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Mechanism of the Oxidation–Reduction of the MoVSbNbO Catalyst: In Operando X-ray Absorption Spectroscopy and Electrical Conductivity Measurements

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The mechanism of the oxidation–reduction of the MoVSbNbO catalyst has been studied in dynamic conditions using X-ray absorption spectroscopy (XAS) and electrical conductivity measurements. XAS at Sb L₁- and V/Mo K-edges permitted a better understanding of the chemical processes taking place in the M1 phase of the MoVSbNbO catalyst at different temperatures and atmosphere compositions. The reduction of antimony was already observed during the annealing of the M1 phase in He at 100 °C, which might be explained by the presence of hydrogen in the bronze-like structure of the M1 phase. Under operando conditions at 380 °C, we have found that Sb and V change their oxidation states depending on the C₃H₈/O₂ ratio in the atmosphere. These changes occur simultaneously and with the same kinetics. Under the same conditions, variations in the oxidation state of Mo were not observed. These results prove that different types of oxygen (from the hexagonal channels and from the MO₆ octahedral network) must be involved in the catalytic process although their relative contributions are different. It was found that the electrical conductance of the M1 phase correlates with the oxidation states of Sb and V and the concentration of oxygen vacancies.

1. Introduction

Numerous studies have recently focused on the multicomponent MoVSb(Te)NbO mixed oxide catalysts for selective propane oxidation and ammoxidation.^{1–3} These catalysts typically contain two phases called M1 and M2. MoO₃, Mo-(V,Nb)₅O₁₄, or TeMo₅O₁₆ can also be found, depending on the preparation conditions and initial stoichiometry.^{4–6} It is generally accepted that only the M1 phase is catalytically active and selective. The M1 phase crystallizes in the orthorhombic system with a formula that has been reported as (AO)_{2–2x}(A₂O)_xM₂₀O₅₆, where A = Sb or Te, M = Mo, V, Nb, and 0 < x < 1. The V/Mo and Nb/Mo ratios can vary but are generally close to 0.3 and 0.1.^{4,5} The detailed structure and composition of the M1 phase was recently determined.^{7–9} It was shown that the structure corresponds to a network of MO₆ octahedra (M = Mo, V, Nb) sharing corners and edges (Figure 1). Niobium cations are pentavalent whereas molybdenum and vanadium can have d⁰ and d¹ electronic configurations that correspond with the Mo⁶⁺/V⁵⁺ and Mo⁵⁺/V⁴⁺ states. MO₆ octahedra form pentagonal, hexagonal, and heptagonal channels in the [001] direction. The pentagonal channels contain niobium and oxygen, the hexagonal channels are occupied by antimony or tellurium and oxygen, and the heptagonal channels are empty. To be an efficient oxidation catalyst, the M1 phase has to be able to undergo oxidation and reduction to a certain degree without changes in its structure. However, a structure built from corner-sharing octahedra should not support a high concentration of oxygen vacancies. Niobium is always present in the stable Nb⁵⁺ oxidation state, so the pentagonal channels cannot contain oxygen defects. In the case of Sb-containing M1 phase oxygen,

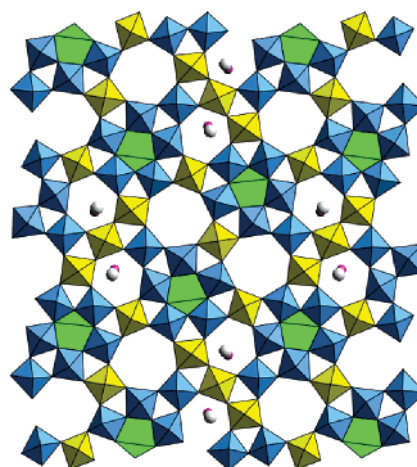


Figure 1. Schematic representation of the structure of M1 along the [001] direction as determined in the case of Te containing phase.⁹ Green color corresponds to NbO₇, blue to MoO₆, and yellow to MO₆, occupied by both Mo and V cations.

nonstoichiometry must be mainly observed in the hexagonal channels, where antimony forms the [SbO_x]_∞ infinite chains parallel to the [001] direction. A schematic representation of completely oxidized hexagonal channels that contain only Sb⁵⁺ and [Sb⁵⁺O]₃⁺ is given in Figure 2a. Oxygen vacancies can be formed between two antimony atoms. Removal of oxygen leads to the reduction of Sb⁵⁺ to Sb³⁺ and to formation of the [Sb³⁺O_{0.5}]₂⁺ structure shown in Figure 2b. It should be mentioned that theoretically only half of the oxygen atoms can be removed from the channels, otherwise the coordination number of Sb³⁺ would be too low. Since the [Sb⁵⁺O]₃⁺ and [Sb³⁺O_{0.5}]₂⁺ structures are charged differently, removal of oxygen from the hexagonal channels should be accompanied by the oxidation of Mo or V atoms from the octahedral network,

