physics of Nanostructures,
Universitätsstrasse 25, 33615 Bielefeld, Germany

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100947.

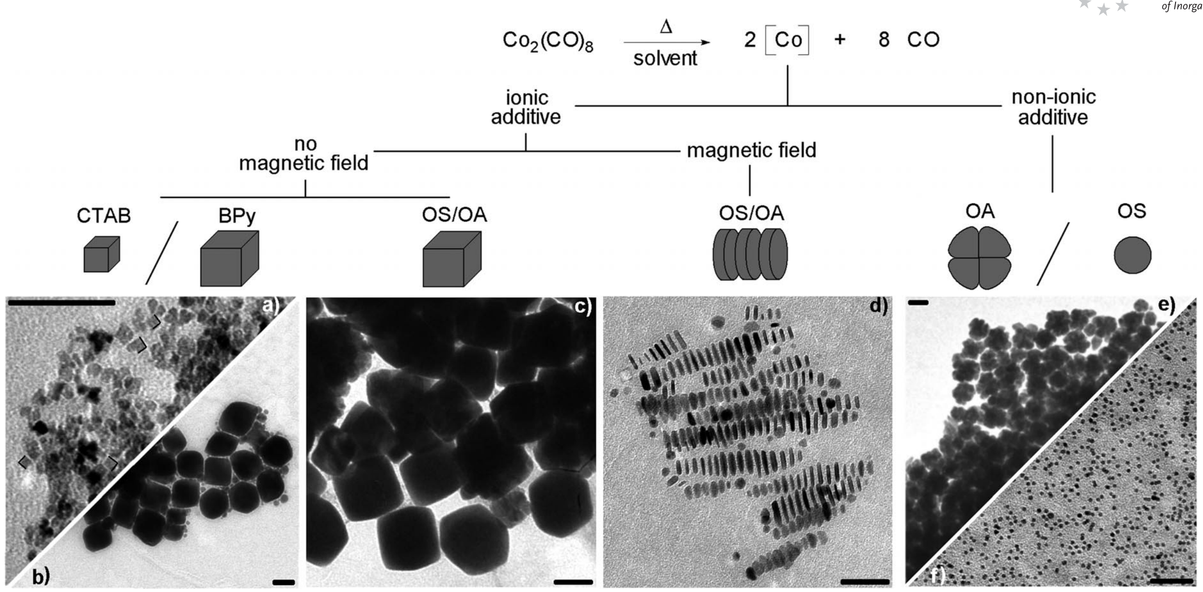

Figure 1. Schematic overview of the morphologies of Co nanoparticles obtained by the thermal decomposition of $Co_2(CO)_8$ under the influence of ionic additives with and without an external magnetic field and under the influence of non-ionic additives. TEM images show the respective morphologies. The chosen additives are: (a) cetyltrimethylammonium bromide (CTAB; the cubic structure of some particles is exemplarily marked), (b) 4-benzylpyridine (BPy), (c and d) an OS/OA mixture in the absence (c) and in the presence of a magnetic field (d), (e) OA, and (f) OS.[8] Scale bar: 50 nm. Additional TEM images with higher magnification are presented in section B of the Supporting Information.

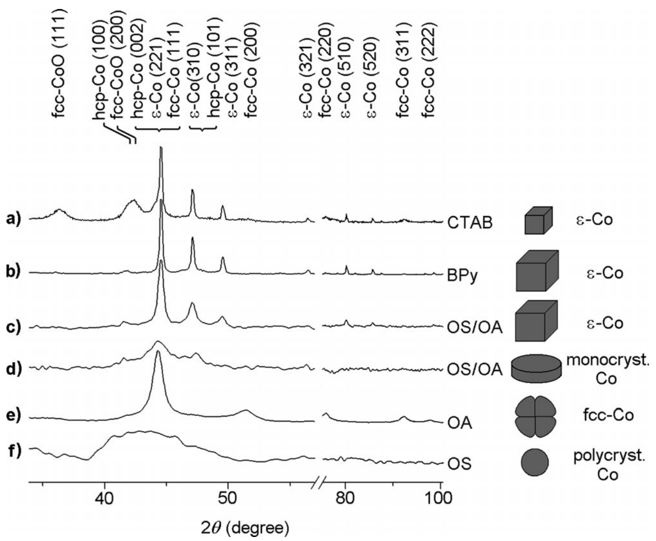

Figure 2. XRD patterns[33] of cobalt nanoparticles with various morphologies synthesized by the thermal decomposition of $Co_2(CO)_8$ in the presence of (a) cetyltrimethylammonium bromide (CTAB), (b) 4-benzylpyridine (BPy), (c and d) an OS/OA mixture () in the absence (c) and in the presence of a magnetic field (d), (e) OA, and (f) OS.

