Synthesis of tailored composite nanoparticles by a continuous integrated CVS/CVD – process at atmospheric pressure

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Introduction

In general, structured oxide-composite particles, containing molybdenum oxides, are of great interest for the use in catalysis [1]. The industrial production of formaldehyde is based on the partial oxidation of methanol in a fixed bed reactor and the use of an iron molybdenum oxide catalyst. Process instabilities and insufficient heat transfer in the catalyst bed due to the high exothermicity of the reaction, lead to the formation of hot spots and deactivation of the catalyst by sintering and sublimation of MoO_3. The use of an alternative fluidized bed process, overcoming these problems and offering additionally advantages like decrease of explosion risk and continuous changing of deactivated catalyst, demands mechanically stable supported catalysts with a well-defined particle morphology [2].

Chemical Vapour Deposition (CVD) offers an alternative solvent free synthesis technique to the conventional multi-step liquid-phase techniques including co-precipitation, impregnation and calcinations for the preparation of such supported catalyst particles. It has been used for several material combinations including noble metals as well as metal oxides and the synthesized particles show comparable catalytic performance [3].

In this work a continuous CVS/CVD-process at atmospheric pressure, which was originally applied for the synthesis of well dispersed Pd nanodots with a narrow size distribution on SiO_2 support [4], was used for the synthesis of MoO_x-Fe_2O_3 and MoO_x-SiO_2 composite particles, which can be used as catalyst for partial oxidation of methanol or the esterification of acetic acid [5], respectively.

Experimental

The experimental setup for the production of the MoO_x-Fe_2O_3 particles in a combined CVS/CVD process is shown in figure 1. In the first CVS step, a nitrogen flow is loaded with a defined amount of the precursors iron-pentacarbonyl or tetraethyl(ortho)silicate (TEOS) in a temperature-controlled bubbler, mixed with oxygen and dilution nitrogen and fed into a hot wall reactor, where the precursors thermally decomposed and the oxidized particles were formed by homogeneous nucleation. A nitrogen flow, loaded with a defined amount of water vapour, could be added to change the water concentration in the CVS-process step and therefore influence the OH group surface density of the particles. This surface modification should be used to control the selective deposition of the precursor as shown for the deposition of Pd dots on SiO_2 particles by adjusting the oxygen flow rate [4]. For the MoO_x-SiO_2 composite particles an additional sintering furnace in the CVS step was used to ensure spherical SiO_2 particles. Further downstream a silica diffusion dryer is used to remove gas-

phase water, which was added (or generated during the TEOS decomposition). To coat the support particles, a temperature- controlled sublimator was used to load a flow of nitrogen with molybdenum hexacarbonyl vapor and was directly connected to the first inlet of an electrically heated CVD reactor, which was made of glass and set to a defined temperature. In the CVD reactor, the support particles were mixed with the $Mo(CO)_6$ vapor and coated via decomposition of the precursor. An optional tube furnace was used for subsequent temperature treatment of the aerosol to further oxidize molybdenum oxide coating and to enhance the formation of mixed crystalline phases, which exhibit higher catalytic activity [1].

