# XANES Study of Hydrothermal Mo−V-Based Mixed Oxide M1-Phase Catalysts for the (Amm)oxidation of Propane

N. Raveendran Shiju,[†] Adam J. Rondinone,[†] David R. Mullins,[‡] Viviane Schwartz,[‡]
Steven H. Overbury,[‡] and Vadim V. Guliants*[,†]

*Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0012,*
*and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*

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The hydrothermal Mo−V-based mixed oxide catalysts possessing the M1-phase structure were investigated by XANES and in situ X-ray diffraction under ambient and dynamic redox conditions in the presence of $O_2$ and $H_2$ at 693 K. Under ambient conditions, XANES, with the use of model compounds, suggested oxidation states of Nb, Te, Mo, and V close to 5+, 4+, 6+, and 4+, respectively, in the bulk M1 phase. The oxidation state changes of Nb, Te, and Mo were not detected under the dynamic redox conditions employed, while the pre-edge peak of vanadium in the M1 phase exhibited small, reproducible shifts, suggesting that $VO_x$ is the active catalytic species in the bulk M1-phase catalysts for selective (amm)oxidation of propane.

## Introduction

Acrylonitrile and acrylic acid are important petrochemical intermediates currently produced by the ammoxidation and oxidation of propene, respectively.[1] A process based on direct ammoxidation of propane is highly desirable because of the widespread availability and low cost of this alkane feedstock. However, the selective (amm)oxidation of propane is still awaiting the development of a suitable catalyst. Several catalyst systems are being investigated, and the most promising candidate reported to date is the Mo−V−Te−Nb−O oxide system, originally discovered by Mitsubishi Chemicals.[2] This catalyst can be used in both selective ammoxidation and oxidation of propane, while other catalysts, such as the V−Sb−Al mixed oxides, are only active and selective in the propane ammoxidation process.[3−9] The major phases of the Mo−V-based mixed oxide system are orthorhombic (so-called M1) and pseudohexagonal (M2) phases, the former being active and selective in both reactions. Whereas the unique structural and compositional features that make this catalyst system highly selective in propane ammoxidation are still being investigated, the complexity of this system requires characterization by a variety of spectroscopic techniques.[10−19] The structure of the M1 phase, synthesized by the slurry method, was recently reported as consisting of a network of $MO_6$ octahedra (M = Mo, V, Nb) forming hexagonal and heptagonal channels.[19] Mo and V are proposed to exist in both $d^0$ and $d^1$ electronic configurations and occupy the majority of cation sites in the M1 structure. Tellurium cations mainly occupy the hexagonal channels and partially the heptagonal channels. This catalyst system can be synthesized by slurry (dry-up) or hydrothermal methods, and the majority of previous structural investigations of this catalyst system were conducted on catalysts prepared by the slurry method containing appreciable amounts of the M2 phase. The hydrothermal synthesis method provides improved control over the formation of the

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* To whom correspondence should be addressed. Fax: (513) 556-3473. E-mail: vguliant@alpha.che.uc.edu.

[†] University of Cincinnati.

[‡] Oak Ridge National Laboratory.

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M1 phase and results in essentially pure M1 phase.[20−22] However, the structure of the M1-phase catalyst and the oxidation states of constituent metal cations during the dynamic redox conditions have not been investigated yet. X-ray absorption spectroscopy (XAS) is a powerful technique that enables investigation of the local structure and oxidation states of constituent metal ions of the Mo−V-based mixed oxide catalysts. In this study, we employed XAS to probe the oxidation states of the hydrothermal M1 phases under ambient and dynamic conditions. The phase composition of the M1 catalysts was investigated in an in situ XRD study conducted under similar experimental conditions.

