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GENERATION OF BINARY $\text{CoO}_x/\text{SiO}_2$ NANOPARTICLES FROM ORGANO-COMPOUND PRECURSORS

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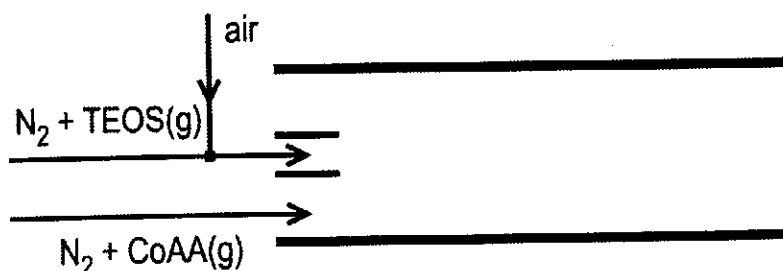
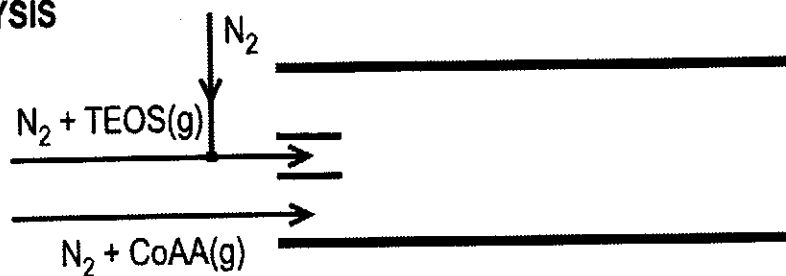
INTRODUCTION

In recent years cobalt and cobalt oxide nanoparticles have attracted substantial research effort because of their potential applications such as protective materials, catalysts, magnetic data recorders, batteries and gas sensors (Jang *et al.*, 2004). To improve their functionality and biocompatibility nanoparticles are frequently coated with SiO_2 (Teleki *et al.*, 2008). In this work, we studied $\text{CoO}_x\text{-SiO}_2$ binary nanoparticles synthesis by metal organics chemical vapor deposition (MOCVD) using organo-compound precursors cobalt acetylacetonate (CoAA) and tetraethyl orthosilicate (TEOS).

EXPERIMENTAL

Particles were synthesized in an externally heated tube flow reactor with i. d. 25 mm and the length of heated zone 1 m. Experiments were performed in an inert atmosphere using nitrogen as a carrier gas (pyrolysis) as well as in oxidizing atmosphere at 10 vol. % of oxygen in the reaction mixture (oxidation), see Fig. 1.

PYROLYSIS



OXIDATION

Fig. 1 Scheme of inlet section arrangements for pyrolysis and oxidation of CoAA.

Particle production and their characteristics were studied in dependence on reactor temperature (T_R : 600 – 900 °C), concentrations (vapor pressures) of precursors (P_{CoAA} : 0.32 – 2.06 Pa; P_{TEOS} : 0 – 5.67 Pa), oxygen concentration (c_O : 0 or 10 %), and reactor flow rate (Q_R). Precursor concentrations in the reaction mixture were controlled by the variation of the saturator temperature (CoAA) or by carrier gas flow rate through the saturator (TEOS), and they were calculated on the basis of experimental data of Götze *et al.* (1970) from the equation:

$$P_{CoAA} (Pa) = 133.322 \times 10^{\left(9.5909 - \frac{4297.31}{T_s (K)}\right)} \quad (1)$$

and from the equation presented at Okuyama *et al.* (1986):

$$P_{TEOS} (Pa) = 133.322 \times e^{\left(19.3 - \frac{5555}{T_s (K)}\right)} \quad (2)$$

The particle production was monitored by scanning mobility particle sizer (SMPS, *TSI model 3936*) and samples for particle characterization were deposited onto TEM grids using nanometer aerosol sampler (NAS, *TSI model 3089*) and on Sterlitech Ag filters. Particle morphology was studied by high resolution transmission electron microscopy (HRTEM, *JEOL 3010*), crystallinity by selected area electron diffraction (SAED) and X-ray diffraction (XRD, *PANalytical X'PertPRO*), and chemical composition was analyzed by energy dispersive spectrometry (EDS, *INCA/Oxford*) connected to HRTEM and X-ray photoelectron spectroscopy (XPS, *ADES-400, VG Scientific*).

