# Preparation of vanadium and vanadium oxide clusters by means of inert gas aggregation

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Vanadium clusters were prepared by the inert gas aggregation technique by evaporating V of high purity. Structural characterization was performed by high-resolution transmission electron microscopy. Apart from vanadium clusters of bcc structures in different orientations, crystalline VO clusters of NaCl structures were observed, which was attributed to the reaction with free oxygen present on the amorphous carbon substrates. The latter could be detected by electron energy-loss spectroscopy. The exposure of the samples to air caused a change to amorphous structures, which re-crystallized under the electron beam. This effect was interpreted as a reaction with water present in the air.

**KEY WORDS:** clusters; high-resolution electron microscopy; oxidation.

## 1. Introduction

Vanadium oxide clusters in a supported form or as part of a multiple-phase system have recently become significant as the catalytic active component 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 system vanadium titanium oxide [1,2] and vanadyl pyrophosphate [3,4]. Therefore, $V_xO_y$ clusters can serve as two-dimensional catalysts. Of importance also is an accurate analysis of the structural behavior. A review article [5] dealing with selective catalytic reduction of $NO_x$ indicates the importance of a fundamental knowledge of catalysis utilizing vanadium clusters. Nevertheless, there are many open questions on vanadium oxide clusters [6,7]. We tried to prepare pure vanadium clusters by directly evaporating V, which subsequently were oxidized. This technique and the structural characterization are described below.

## 2. Experimental

Vanadium clusters in the size range between 1 and 10 nm diameter have been prepared by the inert gas aggregation technique [8,9]. In order to prepare the clusters under clean conditions and for further spectroscopic investigations, which will not be discussed here, a newly designed cluster nucleation cell was constructed which made it possible to create UHV conditions after depositing the clusters. The principle of the cell is described in detail elsewhere [10,11]. Vanadium (Goodfellow Vanadium wire, 1.0 mm diameter, 99.9% purity) was evaporated from a Knudsen cell of molybdenum by direct heating (400 A current, 4 V voltage) at a temperature higher than 1800 °C into a liquid nitrogen-cooled argon atmosphere at $1.5 \times 10^{-1}$ mbar pressure. The cluster flow was monitored by means of a quartz microbalance (Inficon XTM). In order to avoid coagulation, the cluster flow was kept at 0.04 nm/s. The clusters were deposited on an amorphous carbon film of 4 nm thickness; the deposition time was 8 s. The samples were transferred under a nitrogen atmosphere into the electron microscope with a transfer system (Gatan) in order to avoid chemical reactions (oxidation) with air. The transfer system could also be used as a reaction chamber. For high-resolution transmission electron microscopy (HRTEM) a Philips 200 kV microscope equipped with a field emission gun was used (CM 200 FEG, $C_s = 1.35$ mm). The information limit of this microscope was better than 0.18 nm. In order to study oxidation of vanadium clusters, the samples were exposed to air for 170 h under ambient conditions after electron microscopic studies. The samples were then again inserted into the microscope for further studies.

For interpretation the images were digitized. The pixel size used was 0.0284 nm and the images were digitized in $256 \times 256$ or in $512 \times 512$ square pixels. In order to enhance the quality and contrast of the images, image processing was performed [12–14]. For this purpose, the power spectra (square of the Fourier transform of the images) had to be calculated. From these data, information on structures, lattice parameters and orientations with respect to the substrate could be obtained. For the digitization a densitometer (Image Science GmbH, Berlin) equipped with a CCD camera was used. Sometimes,

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images were taken with the CCD camera of the microscope with a pixel size of 0.0222 nm. The images were directly stored after digitizing into the computer for further interpretation. In order to explain structures of the clusters, computer simulations by using the multi-slice technique [15] were carried out. However, very often the technique of single-crystal diffraction was sufficient. A well-known technique for structural characterization is the comparison of calculated images in different orientations with the experimental image [16].

## 3. Results and discussion

Overview images of pure vanadium clusters deposited on amorphous carbon films showed a very low density of clusters, which guarantees that no coagulation during their growth or on the substrate had taken place.