For characterization the particles were collected on a filter and a TEM grid. TEM-Images were made using a Philips CM12 (120keV) and EDX analyses was done with a Bruker, Quantax 400 detection system. The FTIR spectra of the samples were recorded with a Bruker,Vector 22, using the KBr disk technique. The degree of deposition and coating thickness was measured online in the aerosol phase by a single-stage low pressure impactor (SS-LPI) in the pressure scanning mode. To apply this method, a certain density ratio of the coating and support material is needed and could therefore be used only for the MoO_x-SiO_2 particles. For detailed information see [8].
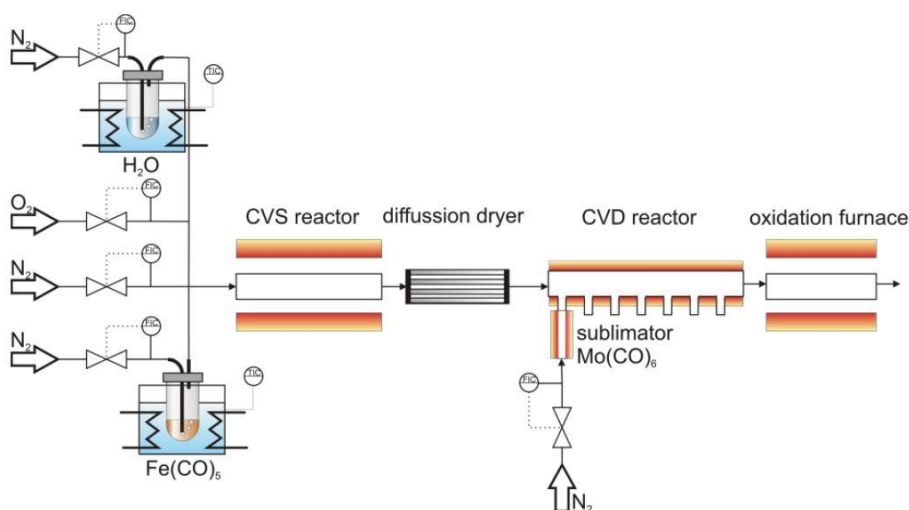

Fig.1: Experimental setup for the preparation of MoO_x-Fe_2O_3 composite particles

Results

Preparation of the support particles

Fe_2O_3-Particles were synthesized at two different temperatures in the CVS reactor and different crystalline phases and morphologies were obtained, as shown in figure 2. For 600°C agglomerates with a primary particle size of 4-7nm and a specific surface area of 89,1 m^2/g were obtained. The crystalline phase could be assigned to alpha-Fe_2O_3 by FTIR- and XRD-measurements. Thermo-gravimetric analysis [8] (Netzsch TG 209/2/F) of 7mg samples, synthesized at 600°C and a water concentration of 0, $3 \cdot 10^{-4}$ and $6 \cdot 10^{-4}$ mol/l, was used to determine the OH surface group density and values of 3, 7 and 16 #/nm^2 were found, respectively. The later value corresponds to a fully hydroxylated surface [7].

In contrast, chainlike agglomerates consisting of higly crystalline (gamma-Fe_2O_3) primary particles with an edge length of 100-200nm and S_{BET}=7,5 m^2/g were formed at 1500°C. TGA analyses for these particles could not be performed due to the small specific surface area. The SiO_2 particles, synthesized at 1000°C and sintered at 1500°C, were spherical and amorphous with an OH group surface density of 1-6 #/nm^2, depending on added oxygen flow rate [4].
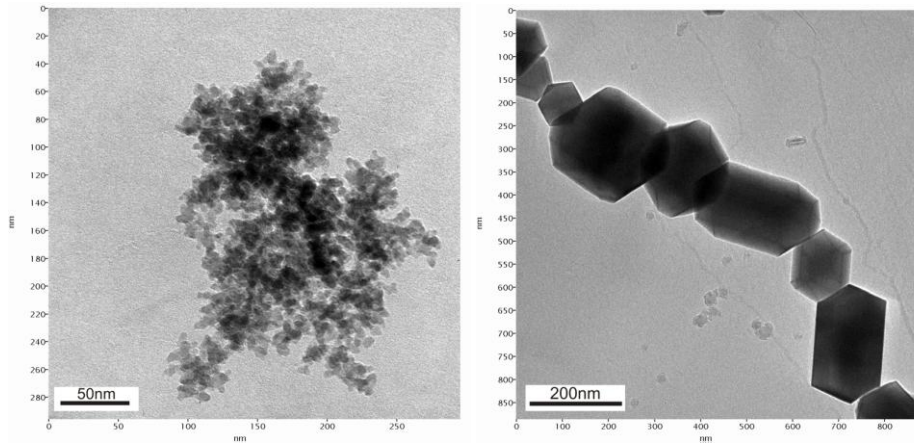

Fig.2: Fe_2O_3 particles synthesized by CVS at 600°C (left) and 1500°C (right)

