# Tribochemical modification of the microstructure of $V_2O_5$

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The tribochemical activation of vanadium pentoxide $V_2O_5$ is studied by means of X-ray diffraction, electron microscopy and electron energy-loss spectroscopy. The two-stage process can be described as crushing of large crystals into small ones (macroscopic process) followed by amorphisation and reagglomeration of the fragments (microscopic process). No milling equilibrium state can be found. Energy-loss spectra reveal the reduction of vanadium *via* oxygen loss. The formation and distribution of $V^{4+}$ or $V^{3+}$ species depends on the history of milling.

**KEY WORDS:** $V_2O_5$; tribochemical activation; oxidation state; reduction; defect and surface structure; electron microscopy; electron energy-loss spectroscopy

## 1. Introduction

In recent years, tribochemical activation has been used in catalyst research [1–3] for the preparation of mixed or supported metal oxide catalysts. Conventionally, such catalysts are prepared by impregnation, co-precipitation or grafting of one component onto a support [1]. Ball-milling preparation, which is technically simple and environmentally friendly, can be performed either by the simultaneous grinding of two or more oxide powders, or by the milling of only one prior to mixing and calcination. In addition, ball-milling is an effective method for the modification of the defect structure and the electronic properties of catalytic materials. Ball-milling can reduce particle sizes, increase the specific surface area of catalysts, and change the chemical state of constituent atoms. Improvements in the catalytic performance of ball-milled catalysts have been reported. For instance, the yield for $n$-butane oxidation to maleic anhydride (MA) increases by about 5% using a dry milled $V_2O_5$ precursor *vs.* the yield obtained with untreated $V_2O_5$, and yield increases even higher for wet milled $V_2O_5$ [2]. The catalytic performance of vanadyl pyrophosphate (VPP) catalysts is also influenced by ball-milling: the MA selectivity and maximum MA yields increase noticeably [3].

To use observations of increased yield after ball-milling for an improved structure–function relationship in V-based selective oxidation catalysts, a description of the real structure of tribochemically activated $V_2O_5$ is useful as a reference data set. The effect of the milling of $V_2O_5$ on the local environment of vanadium has been studied by solid-state $^{51}V$ NMR, ESR spectroscopy, and complementary methods [1]. It was found that most of the vanadium atoms in milled $V_2O_5$ are still in the $V^{5+}$ state, with small amounts of $V^{4+}$ and $V^{3+}$, which are most likely distributed inhomogeneously. No $V^{5+}$ ions in tetrahedral coordination were formed during milling. Zazhigalov *et al.* [2] studied the influence of the tribochemical treatment on the activity of V-containing oxide systems. They found that vanadium hydrogenphosphate hemihydrate can be thermally transformed into a VPP catalyst by milling and that milling induces anisotropic deformations.

The available integral information needs to be complemented by experiments probing the nanoscopic structural range. Since the catalytic performance is strongly dependent on the microstructure and the electronic state of the surface of small particles, such investigations are also important for the development of more efficient catalysts. In the present work, we report on the tribochemical modification of $V_2O_5$ as studied by scanning and transmission electron microscopy (SEM and TEM), electron diffraction, and high-resolution imaging techniques. Electron energy-loss spectroscopy (EELS) was used to study local changes in the oxidation states of vanadium. X-ray diffractometry was also applied to give complementary information on integral structural changes of milled samples.

## 2. Experimental

Vanadium oxide $V_2O_5$ was from J.T. Baker Chemicals B.V. and had a purity of $>99\%$. Ball-milling was carried out in a planetary ball-mill: 60 g of $V_2O_5$ together with six agate balls (1.5 cm diameter, 11 g) were placed into an agate vessel (250 $cm^3$ 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.

X-ray powder diffraction was recorded using a STOE STADIP X-ray diffractometer. SEM studies were performed on a Hitachi S-4000 scanning electron microscope operating

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at 5 kV. For TEM investigations, unmilled and milled samples were dispersed onto copper mesh grids covered with holey carbon films. A Philips CM200 FEG transmission electron microscope, operating at 200 kV, and equipped with a GATAN image filter GIF100, was used. All selected area diffraction patterns are taken from an area of about 900 nm in diameter. The image filter, operated in the spectroscopy mode, was used to record EELS spectra. All spectra were recorded from very fine particles and from the thin edge area of large particles to avoid any artefacts due to large thickness, and were corrected for backgrounds and multiple scattering [4]. In order to avoid any artefacts such as electron-beam induced structural changes, high-resolution images were taken using electron dose as low as possible. EELS spectra were recorded with 2 $A/cm^2$ current density for 5 s. According to a previous study about stability of $V_2O_5$ under electron beam irradiation, no chemical changes under those conditions are visible [5].