## Experimental Section

The catalysts were synthesized by hydrothermal treatment of the slurry obtained by mixing appropriate amounts of source compounds, such as ammonium molybdate, vanadyl sulfate, niobium oxalate, and telluric acid for Mo−V−Te−Nb−O and tellurium oxide for Mo−V−Te−O.[23] Hydrothermal synthesis was carried out at 448 K for 20, 72, and 48 h for Mo−V−O, Mo−V−Te−O, and Mo−V−Te−Nb−O, respectively. After synthesis, the obtained solids were filtered, washed several times with deionized water, and dried overnight at 353 K. The solids were then calcined in a flow of ultrapure $N_2$ at 773 K for the Mo−V−O and Mo−V−Te−O phases and at 873 K for the Mo−V−Te−Nb−O phase to yield crystalline, phase-pure samples, as confirmed by X-ray diffraction (Siemens D500, Cu Kα). The ammoxidation reaction was carried out in a fixed bed tubular flow reactor at atmospheric pressure using 0.2 g of the calcined catalyst diluted with 0.5 g of SiC. The catalyst was ground in an agate mortar prior to catalytic tests. The diluted catalyst was placed into the reactor, heated to the desired temperatures under He flow, and exposed to the reaction feed. The feed was composed of $C_3H_8$, $NH_3$, $O_2$, and He in a molar ratio of 6:7:17:70 at a total flow rate of 20 mL/min. The reactants and products were analyzed by an online GC system (Shimadzu 14A) equipped with FID and TCD. The total carbon balances agreed within $\pm 5\%$. The X-ray absorption spectroscopic experiments were conducted on beamline X18-B at the National Synchrotron Light Source (NSLS) with the electron storage ring operating at an electron energy of 2.8 GeV and a current in the range of 110−240 mA. The spectra were collected in the transmission mode using a Si(311) double-crystal monochromator. The X-ray intensities were monitored using ionization chambers filled with appropriate mixtures of nitrogen and argon gases. The energy calibration was carried out by measuring metallic foils for Mo, V, and Nb K edges. For the Te edge, $TeO_2$ and $H_6TeO_6$ were used as references. For the measurements, the samples were ground, homogenized, and tabletted under pressure after being mixed with BN. The dynamic experiments were conducted at 693 K in a mixture of 10% $O_2$ in He or 4% $H_2$ in He. The software program IFEFFIT, along with its complementary GUIs Athena and Artemis, was used for the data analysis.[24] The in situ X-ray powder diffraction analysis was done using Cu Kα radiation with a PANalytical X'pert Pro powder diffractometer equipped with an X'celerator position-sensitive detector. Powder samples were mounted inside a Parr XRD900 heating stage and run at room temperature under vacuum and at 693 K in 10% $O_2$ in He and 4% $H_2$ in He for 10 min. Data were collected over the range of 5−55° ($2\theta$) with a step size of 0.017° and refined using GSAS.[25] The SEM images were obtained using a Philips XL-30 field emission ESEM instrument.

## Results and Discussion

The M1 phases employed in this study were prepared by hydrothermal synthesis at 448 K. The synthesis times were 20, 48, and 72 h for the Mo−V−O, Mo−V−Te−Nb−O, and Mo−V−Te−O M1 phases, respectively. The precursors obtained after hydrothermal synthesis were calcined in an inert atmosphere (ultrapure $N_2$) at 773−873 K. The X-ray diffraction patterns of the samples are in agreement with those reported for the M1 phase characterized by the Bragg peaks at $2\theta \approx 6.6°$, 8.0°, and 9.0°, sharp peaks at $2\theta = 22°$ and 45°, and a broad peak around 27° (Figure S1, Supporting Information). The Mo−V−Te−Nb−O sample used in this study consisted of 92% M1 phase and 8% M2 phase, according to the full profile refinement of its X-ray powder diffraction pattern. The Mo−V−Te−O catalyst contained 93% M1 phase and 7% M2 phase. These M1-phase catalysts were studied in the ammoxidation of propane and showed high activity and selectivity toward the formation of propylene, acrylonitrile, and acrylic acid (Figure S2, Supporting Information). The SEM images confirmed the rod-shaped morphology of the M1-phase catalyst particles (Figure S3, Supporting Information).

The crystal structure of the M1 phase, prepared using a reductant and oxoacid as well as the slurry (dry-up) method, has been studied using several techniques such as X-ray powder diffraction, TEM, and neutron powder diffraction.[19] This phase is characterized by an orthorhombic crystal structure (space group *Pba*2, No. 32) and lattice parameters $a = 21.134(2)$ Å, $b = 26.658(2)$ Å, and $c = 4.0146(3)$ Å. According to this study, the structure consists of a framework of transition-metal oxide octahedra and $-(\mathrm{Te-O})_n^{2+}-$ chains located in the hexagonal channels (Figure S4, Supporting Information). The metal oxide octahedra are proposed to contain Mo and V in mixed valence $Mo^{6+}/Mo^{5+}$ and $V^{5+}/V^{4+}$ states. DeSanto et al. suggested that these octahedra are stabilized and structurally isolated by $Nb^{5+}$, while Te is proposed to be in the 4+ oxidation state.[19]