RESULTS

Particle production

The particle production was affected by all investigated parameters including the chemistry of precursor decomposition, in particular by concentrations of precursors (P_{CoAA} , P_{TEOS}). The examples of the influence of T_R and P_{TEOS} on particle size distributions (PSD's) are shown in Fig. 2 and Fig. 3.

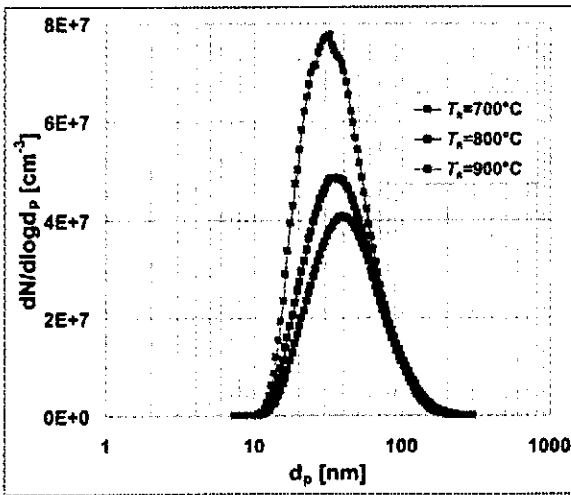


Fig. 2: Influence of T_R on PSD's at $P_{CoAA}=0.32$ Pa, $P_{TEOS}=1.89$ Pa, $c_O=10$ vol. %, $Q_R=1000$ cm³/min, OXIDATION.

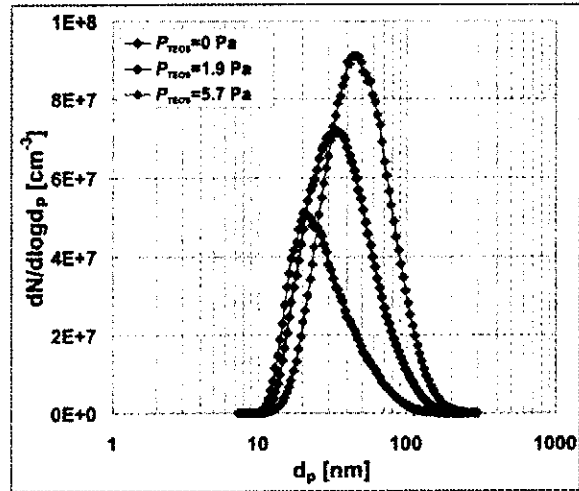


Fig. 3: Influence of P_{TEOS} on PSD's at $T_R=900$ °C, $P_{CoAA}=0.32$ Pa, $c_O=10$ vol. %, $Q_R=1000$ cm³/min, OXIDATION.

Particle characteristics

Particle characteristics were predominantly a function of the chemistry of precursor decomposition, but they were also affected by reactor temperature and concentration of precursors. Experimental conditions of the samples chosen for particle characterization are shown in Table 1.

Table 1 Process parameters of the CoAA samples and crystalline structures detected by SAED [#], XRD [*] and/or HRTEM [&].

Sample No.	T_R [°C]	P_{CoAA} [Pa]	P_{TEOS} [Pa]	Q_R [cm ³ /min]	c_0 [vol. %]	Carrier gas/reagent	Crystalline phases
CoAA9	700	0.32	1.89	1000	10	N ₂ /O ₂	CoO [#]
CoAA15	700	0.61	1.89	800	0	N ₂	Co ₃ O ₄ ^{#,&}
CoAA18	900	0.61	5.67	800	0	N ₂	n.a.
CoAA22	900	2.06	1.89	800	0	N ₂	Co ^{&}
CoAA23	900	2.06	5.67	800	0	N ₂	Co ^{&} , Co ₃ O ₄ ^{&}
CoAA24	900	2.06	5.67	800	10	N ₂ /O ₂	CoO [*] , Co ₃ O ₄ ^{#,*}

Morphology

Particle morphology can be seen on TEM images in Fig. 4 and Fig. 5. At lower T_R , particles had broader size distribution, typically from 5 to 25 nm (Fig. 4), at T_R 900 °C, the typical particle size varied between 5 and 10 nm (Fig. 5).