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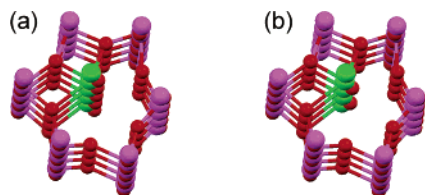
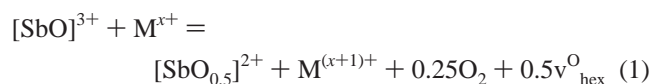


Figure 2. Schematic representation of completely oxidized $[\text{SbO}]^{3+}_{\infty}$ (a) and reduced $[\text{SbO}_{0.5}]^{2+}_{\infty}$ (b) chains in the hexagonal channels of the M1 structure. Green atoms correspond to Sb, red to O, and purple to Mo or V.

as shown in the following



where $\text{M} = \text{V}, \text{Mo}$ and $v_{\text{hex}}^{\text{O}}$ is the oxygen vacancy in the hexagonal channel.

In our previous work⁷ we proposed that hexagonal channels play a role as oxygen reservoirs in the M1 structure that determine its high catalytic efficiency in the process of selective propane oxidation by the Mars and van Krevelen mechanism. Since the concentration of oxygen in the hexagonal channels should be directly related to the oxidation state of Sb, whereas oxygen nonstoichiometry in the lattice octahedral network should depend on the oxidation states of V and Mo, knowledge of the reactivity of these metals can be used as a direct probe of the activity of different oxygen sites in the redox process. It was shown in ref 7 that X-ray absorption spectroscopy (XAS) is a very useful and unique technique for the determination of the oxidation states and local environments of V, Sb, and Te in $\text{MoVSb}(\text{Te})\text{NbO}$ catalysts. However, all of the previous studies were performed *ex situ* at room temperature. The goal of this work was to clarify the role of lattice and channel oxygen in the catalytic mechanism of propane oxidation by measuring XAS at the K-edges of V and Mo and the L_{1-} edge of Sb under real working conditions (*operando*).¹⁰ Since the M1 phase is a semiconductor, its electrical conductivity should depend on oxygen stoichiometry. Combined XAS and conductivity measurements allowed us to study catalytic and electronic properties of the active phase in dynamic conditions, which had never been done before.

A program of successive treatments under different reaction conditions was chosen to characterize the active phase and to attempt to answer the following questions:

- (1) What is the nature of the chemical processes taking place in the catalyst under real working conditions and are they reversible?
- (2) What is the origin of the oxygen (from hexagonal channels or from the octahedral network) participating in the catalytic process?
- (3) How fast are the processes controlling the mobility of oxygen in the catalyst structure?
- (4) Are there correlations between the electrical conductivity and oxygen stoichiometry?

2. Experimental Section

2.1. Synthesis and Characterization. The M1 phase with the composition $[\text{SbO}]_{1.0}[\text{SbO}_{0.5}]_{0.8}\text{V}_{3.4}\text{Mo}_{14.5}\text{Nb}_{2.2}\text{O}_{56}$ was synthesized from aqueous slurry containing Mo, V, Sb, and Nb in the following ratio: $\text{Mo/V/Sb/Nb} = 1/0.33/0.15/0.11$. Ammonium heptamolybdate and vanadate, antimony trioxide, and niobium oxalato-niobate were used as the precursors. The slurry was dried at 150 °C and successively heat treated in air at 300 °C