## 3. Results

### 3.1. Microstructure

X-ray powder diffraction patterns of the four milled samples show a decrease of integral intensities of individual Bragg peaks, an increase of the full width at half maximum, and an increase of the background of all milled samples. These features can be attributed to the reduction of particle sizes, the build-up of lattice defects and strain/stress in the bulk of the crystallites, and the increase of amorphous components in the milled powder [2]. No changes in lattice constants can be determined, indicating that milling induces deformations and defects at a local level, but does not affect the average unit cell volume and lattice constants.

SEM micrographs in figure 1 reveal the morphological development of $V_2O_5$ after various periods of milling in the planetary ball-mill. $V_2O_5$ crystallites, as received, are shown in figure 1(A). For up to 3 h of milling the main effect is the crushing of large crystallites (figure 1(B)). Further milling up to 10 h leads to the formation of fine particles with a narrow size distribution (figure 1 (C) and (D)). Increasing milling time to 20 h leads to reagglomeration of small particles, as shown in figure 1(E).

Selected-area electron diffraction patterns in figure 2 reveal the drastic loss of internal structural ordering. The pattern in figure 2(A) can be identified as the 001 pattern of orthorhombic $V_2O_5$. While the pattern of the 2 h milled sample (figure 2(B)) still can be recognised as the 001 pattern decorated with additional spots due to the crushed particles, the pattern of the sample after 5 h milling (figure 2(C)) becomes speckled. After 10 h milling, rings made up of discrete spots appear in the diffraction pattern (figure 2(D)). Such discrete rings are formed when incident electrons are diffracted by randomly distributed nanoscopic particles. After milling for 20 h, the diffraction pattern develops into a more continuous ring pattern since the long range ordering and particle sizes further decrease, reaching the level

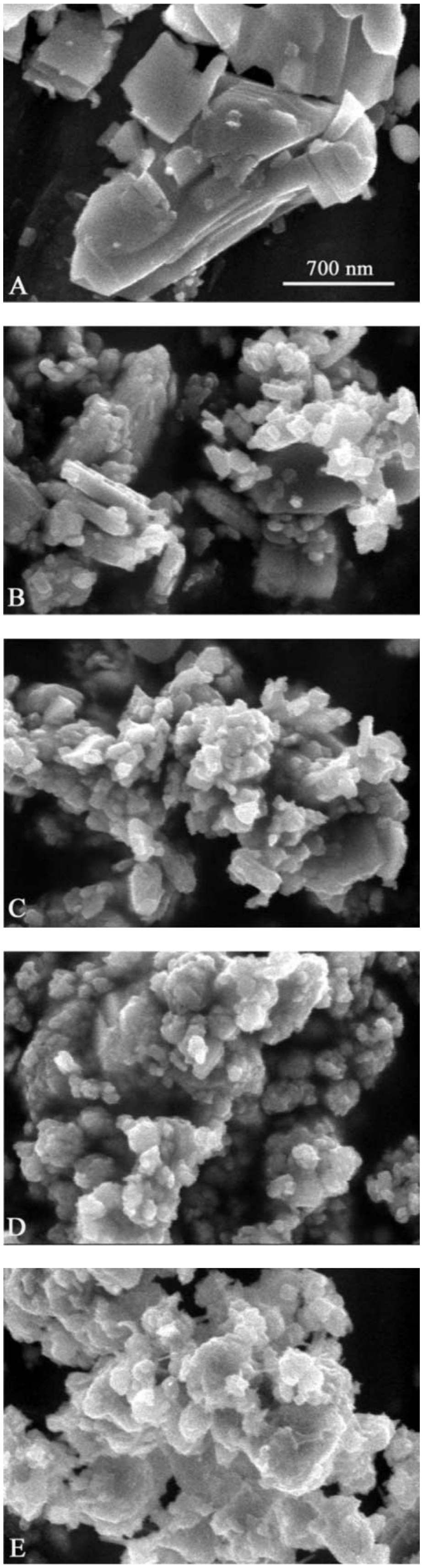

Figure 1. SEM images of vanadium pentoxide samples: (A) as received; (B), (C), (D), and (E) after 3, 5, 10, and 20 h milling, respectively; a scale bar is given in A.

