**Nanoparticle Formation by Thermal Decomposition and Oxidation of Manganese(II) Acetylacetonate**

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# NANOPARTICLE FORMATION BY THERMAL DECOMPOSITION AND OXIDATION OF MANGANESE(II) ACETYLACETONATE

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## INTRODUCTION

Over the last decade, Mn and $MnO_x$ nanoparticles has been extensively investigated due to their great importance in catalysis, electrochemistry, ion exchange materials, batteries and other areas (Si *et al.*, 2005; Han *et al.*, 2006). This work describes preliminary experiments producing manganese nanoparticles by metal organic chemical vapor deposition (MOCVD) using manganese(II) acetylacetonate (MnAA) as a precursor.

## 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 2 and 10 vol. % of oxygen in the reaction mixture (oxidation) see Fig. 1.

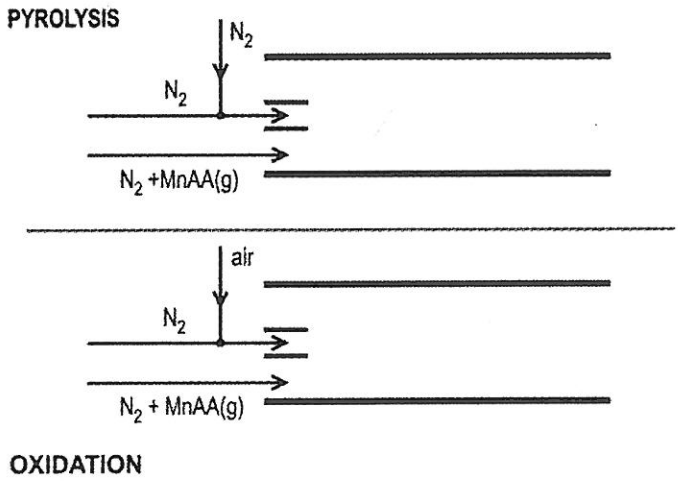


Fig. 1: Scheme of the inlet section arrangements for pyrolysis and oxidation of MnAA.

Particle production and their characteristics were studied in dependence on reactor temperature ($T_R$: 500 – 1000 °C), precursor vapor pressure ($P_{MnAA}$: 0.82 – 5.47 Pa), oxygen concentration ($c_O$: 0, 2 a 10 vol. %), and reactor flow rate ($Q_R$: 600 – 1000 $cm^3$/min). $P_{MnAA}$ was controlled by the variation of the

saturator temperature ($T_S$) and it was calculated on the basis of experimental data of Götze *et al.* (1970) from the equation:

$$P_{MnAA}(Pa) = 133.322 \times 10^{\left[8.9661 - \frac{4612.6}{T_S(K)}\right]} \quad (1)$$

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), X-ray diffraction (XRD, *PANalytical X'PertPRO*) and by HRTEM, and chemical composition by energy dispersive spectrometry (EDS, *INCA/Oxford*) connected to HRTEM and X-ray photoelectron spectroscopy (XPS, *ADES-400, VG Scientific*).

## RESULTS

### Particle production

The SMPS monitoring showed that generation of particles depends in particular on precursor concentration and also on the chemistry of precursor decomposition. Number concentration and mean particle size increase with increasing $P_{MnAA}$ ($T_S$), see Fig. 2, and more and larger particles/clusters are generated by pyrolysis than by oxidation (Fig. 3). Number concentration also slightly increases with $T_R$ and $Q_R$, while mean particle size decreases. Examples of the influence of $T_S$, $T_R$ and $c_O$ are shown in Fig. 2 and Fig. 3.

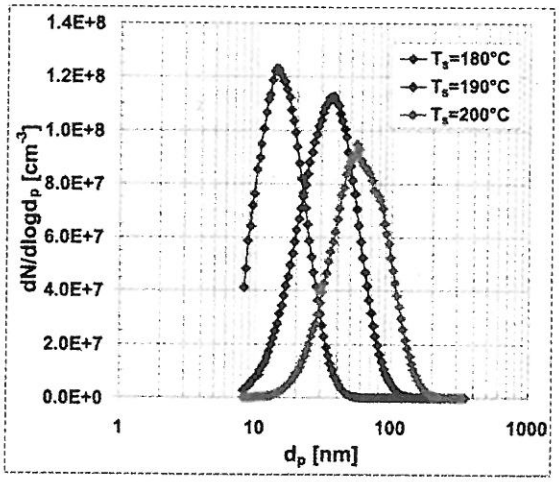


Fig. 2 Influence of $T_S$ on PSD's at $T_R$=900 °C, $Q_R$=800 cm$^3$/min, $c_O$=0, PYROLYSIS.