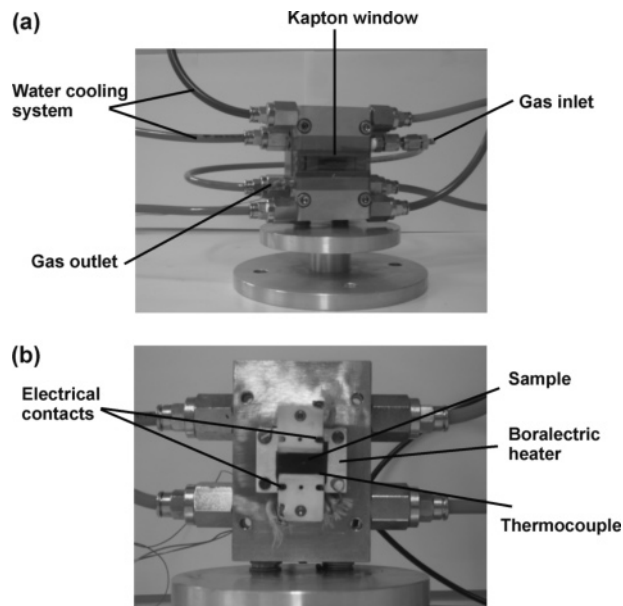


Figure 3. Photos of the cell showing views from outside (a) and inside (b).

and in a nitrogen atmosphere at 600 °C for 2 h. To dissolve the M2 phase formed during the synthesis, the resulting solid was held in 15% hydrogen peroxide while stirring at room temperature for 5 h. Then it was washed in water, dried at 110 °C, and heated in a nitrogen atmosphere at 600 °C for 2 h.

The crystal structure of the M1 phase was determined using X-ray diffraction (Bruker D5005 diffractometer, Cu $K\alpha$ radiation). The concentrations of metals were measured by inductively coupled plasma atomic absorption.

To perform XAS and electrical conductivity measurements on the same samples, the M1 phase (80–100 mg) was mixed with water and deposited onto the Al_2O_3 plates (20 × 20 mm²) using a screen-printing technique.

2.2. Design of In Situ Cell. In situ experiments were conducted using a 20 mL cell with a 25 μm Kapton window that allowed us to measure XAS at the L_{1-} edge of Sb (4.698 keV) and K-edges of V (5.465 keV) and Mo (20.000 keV). Figure 3 illustrates the cell. The electrical conductance of the sample was measured at fixed voltage (1 V) between two Au electrodes. It was possible to heat the sample in the cell up to 400 °C. The studies were carried out under atmospheric pressure at a 30 mL/min gas flow rate. A system of six Bronkhorst mass flow controllers and a Valco two-position switching valve was used to produce gas mixtures containing different concentrations of C_3H_8 and O_2 in He. Reactivity of the catalyst was controlled by online gas-phase analysis using a mass spectrometer (Pfeiffer). This allowed us to measure the conversion of propane and to qualitatively analyze the reaction products.

2.3. XAS Experiments. The XAS studies have been done at ID26 (High Brilliance XAFS-XES beamline) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The electron energy was 6.0 GeV, and the ring current varied between 150 and 200 mA. Depending on the energy, the measurements were performed at the first and third harmonics of the u35 undulator. A pair of Si(220) single crystals were used in the fixed exit Kohzu monochromator. At low energies (Sb L_{1-} edge and V K-edge), harmonic rejection was performed using two silicon mirrors. For high energies (Mo K-edge), two platinum-coated mirrors were applied for the same purpose. Energy was calibrated with pure metal V and Mo foils. During the energy scans the monochromator and undulator moved

TABLE 1: List of Different Treatments of the M1 Catalyst

treatment	gas atmosphere ^a	temperature (°C)
A	He	25
B	He	100
C	He	200
D	He	300
E	He	380
F	10/5/85	380
G	O ₂	380
H	He	380
I	10/5/85	380
J	7.5/7.5/85	380
K	10/5/85	380
L	10/5/85	25
M	He	100

^a 10/5/85 and 7.5/7.5/85 are the gas mixtures with the corresponding O₂/C₃H₈/He ratios.

continuously (quick EXAFS). Sb L₁-edge and V K-edge XANES (X-ray absorption near edge structure) were measured simultaneously during a 63 s scan from 4.660 to 5.600 keV with a 0.3 eV step. Mo K-edge spectra were collected for 25 s from 19.8 to 20.1 keV with a 0.25 eV step. Full XAS spectra (1 000 eV range) were also measured in the steady-state conditions and used afterward for the normalization of the XANES data. We conducted the experiments in the fluorescence mode. The detector (Camberra Si diode) was mounted at 90° with respect to the incident beam. The distance between the detector and the sample was equal to 80 mm, and the diameter of the active surface of the diode was 20 mm.

It was possible to rotate the sample with respect to the beam and measure the fluorescence at different angles. All the spectra presented in this work were measured at 90°, possibly allowing us to minimize self-absorption and to increase the contribution of the sample surface in the XANES spectra.¹¹ The spectra of Sb₂O₄, FeSbO₄, (VO)₂P₂O₇, V₂O₅, MoO₃, and TeMo₅O₁₆ were collected at room temperature and used as the references.