Cetyltrimethylammonium Bromide (CTAB)

The synthesis of Co nanoparticles in the presence of CTAB (0.16 mM) led to the formation of small nanocubes of ε-Co with an edge length of 4.1 ± 1.9 nm (TEM image in Figure 1a and XRD pattern in Figure 2a). The XRD pattern indicates small contributions of fcc cobalt(II) oxide as a result of oxidation at the particle surface during the measurement. The crystallite size was determined as 34.9 nm.[32]

Benzylpyridine (BPy)

The synthesis of Co nanoparticles in the presence of BPy (0.12 mmol) led to the formation of nanocubes of ε-Co with an average edge length of 57.6 ± 21.5 nm (TEM image in Figure 1b and XRD pattern in Figure 2b). The crystallite size of 26.3 nm indicates a polycrystalline texture.

During the usual work-up, a deep green solution was obtained after centrifugation. The conductivity of this solution was measured to be 0.5 $\mu S\,cm^{-1}$. Evaporation of the solvent led to an air-sensitive, viscous, red-brown residue. Its IR spectrum shows absorptions at 1895, 1863 and 1701 cm^{-1}, which can be assigned to the $Co(CO)_4^-$ unit.[34–36] Hieber has reported that $Co_2(CO)_8$ disproportionates with pyridine (Py) already at room temperature to give the red-brown salt $[CoPy_6]^{2+}[Co(CO)_4]^-_2$.[37] We conclude that, during the synthetic procedure (see Experimental Section) the soluble ionic compound $[Co(BPy)_6]^{2+}$-$[Co(CO)_4]^-_2$ is formed in addition to the Co nanocubes (for further details, see section C of the Supporting Information).

Mixtures of Oleic Acid (OS) and Oleylamine (OA)

The synthesis of Co nanoparticles in the presence of a mixture of OS (0.12 mmol) and OA (0.12 mmol) led to the formation of polycrystalline nanocubes of ε-Co with an average edge-length of 68.6 ± 14.0 nm (TEM image in Figure 1c and XRD pattern in Figure 2c). The average crystallite size was determined to be 22.2 nm (Figure 2c). Other OS/OA ratios also led to the formation of nanocubes. Interestingly, the size of the nanocubes strongly depends on the OS/OA ratio: Figure 3 shows that the average edge-length decreases with an increase of the OA component.

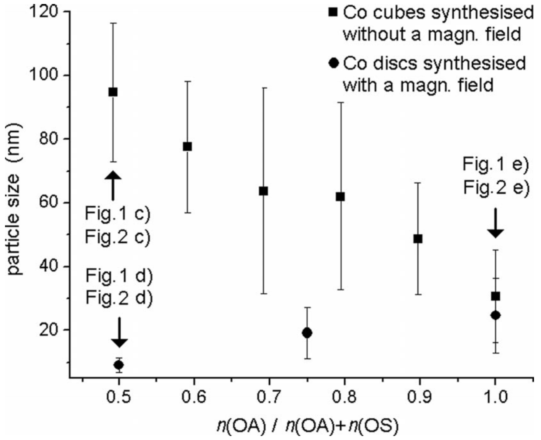

Figure 3. Edge length of Co nanocubes (squares) and diameter of Co nanodiscs (dots) depending on the mixing ratio of the additives (OS/OA). Nanocubes (in the absence of a magnetic field; squares) and nanodiscs (in the presence of a magnetic field; dots) were obtained.

The synthesis of Co nanoparticles in the presence of only a single additive (long-chain amine or carboxylic acid) has already been described in the literature in detail: The use of hexadecylamine (HDA) as additive leads to polycrystalline hcp-Co spheres and that of OS to monocrystalline ε-Co spheres.[11] For comparison, we have performed similar experiments with OA (0.32 mmol) and with OS (0.52 mmol) as single additives. As expected, the formation of spherical nanoparticles was observed. In the presence of OA, small crystallites of fcc-Co are formed, which aggregate to larger particles (27.7 ± 13.1 nm, Figures 1e and 2e). In the presence of OS, polycrystalline Co particles are observed (4.3 ± 1.1 nm, Figures 1f and 2f). The small particles and the resulting broad Bragg reflections do not allow a structure assignment.