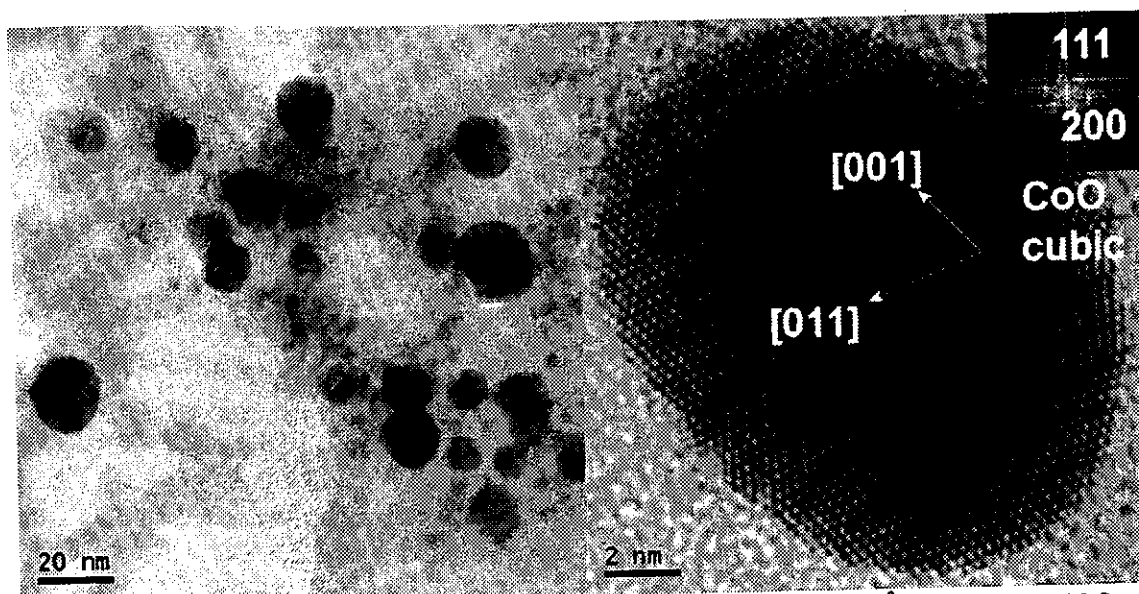


Fig. 4: HRTEM images of the sample CoAA9. $T_R=700$ °C, $Q_R=1000$ cm³/min, $P_{CoAA}=0.32$ Pa, $P_{TEOS}=1.89$ Pa, $c_0=10$ vol. %.

Crystallinity

Crystalline structure can be seen on TEM images in Fig. 4 and Fig. 5, and it is summarized in Table 1. Particles produced by pyrolysis were XRD amorphous and selected area electron diffraction (SAED) patterns were usually rather weak. HRTEM images revealed lattice fringes in the cores of particles, which were typically indexed as hexagonal Co or, in some cases, cubic Co₃O₄. Samples prepared by oxidation showed much better developed SAED patterns and also XRD confirmed cubic CoO and cubic Co₃O₄ crystalline structures.

Composition

XPS analysis showed Si in the oxide state in the surface layer of particles prepared both in an inert and oxidizing atmosphere. Co-O bonds were identified in the samples prepared by oxidation and mixture of Co-Co (metallic clusters) and Co-O as well as C-CH_x, C-O and C=O bonds were detected in particles prepared by pyrolysis.