XANES spectra were normalized and background-corrected using the IFFEFIT program.¹² To quantify the Sb³⁺/Sb⁵⁺ ratio and variations of V XANES, the principal component analysis of the normalized XANES data was performed using ITFA_v1_3 software.¹³ The analysis of XANES spectra of V and Mo was based on the observations of the pre-edge and edge positions. The center of mass and the total area of V pre-edge were calculated using the PeakFit program.

2.4. Treatments of the Samples. The samples were treated at different temperatures (25–380 °C) and atmospheres (pure He, pure O₂, and two gas mixtures containing propane and oxygen in different ratios). The former mixture (O₂/C₃H₈/He = 10/5/85) is the most common for the process of propane oxidation to acrylic acid; the latter (O₂/C₃H₈/He = 7.5/7.5/85) is enriched with propane. In the following text we will denote them as “10/5/85” and “7.5/7.5/85” gas mixtures, respectively. The list of successive treatments is shown in Table 1. The propane conversion at 380 °C with the 10/5/8 gas mixture was around 16%, which is slightly lower than that obtained in a fixed-bed reactor in the same conditions (19%). This may be due to the fact that the gas feeds did not pass through the catalytic bed but only touched it. It should also be mentioned that these conversions are slightly lower than those commonly reported in the literature because no water was added to the feeds. The carbon-containing products detected by mass spectrometry correspond to those generally observed, acrylic and acetic acids, CO, CO₂, and propene.

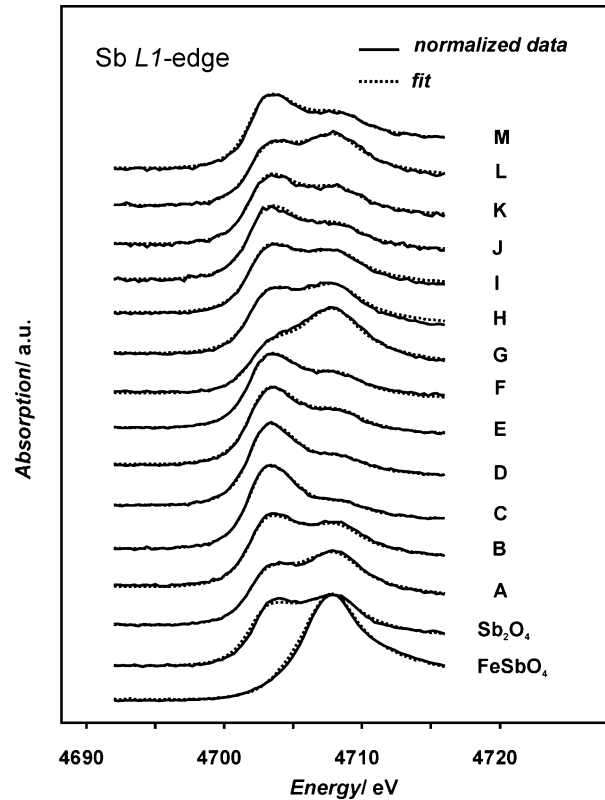
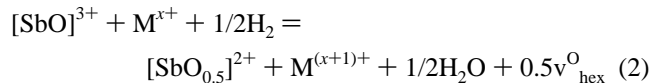


Figure 4. Sb L₁-edge XANES spectra of the M1 phase under different redox conditions and the spectra of the reference samples. The letters A–M correspond to the conditions listed in Table 1. Solid lines show experimental data; dotted lines show best fit.

3. Results and Discussion

3.1. Sb L₁-Edge XANES and Electrical Conductivity Measurements. The Sb L₁-edge XANES spectra of the M1 phase equilibrated during 1–1.5 h under different redox conditions (see Table 1) are shown in Figure 4. All the spectra were measured in situ at working temperatures and compositions of the gas phase. The spectra of the reference samples FeSbO₄ (Sb⁵⁺) and Sb₂O₄ (50% Sb³⁺ + 50% Sb⁵⁺) are also shown in this figure.

Figure 5 shows the fraction of Sb³⁺ in the Sb³⁺/Sb⁵⁺ mixture calculated from the XANES data using ITFA_v1_3 software. One can see that antimony changes its oxidation state very easily even at 100 °C in a He atmosphere. Taking into account that the temperature is very low, this result may be explained by the presence of hydrogen in the bronze-like structure of the M1 phase¹⁴ that was already observed before using neutron diffraction.¹⁵ The process may be summarized as



where M = V, Mo and v_{hex}^O is the oxygen vacancy in the hexagonal channel.