In mixtures of organic carboxylic acids and amines, the formation of the corresponding salts is expected ($RCOOH + RNH_2 \rightleftarrows RNH_3^+ + RCOO^-$). The presence of ionic species has been confirmed by IR spectroscopic and conductivity measurements. In IR spectroscopic studies of the system OS/OA, vibrations assignable to the COOH unit appear in pure OS at 1703 and 933 cm^{-1}, whereas vibrations assignable to the COO$^-$ unit in the corresponding salt formed in an OS/OA mixture appear at 1557 and 1396 cm^{-1} (for further details see section D of the Supporting Information). Conductivity measurements in the OS/OA system were not conclusive because of the restricted ion mobility. Alternatively, we have measured the conductivity of the system consisting of hexanoic acid (HS) and hexylamine (HA). A mixture of 3 mmol HS and 3 mmol HA in 12 mL 1.2-dichlorobenzene showed a conductivity of 1.2 ± 0.3 μS cm^{-1} at 30 °C, which increased linearly with increasing temperature up to 2.3 ± 0.3 μS cm^{-1} at 100 °C (see section C of the Supporting Information). As expected, solutions of the pure components did not show any conductivity.

Weak Magnetic Field during Synthesis

The influence of a weak magnetic field on the shape of the Co particles was investigated exemplarily in a system containing an OS/OA mixture as additive. The synthesis was performed in the presence of a heterogeneous magnetic field of 0.03 T. A permanent magnet ($Nd_2Fe_{12}B$, 30 × 5 × 10 mm) was positioned horizontally underneath the reaction flask. Nanodiscs of ε-Co with an average diameter of 9.1 ± 2.3 nm and with an average thickness of 4.5 ± 1.8 nm were formed. The discs are organized in form of chains by magnetic dipole interactions.[10,11] Tilted chain segments confirm the existing disc shape (Figure 1d). The disc size is influenced only to a small extent by the OS/OA ratio; the size increases with the increase of the OA component (Figure 3). XRD investigations prove the presence of monocrystalline Co with a crystallite size of 5.8 nm (Figure 2d). A structure assignment (ε- or hcp-Co) remains uncertain because of broad Bragg reflections.

Conclusions

Our experiments clearly show that the presence of ionic species and of magnetic fields during the thermal decomposition of $Co_2(CO)_8$ allows to control the morphology of the resulting Co nanoparticles. Ionic additives lead exclusively to the formation of nanocubes. The ionic species are added in the form of a stable salt (CTAB) or are formed by a chemical reaction between the additive and the precursor molecule [BPy/$Co_2(CO)_8$] or between additives (OS/OA). In the OS/OA additive system, the additional presence of a weak inhomogeneous magnetic field leads to the formation of nanodiscs, which assemble to chains.

Only very recently, Scariot et al. have observed that nanocubes are formed in the thermal decomposition of $Co_2(CO)_8$ performed in an ionic liquid as solvent.[16] Our experiments demonstrate that an inert organic solvent and the presence of ionic additives is sufficient to initiate a comparable selectivity in particle formation. Puntes et al. have reported that the thermal decomposition of $Co_2(CO)_8$ in the presence of the additive mixture OS/HDA leads to hcp-Co nanodiscs.[11] We assume that a magnetic stirring bar has been used in these experiments.[38] According to our observations, the weak inhomogeneous magnetic field of a stirring bar is sufficient to induce a change in shape from nanocubes to nanodiscs.

In future work, the mechanisms that are responsible for the influence of electric charges and heterogeneous magnetic fields on the formation of anisotropic nanoparticles have to be investigated in detail. With regard to the influence of electric charges, we suppose that a mechanism similar to that observed for the formation of tin cubes in the presence of ionic additives is operative.[1] Concerning the influence of magnetic fields, the underlying effect is not yet understood. The presence of paramagnetic intermediates during the formation of the particles is indicated. In the literature, there are hints for the existence of paramagnetic species in the thermal decomposition of $Co_2(CO)_8$.[39,40]

In a more general context, investigations need to be carried out to determine whether our results on the control of the shape of tin and cobalt particles formed can be transformed to other chemical systems used for the preparation of nanoparticles.[41]

Experimental Section

Synthesis and Characterization of the Cobalt Nanoparticles and the Additive Mixtures