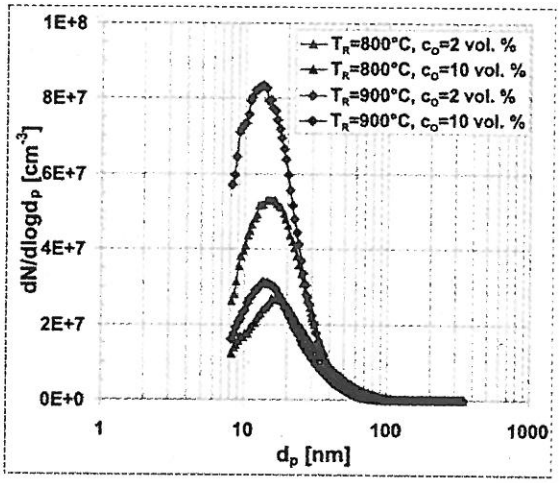


Fig. 3Influence of $T_R$ and $c_O$ on PSD's at $P_{MnAA}$=3.50 Pa, $Q_R$=800 cm$^3$/min, OXIDATION.

### Particle characterization

Experimental conditions of the samples for particle characterization are shown in Table 1.

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

| Sample No. | $T_R$ [°C] | $P_{CoAA}$ [Pa] | $Q_R$ [cm$^3$/min] | $c_O$ [vol. %] | Carrier gas/reagent | Crystalline phases |
|---|---|---|---|---|---|---|
| MnAA6 | 900 | 0.82 | 800 | 0 | $N_2$ | n.i.[&] |
| MnAA9 | 1000 | 2.20 | 800 | 0 | $N_2$ | **Mn**[&], $Mn_2O_3$[&] |
| MnAA11 | 600 | 2.20 | 800 | 10 | $N_2/O_2$ | n.a.[#,&] |
| MnAA13 | 800 | 2.20 | 800 | 10 | $N_2/O_2$ | n.a.[#,&] |
| MnAA15 | 800 | 3.05 | 800 | 2 | $N_2/O_2$ | n.a.[#,&] |
| MnAA17 | 900 | 5.47 | 800 | 10 | $N_2/O_2$ | n.a.[#,&] |

Morphology

**Pyrolysis:** Particles were typically agglomerated into clusters with primary particle size between 5 and 10 nm, and with clusters size increasing with increasing $P_{MnAA}$. An example of generated particles is shown in Fig. 4.

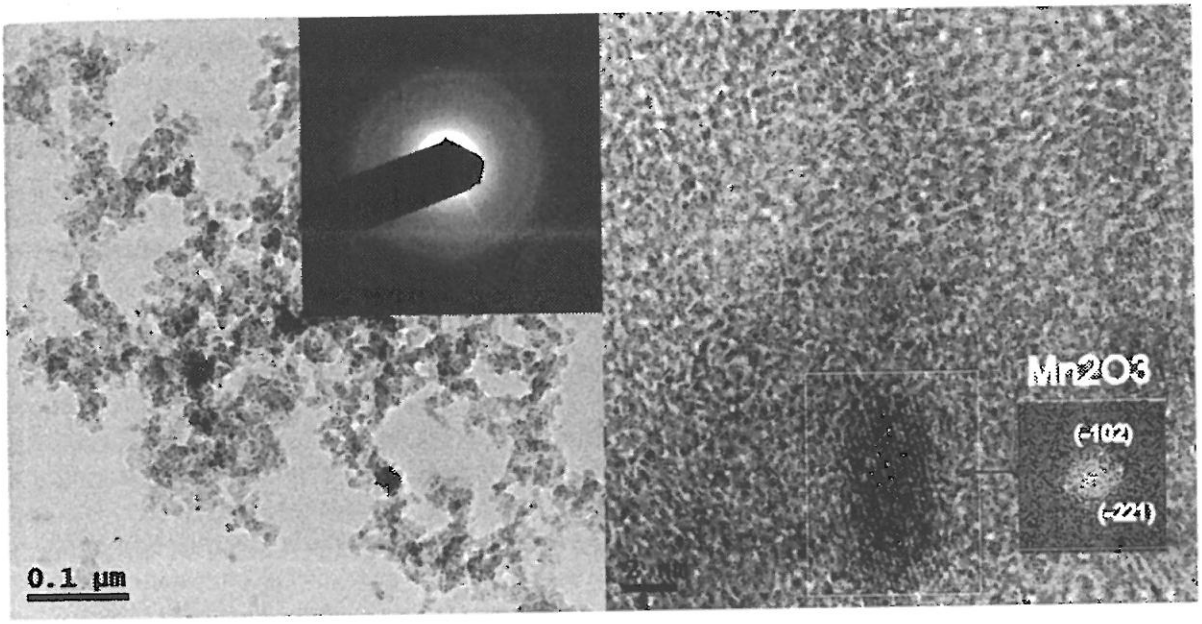


Fig. 4 HRTEM images and SAED pattern of the sample MnAA9, $T_R$=1000 °C, $Q_R$=800 cm$^3$/min, $P_{MnAA}$=2.20 Pa, $c_O$=0.