XANES spectra of transition-metal oxides are characterized by the pre-edge peak caused by the s → d transition. The intensity depends on the coordination symmetry of oxygen atoms around the central metal atom. The peak is intense for a tetrahedral coordination and low for an octahedral coordination. The fine structure near the edges of the X-ray absorption spectrum is determined by the electron structure and the geometric arrangement of the neighboring atoms of an absorbing atom. The pre-edge feature is clearly visible in the Nb K edge spectra of the Mo−V−Te−Nb−O M1 phase and $Nb_2O_5$, collected at ambient conditions, shown in Figure 1. The intensity of the pre-edge, which is due to the transition from the Nb 1s orbital to the 4d orbital manifold, is low. The absorption edges of this M1 phase (19003.6 eV) and $Nb_2O_5$ (19003.8 eV) are

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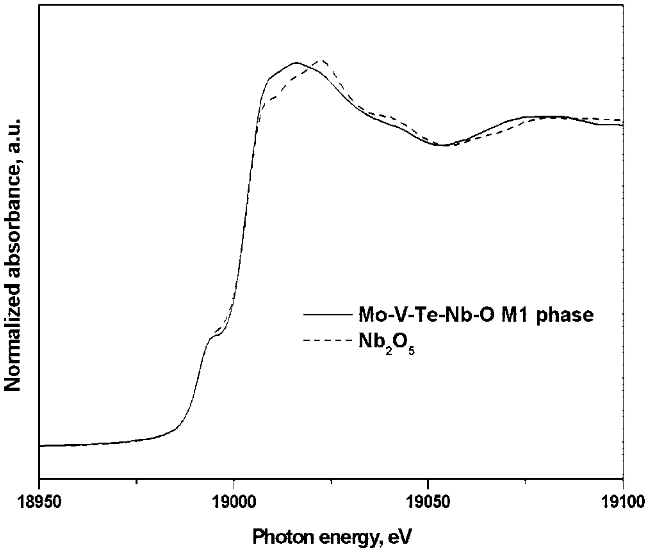

**Figure 1.** Nb K near-edge X-ray absorption spectra of $Nb_2O_5$ and the Mo−V−Te−Nb−O M1 phase.

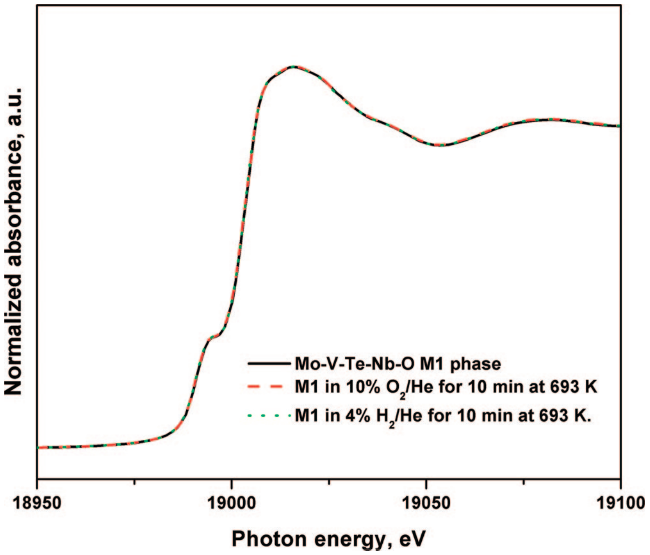

**Figure 2.** Nb K near-edge X-ray absorption spectra of (——) the Mo−V−Te−Nb−O M1 phase, (---) the Mo−V−Te−Nb−O M1 phase after its exposure to 10% $O_2$ in He for 10 min at 693 K, and (···) the Mo−V−Te−Nb−O M1 phase after its subsequent exposure to 4% $H_2$ in He for 10 min at 693 K.

nearly identical, indicating the presence of pentavalent Nb in the M1 phase. This is in agreement with the proposed structural model of the M1 phase where the bond valence sum calculations suggest that Nb is in the 5+ oxidation state.[19] Also no $Nb^{4+}$ was detected in the previous EPR studies of the Mo−V−Te−Nb−O M1 (slurry) phase.[15]