In an argon atmosphere, a solution (3 mL) containing 1,2-dichlorobenzene and the respective additive were heated to 182 °C by a hemispherical heating mantle while stirring with a sealed mechanical stirrer. Then, a solution of $Co_2(CO)_8$ in 1,2-dichlorobenzene (1 mL, 0.28 mmol) was quickly injected. After a reaction time of 15 minutes, the black colloidal particle suspension obtained was treated by following a usual work-up procedure: addition of acetonitrile (6 mL), centrifugation [3 min relative centrifugal force (RCF) 7500 $m\,s^{-2}$], substitution of the supernatant solution by pure 1.2-dichlorobenzene and redispersion. Transmission electron microscopy (Philips CM 200 TWIN) was used to characterize the morphology of the as-prepared nanoparticles, while X-ray diffraction (Philips X'pert) was used to characterize their crystalline structure and to determine the crystallite size with the help of the Scherrer equation.

The TEM samples were prepared by applying a drop of the particle solution (0.1 µL) on the carbon-coated copper grid, removing parts of the particle solution by a filter paper, and drying the remaining liquid film under vacuum. The XRD samples were prepared by applying the particle solution (250 µL) on a Si-111 wafer (10 × 10 mm) and removing the solvent in the vacuum.

IR spectroscopy (Bruker Vektor 22) and conductivity measurements (Schott CG853) were used to characterize the additive mixtures. Further experimental and analytical details are given in the Supporting Information.

Supporting Information (see footnote on the first page of this article): Preparation of the cobalt particles, transmission electron microscopy of the cobalt particles, identification of hexa(4-benzylpyridine)cobalt(II) bis(tetracarbonylcobaltate), and IR spectroscopy and conductivity measurements of the additive mixtures.

Acknowledgments

We wish to thank the University of Bielefeld and the Faculties of Chemistry and Physics for support with experiments and analyses, and the Deutsche Forschungsgemeinschaft (DFG) for financial support within the framework of the FOR 945 project 3. We are indebted to Nadine Mill for her experimental work.

