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# A size-selective synthesis of air stable colloidal magnetic cobalt nanoparticles

H. Bönnemann<sup>a,\*</sup>, W. Brijoux<sup>a</sup>, R. Brinkmann<sup>a</sup>, N. Matoussevitch<sup>a</sup>, N. Waldöfner<sup>a</sup>,  
N. Palina<sup>b</sup>, H. Modrow<sup>b</sup>

<sup>a</sup> Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm Platz 1, 45470 Mulheim an der Ruhr, Germany

<sup>b</sup> Physikalisches Institut der Universität Bonn, Nussallee 12, 53115 Bonn, Germany

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Dedicated to Pierre Braunstein, one of the fathers of present day nanochemistry in Europe

## Abstract

A novel, size-selective preparation route leads to air stable ‘monodisperse’ colloidal cobalt nanoparticles via the thermolysis of  $\text{Co}_2(\text{CO})_8$  in the presence of aluminum alkyls. X-ray absorption near edge structure measurements have proved that this preparation pathway provides long term stable zerovalent magnetic Cobalt particles. In addition, these measurements show that the chemical nature of the surfactant used exerts a significant influence on the stability and the local electronic and geometric structure of the analyzed nanoparticles.

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## 1. Introduction

Magnetic fluids (MFs) with narrow size distributions exhibit useful properties for a number of technical and biomedical applications. The magnetic properties of MFs depend strongly on the size of the particles and the concentration of the magnetic material in dispersion. The well known magnetite MFs have a good stability. However, the magnetic properties of these materials are not sufficient for a number of purposes. Consequently, stable MFs on the basis of nanosized colloidal cobalt(0) particles are very interesting materials. For the preparation of nanoscopic Co(0) particles the thermolysis of  $\text{Co}_2(\text{CO})_8$  is a very convenient and generally applied

method [1,2]. Unfortunately, the Co particles obtained by this route show an unwanted broad size distribution (Fig. 1).

Another important issue is the stability of the zerovalent nanometal against air and moisture. Without the protection of the cobalt(0) nanoparticle surface by a layer of anticorrosive materials, e.g., gold [3], the magnetization of saturation of conventional Co(0) particles obtained by conventional thermolysis of  $\text{Co}_2(\text{CO})_8$  decays rapidly when exposed to air after the peptisation with KorantinSH (see No. 1 in Table 2). We have found that in the presence of organo aluminum compounds it is possible to control the size and the ‘monodispersity’ of the zerovalent magnetic nanoparticles resulting from the thermolysis of  $\text{Co}_2(\text{CO})_8$  [4]. After a smooth oxidation with air the particles may be isolated and peptised with the help of surfactants to give remarkably stable MFs which can be handled under ambient conditions.

\* Corresponding author. Tel.: +49-208-306 2374; fax: +49-208-306 2983.

E-mail address: [boennemann@mpi-muelheim.mpg.de](mailto:boennemann@mpi-muelheim.mpg.de) (H. Bönnemann).

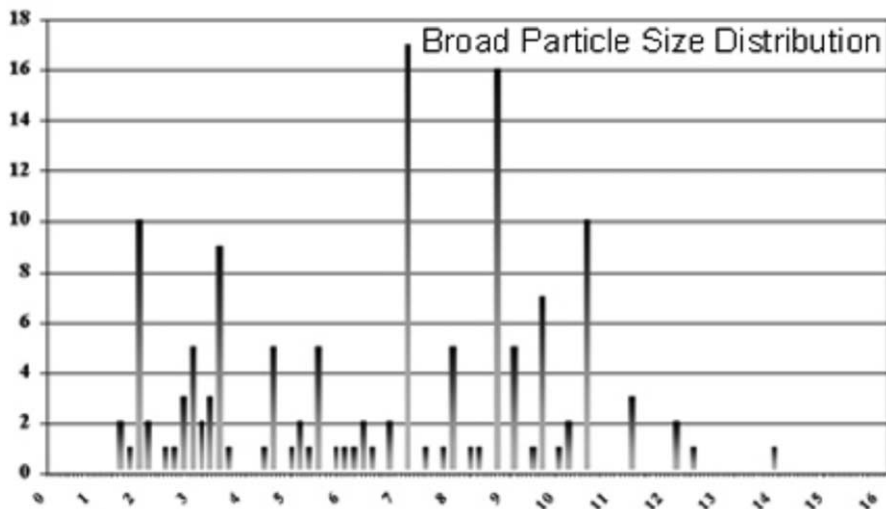


Fig. 1. Broad particle size distribution (peptisation with KorantinSH during the decomposition of  $\text{Co}_2\text{CO}_8$  ( $110^\circ\text{C}$ ) in toluene).