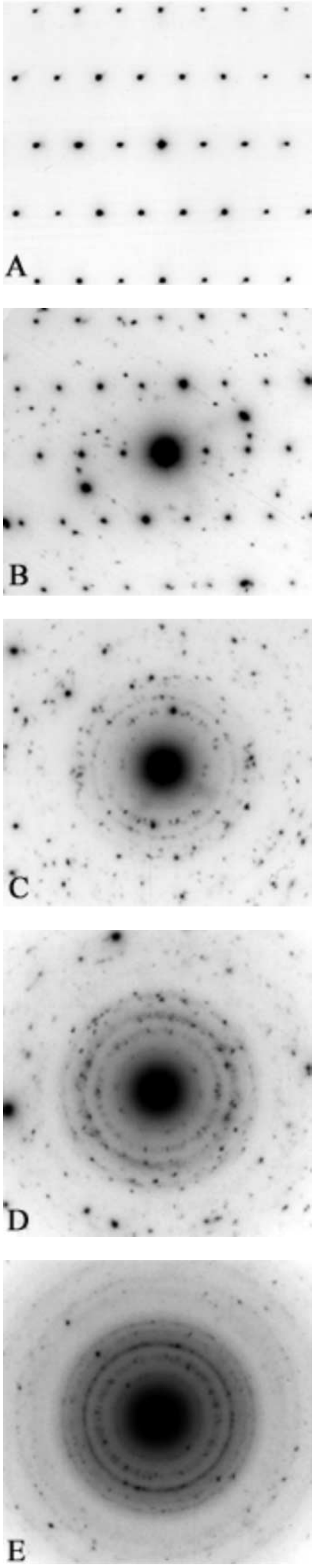

Figure 2. Selected area diffraction pattern of vanadium pentoxide: (A) as received $V_2O_5$; (B), (C), (D), and (E), after 3, 5, 10 and 20 h milling, respectively.

of amorphous matter (figure 2(E)). The diffuse background caused by the amorphous components in the samples becomes very prominent, especially in the pattern of the 20 h milled sample (figure 2(E)).

Electron micrographs of 10 and 20 h milled samples are reproduced in figure 3 (A) and (B), respectively. In figure 3(A) small particles of about 10 nm in size can be seen. They are not visible in figure 1 due to the limited resolution of SEM. Almost all particles exhibit a plate-like shape, as do those found in the untreated $V_2O_5$ sample. Also samples milled for 3 and 5 h contain similar particles. This confirms the finding by X-ray diffraction that fracture takes place in all directions [2]: the shape of particles up to 10 h milling time remains nearly the same, but their size decreases. However, the electron micrograph of the 20 h milled sample in figure 3(B) does not show clear profiles of individual particles. A scarf-like contrast was obtained, which was never observed in the samples milled for up to 10 h. It is therefore concluded that milling for periods longer than 10 h leads to reagglomerations.

High-resolution images of the thin scarf-like pieces in figure 3(B) are shown in figure 4. They reveal two kinds of contrast: (i) contrast with lattice fringes of small particles (figure 4(A)), most of them being less than 5 nm in size, aggregated to large particles as shown in the SEM image in figure 1(E) and (ii) contrast that does not show any long-range order or periodic structures (figure 4(B)). This two-fold micro-morphology is the explanation of the overlay of continuous diffraction rings with small spots in the electron diffraction patterns and of the strong background recorded both in X-ray diffraction and in electron diffraction patterns. An amorphous layer of about 5 nm in thickness can also be found on the surface of large particles (figure 4(C)). Careful investigation of the high-resolution micrographs in figure 4 (B) and (C) reveals the existence of short-range order (marked by circles) in the apparently amorphous regions. The platelets contain an irregular array of oxide clusters with a well-defined internal structure.

In order to understand how the reagglomeration process proceeds, we studied the deformation of the crystalline lattice after various periods of milling. The image in figure 5(A) reveals the lattice distortion after 5 h milling. As the milling continues, particles are crushed and the lattice distortion becomes clearly visible (figure 5(B)). Nearly all investigated small particles of the 10 h milled samples show imperfect lattice fringes in high-resolution images. The image in figure 5(C), taken from the 20 h milled sample, shows a particle whose lattice has been nearly totally destroyed, representing a state before the particle becomes amorphous. Further milling will then lead to the complete amorphization of the particle and to the reagglomeration with other particles. The reagglomeration can take place as a relaxation effect to release the energy stored in the defect structures such as those seen in figure 5(C).

