

Synthesis and Modification of structured molybdenum oxide-composite nanoparticles in an integrated CVS/CVD process

Weis F., Seipenbusch M. and Kasper G.

Institute for Mechanical Process Engineering and Mechanics,
Karlsruhe Institute of Technology (KIT), 76131, Karlsruhe, Germany

Keywords: aerosol coating, oxide-composite, nanoparticle, modification, CVD

In general, structured molybdenum containing oxide-composite particles are of great interest as catalysts in different reactions such as oxidative dehydrogenation or the partial oxidation of hydrocarbons. For optimized activity a high dispersion of the active Mo oxide on a support material is desirable. The support can either be inert like SiO_2 and Al_2O_3 or it can be reactive itself like Fe_2O_3 . The industrial production of formaldehyde for instance is based on the partial oxidation of methanol and the use of an iron molybdenum oxide catalyst. The formation of the mixed oxide phase iron molybdate requires the interdiffusion between the two oxide phases. Chemical Vapour Deposition (CVD) offers one step and solvent free synthesis technique as an alternative to the conventional multi-step liquid-phase techniques which require coprecipitation, impregnation and calcination for the preparation of such supported catalyst particles. CVD has been used for several material combinations including noble metals as well as metal oxides and the synthesized particles show comparable catalytic performance (Serp et al., 2002).

In this work an integrated CVS/CVD gas process at atmospheric pressure was adapted to synthesize molybdenum oxide supported on SiO_2 or Fe_2O_3 .

This process was already successfully used for the synthesis of Pd/ SiO_2 particles with a narrow size distributions of well dispersed Pd-nanodots on the SiO_2 -surface (Binder et al., 2007).

The support particles were synthesized by Chemical Vapour Synthesis (CVS) in a hot wall reactor. A nitrogen-oxygen mixture was used as carrier gas and the precursors used for the Fe_2O_3 - and SiO_2 -substrate particles were iron-pentacarbonyl and tetraethyl(ortho)silicate (TEOS), respectively. Depending on the temperature in the CVS step different crystalline phases (alpha and gamma) were obtained for the iron oxide particles. SiO_2 -particles were found to be amorphous.

In a second step the support particles were directly coated downstream with Mo-oxide in the gas phase by Chemical Vapour Deposition (CVD) using molybdenum hexacarbonyl as a precursor and oxygen as reactive gas. Subsequent temperature treatment of the aerosol in an additional hot wall reactor was used to further modify the oxidation state of the molybdenum oxide coating and to enhance the formation of a mixed oxide for the $\text{MoO}_x\text{-Fe}_2\text{O}_3$

particles as mentioned above. The influence of subsequent aerosol treatment was shown by a change of the relevant peaks in FTIR spectra.

Coating of the particles was analyzed online in the aerosol phase by a single-stage low pressure impactor (SS-LPI) in the pressure scanning mode or offline by HR-TEM. Well defined core-shell-structures with a coating thickness in the nanometer range could be obtained as shown in figure 1 for the $\text{MoO}_x\text{-SiO}_2$ particles.

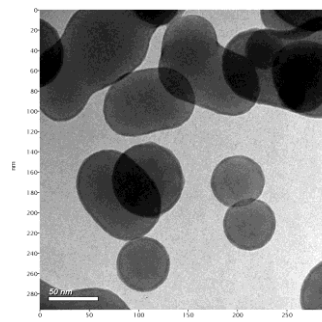


Figure 1: $\text{MoO}_x\text{-SiO}_2$ particles synthesized by an integrated CVS/CVD-process

Complete encapsulation of the support particles and a good dispersion of the Mo oxide on the support particles were further ensured by elemental mapping using electron energy-loss spectroscopy energy (EELS) as shown in figure 2 for the iron molybdenum oxide particles.

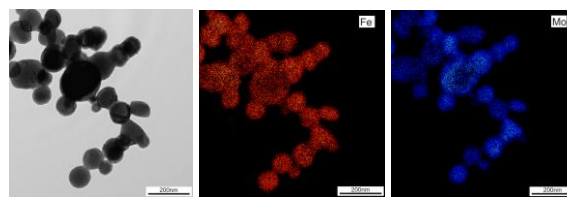


Figure 2: EELS imaging of iron molybdenum oxide particles

This project was supported by Deutsche Forschungsgemeinschaft (DFG).

Serp P., Kalck P., Feurer, R.(2002) *Chemical Reviews*, 102(9); 3085-3128

Binder A., Heel, A., Kasper, G. (2007) *Chem. Vap. Deposition*, 13; 48-54