To study the effect of catalytic conditions on the state of Nb in the catalyst, the M1-phase sample was subjected to oxidizing and reducing conditions at 693 K. The Nb K edge XANES spectra were collected after the Mo−V−Te−Nb−O M1 phase was exposed to oxidizing (a 10% $O_2$ in He mixture for 10 min at 693 K) and reducing (a 4% $H_2$ in He mixture for 10 min at 693 K) conditions. No observable changes were detected in the spectra during these redox treatments (Figure 2). Considering together the facts that niobium is highly resistant to reduction and its proposed function is to stabilize and structurally isolate the active sites in the M1 structure rather than directly participate in the catalysis, niobium most likely retains its pentavalent state during the reaction conditions.

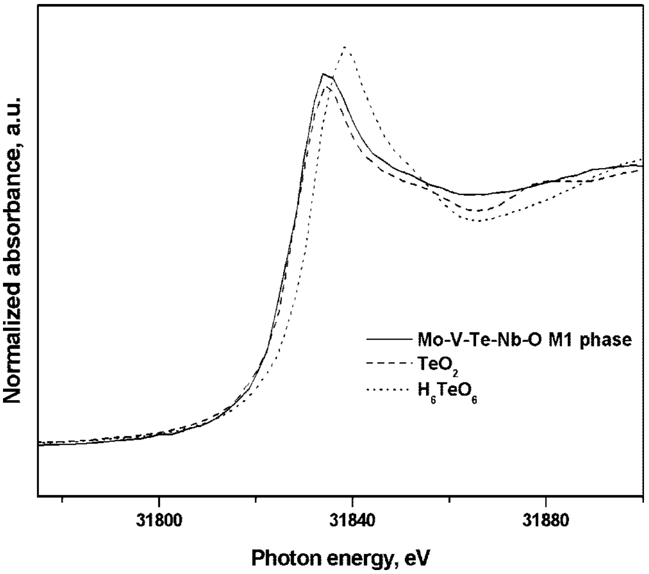

**Figure 3.** Te K near-edge X-ray absorption spectra of (···) $H_6TeO_6$, (——) the Mo−V−Te−Nb−O M1 phase, and (---) $TeO_2$.

Te K edge spectra of the M1 phase, telluric acid ($Te^{6+}$), and $TeO_2$ ($Te^{4+}$) are shown in Figure 3. The edge energy position for the M1 phase (31829.6 eV) is much closer to that of $TeO_2$ (31828.8 eV) rather than $H_6TeO_6$ (31831.7 eV), indicating a predominant oxidation state of 4+ for Te in the M1 phase. Millet et al. investigated the Mo−V−Te−Nb−O catalyst using Mössbauer and XPS spectroscopies and showed that the catalysts contained only $Te^{4+}$ in the bulk and mainly $Te^{6+}$ at the surface.[13] Their catalyst, prepared by the slurry method, contained a mixture of M1 (ca. 60%) and M2 phases. The EXAFS studies of this catalyst also suggested that the tellurite entities corresponded to the $TeO_4E$ trigonal bipyramid in the M1 phase and $TeO_3E$ distorted trigonal pyramid in the M2 phase. Te was also observed to be present in only the 4+ oxidation state in the bulk of an M1/M2-phase mixture (Mo−V−Te−Nb−O) in a later study.[15]

We have further investigated the effect of redox conditions on the Te oxidation state, and the Te K edge XANES spectra of the Mo−V−Te−Nb−O M1 phase collected are shown in Figure 4. No changes were observed in the spectra after exposure to a 10% $O_2$/He mixture or a 4% $H_2$/He mixture at 693 K, suggesting that the oxidation state of Te remained unchanged during these treatments. This is consistent with the observation by Millet et al. that the Te LIII edge XANES spectra of the above-mentioned catalyst were similar before and after catalytic reaction, which confirmed that the local environment of Te was not affected by the catalytic reaction conditions.[13] Also, Te in the M1/M2-phase mixture was found to remain as $Te^{4+}$ before and after propane oxidation reaction using Mössbauer spectroscopy.[15] On the other hand, oxidation state changes were observed under catalytic conditions for Sb, which occupies the same crystallographic sites in the bulk crystal structure of the MoVSbNbO M1 phase.[17] The Sb reduction was observed even during the