## 2. Experimental

### 2.1. XANES measurements

Co K-edge X-ray absorption near edge structure (XANES) measurements were performed at beamline BN3 at the electron stretcher and accelerator ring (ELSA) in Bonn, operating in 2.3 GeV mode. The apparatus at this beamline and data extraction [5] as well as the type of the cell [6] used for the measurements have been described previously. For monochromatization, Ge220 crystals were used, allowing for a stepwidth of 0.6 eV between the data points. The integration time per data point was 500 ms. For energy calibration, the first inflection point of the XANES spectrum of a hcp Co foil was assigned to a value of 7709 eV.

### 2.2. Source of chemicals

$\text{Al}(\text{C}_8\text{H}_{17})_3$  from Witco Company

$\text{Co}_2(\text{CO})_8$  from Aldrich  
 Vacuum pump oil L9 from Edwards  
 Surfactant LP-4 from ICI Ltd  
 KorantinSH from BASF AG  
 Oleic acid from Aldrich  
 AOT from SERVA  
 Silicon oil DC-702 from Dow Corning

## 3. General procedure for air stable, monodisperse ( $10 \pm 1.1$ nm) Co particles by thermolysis of $\text{Co}_2(\text{CO})_8$ in the presence of $\text{Al}(\text{C}_8\text{H}_{17})_3$ (Co:Al = 10:1) and subsequent smooth air oxidation

### 3.1. Thermolysis

In a 500 ml three-necked flask fitted with a mechanical stirrer and a reflux condenser 17.1 g (100 mM)  $\text{Co}_2(\text{CO})_8$  were introduced under a flow of argon. 4.4 ml (10 mM)  $\text{Al}(\text{C}_8\text{H}_{17})_3$  dissolved in 300 ml of toluene were

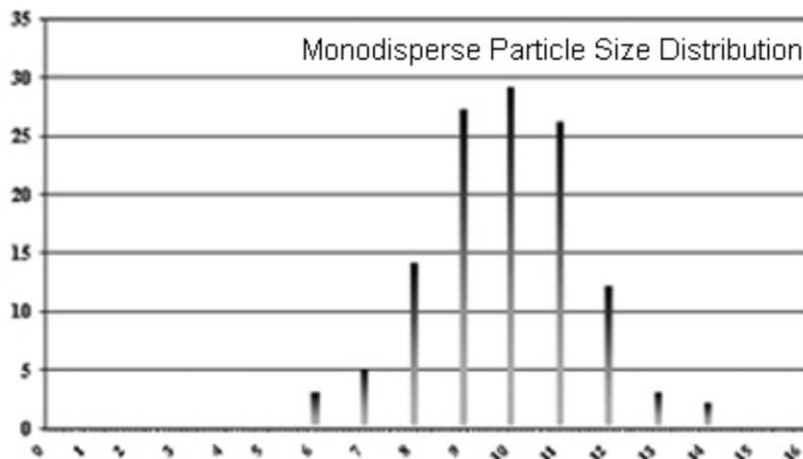


Fig. 2. Monodisperse Cobalt organosol ( $10 \pm 1.1$  nm) via decomposition of  $\text{Co}_2\text{CO}_8$  ( $110^\circ\text{C}$ ) in the presence of  $\text{Al}(\text{C}_8\text{H}_{17})_3$  (Co:Al = 10:1,  $T = 110^\circ\text{C}$ ) peptised with KorantinSH (see Sections 3.1, 3.2 and 3.3).