Since the concentration of Sb³⁺ should be proportional to the concentration of oxygen vacancies in the hexagonal channels, this result proves an extremely high oxygen mobility. Moreover, it clearly demonstrates that it is impossible to study this catalyst ex situ.

At 300–380 °C in He, antimony reoxidizes but to much less extent than it was reduced. At this temperature it is possible that oxygen from the octahedral network becomes mobile, goes out in the channel of the structure, and oxidizes antimony in

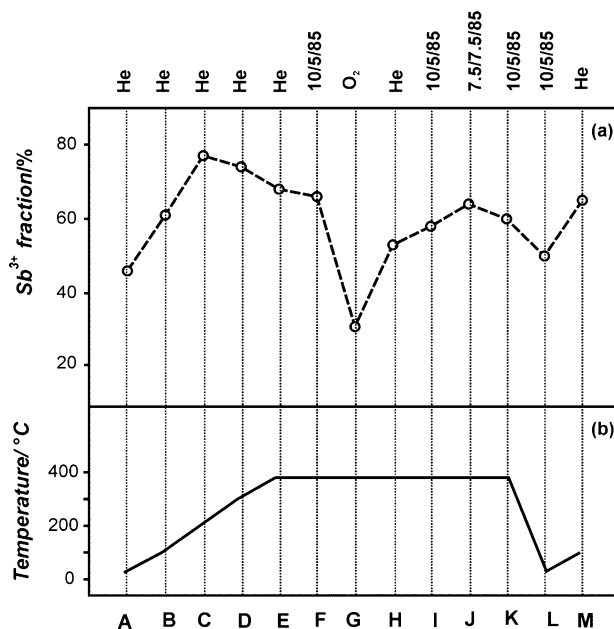


Figure 5. (a) Fraction of Sb³⁺ cations in the structure of the M1 phase under different redox conditions. (b) Temperature plot. Notes at the top of the figure indicate different conditions listed in Table 1.

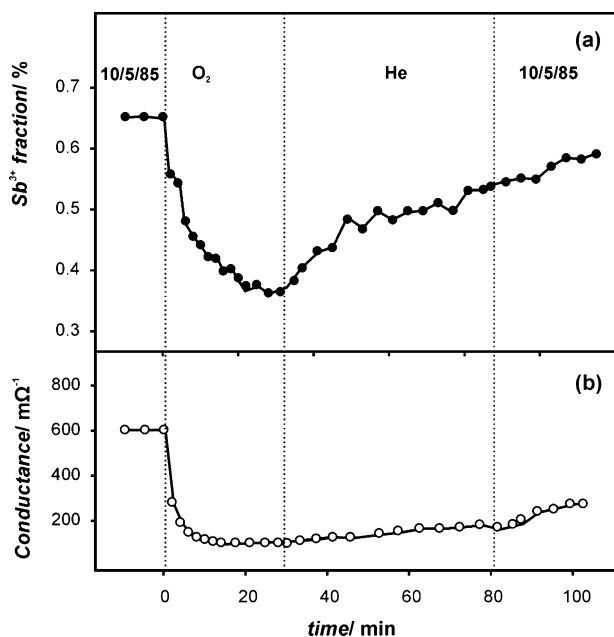
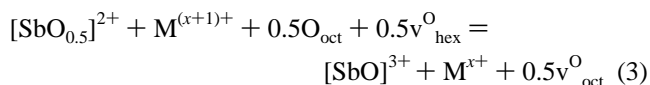


Figure 6. Kinetics of oxidation and reduction of antimony and the variation in electrical conductance of the M1 phase at 380 °C.

the hexagonal channels



where M = V, Mo and $\text{v}_{\text{hex}}^{\text{O}}$ and $\text{v}_{\text{oct}}^{\text{O}}$ are oxygen vacancies in the hexagonal channels and octahedral network. This process could correspond to a re-equilibration of oxygen concentration in the total structure.

At 380 °C antimony also reversibly changes its oxidation state depending on the partial pressures of oxygen and propane in the atmosphere. This proves that oxygen from the hexagonal channels participates in the catalytic process. The kinetics of the oxidation and reduction of Sb together with the simultaneous data of conductivity measurements are presented in Figure 6.