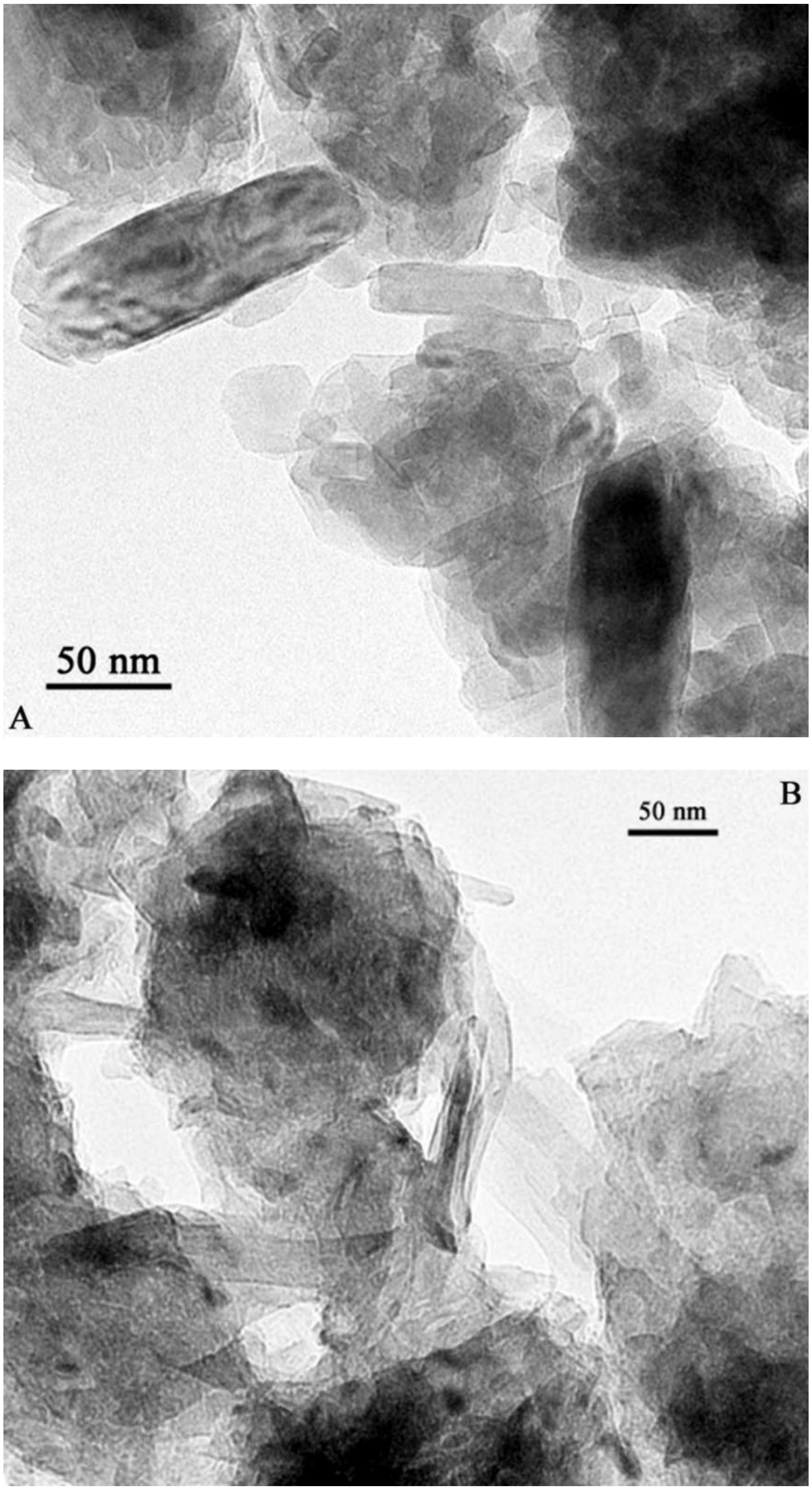

Figure 3. Electron micrographs of vanadium pentoxide after 10 (A) and 20 h (B) milling.