Table 1  
Dependence of the co-particle size on the type of  $\text{AlR}_3$

Type of $\text{AlR}_3$	$d$ [nm]
$\text{Al}(\text{CH}_3)_3$	3–4, 5
$\text{Al}(\text{C}_2\text{H}_5)_3$	6, 5–8, 5
$\text{Al}(\text{C}_8\text{H}_{17})_3$	8, 5–10, 5

added at once (initial ratio  $\text{Co}:\text{Al} = 10:1$ ) and the mixture was stirred and heated to  $110^\circ\text{C}$ . The temperature was kept at  $110^\circ\text{C}$  for 18 h. With  $\text{CO}$  evolution, the colour of the solution changed to dark brown and then a black precipitate was formed from the clear solution. The contents were cooled to  $20^\circ\text{C}$  and another 1.5 ml  $\text{Al}(\text{C}_8\text{H}_{17})_3$  ( $\sim 30\%$  of the initial quantity) were added to this mixture. The temperature was increased to  $110^\circ\text{C}$  and kept for 3 h more. After cooling to room temperature, the contents were stirred for another 16 h.

### 3.2. Smooth air oxidation

The mixture resulting from 3.1 was slowly oxidized by synthetic air bubbled through a capillary into the mixture during approximately 6 h. The product was stirred over night and the precipitate was allowed to settle down during 2 h. The supernatant was decanted and the Co particles were isolated in wet form.

The particles were dried in vacuo and 5.2 g of air stable Co powder were obtained which can be handled under ambient conditions.

### 3.3. Peptisation

Co particles obtained according to 3.2 (wet or in dried powder form) were peptised using suitable surfactants, e.g. KorantinSH, oleic acid, LP-4, AOT, etc. in toluene, kerosine, vacuum oil L9, and silicon oil DC-702.

#### 3.3.1. Example 1

Three grams of Co particles were peptised under ambient conditions by adding 10 ml of toluene containing 3% KorantinSH to give an air stable MF.

#### 3.3.2. Example 2

Three grams of Co particles were peptised in 10 ml of vacuum oil L9 or alternatively in silicon oil DC-702 containing 2–3% LP-4 giving an oil based air stable Co MF.

## 4. Physical analysis of Co particles ( $10 \pm 1.1$ nm) prepared following 3.1 without oxidative stabilization

The Co particles were isolated in wet form and analyzed by XANES (See Fig. 7(a)).

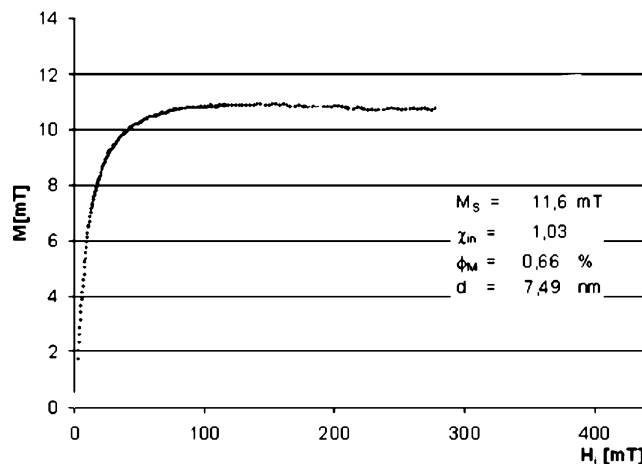


Fig. 3. Saturation magnetization curve of a sample according to Section 3.3.

(1) *Peptisation of Co particles obtained following 3.1 with KorantinSH in toluene:* The Co particles were suspended in 50 ml of toluene and peptised by adding 2 ml of KorantinSH as the surfactant and sonicated for 10 min in an ultrasound bath. A clear dark brown Co MF was formed. After drying in vacuo, 67.85% Co and 0.98% Al were found by elemental analysis.

The particle size was found to be  $10 \pm 1.1$  nm (see the particle size distribution in Fig. 2 and the micrographs in Figs. 5 and 6).

(2) In a second run the precipitate was washed two times with 20 ml of toluene in order to remove adjacent  $\text{Al}(\text{C}_8\text{H}_{17})_3$ . The Co particles were subsequently peptised with 2 ml of KorantinSH, analyzed by XANES (see Fig. 7(c)) and exposed to air.