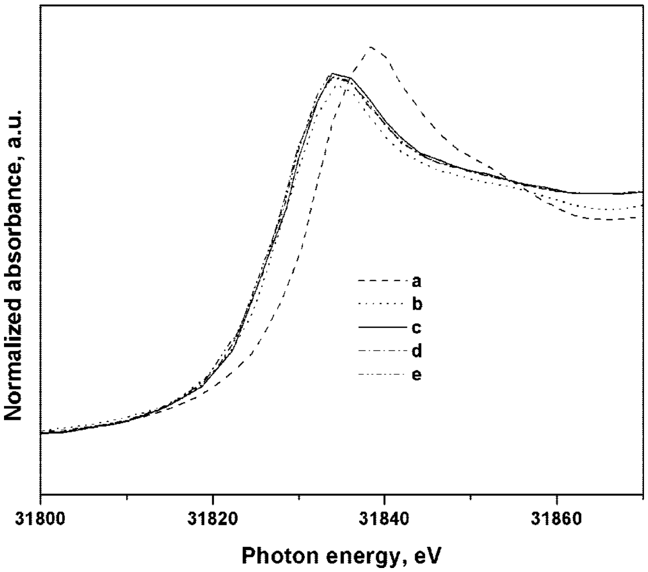

**Figure 4.** Te K near-edge X-ray absorption spectra of (a) $H_6TeO_6$, (b) $TeO_2$, (c) the Mo−V−Te−Nb−O M1 phase, (d) the Mo−V−Te−Nb−O M1 phase after its exposure to 10% $O_2$ in He for 10 min at 693 K, and (e) the Mo−V−Te−Nb−O M1 phase after its subsequent exposure to 4% $H_2$ in He for 10 min at 693 K.

annealing of the M1 phase in He at 373 K. Tellurium and antimony have been proposed to be responsible for the abstraction of an α-hydrogen from the chemisorbed propyl radical formed from propane and subsequently from the propylene intermediate to form the allyl intermediate.[18] These steps require the immediate regeneration of the tellurium site after the abstraction of the first hydrogen. As mentioned above, $Te^{6+}$ proposed to be present at the surface in previous studies may play a role in the hydrogen abstraction. According to our observations, the bulk Te remained tetravalent under the redox conditions of our studies.

Figure 5 shows the Mo K near-edge spectra of two-, three-, and four-component M1 phases (20016.4, 20016.0, and 20016.1 eV, respectively) and two reference compounds, $MoO_3$ (20016.3 eV) and $MoCl_5$ (20010.9 eV). Mo complexes with tetrahedral geometry show pre-edge peaks of relatively high intensity, attributed to the 1s(Mo) → 4d(Mo) + 2p(O) transition, which is dipole-allowed for the tetrahedral symmetry. For a regular octahedron (e.g., in $MoO_2$), this transition is very weak and nearly invisible at the Mo K edge having large natural broadening. When the coordination is distorted octahedral, this transition is visible as a weak pre-edge or shoulder, as in α-$MoO_3$. The absorption edges of the catalytic M1 phases are shifted to higher energies compared to that of $MoCl_5$ and exhibit clear similarity to that of $MoO_3$. The occurrence of a prepeak and the energy values indicate that Mo exists in a distorted octahedral coordination in the 6+ oxidation state in all M1 phases. An oxidation state of Mo between +5.6 and +6 in the Mo−V−Sb−Nb−O M1 phase (a slurry catalyst treated with $H_2O_2$) was reported in a previous study.[17] The same authors also presented ESR spectroscopic evidence for $Mo^{5+}$ in the Mo−V−Te−Nb−O M1 phase, synthesized by a slurry method and treated with $H_2O_2$.[15] The $Mo^{5+}$ content was found to be 7% of the total Mo by integrating the ESR signals and subtracting the contribution of the $V^{4+}$ species. However, according to our observations, the Mo oxidation state was 6+ in the two-, three-, and four-component M1 phases within the accuracy of the XANES method.