### *3.2. Oxidation state*

In order to find out whether the observed structural changes are accompanied with chemical or electronic changes, vanadium 2p spectra were retrieved from the measured EELS data. Up to ten spectra of each sample at different positions were recorded. Typical spectra of samples after 3 h and 20 h milling, taken at different positions in each sample, are shown in figure 6, together with the spectrum of untreated $V_2O_5$. This spectrum is characterised by the vana-

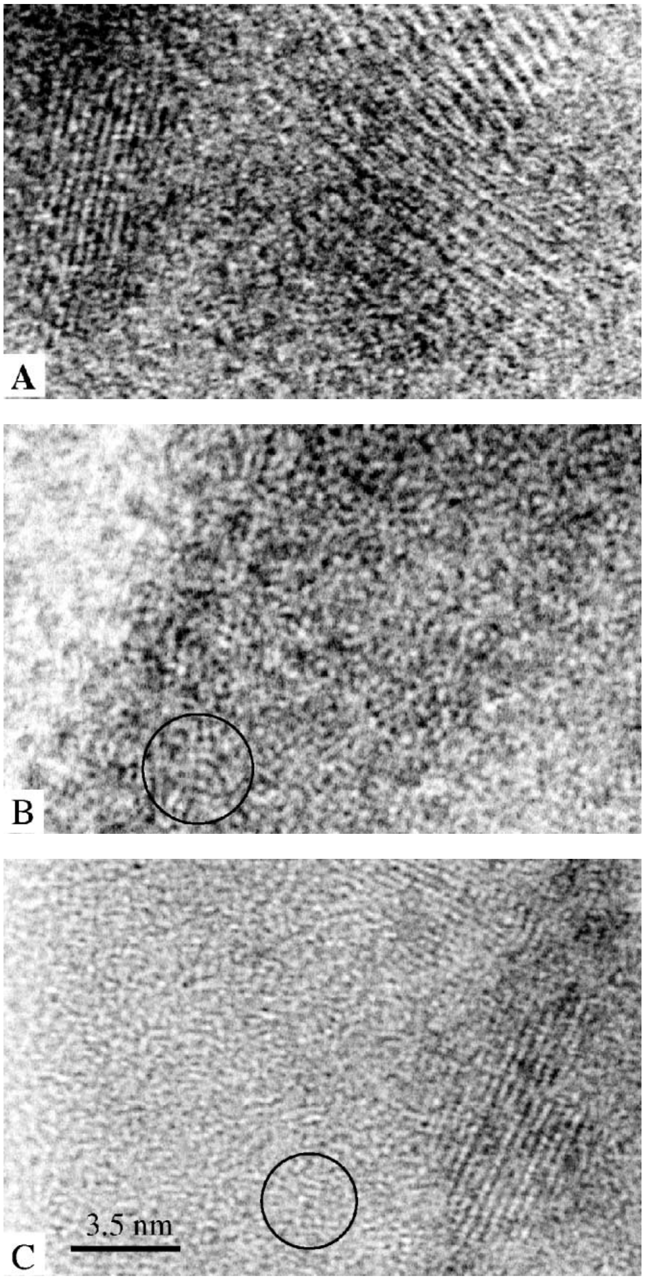

Figure 4. High-resolution images of the vanadium pentoxide after 20 h milling: (A) reagglomerated fine particle, (B) amorphous part and (C) edge of a large particle. The circles in (B) and (C) mark areas with short-range order.

dium 2p → 3d transition (V L-edge): the two peaks, located at 519 and 525.7 eV, are the V $L_3$- and $L_2$-edges, attributed to the transitions from the V $2p_{3/2}$ and V $2p_{1/2}$ core levels to the unoccupied V 3d bands, respectively [6].

In comparison with the spectrum of untreated $V_2O_5$, significant changes in the spectra of milled samples are shifts of the V $L_2$- and $L_3$-edges to lower energy loss. These changes are evidence that milling induces the chemical reduction of vanadium ions *via* the loss of oxygen. The chemical shift depends on milling time. For samples milled for 3 and 5 h, spectra which are identical with the spectrum of untreated $V_2O_5$ can still be recorded. In spectra of the sample after 20 h milling the chemical shift of the V $L_2$- and $L_3$-edges to lower energy becomes significant. The chemical shifts measured for one sample at different positions vary, reflecting the chemical inhomogeneity of the samples introduced by milling. The measured V $L_3$-edge positions of all milled samples are summarised in table 1.