## 5. Preparation of Co MF in vacuum pump oil L9

5.1. *Decomposition of  $\text{Co}_2(\text{CO})_8$  by thermolysis in a mixture of toluene and vacuum oil L9 in the presence of  $\text{Al}(\text{C}_8\text{H}_{17})_3$  ( $\text{Co}:\text{Al} = 10:1$ ,  $T = 110^\circ\text{C}$ )*

In 500 ml three-necked flask fitted with a mechanical stirrer and reflux condenser 51 g (300 mM)  $\text{Co}_2(\text{CO})_8$  were placed under a flow of argon. To this, 13.2 ml (30 mM)  $\text{Al}(\text{C}_8\text{H}_{17})_3$  dissolved in a mixture of 300 ml of toluene and 50 ml of vacuum pump oil L9 were added at once under ambient conditions. The mixture was stirred and heated to  $110^\circ\text{C}$ .

This temperature was kept for 4 h, subsequently increased to  $150^\circ\text{C}$  for 2 h. Under  $\text{CO}$  evolution the colour changed to dark brown and a black precipitate was formed from the solution. The contents were cooled to  $20^\circ\text{C}$  and stirred for another 16 h. After this the precipitate was allowed to settle during 2 h, the super-

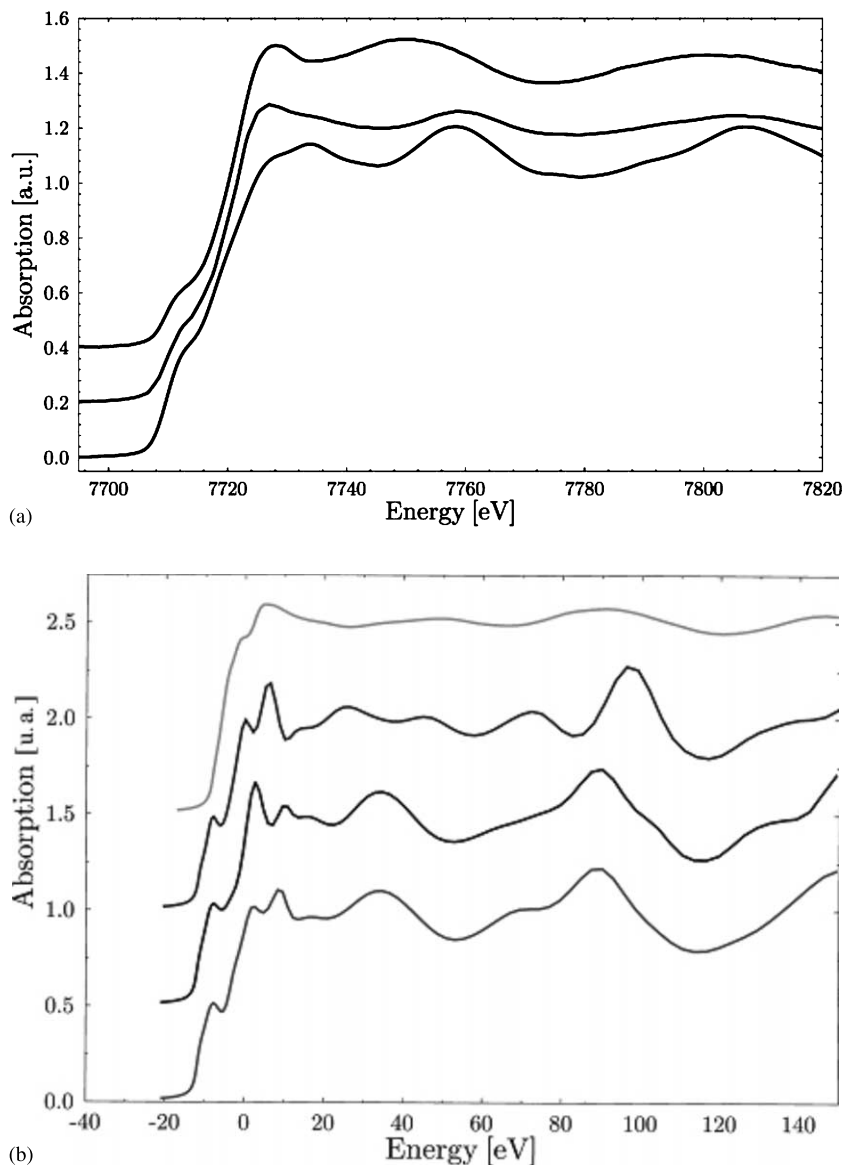


Fig. 4. (a) Co K-XANES of (bottom to top) samples peptized in vacuum oil, Co foil and samples prepared with KorantinSH (see Section 4). (b) Calculated Co K-XANES spectra of (bottom to top) hcp Co, fcc Co, bcc Co (hypothetical), Co in beta-Mn structure (hypothetical).

natant was decanted and the Co particles were isolated in wet form.