Fe_2O_3-MoO_x composite particles

For the coating step different CVD reactor temperatures in the range of 100-450°C were tested. Best results and uniform core shell structures were obtained for T_{CVD}=150°C, as shown in figure 3 and was therefore chosen for further investigations. Lower temperatures gave poor $Mo(CO)_6$ decomposition and higher temperature values resulted in homogenous nucleation of MoO_x particles and no coating of the support particles could be observed.
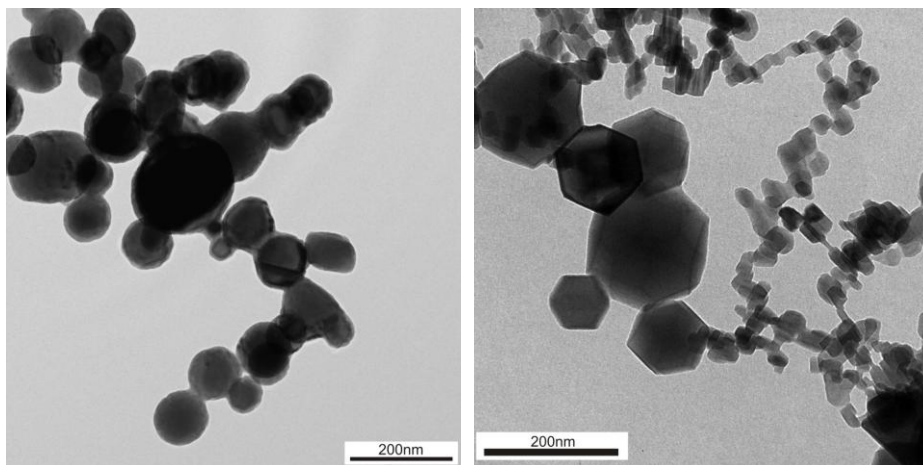

Fig.3: TEM-Images of Fe_2O_3-MoO_x composite particles coated at $T_{CVD,Mo(CO)6}$=150°C (left) and 450°C (right). $T_{CVS,Fe(CO)5}$=1500°C and $T_{Subl,MO(CO)6}$=60°C for both samples

By changing the temperature of the sublimator ($T_{Subl,Mo(CO)6}$=40-60°C) and therefore the $Mo(CO)_6$ loading of the nitrogen flow, samples with an increasing Mo/Fe mass ratio (determined by EDX and ICP-OES) could be synthesized, corresponding to the exponential increase of the sublimation rate, which was determined by gravimetric analyses of the mass of $Mo(CO)_6$ powder. ICP-OES and EDX measurements showed good agreement with the EDX values being slightly higher, because of the surface-related character of the technique.
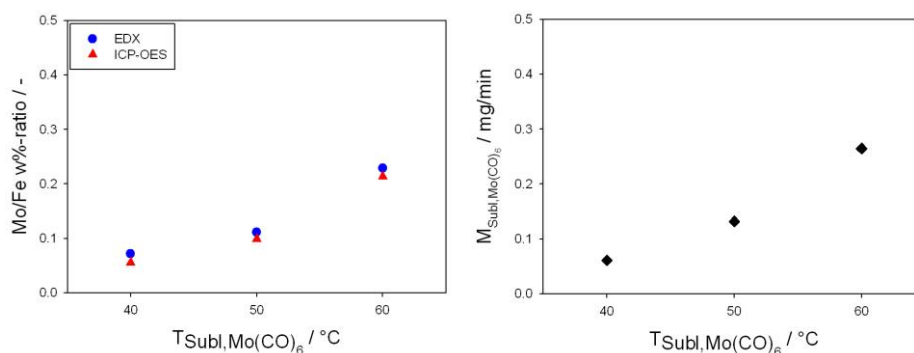

Fig.4: Mo/Fe mass ratio of Fe$_2$O$_3$-MoO$_x$ composite particles synthesized at $T_{CVS,Fe(CO)5}$=1500°C and $T_{CVD,Mo(CO)6}$=150°C (left) and Mo(CO)6 sublimation rates (right) for different sublimator temperatures

Subsequent temperature treatment of the aerosol in an additional flow reactor was used to further oxidize the MoO$_x$-shell and to enhance the formation of a Fe-Mo mixed oxide shell, which is indicated by an increase in the relevant peaks seen in the FTIR spectra and a change in the particle surface morphology observed on TEM images.

Acknowledgement

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