According to the proposed hypothetical mechanism of propane ammoxidation, the $Mo^{6+}$ site coordinates the allyl radical and aids in the insertion of the NH moiety into the radical.[18] However, no detectable changes were observed in the XANES spectra collected after the M1 phases were exposed to oxidizing (a 10% $O_2$ in He mixture for 10 min at 693 K) and reducing (a 4% $H_2$ in He mixture for 10 min at 693 K) environments, indicating that any oxidation state changes experienced by the Mo species under dynamic conditions were below the detection limit of this technique (Figure 6). Similar observations were made by Safonova et al. in their XAS and electrical conductivity study of the Mo−V−Sb−Nb−O M1 phase under dynamic conditions.[17]

Previous studies of vanadium compounds reported that the pre-edge (forbidden transition 1s → 3d) and main-edge (dipole-allowed transition 1s → 4p) positions and their intensity can be correlated with the oxidation state and coordination geometry of the vanadium cation.[26] When the vanadium oxidation state increases, the pre-edge peak and main-edge positions shift to higher energies to different extents. The pre-edge intensities indicative of V coordination are very low for symmetrical vanadium−ligand coordinations with inversion symmetry, such as in regular "$VO_6$" octahedra. The symmetry decreases progressively for distorted octahedral, square-pyramidal, and tetrahedral geometries, and an increase in pre-edge intensities is correspondingly observed. Very strong pre-edge intensities were reported for $NH_4VO_3$ with an almost regular tetrahedral "$VO_4$" coordination. A large pre-edge intensity is present in $V_2O_5$ where the V−O coordination sphere may be described as a strongly distorted square-pyramidal "$VO_5$" unit, with one short vanadyl bond (V=O) at 1.59 Å perpendicular to the plane formed by the four other oxygen neighbors. $VOSO_4 \cdot 3H_2O$ has a distorted $VO_6$ coordination with a short vanadyl bond at 1.56 Å and a long V−O bond at 2.28 Å both perpendicular to the more or less symmetrical square plane of the $VO_6$ unit, and its pre-edge intensity is lower (in comparison to the maximum absorption) than that of $V_2O_5$. However, it must be noted that not only the symmetry but also other parameters may influence the prepeak and the technique only provides an average picture of the V environment. Nevertheless, these results may be used to understand the V environment in the present samples qualitatively. The prepeak in the Mo−V−Te−Nb−O M1 phase is less pronounced (Figure 7) and indicates that, although V may still be in a distorted octahedral coordination, it has a higher symmetrical environment as compared to that in $VOSO_4$.

The position of the pre-edge peak is similar for the Mo−V−Te−Nb−O M1 phase (5468.8 eV) and $VOSO_4$ (5468.9 eV), while that of $V_2O_5$ (5469.7 eV) is shifted to higher energies (Figure 7). This suggests that V most likely exists in the 4+ oxidation state in the M1 phase. In a previous

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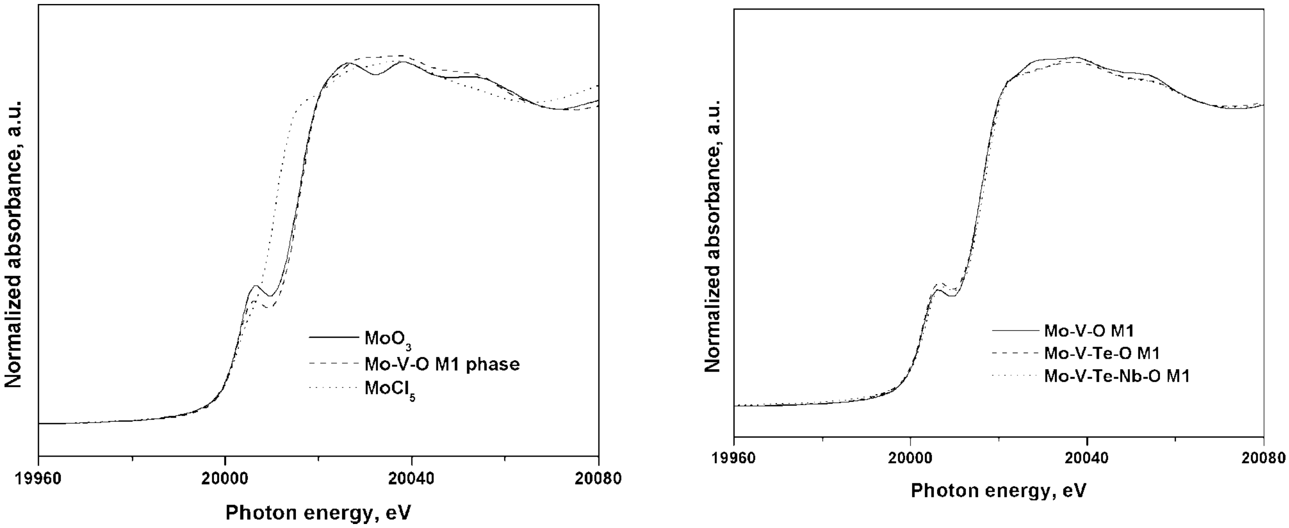

**Figure 5.** Mo K near-edge X-ray absorption spectra of $MoO_3$, $MoCl_5$, and the Mo−V−O, Mo−V−Te−O, and Mo−V−Te−Nb−O M1 phases.