### 5.2. Peptisation of the Co particles by KorantinSH and LP4 in vacuum pump oil L9

After drying in vacuo, the Co particles of 5.1 were suspended in 50 ml of vacuum pump oil L9 containing 2.5 ml KorantinSH and 0.5 g of LP 4 as the surfactants. Under rapid stirring a dark brown Co MF was formed in L9. The resulting sample was subsequently analyzed by XANES.

## 6. Results and discussion

Using the procedures described in Section 3.1 and Section 3.2, the thermolysis of  $\text{Co}_2(\text{CO})_8$  in the presence of  $\text{Al}(\text{C}_8\text{H}_{17})_3$  followed by peptisation with KorantinSH gave a cobalt organosol of  $10 \pm 1.1$  nm size (the particle size distribution quoted was determined by TEM, see Fig. 2).

Further investigations have revealed the following parameters in the above described procedure to be crucial (for details see below):

- the reaction time and temperature applied
- the chain length of  $R$  in  $\text{AlR}_3$

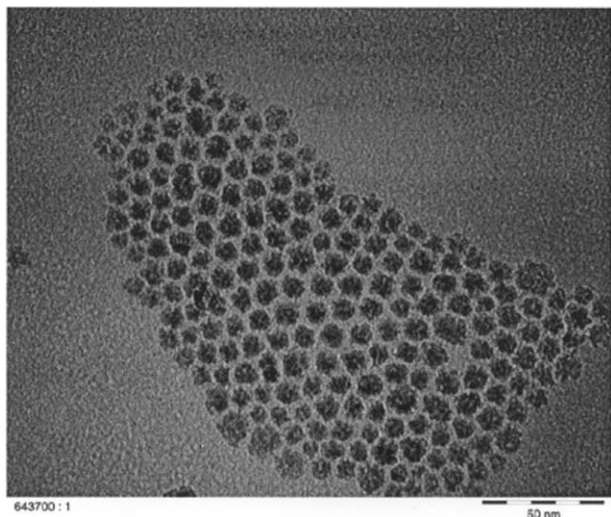


Fig. 5. TEM micrograph of 10 nm cobalt particles (Section 3.3).

- the molar ratio of  $\text{Co}_2(\text{CO})_8$ :  $\text{AlR}_3$
- the surfactant

#### 6.1. Reaction time and temperature

The decomposition of  $\text{Co}_2(\text{CO})_8$  was performed at low (30–50 °C) and at high temperature (130–150 °C). At low temperature the decomposition takes a long time; at temperatures > 130 °C unwanted side products such as carbonyl complexes, e.g.  $\text{Co}_4(\text{CO})_{12}$ , are formed. The optimum thermolysis conditions for  $\text{Co}_2(\text{CO})_8$  in toluene are: 105–110 °C for 4–16 h.

#### 6.2. Chain length of R in $\text{AlR}_3$

Different types of  $\text{AlR}_3$  were applied to the optimum thermolysis of  $\text{Co}_2(\text{CO})_8$  in toluene, and an inspection of Table 1 shows that there is a marked influence of the alkyl chain length on the size of the resulting Co particles.

#### 6.3. Molar ratio of $\text{Co}_2(\text{CO})_8$ to $\text{AlR}_3$

The size of the Co particles may also be controlled by the molar ratio of  $\text{Co}_2(\text{CO})_8$  to  $\text{AlR}_3$ . Fig. 5 shows the HRTEM image of Co particles ( $10 \pm 1.1$  nm) obtained at the molar ratio of Co to  $\text{Al}(\text{C}_8\text{H}_{15})_3$  as 10:1. In contrast, at a molar ratio of Co:Al = 1:2 the thermolysis of  $\text{Co}_2(\text{CO})_8$  in the presence of  $\text{Al}(\text{C}_8\text{H}_{15})_3$  yields Co particles of only 5.4 nm size.