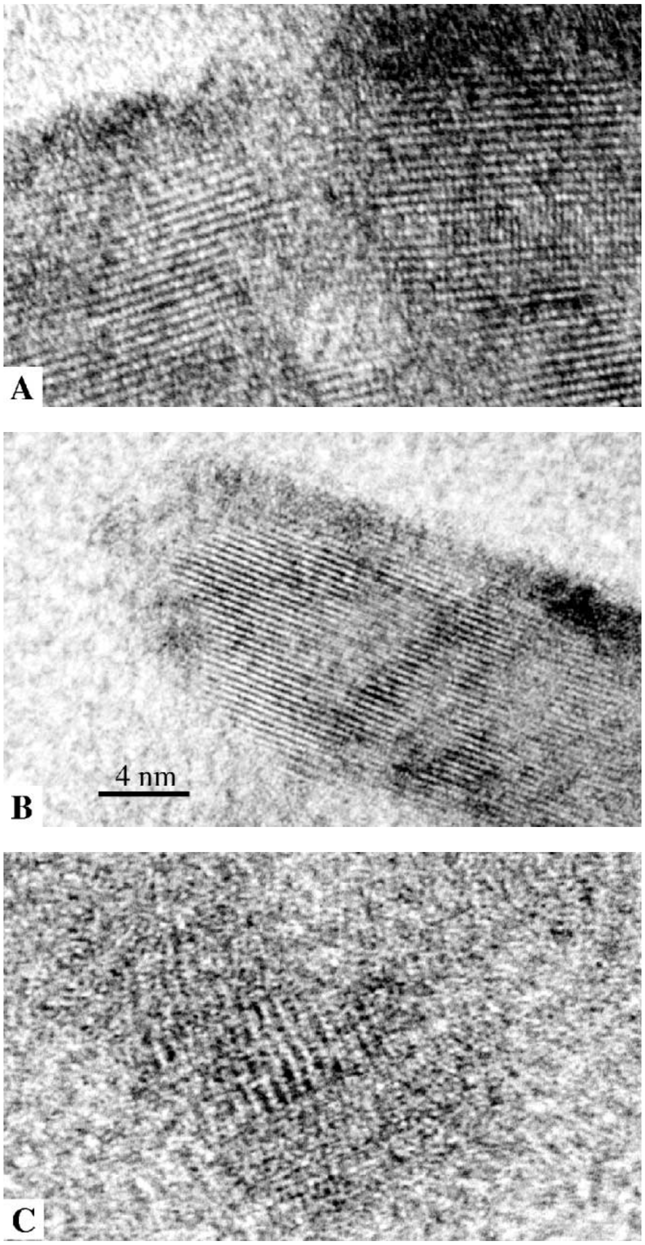

Figure 5. Lattice fringes of vanadium pentoxide: (A) after 5 h milling, (B) after 10 h milling, and (C) after 20 h milling.

For transition metal oxides, the L- or M-edge features can be used to determine the oxidation states [7]. Figure 7 shows the correlation of vanadium $L_3$-edge positions with the oxidation state of vanadium in binary vanadium oxides, determined from the measurements on vanadium oxides VO, $V_2O_3$, $VO_2$, $V_2O_5$, and $V_6O_{13}$ [8]. Using this correlation curve, the average oxidation states of vanadium ions after milling can be estimated (see table 1).

Table 1
V $L_3$-edge positions and average oxidation states of untreated and milled vanadium pentoxides.

| Sample | $V_2O_5$ | 3 h | 5 h | 10 h | 20 h |
|---|---|---|---|---|---|
| V $L_3$-peak positions (eV) | 519.0 | 519.0–518.7 | 519.0–518.6 | 518.8–518.2 | 518.5–517.8 |
| Oxidation state | 5 | 5–4.3 | 5–4.1 | 4.6–3.7 | 4–3.4 |