**Oxidation:** Mixture of spherical and facetted particles. Size of spherical particles varied between 10 and 30 nm, facetted particles were larger, 20 – 50 nm. Both spherical and facetted particles were partially agglomerated. Portion of facetted particles increases with increasing $T_R$ and $c_O$. An example of particles is shown in Fig. 5.

Crystallinity and composition

Particles prepared by pyrolysis were XRD amorphous and SAED patterns were rather week. HRTEM images detected lattice fringes in the cores of particles, which were mostly indexed as cubic Mn (an example is shown in Fig. 4).

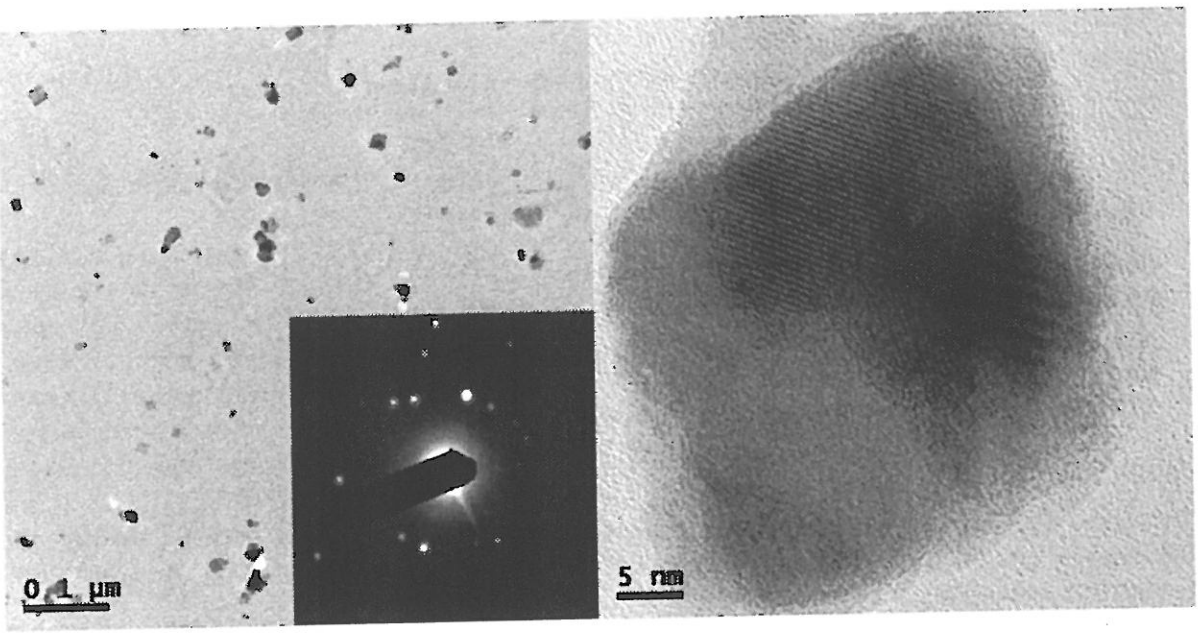


Fig. 5 HRTEM images and SAED pattern of the sample MnAA17. $T_R$=900 °C, $Q_R$=800 cm$^3$/min, $P_{MnAA}$=5.47 Pa, $c_O$=10 vol. %.

Particles produced by oxidation, were much more crystalline. Electron diffraction patterns consist of spots, which are difficult to index, and lattice fringes were visible through the whole size of particles (Fig. 5). EDS analysis discovered Mn, O and C in the samples with much higher oxygen concentration in the particles prepared by oxidation. XPS analysis of the 5 nm thick surface layer of the samples showed carbon present in bonds C-C, C-H and C-O and manganese in bonds Mn-O.

## CONCLUSIONS

$Mn/MnO_x$ nanoparticles were synthesized in an externally heated tube reactor by decomposition of MnAA in both inert and oxidative atmosphere. Size of primary particles varied in dependence on experimental conditions between 5 and 50 nm. We can suppose formation of Mn nanoparticles encapsulated in partially decomposed MnAA by pyrolysis and $MnO_x$ nanoparticles by oxidation.

## ACKNOWLEDGEMENTs

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