#### 6.4. Type of surfactant

Using conventional dispersing agents, e.g. lauric acid, oleic acid, AOT, KorantinSH (BASF) or *N*-lauroylsarcosin Na-salt ('Sarcosyl', Merck) the dispersion of Co particles yields MFs in toluene or kerosine, pump oil or

silicon oil with a high saturation magnetization at low particle concentrations. For example, at only 0.6 Vol.% cobalt prepared after procedure 1 in a MF in vacuum oil shows a value of 11.6 mT (Fig. 3).

How important the surfactant is for the resulting nanostructure of the product becomes evident from Co K-edge XANES spectroscopy, which provides a 'fingerprint' characterization of both the electronic and geometric environment of the absorbing atoms. Comparing e.g. the Co K-XANES spectra of particles dispersed in vacuum oil and KorantinSH in Fig. 4(a), significant differences are observed. These effect not only the region of the absorption edge, which is sensitive to changes in the electronic structure, but also form and position of the shape resonances, which are a sensitive indicator of differences in the coordination geometry of the Co atoms within the sample. In more detail, we find that the energy position of the first inflection point in the spectra remains identical to the one observed for the reference foil, i.e., 7709 eV. While this observation suggests that we are dealing with zerovalent Co, clearly the electronic structure is in both cases significantly different to the one observed for hcp Co. Whereas the shape resonances indicate that in the sample dispersed in vacuum oil the atomic configuration around the absorbing Co atom is rather similar to the hcp case, there is a clear energy shift in the position of the shape resonances, indicating a different atomic configuration. At the same time, the ordered structure observed in the TEM pictures and the magnetic properties suggest, that we are still dealing with a configuration in which Co is mainly surrounded by Co atoms. In an attempt to gain an understanding of the observed changes, FEFF8 calculations [7] were performed not only for the known hcp and fcc Co phases, but also for hypothetical bcc and  $\beta$ -manganese phases of nanoparticles discussed recently in Refs. [8–10]. The results of these calculations are shown in Fig. 4(b). They suggest that the sample dispersed in vacuum oil is present in the fcc phase. The only way to induce a shape resonance at a similar energy position relative to the absorption edge as observed for the particles dispersed in KorantinSH is resorting to a mixture of fcc and bcc structure. Similar structures are discussed in Ref. [10].

An attempt to obtain a more detailed structural model for the different types of Co core including EXAFS analysis of the samples is underway.

## 7. Properties of the magnetic cobalt nanoparticles

### 7.1. Particle size

Comparative TEM examinations have revealed that smooth oxidation of the Co particles does not alter the size nor the size distribution. The pre-prepared Co