---

[1] A. Dreyer, I. Ennen, T. Koop, A. Hütten, P. Jutzi, *Small* **2011**, *7*, 3075–3086.
[2] D. Sudfeld, K. Wojczykowski, W. Hachmann, P. Jutzi, G. Reiss, A. Hütten, *J. Appl. Phys.* **2003**, *93*, 7328.
[3] A. Hütten, D. Sudfeld, K. Wojczykowski, P. Jutzi, G. Reiss, *J. Magn. Magn. Mater.* **2003**, *262*, 23.
[4] A. Hütten, D. Sudfeld, I. Ennen, G. Reiss, K. Wojczykowski, P. Jutzi, *J. Magn. Magn. Mater.* **2005**, *293*, 93.
[5] A.-H. Lu, E. L. Salabas, F. Schüth, *Angew. Chem.* **2007**, *119*, 1242–1266; *Angew. Chem. Int. Ed.* **2007**, *46*, 1222–1244.
[6] Y. Xia, Y. Xiong, B. Lim, S. K. Skrabalak, *Angew. Chem.* **2009**, *121*, 62–92; *Angew. Chem. Int. Ed.* **2009**, *48*, 60–103.
[7] N. A. Frey, S. Peng, K. Cheng, S. Sun, *Chem. Soc. Rev.* **2009**, *38*, 2532.
[8] J. R. Thomas, *J. Appl. Phys.* **1966**, *37*, 2914.
[9] V. F. Puntes, K. M. Krishnan, A. P. Alivisatos, *Top. Catal.* **2002**, *19*, 145.
[10] V. F. Puntes, K. M. Krishnan, A. P. Alivisatos, *Science* **2001**, *291*, 2115.
[11] V. F. Puntes, D. Zanchet, C. Erdonmenz, A. P. Alivisatos, *J. Am. Chem. Soc.* **2002**, *124*, 12874.
[12] G. Cheng, J. D. Carter, T. Guo, *Chem. Phys. Lett.* **2004**, *400*, 122.
[13] G. Cheng, D. Romero, G. T. Fraser, A. R. Hight Walker, *Langmuir* **2005**, *21*, 12055.
[14] G. Cheng, C. L. Dennis, R. D. Shull, A. R. Hight Walker, *Langmuir* **2007**, *23*, 11740.
[15] G. Cheng, R. D. Shull, A. R. Hight Walker, *J. Magn. Magn. Mater.* **2009**, *321*, 1351–1355.
[16] M. Scariot, D. O. Silva, J. D. Scholten, G. Giovanna Machado, S. R. Teixeira, M. A. Novak, G. Ebeling, J. Dupont, *Angew. Chem.* **2008**, *120*, 9215–9218; *Angew. Chem. Int. Ed.* **2008**, *47*, 9075–9078.
[17] F. Dumestre, B. Chaudret, C. Amiens, M. C. Fromen, M.-J. Casanove, P. Renaud, P. Zurcher, *Angew. Chem.* **2002**, *114*, 4462–4465; *Angew. Chem. Int. Ed.* **2002**, *41*, 4286–4289.
[18] J. P. Chen, C. M. Sorensen, K. J. Klabunde, G. C. Hadjipanayis, *Phys. Rev. B* **1995**, *51*, 11527.
[19] C. Petit, A. Taleb, M. P. Pileni, *J. Phys. Chem. B* **1999**, *103*, 1805–1810.
[20] S. Sun, C. B. Murray, *J. Appl. Phys.* **1999**, *85*, 4325.
[21] C. B. Murray, S. Sun, H. Doyle, T. Betley, *MRS Bull.* **2001**, 985.
[22] C. B. Murray, S. Sun, W. Gaschler, H. Doyle, T. A. Betley, C. R. Kagan, *IBM J. Res. Dev.* **2001**, *45*, 47–56.
[23] N. A. Frey, S. Peng, K. Cheng, S. Sun, *Chem. Soc. Rev.* **2009**, *38*, 2532.
[24] S. A. Majetich, M. Sachan, *J. Phys. D: Appl. Phys.* **2006**, *39*, R407.
[25] S. Yamamuro, K. Sumiyama, *Chem. Phys. Lett.* **2006**, *418*, 166.
[26] X. Yang, F.-y. Lai, J.-z. Zhang, Q.-w. Chen, *J. Phys. Chem. C* **2009**, *113*, 7123–7128.
[27] F. Wang, H. Gu, Z. Zhang, *MRS Bull.* **2003**, *38*, 347–351.
[28] R. Abu-Much, A. Gedanken, *Chem. Eur. J.* **2008**, *14*, 10115–10122.
[29] E. K. Athanassiou, P. Grossmann, R. N. Grass, W. J. Stark, *Nanotechnology* **2007**, *18*, 165606(7pp).
[30] Concluded from the information given in the literature for the experimental details.
[31] B. Vogel, PhD Thesis, University of Bielefeld, **2011**.
[32] The larger size of the crystallites might be caused by a self-organization induced by the magnetic moment of the cubes to iso-oriented crystals during the evaporation of the solvent in the process of XRD sample preparation. A self-organization of small Co dics (4 × 25 nm) has already been observed in the literature and is documented by XRD data.[10,11]
[33] The diffractograms were measured with a copper X-ray source ($K_\alpha 1$: 1.54056 Å, $K_\alpha 2$: 1.54439 Å). XRD reference data from X′Pert High Score (hcp-Co 00–005–0727; fcc-Co 00–015–0806; fcc-CoO 00–048–1719) and from the literature (ε-Co).[15]
[34] G. Fachinetti, G. Fochi, T. Funaioli, P. F. Zanazzi, *J. Chem. Soc., Chem. Commun.* **1987**, 89.

[35] A. Sisak, L. Markó, *J. Organomet. Chem.* **1987**, *330*, 201–206.
[36] G. Fachinetti, G. Fochi, T. Funaioli, *J. Organomet. Chem.* **1986**, *301*, 91–97.
[37] W. Hieber, J. Sedlmeier, *Chem. Ber.* **1954**, *87*, 25–34.
[38] The authors[11] give no experimental details with regard to the stirring equipment.
[39] R. M. de Silva, V. Palshin, K. M. Nalin de Silva, L. L. Henry, C. S. S. R. Kumar, *J. Mater. Chem.* **2008**, *18*, 738–747.
[40] A. Lagunas, C. Jimeno, D. Font, L. Solà, M. A. Pericàs, *Langmuir* **2006**, *22*, 3823–3829.
[41] We assume that the formation of hcp-Co rods (ca. 9 × 40 nm) during the decomposition of Co(η^3-C_8H_{13})(η^4-C_8H_{12}) with H_2 in anisole and in the presence of the additive mixture OS/OA[17] is caused by salt formation and by the presence of an inhomogeneous magnetic field generated by a magnetic stirrer.

Received: September 7, 2011