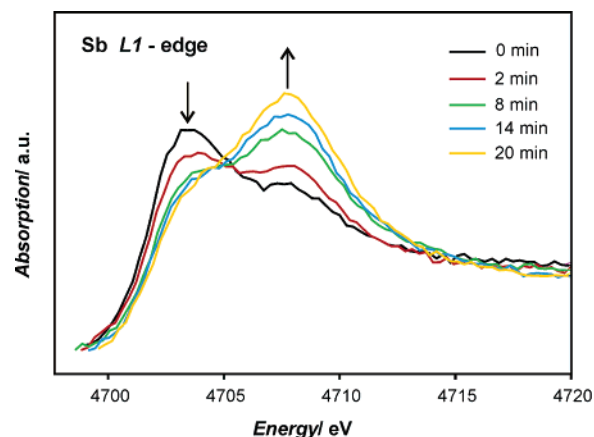


Figure 7. Time variation of Sb L₁ XANES spectra of the M1 phase in O₂ at 380 °C.

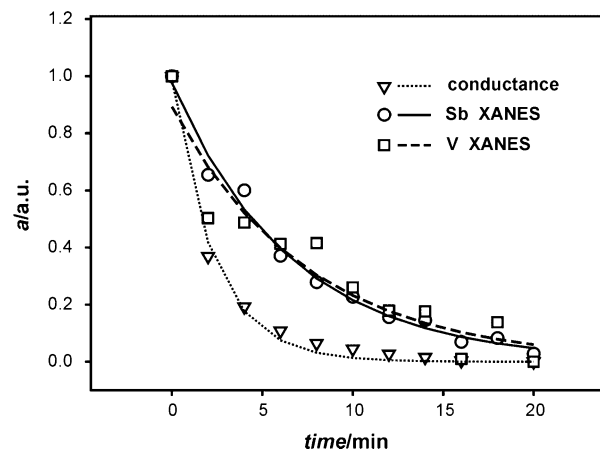


Figure 8. Analysis of variation of conductance and XANES spectra (at Sb L₁- and V K-edges) of the M1 phase in O₂ at 380 °C using an exponential decay function. Points show the experimental data; lines indicate the best fit.

TABLE 2: Parameters of the V K Pre-edge

sample	center of mass (eV)	total area (au)
M1 in 10/5/85	5 470.7	1.2392
M1 in O ₂	5 470.8	1.3581
V ₂ O ₅	5 472.0	2.2950
(VO) ₂ P ₂ O ₇	5 470.7	0.8064

The XANES spectra during exposure of the sample in O₂ atmosphere are shown in Figure 7. The M1 phase reaches equilibrium in 20–25 min. This length of time is required for the diffusion of oxygen from the bulk to the surface of the M1 crystallites through the hexagonal channels. The electrical conductivity changes synchronously with the Sb oxidation state and the concentration of oxygen vacancies in the structure, which is normal for the n-type semiconductors. The processes of Sb oxidation and conductivity variation in the O₂ atmosphere were further analyzed using an exponential decay function:

$$a = \exp(-kt) \quad (4)$$

The fitted data are shown in Figure 8. One can see that in an O₂ atmosphere electrical conductance changes faster (the constant k is equal to 0.43 min⁻¹) than the oxidation state of antimony ($k = 0.15$ min⁻¹). This means that the relationship between the number of oxygen vacancies in the M1 structure and the concentration of free electrons is not linear. This effect is normal for the polycrystalline semiconductors and may be

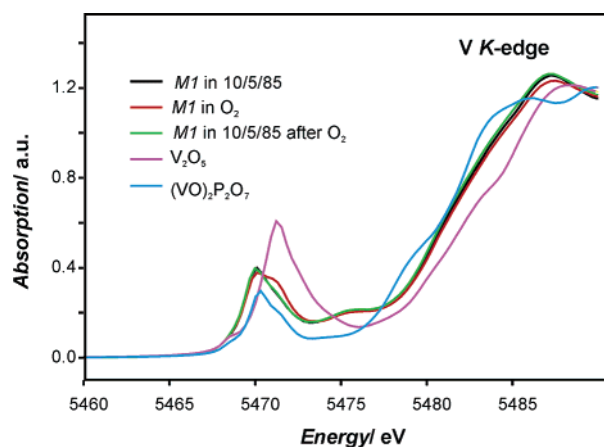


Figure 9. V K-edge XANES spectra of M1 phase in a 10/5/85 mixture and O₂ at 380 °C compared with the spectra of the reference samples.

explained by the presence of potential barriers between the crystallites of the semiconductor phase.¹⁶

When the oxygen-to-propane ratio was reduced from 10/5 to 7.5/7.5, a slight reversible reduction of antimony was observed, showing that the catalyst bulk is sensitive to the redox atmosphere and correspondingly equilibrated.