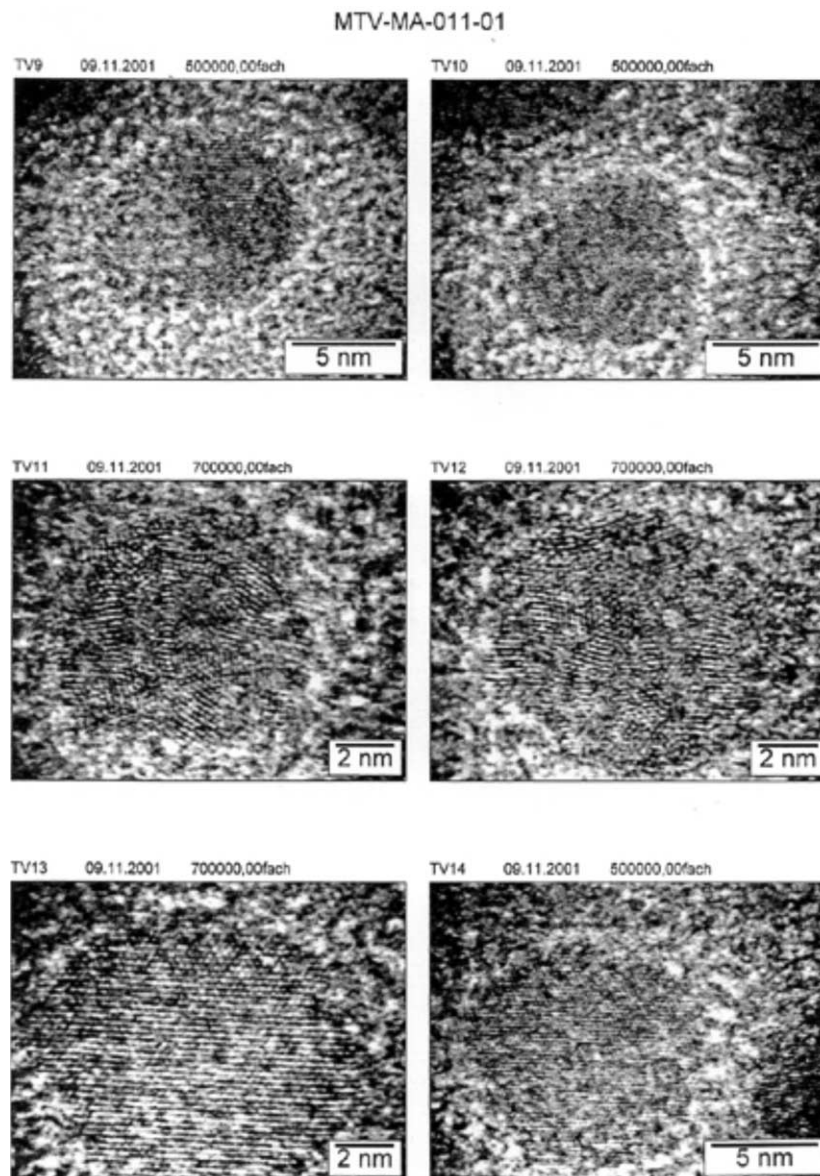


Fig. 6. HRTEM micrographs of 10 nm cobalt particles (Section 3.3).

particles may be stabilized by KorantinSH according to Section 3.3 to give a long term stable MF. Typical TEM- (Fig. 5) and HRTEM-pictures (Fig. 6) of the MF are shown below.

#### 7.2. Stability of the resulting MFs under air at room temperature

The magnetic stability of the following Co colloid samples was investigated by measuring the loss of the magnetic properties during time under ambient conditions (i.e. exposition to air).

- 1)  $\text{Co}_2(\text{CO})_8$  thermolysis in the presence of KorantinSH only (see size histogram Fig. 1)
- 2)  $\text{Co}_2(\text{CO})_8$  thermolysis in the presence of  $\text{Al}(\text{C}_8\text{H}_{17})_3$  (Co:Al = 10:1, Section 3.1, see size histogram Fig. 2)
- 3) Co particles from No. 2 dispersed in toluene with KorantinSH
- 4) Co particles washed with toluene, dispersed with KorantinSH (Section 4(2))
- 5) Co particles dispersed in vacuum pump oil L9 containing KorantinSH and LP4 (Section 5.2)

As can be seen from Table 2 the magnetic properties rapidly decay in case of No. 1 and 2 where the Co particles were stabilized only with KorantinSH or  $\text{Al}(\text{C}_8\text{H}_{17})_3$ , respectively. In contrast, the magnetic properties of Co particles stabilized with  $\text{Al}(\text{C}_8\text{H}_{17})_3$  and subsequently peptised with KorantinSH (No. 3) remained remarkably constant over 5 months under air.

Table 2

Decay of the magnetization of saturation of co-colloids after the exposition to air for weeks and months (description of colloids 1–5 see above)

No.	Magnetization of saturation $M_s$ (kA m <sup>-1</sup> )					XANES
	As prepared	1 week	2 week	3 month	5 month	
1	4.04	4.01	3.79	2.42	1.8	Fig. 1
2	4.32	3.11	3.2	2.51	2.1	Fig. 7
3	5.53	5.51	5.53	5.47	5.22	
4	3.83	3.80	3.82	3.78	3.41	Figs. 4 and 7
5	n.d.	n.d.	n.d.	n.d.	n.d.	Fig. 4

If the  $\text{Al}(\text{C}_8\text{H}_{17})_3$  is washed away from the Co particles immediately after the synthesis (No. 4), the magnetic stability was markedly reduced after exposing the particles to air. This indicates that none of the stabiliz-

ing components alone is enough to conserve the zerovalent state of the cobalt.