Figure 1 shows a particle of about 6 nm diameter together with its power spectrum. The particle could be identified as pure vanadium in the [001] orientation of bcc structure. The particle consists of two domains. One domain shows two reflections in the corresponding power spectrum of the 110 family, *i.e.*, at 0.210 and 0.215 nm with an interplanar angle of 87°, and the other region shows only one 110 reflection at 0.214 nm. By comparison with the bulk data it can be concluded that the cluster is slightly deformed. The corresponding bulk data are $d_{110} = 0.2141$ nm with an interplanar angle between the 110 reflections of 90°.

Figure 2 shows another example of a vanadium cluster—also of about 6 nm in diameter—of bcc structure in the [110] orientation. In the upper part of the particle an amorphous region can be seen. The $\bar{1}10$ reflection and the 002 reflection correspond to lattice parameters of $d_{\bar{1}10} = 0.213$ nm and $d_{002} = 0.144$ nm (bulk $d_{002} = 0.1514$ nm). The interplanar angle is 87°, which is close to the 90° for the bulk material. Again, small distortions are observed. It should be pointed out that imaging of the $d_{002}$ netplane at 0.144 nm shows excellent resolution condition.

Surprisingly, particles with large deviations of the lattice parameters from pure vanadium could be observed. Figure 3 shows such an example. This particle can be identified as VO in the [110] orientation with rock salt structure (Fm$\bar{3}$m). The $1\bar{1}1$ and 002 reflections correspond to 0.240 nm and 0.204 nm, respectively (bulk $d_{1\bar{1}1} = 0.2379$ nm and $d_{002} = 0.2060$ nm). The angle between the planes is 50° (bulk 54.7°), which indicates heavy distortions within the particle.

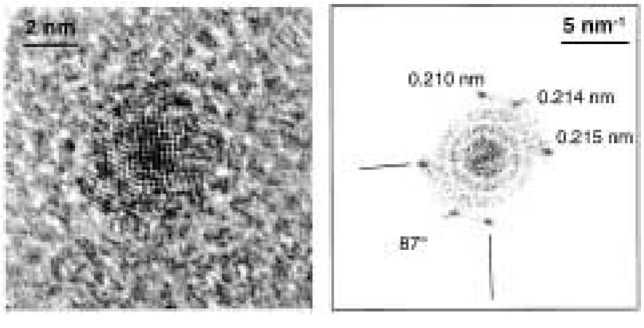

Figure 1. HRTEM image and power spectrum of vanadium with bcc structure in the [001] orientation.

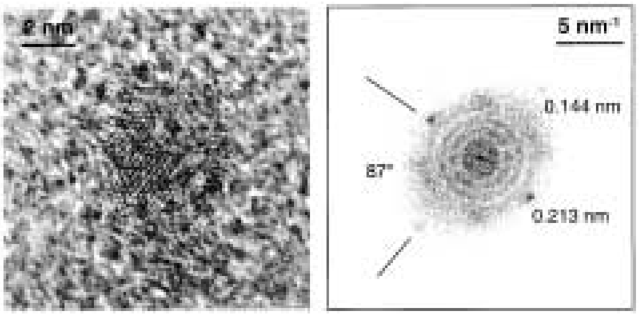

Figure 2. HRTEM image and power spectrum of vanadium with bcc structure in the [110] orientation with an amorphous region (top right).

The reason for the oxide formation can be identified using our electron energy-loss spectroscopy (EELS) facilities. The EELS spectroscopy of a pure amorphous carbon film shows an oxygen K-edge at 540 eV energy loss, as can be seen in figure 4. The small amount of free oxygen on the carbon film has reacted with some of the originally pure V clusters leading to VO clusters.