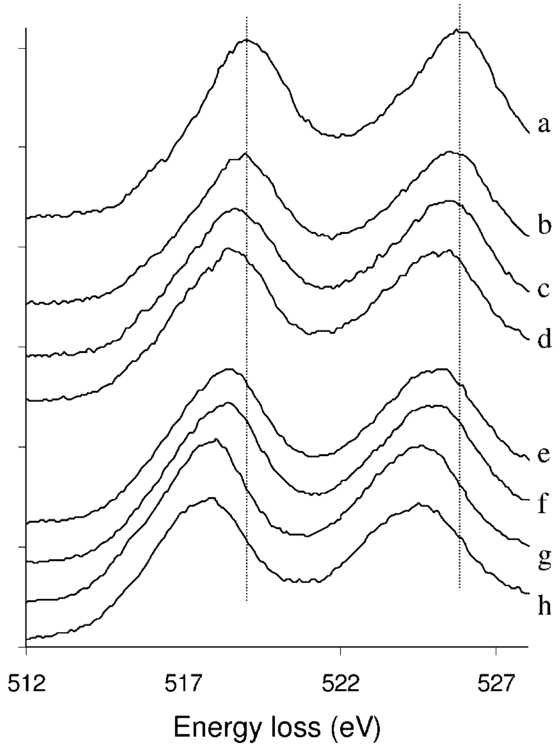

Figure 6. EELS spectra of vanadium pentoxide: (a) untreated, (b)–(d) after 3 h milling, and (e)–(h) after 20 h milling.

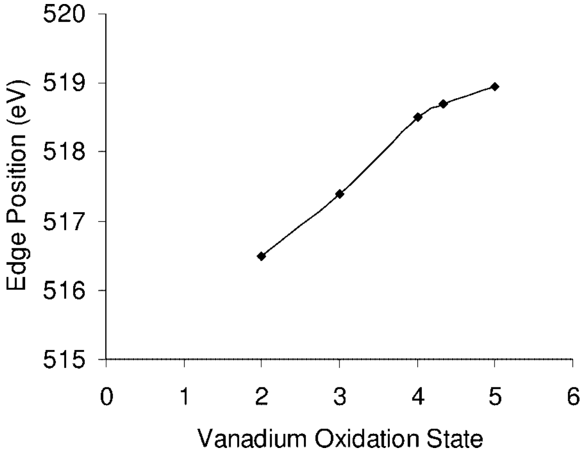

Figure 7. Correlation between V $L_3$-edge position and vanadium oxidation state. The curvature at high oxidation states is due to the final state effects of the empty d-shell of vanadium [9].

From table 1 we can see that the sample milled for 3 h contains unreduced small particles (oxidation state 5) and reduced small particles (average oxidation state 4.3). Milling up to 5 h induces further reduction of vanadium (down to 4.1), but unreduced particles can still be found. It is supposed that the unreduced particles in these two samples are formed during the milling by crushing of large particles. In the sample milled for 10 h, however, all the analysed particles are reduced; the highest average oxidation state is 4.6 and the lowest oxidation state is 3.7. Milling for 20 h gives rise to the total reduction of the $V^{5+}$ state and only $V^{4+}$ and $V^{3+}$ states can be detected. The main effect of milling up to 5 h is therefore the crushing of crystallites into small ones, with a minor loss of oxygen. For milling up to 20 h, the mechanical deformation and chemical reduction are equally effective. The inhomogeneity of oxidation states in all four milled samples can be explained as a dependence of the chemical state on the history of milling: the mechanical distortion of long range order is followed by a chemical reduction to an average vanadium oxidation state below 5+ with two time constants in the order of several hours.

## 4. Discussion

Our investigation reveals that tribochemical modification of $V_2O_5$ in a planetary agate ball-mill can be divided into two stages, as illustrated in figure 8. The first stage ranges from initial milling to about 5 h where large particles are crushed, with a minor loss of oxygen. This is a macroscopic process of mechanical deformation and fracture. The second stage describes the transformations induced by extended milling times up to 20 h when particles undergo fine grinding and reduction. Lattice defects become severe and the size distribution tends to narrow. Finally, amorphisation and reagglomeration take place leading to scarf-like particles, accompanied by the reduction of $V^{5+}$ in small particles to $V^{4+}$ and $V^{3+}$. This is a microscopic process which may have been ignored in earlier investigations. As revealed by high-resolution imaging, amorphisation and reagglomeration occur in a nanoscopic size range. Physically, in the first period the energy supplied by ball-milling is partly exhausted by crushing the crystallites. In the second period, the mechanical energy is partly stored as strain energy in particles. Most particles studied for this period show a heavily deformed lattice. Therefore, it seems that amorphisation and reagglomeration are consequences of extensive tribochemical modification of $V_2O_5$.