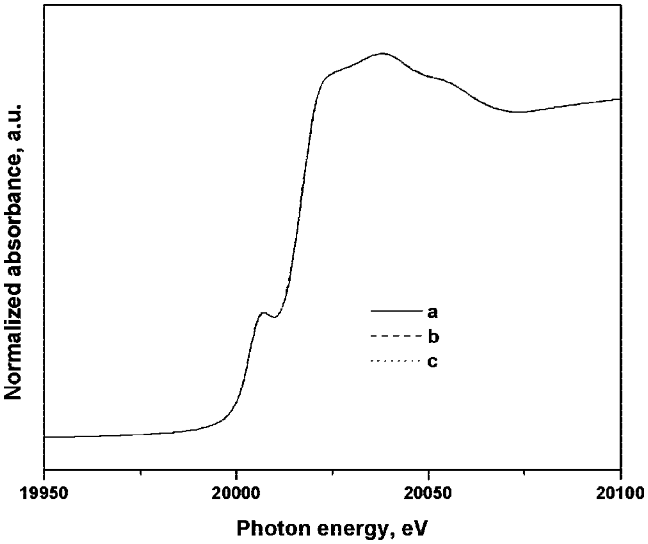

**Figure 6.** Mo K near-edge X-ray absorption spectra of (a) the Mo−V−Te−Nb−O M1 phase, (b) the Mo−V−Te−Nb−O M1 phase after its exposure to 10% $O_2$ in He for 10 min at 693 K, and (c) the Mo−V−Te−Nb−O M1 phase after its subsequent exposure to 4% $H_2$ in He for 10 min at 693 K.

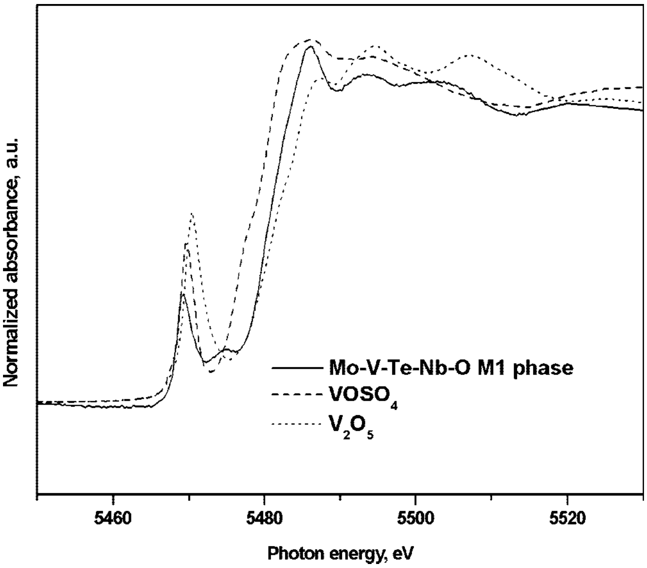

**Figure 7.** V K near-edge X-ray absorption spectra of (---) $VOSO_4 \cdot 3H_2O$, (——) the Mo−V−Te−Nb−O M1 phase, and (•••) $V_2O_5$.

study of the M1 phase prepared by a slurry method, the V oxidation state was suggested to be 4+ on the basis of the prepeak positions.[15] The positions were the same for the M1 phase and $(VO)_2P_2O_7$ and lower in energy as compared to that of $V_2O_5$. The prepeak observed for our Mo−V−Te−Nb−O M1 phase was wider than that of $VOSO_4$, probably suggesting the presence of some $V^{5+}$ in the structure. A distribution of the V−O bond distances for different V crystallographic sites in the M1 structure around the vanadium ions may give rise to such a prepeak widening.

