

# Morphological Characterization of V<sub>2</sub>O<sub>5</sub> Catalysts Prepared by Ball Milling

D.S. Su<sup>a</sup>, G. Weinberg<sup>a</sup>, R. Schlögl<sup>a</sup>, H. Knözinger<sup>b</sup>

a: Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6,  
D-14195 Berlin, Germany

b: Institut für Physikalische Chemie, Universität München, Butenandtstrasse 5-13 (Haus E),  
D-81377 München, Germany

Ball mill was used in recent years for preparations of metal oxide catalysts [1]. It is obvious that the aim of milling is to reduce the size of the powder components and therefore to increase the surface area of catalysts. It is, however, also obvious that milling can also introduce lattice defects, destroy the surface structure, result in the loss of oxygen or can even induce phase transitions. Understanding the effects of milling of metal oxides become therefore unavoidable for the understanding of the chemical reactivity of prepared catalysts. Raman spectroscopy, ESR spectroscopy and MAS <sup>51</sup>V NMR techniques were used to characterise the oxidation state of vanadium in V<sub>2</sub>O<sub>5</sub> prepared by milling for various times [1]. In the present work, scanning and transmission electron microscopes (SEM and TEM), electron diffraction and high-resolution imaging techniques were used to elucidate the effects of ball-milling on the morphology of V<sub>2</sub>O<sub>5</sub> powders. Electron energy-loss spectroscopy (EELS) was used to study the oxidation state of vanadium.

Vanadium oxide V<sub>2</sub>O<sub>5</sub> was from J. T. Baker Chemicals B. V. and had a purity of >99%. 60 g of V<sub>2</sub>O<sub>5</sub> together with six agate balls (1.5 cm diameter, 11g) were placed into an agate vessel (250 cm<sup>3</sup> volume). Milling was performed for up to 20 h at approximately 150 revolutions per minute. Samples studied in the present work were taken after 3, 5, 10 and 20 h.

SEM-images in Fig.1 show the morphologies of the four samples. The particle size becomes, as expected, smaller and aggregations occur as the milling time increases. Electron diffraction patterns in Fig.2 reveal how dramatically the particle-size decreases: while the pattern from 3h milled sample still exhibits discrete spots, the pattern in Fig. 2b becomes speckled and rings made up of discrete spots appear in pattern 2c. Such rings are formed when incident electrons are diffracted by random distributed small particles. The rings develop to more continuous ring pattern as the particles sizes further decrease (Fig, 2d). High-resolution imaging reveals that, after milling more than for 10 h, most particles exhibit a disordered surface; lattice defects are formed in the bulk (Fig.3a). For the sample prepared by 20 h milling, the disordered surface layer of small particles become thicker; some particles exhibit belt lattice fringes (Fig. 3b).

EELS-spectra from very fine particles and from the surface area of large particles milled for 10 h and 20 h are shown in Fig.4 a and 4b respectively. Due to the oxygen loss during millings the intensities of the O K-edge decrease. The peak positions of the V L<sub>3</sub>-edges from the 10 h milled particles varies from 518.2 to 518.8 eV and those from 20 h milled samples varies from 517.8 to 518.5 eV. According to Chen et al [2], the corresponding oxidation states of vanadium are between 3.7 to 4.6 and between 3.0 to 3.7 respectively. Since the formal oxidation state of vanadium in V<sub>2</sub>O<sub>3</sub> is 3, the present results reveal that the vanadium atoms in fine particles or at the surface of the 10 and 20 h milled samples have been reduced to oxidation states much lower than those measured by other experiments [1].