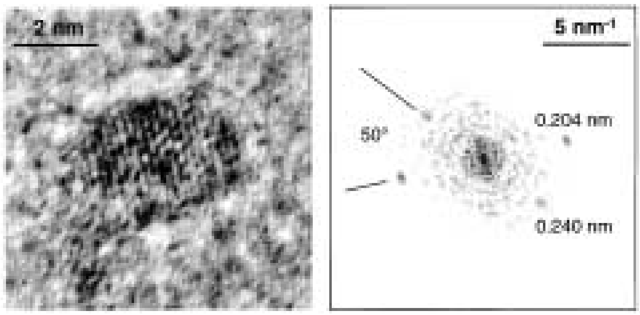

Figure 3. HRTEM image and power spectrum of a VO cluster in the [110] orientation.

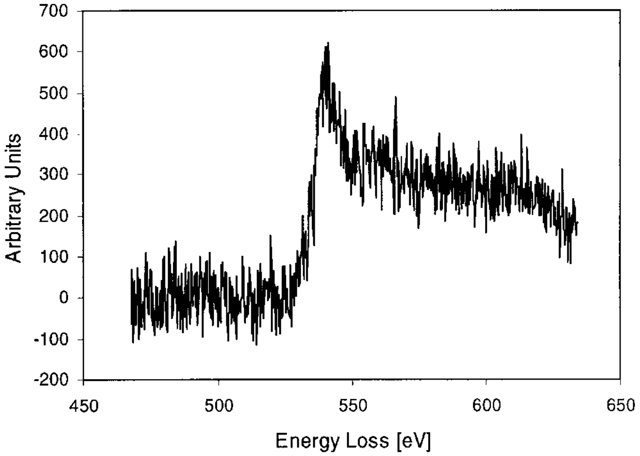

Figure 4. EELS spectrum of a carbon film without vanadium depositions with the O–K spectrum at 540 eV energy loss.

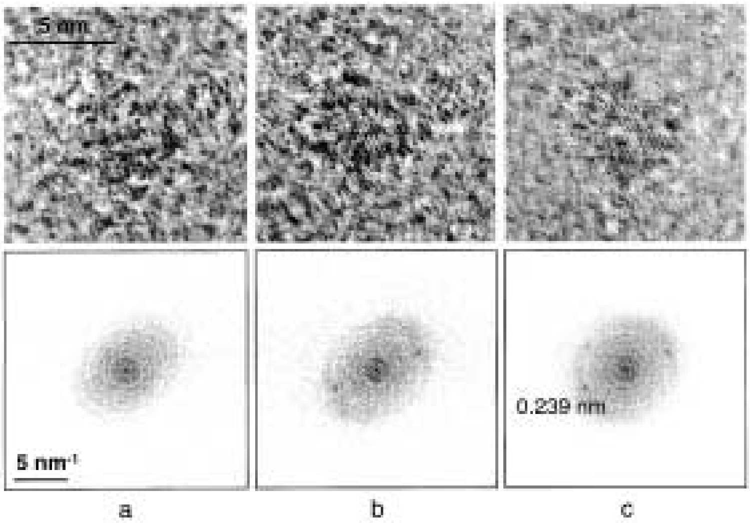

Figure 5. Recrystallization of oxidized vanadium clusters together with the power spectra for different dose rates of irradiation. (a) Without additional irradiation, (b) after 1 min of irradiation, (c) after 3 min of irradiation.

This may be taken as proof of the very high reactivity of the vanadium clusters.

The vanadium cluster samples (which included also some oxidized particles) were then exposed to air for 168 h under ambient conditions. After this procedure, the structures of the particles turned out to be amorphous, as can be seen in figure 5(a). Only after further irradiation did re-crystallization occur, which was observable after about 1 min (figure 5(b)). Following a further 2 min of irradiation, no further changes in the crystallinity could be observed, as can be seen in figure 5(c).

The finding of originally amorphous structures of the oxidized clusters contradicts the finding of the crystalline structures of vanadium oxides without exposing the clusters to air. It is believed that the influence of water contained in the air causes the amorphous structures, which will then be removed after irradiation (heating) with electrons. However, no proof thereof can be given at the present stage. Further investigations will be performed.

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