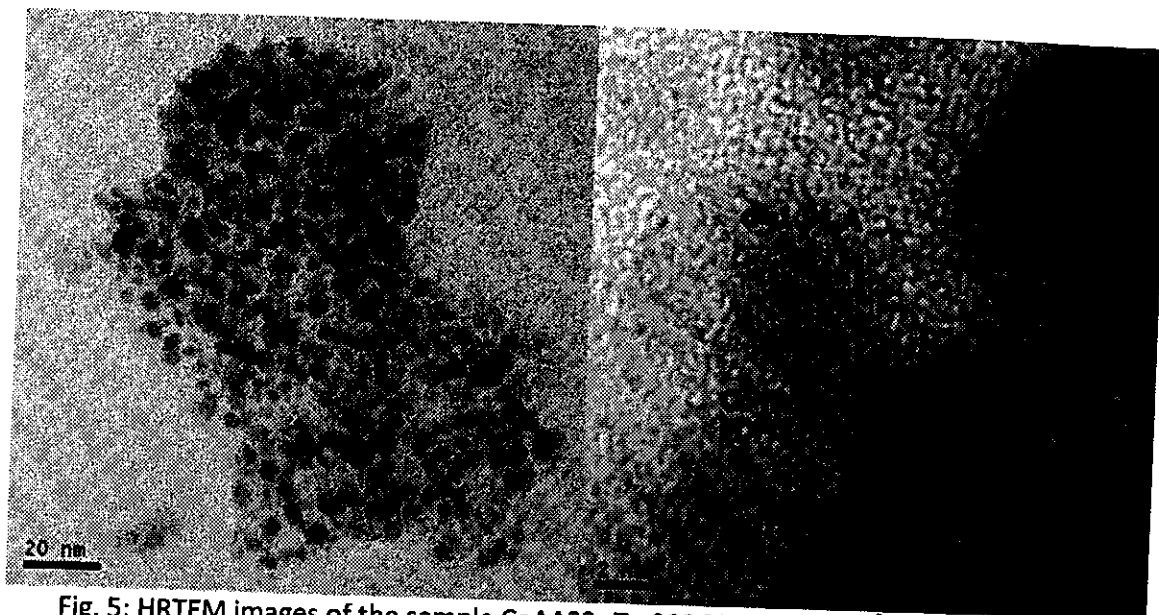


Fig. 5: HRTEM images of the sample CoAA22. $T_R=900\text{ }^{\circ}\text{C}$, $Q_R=800\text{ cm}^3/\text{min}$, $P_{\text{CoAA}}=2.06\text{ Pa}$, $P_{\text{TEOS}}=5.67\text{ Pa}$, $c_O=0$.

CONCLUSIONS

Binary $\text{CoO}_x\text{-SiO}_2$ nanoparticles were synthesized in an externally heated tube reactor by simultaneous decomposition of CoAA and TEOS in both inert and oxidative atmosphere. Size of primary particles varied between 5 and 25 nm. Crystalline structure corresponds to hexagonal Co or, in some cases, cubic Co_3O_4 in the case of pyrolysis and to cubic CoO and Co_3O_4 in the particles prepared by oxidation. We can assume that Co nanoparticles encapsulated in SiO_2 and partially decomposed CoAA were synthesized in an inert carrier gas, and mixture of CoO and Co_3O_4 covered by SiO_2 were prepared in an oxidizing atmosphere.

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REFERENCES

- Jang H.D., Hwang D.W., Kim D.P., Kim H.C., Lee B.Y., Jeong I.B., Preparation of cobalt nanoparticles by hydrogen reduction of cobalt chloride in the gas phase, *Mater. Res. Bull.*, **39**, 63-70 (2004).
- Teleki A., Heine M.C., Krumeich F., Akhtar M.K., Pratsinis S.E., In situ coating of flame-made TiO_2 particles with nanothin SiO_2 films, *Langmuir*, **24**, 12553-12558 (2008).
- Götze H.-J., Bloss K., Molketin H., Dampfdruckbestimmung von acetylacetonaten, *Zeitschrift Phys. Chem. Neue Folge*, **73**, 314-320 (1970).
- Okuyama K., Kousaka Y., Tohge N., Yamamoto S., Wu J.J., Flagan R.C., Seinfeld J.H., Production of ultra-fine metal oxide particles by thermal decomposition of metal alkoxide vapor, *AIChE J.*, **32**, 2010-2019 (1986).