At the end of the experiments, the catalyst was cooled at room temperature under the reaction gas mixture. After the switch to a pure He atmosphere, the catalyst was again heated at 100 °C. A reduction of antimony similar to that observed at the beginning of the experiment was observed. This demonstrates the reversibility of eq 2 and again points out to the need for studying the oxidation state of the metallic elements of the catalysts in operando conditions.

3.2. V K-Edge XANES. Despite the fact that V K-edge XANES spectra were measured in the same reaction conditions as the spectra of antimony, the variations observed were much less pronounced. At low temperatures (below 380 °C) we have not observed any reactivity of vanadium. If it had participated in eq 2 as the M cation, we would have observed the oxidation of 17.6% of V and this would have been unambiguously detected. Therefore, we believed that it is Mo that is involved in the reaction. Taking into account the proportion of Mo in the oxides and the stoichiometry of eq 2, only 3.7% of molybdenum would be oxidized, which is almost undetectable by XANES. At a catalytic temperature (380 °C), small but reversible changes in the V K-edge were observed when the M1 phase was alternately exposed to 10/5/85 and O₂ atmospheres. The corresponding spectra of the M1 phase in the steady-state conditions together with spectra of the reference samples (VO)₂P₂O₇ (V⁴⁺) and V₂O₅ (V⁵⁺) are shown in Figure 9. One can see that in the presence of the 10/5/85 gas mixture the oxidation state of vanadium is very close to 4+. In O₂ atmosphere a small shoulder appears reversibly on the right side of the pre-edge which indicates the partial oxidation of V⁴⁺ into V⁵⁺. The calculated parameters of the V pre-edge are given in Table 2.

According to the shift of the pre-edge center of mass,⁷ we can roughly estimate¹⁷ that less than 10% of vanadium atoms change their oxidation states when the gas composition in the cell is altered.

This process indicates that vanadium and oxygen from the octahedral network participate in the catalytic reaction. The corresponding equilibrium may be summarized as

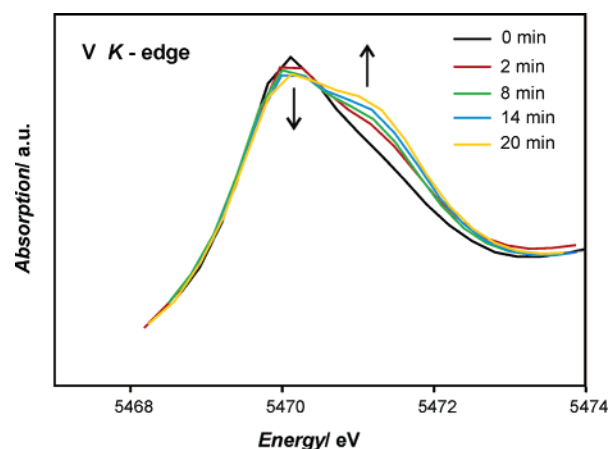
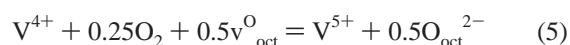


Figure 10. Time variation of V K-edge XANES spectra of the M1 phase in O₂ atmosphere at 380 °C.

