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Vanadium Oxide Clusters

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Vanadium Oxide clusters in a supported form or as part of a multiple phase system have recently become significant as catalytic active components in many selective oxidation reactions. The research on catalysts, which mainly contain V_xO_y as active components and which are applied in the partial oxidation of hydrocarbons concentrates on the systems Vanadium Titanium Oxide¹ and Vanadyle Pyrophosphate². Therefore, V_xO_y clusters can serve as 2-dimensional model catalysts. The inert gas aggregation technique³ was used, which allowed the preparation of metal clusters under clean conditions. V_2O_5 was evaporated by direct heating of an open crucible into an Argon atmosphere of about 1 mbar partial pressure, which was cooled down by liquid Nitrogen in order to obtain a supersaturation for the creation of nuclei and for further cluster growth. The prepared clusters were deposited on amorphous carbon films after the Argon gas had been pumped off by means of a Helium cooled cryo-pump. By using a Gatan transfer holder, the samples were transferred under Nitrogen into the electron microscope (Philips CM200 FEG) for structural characterisation. In order to study the type of the chemical binding, electron energy loss (EELS) was performed. The main results can be summarised as follows: depending on the temperature of the substrate during the cluster deposition, partly crystalline particles could be observed, but also samples without atomic resolution. The clusters presented here with atomic resolution were not stable under the electron beam. Originally crystalline particles changed to amorphous structures. Therefore, low dose experiments were performed. However, structural characterisation turned out to be extremely difficult. By using the EELS-technique it could be shown that the originally as V_2O_5 evaporated material showed spectra different from the evaporated material. It could be shown that reduction occurred and the final structure was between V_2O_5 and VO. After larger irradiation times only VO was observed. It is not clear whether a reduction took place already prior to the deposition or due to the interaction with the electrons or also during the evaporation process. Furthermore, it could be observed that under the electron beam changes in the EELS-spectra occurred. Pure Vanadium was also evaporated which caused the nucleation of crystalline Vanadium clusters, which were later, after structural characterisation, oxidised. Typical examples of such particles are shown in the figures a-c together with the power spectra. Fig. a shows a Vanadium cluster of about 3 nm diameter with bcc structure in the [001] orientation. In fig. b also a Vanadium cluster is shown. The diameter is about 4 nm and the structure is bcc in the [110] orientation. Also amorphous parts are visible. Fig. c represents a particle after oxidation in air. The oxidation state is that of VO. The structure is cubic of NaCl-type and the orientation is [110]. The small deviations of the lattice parameters and the lattice angles from the bulk data are typical for distortions present in small nanoparticles.

References

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