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Reference

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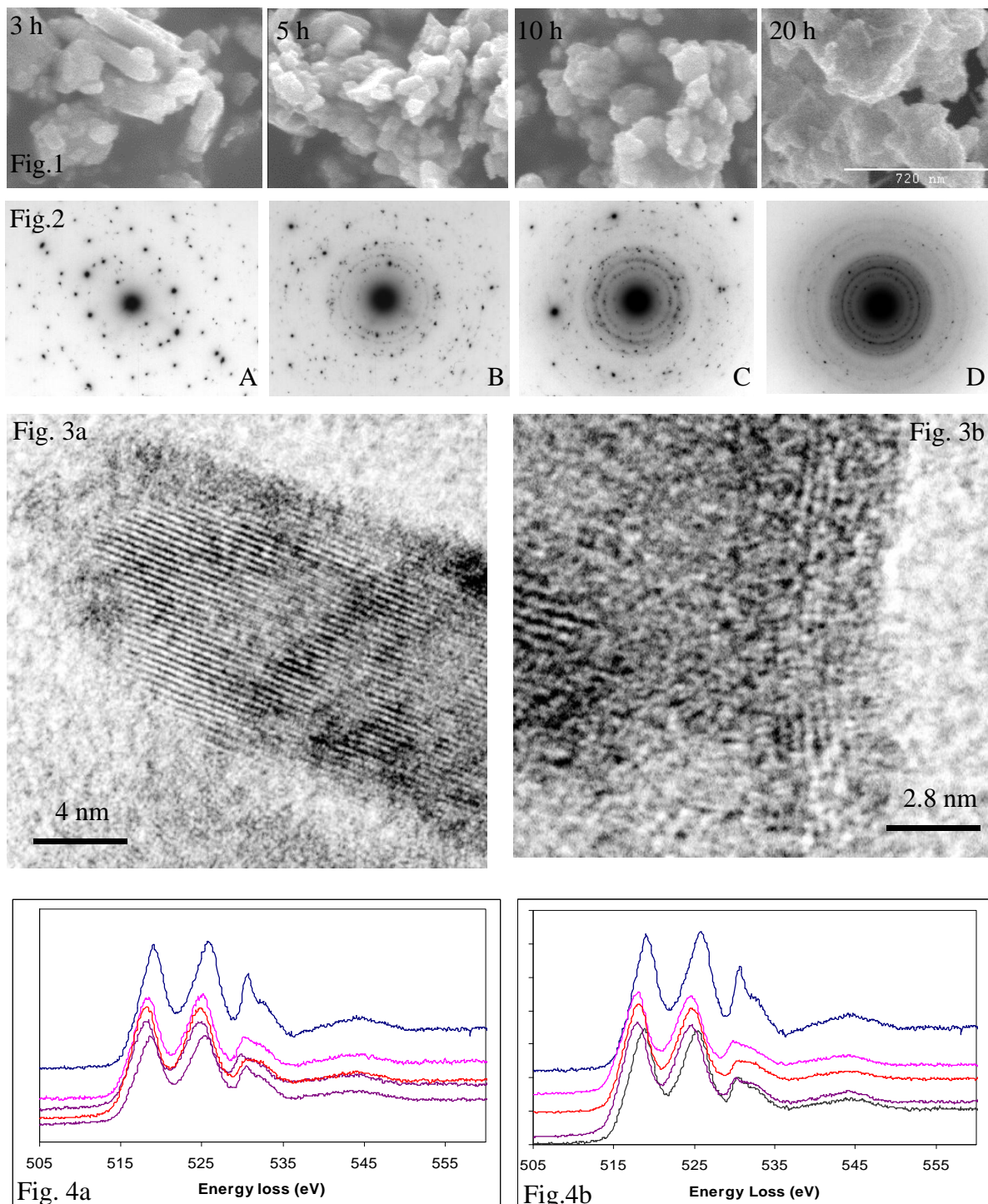


Fig. 1 SEM images of vanadium oxide samples.

Fig. 2 Electron diffraction patterns of vanadium oxide samples.

Fig. 3 HREM-image of 10 h (a) and 20 h (b) milled vanadium oxides samples.

Fig. 4 EELS-spectra of 10 h (a) and 20 h (b) milled vanadium oxides samples. Reference spectra from V<sub>2</sub>O<sub>5</sub> are insert (the upper one).