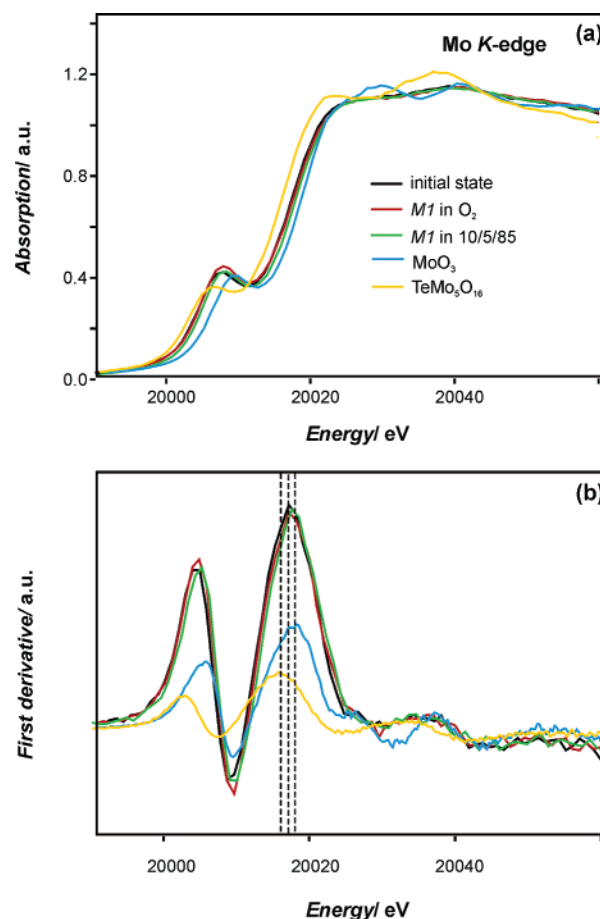


Figure 11. (a) Mo K-edge XANES spectra of M1 phase in the initial state at 25 °C and under steady-state conditions in the 10/5/85 mixture and O₂ atmosphere at 380 °C compared with the spectra of the reference samples. (b) First derivatives of the XANES data. Dashed lines indicate positions of the edge jumps.

Figure 10 shows the dynamics of the variation of the V pre-edge during exposure of the catalyst in O₂. These data were fitted in the pre-edge region (5.468–5.473 keV) as a linear combination of the initial and the final states using the ITFA_v1_3 software. The kinetics was analyzed in the same way as the Sb XANES data using an exponential decay function (the results shown in Figure 8). The value of *k* in eq 4 is equal to 0.13 min^{−1}. Compared with the corresponding Sb data, we can conclude that the oxidation of V proceeds with almost the same speed as the oxidation of Sb. This means that both types

of oxygen (from hexagonal channels and from the octahedral network) are really involved in the redox process. However, oxygen exchange goes easier via hexagonal channels since only Sb changes its oxidation state at low temperatures (100–300 °C). Furthermore, if the contributions to the redox process of the Sb and V cations are compared in terms of electrons donated, the Sb cations contribute almost twice the number of V cations, although they are more than 4 times fewer in number.

3.3. Mo K-Edge XANES. Figure 11a shows the Mo K-edge XANES spectra of the M1 phase in the initial state (25 °C, He) and under the steady-state conditions in 10/5/85 and O₂ atmospheres at 380 °C. The spectra of MoO₃ and TeMo₅O₁₆ are also shown. According to the shape of the XANES spectra¹⁸ and the position of the edge jumps (see the first derivative in the Figure 2b), the oxidation state of molybdenum in the M1 phase must be between +5.6 and +6. This is quite in agreement with the oxidation state calculated from various spectroscopic data (5.65).⁷ It also does not significantly vary with temperature and atmospheric composition. Nevertheless, we cannot conclude that Mo does not participate in the catalytic process. Moreover, we suppose that it is Mo that plays the role of an M cation in reactions 1 and 2. It oxidizes and reduces, providing the electroneutrality of the M1 structure, but we cannot see it because the amount of Mo in the catalyst is much higher than the amounts of Sb and V, and therefore the change in oxidation state is proportionally lower. For example, we observe that between 25 and 200 °C in He, 30% of antimony atoms change their oxidation states from Sb⁵⁺ to Sb³⁺ in reaction 1. In these conditions the oxidation state of Mo should change only by 3.7%. The same explanation is valuable in the case of 380 °C: variation of the oxidation state of Mo by only 5% can provide the electroneutrality of the catalytic structure.

4. Conclusions

We have demonstrated how XAS together with synchronous conductivity measurements can be applied to understand the mechanism of catalytic processes under dynamic operational conditions. The simultaneous use of these techniques allowed us to observe the mobility of different types of oxygen in the complex structure of MoVSbNbO catalyst in operando. The most important conclusions are the following:

(1) Hexagonal channels play the role of oxygen reservoirs in the M1 structure. The mobility of oxygen through these channels may be observed already at 100 °C.

(2) Under catalytic conditions Sb and V change their oxidation states simultaneously, which proves that different types of oxygen coming from the hexagonal channels and from the MO₆ octahedral network must be involved in the redox process. The

contribution of the oxygen anions in the channel is more important, although the rates of exchange seem comparable.

(3) The variation of the oxidation state of Mo is nondetectable, which does not exclude it from participation in the redox process. It may possibly be involved in the oxido-reduction of Sb.

(4) The electrical conductivity measurements show that the M1 phase is an n-type semiconductor and that electrical conductance correlates with the variation of the oxidation states of Sb and V and the corresponding concentration of oxygen vacancies in the M1 structure.

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