Small, yet reproducible changes were observed in the V prepeak when the M1 phase was subjected to redox treatments (Figure 8). The right side of the pre-edge peak shifted slightly to higher energy when the M1 phase was treated in the $O_2$-containing atmosphere at 693 K and shifted back to the original position with subsequent exposure to $H_2$ at the same temperature. These changes were reversible and reproducible after a number of redox cycles, indicating that a redox process affected a small fraction of $V^{4+}$ and $V^{5+}$ states in the catalyst. The average change in oxidation states of samples treated in $O_2$ and $H_2$ atmospheres is found to be ~ 0.35.[15,26] Similar partial oxidation of vanadium was observed previously when the Mo−V−Sb−Nb−O catalyst was heated in an $O_2$ atmosphere.[17]

Reversible changes in the Te, Mo, and V oxidation states are expected to occur during propane ammoxidation over the M1-phase catalysts according to the proposed hypothetical mechanism of propane ammoxidation.[27] Nb is proposed to occupy the pentagonal-bipyramidal sites in the M1-phase structure where it has the active site isolation function and does not directly participate in the redox steps of the propane ammoxidation reaction. However, the results of the present XANES study indicated that not only Nb but also Te and Mo are not easily reduced or oxidized under the dynamic conditions employed in our study. No oxidation state changes

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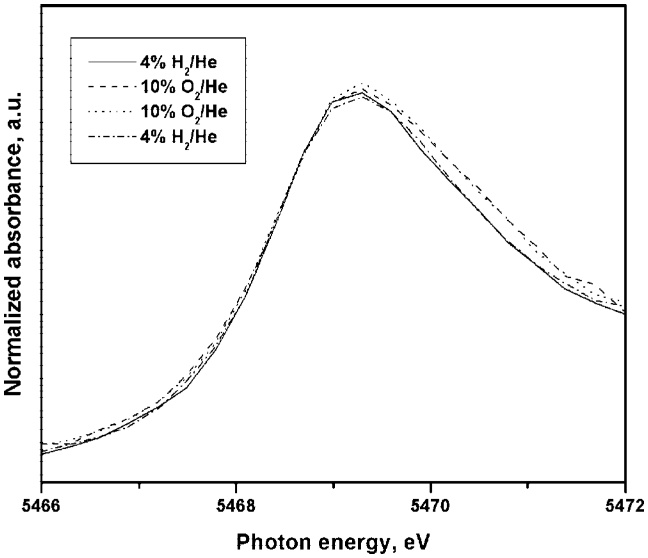

**Figure 8.** V K near-edge X-ray absorption spectra of the Mo−V−Te−Nb−O M1 phase during redox treatments at 693 K showing the pre-edge peaks.

were detected for the Nb, Te, and Mo cations under these dynamic XANES conditions within the accuracy of this bulk spectroscopic technique. Only vanadium was shown to undergo small, but nonetheless finite, oxidation state changes under these dynamic conditions, indicating that it is the most redox active species present in the M1-phase catalysts.

In a previous study using low-energy ion scattering (LEIS), it was observed that the rates of propane consumption and formation of propylene and acrylic acid during propane oxidation over M1-phase catalysts depended on the topmost surface V concentration, whereas no dependence of these reaction rates on either the surface Mo or the surface Te concentration was observed.[28] A subsequent study using LEIS and allyl alcohol chemisorption indicated that the $VO_x$ sites were 3.1 times more preferred than the $MoO_x$ sites in the Mo−V−Te−Nb−O M1-phase catalyst for allyl alcohol chemisorption, even though the Mo was in excess as compared to V.[11] The results obtained in the present study are in agreement with these previous observations and provide further strong support for the critical role played by $VO_x$ species in propane activation over M1-phase catalysts.

## Conclusions

The hydrothermal Mo−V-based mixed oxide catalysts possessing the M1-phase structure were investigated by XANES under ambient and dynamic redox conditions. Under ambient conditions, XANES, with the use of model compounds, suggested oxidation states of Nb, Te, Mo, and V close to 5+, 4+, 6+, and 4+, respectively, in the bulk M1 phase. The oxidation state changes of Nb, Te, and Mo were not detected under the dynamic conditions employed in our experiments, while the pre-edge peak of vanadium in the M1 phase exhibited small, reproducible shifts, suggesting that $VO_x$ is the most reducible/oxidizable catalytic species in the bulk M1-phase catalysts.

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**Supporting Information Available:** Activity data in propane ammoxidation and SEM images and proposed structure of the M1 phase (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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