

Structural and electronic changes of vanadium pentoxide catalysts prepared by ball-milling

DangSheng Su^a, Vladimir Roddatis^a, Gisela Weinberg^a, Edith Kitzelmann^a,
Robert Schlögl^a, Helmut Knözinger^b

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

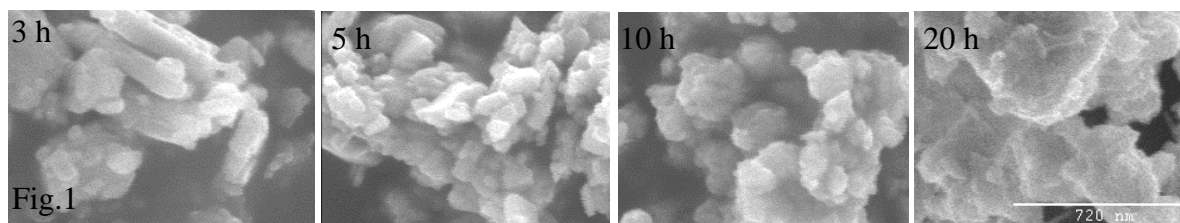
b: Institut für Physikalische Chemie, Universität München, Butenandtstrasse 5-13 (Haus E),
D-81377 München, Germany

- Introduction

Recent years ball-mill was used in catalysis, either as an alternative method for preparations of mixed or supported metal oxide catalysts or as an effective method for the modification of structure and property of catalysts [1, 2]. Generally, it is considered that ball milling can reduce the particle sizes, increase the specific surface area of catalysts and change the chemical state of surface atoms. However, detailed studies on the effects of ball-mill on catalysts down microscopic scale are failed. In the present work, we use scanning and transmission electron microscopes (SEM and TEM), electron energy-loss spectroscopy (EELS) to elucidate the effects of ball-milling on V_2O_5 powders at various milling periods.

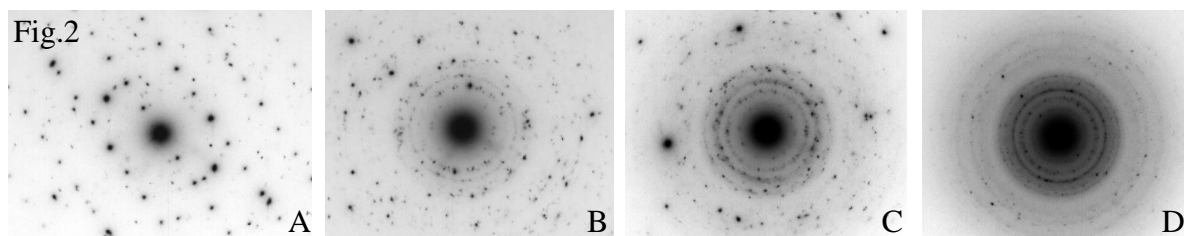
- Experimental and Summary of Results

V_2O_5 crystallites were from J. T. Baker Chemicals B. V. and had a purity of >99%. A planetary ball-mill was used for milling: 60 g of V_2O_5 together with six agate balls (1.5 cm diameter, 11g) were placed into an agate vessel (250 cm³ 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 studies were performed on a Hitachi S-4000 scanning electron microscope operating at 5 kV. TEM and EELS investigations were carried out on a Philips CM200 FEG transmission electron microscope, operating at 200 kV and equipped with a GATAN imaging filter GIF100 that was used to record EELS-spectra.



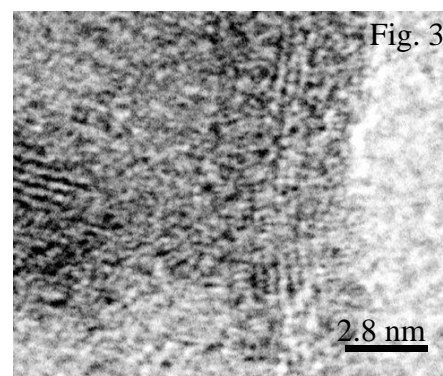
SEM-micrographs in Fig.1 show the morphological development of V_2O_5 at various periods of milling in the planetary ball. In comparison with V_2O_5 powders before milling (not shown), significant change is the decrease of powder size with the increased milling time. The size distributions of milled samples appear more homogenous. Reagglomeration of small particles is found in the 20 h milled sample.

Selected-area electron diffraction patterns in Fig.2 reveal how dramatically the particle-size decreases. While the pattern from 3h milled sample (A) still can be recognised as the 001-pattern decorated with additional spots due to the crushed particles, the pattern in B becomes speckled and rings made up of discrete spots appear in pattern C. The rings develop to more continuous ring pattern as the particles sizes further decrease (D).



Bright-field and high-resolution image reveal that the main milling effects up to 5 h is the crushing of vanadium oxides crystallites, followed by fine grinding of small particles up to 10 h. For milling up to 20 h, long range order in small crystallite are fully destroyed and reagglomeration takes place. High-resolution image in Fig.3 shows amorphous component and lattice defects induced by ball-milling.

EELS-spectra show shifts of V $L_{3,2}$ edges to low energy and a decrease of O K -edge intensity, indicating the reduction of vanadium via the loss of oxygen. Using the relationship between peak position of V L_3 edge and oxidation state of vanadium ions, we found V^{4+} state in samples milled up to 5 h. Both V^{4+} and V^{3+} states were found in the sample after 10 h and 20 h milling.



- Conclusion

Milling reduces the size of particles in V_2O_5 catalyst. With prolonged milling time lattice imperfection get serious and the surface of most particles becomes amorphous. Energy-loss spectra taken from thin particles reveal the loss of oxygen and reduction of vanadium. For milling time shorter than 5 h, vanadium in V^{4+} state is found. For milling longer than 10 h, both V^{3+} and V^{4+} states can be detected.

- Acknowledgement

The work at FHI is supported by SFB 546 of Deutsche Forschungsgemeinschaft (DFG).

- Reference

1. A.A. Shubin, O.B.N. Lapina, E. Bosch, J. Spengler and H. Knözinger: *J. Phys. Chem. B* **103** (1999) 3138
2. M. Fait, B. Bubias, J.-J. Eberle, M. Estenfelder, U. Steinike and M. Scheider: *Catalysis Letters* **68** (2000) 13