Another interesting phenomenon observed in the present study is the inhomogeneity in all milled samples after various durations of milling. In particular, the formation of $V^{4+}$ and $V^{3+}$ species depends on the history of milling: the mechanical distortion of long range order takes place after several hours and the reduction starts at all milling

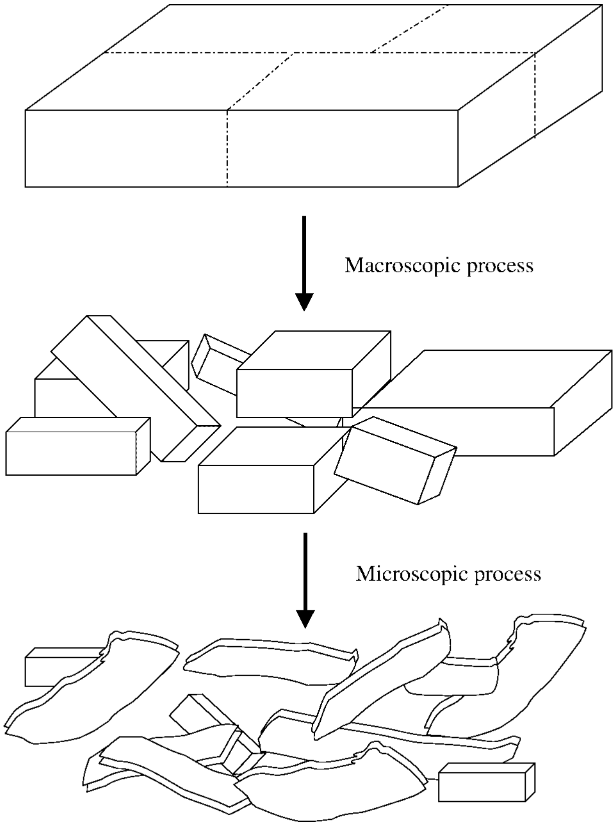

Figure 8. An illustration of the tribochemical modification of $V_2O_5$. In the macroscopic process large particles are crushed into small ones. In the microscopic process amorphorisation and reagglomeration take place.

times, although it becomes strong in the second stage mentioned above. Obviously tribochemical modification of V-based materials may not produce catalysts with homogeneous chemical properties.

A milling equilibrium is reported for some vanadium oxide systems [3] where further milling causes only little macroscopic changes. Our results show, however, a continuous deformation and reduction of vanadium oxides at various periods of milling. Amorphisation and reagglomeration of particles take place. Therefore, the identification of a relevant parameter for controlling the milling becomes inevitable in the preparation of high performance catalysts. One criterion can be the abundance of $V^{4+}$ centres or of phases containing vanadium in the $V^{4+}$ state, since it was found that vanadium oxide systems containing both $V^{5+}$ and $V^{4+}$ in a suitable ratio and abundance exhibit the best catalytic performance [2].

The average oxidation state of the sample after 20 h milling, as determined by means of $^{51}$V-NMR, EPR, and magnetic susceptibility measurements was found to be 4.8 [1]. This value is rather higher than the values summarised in table 1. This is, however, no conflict to our results since the mentioned techniques do detect vanadium ions in the entire sample and do not provide information on the chemical state of vanadium within submicrometer regions. On the other hand, the present study does not analyse thick particles of the specimen. From the fact that our measurements were performed on very thin and small particles (less than 50 nm), it can be concluded that vanadium ions in the bulk of large particles could still be in a high oxidation state close to 5. However, the increase of specific surface area, an expected effect of ball-milling and important for the catalytic performance [1,2], is achieved mainly because of the existence of a large number of small particles, the oxidation states of which are changed in a microscopic process (figure 8).

## 5. Conclusions

The tribochemical activation of vanadium pentoxide, $V_2O_5$, was studied by means of X-ray diffraction, electron microscopy, and electron energy-loss spectroscopy. The process can be described as mechanical deformation (macroscopic process) followed by fine-grinding, amorphisation and reagglomeration (microscopic process). No milling equilibrium state can be found. In the macroscopic process, the particle size decreases through fracture that takes place in all directions. Lattice defects are induced and the outer shell of most particles becomes amorphous. In the microscopic process small particles become completely amorphous and scarf-like particles grow through reagglomeration. Energy-loss spectra reveal the reduction of vanadium via oxygen loss. The formation of $V^{4+}$ and $V^{3+}$ species depends on the history of milling. In samples after 20 h milling, all studied small particles contain vanadium mostly in the $V^{4+}$ and $V^{3+}$ states.

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