This behaviour, especially the high degree of long-term stability of the KorantinSH stabilized samples, is also reflected in the time-dependence of the Co K-XANES spectra displayed in Fig. 7. Evidently, the Co-particles solely stabilized by  $\text{Al}(\text{C}_8\text{H}_{17})_3$  have started to oxidize rather quickly. Already the first measurement, taking place about 10 days after preparation of the particles, shows significant contributions of the structures typical for CoO (at  $\sim 7726$  and  $7773$  eV) and  $\text{Co}_2\text{O}_3$  (at  $\sim 7729$  and  $7781$  eV), respectively, to the spectrum. At the same time, the pre-edge shoulder located at approximately 7709 eV shows that even a long time after the synthesis, some zerovalent Co is still present, which explains the remaining magnetic properties described above. With increasing time, only a slight increase in the oxidation of this type of sample is observed, which could indicate that a shell of oxidized Co surrounds a Co metal core. The delayed onset of the deterioration of magnetic properties of the material stabilized with KorantinSH without  $\text{Al}(\text{C}_8\text{H}_{17})_3$  might be related to reduced diffusion of oxygen through the surfactant shell in this scenario. In contrast to that, even several months after their preparation, no significant contribution of oxide-related phases to the Co K-XANES spectra of samples stabilized using  $\text{Al}(\text{C}_8\text{H}_{17})_3$  and KorantinSH were observed.

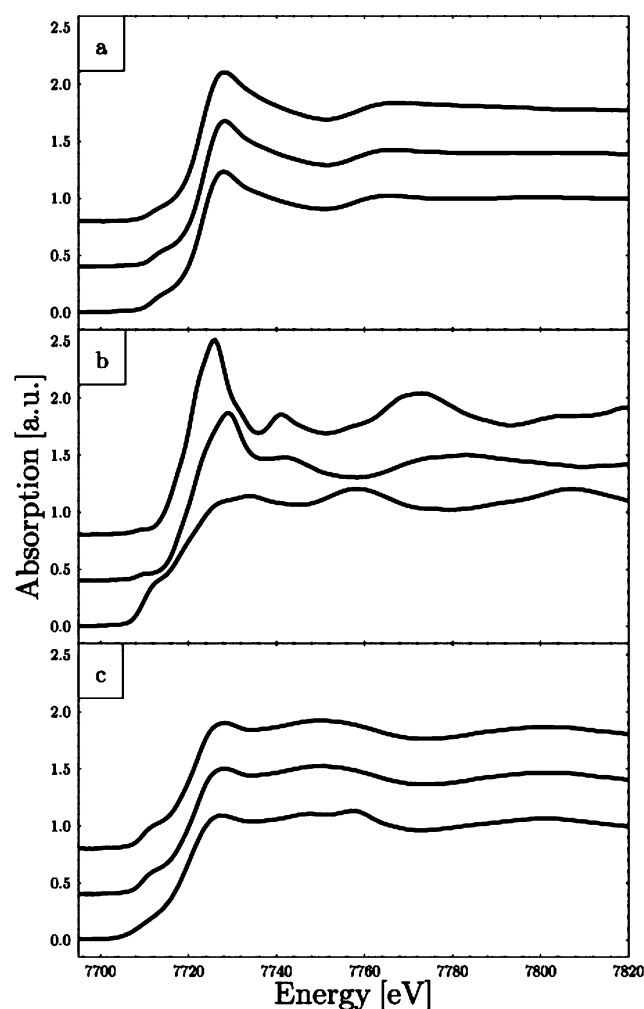


Fig. 7. Co K-XANES spectra of (a) (bottom to top) sample prepared as described in Section 4, approximately 10 days after preparation, approximately 6 weeks after preparation, approximately 14 weeks after preparation; (b) reference spectra for oxidative reactions (bottom to top) Co-foil,  $\text{Co}_2\text{O}_3$ , CoO; (c) (bottom to top) sample prepared as described in Section 4(2), directly after, 4 days after and approximately 14 weeks after preparation.

## 8. Conclusions

The thermolysis of  $\text{Co}_2(\text{CO})_8$  in toluene in the presence of  $\text{AlR}_3$  yields monodisperse Co-particles of various sizes. These precursors can be peptised to give air stable MFs having a high magnetization of saturation at low concentration of Co particles.

Future work will be focussed to elucidate the mode of stabilization which is obviously introduced by a combination of the aluminum organic protecting shell and the surfactant used. A detailed analysis of the structural changes induced in the Co particles is also envisaged. Further, it is necessary to find the optimum concentra-

tion conditions needed to improve the Co MF properties for special applications.

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