

The M1 Phase of MoVTeNbO as a Catalyst for Olefin Metathesis and Isomerization

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Polycrystalline MoVTeNb oxide composed of the M1 phase was studied in the transformation of propene at reaction temperatures between 323 and 573 K in the absence of oxygen and water. Surprisingly, the catalyst showed considerable activity in propene metathesis to ethene and 2-butenes, which was attributed to partial reduction of the catalyst surface under the reaction conditions. The multifunctionality of the M1 phase, which is known as a selective catalyst for the direct oxidation of propane to acrylic acid, was furthermore reflected in the formation of 1-butene and isobutene owing to C4 isomerization. This study demonstrates the diversity of the M1 phase as a catalyst, which is based on surface dynamics and structural stability, and further improves the understanding of the complex reaction network of short-chain hydrocarbons over MoVTeNbO M1 catalysts.

Crystalline MoVTeNbO materials containing the orthorhombic M1 phase (ICSD no. 55097)^[1] as a major component represent the most active and selective catalysts for the direct oxidation of light alkanes.^[2,3] The M1 phase alone is able to accomplish the direct oxidation of propane to acrylic acid, which involves abstraction of four hydrogen atoms, addition of two oxygen atoms, and exchange of eight electrons.^[2,4,5] The multiple catalytic functions of the M1 phase capable of activating various functional groups (e.g., alkanes, alkenes, alcohols, aldehydes) are considered a key aspect that enables the direct formation of acrylic acid with high selectivity.^[6,7] Structural assignment of the catalytic functions is not straightforward, as the catalytic functions of M1 are closely related to the dynamics of the M1 surface changes in response to the reaction atmosphere (e.g., gas composition, temperature).^[8-10] It is likely that the gradient of the gas composition within the catalyst bed influences the catalytic properties of M1. Especially, reaction conditions with a regulated oxygen partial pressure are often applied in propane oxidation to maximize the yield of the desired products.^[11] The formation of an "oxygen-deficient zone" inside the catalyst bed becomes plausible under such conditions, and this leads to extended modification of the catalyst surface that potentially impacts the catalytic performance.^[12] In this con-

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International Iberian Nanotechnology Laboratol Braga 4715-330 (Portugal) text, we explored the conversion of propene over the M1 phase in the absence of oxygen. Surprisingly, we discovered that the MoVTeNbO M1 phase performs the metathesis of propene to form ethene and 2-butenes at a temperature well below that of typical alkane oxidation conditions.

Appreciable conversion of propene into ethene and butenes in an approximately 1:1 ratio was observed above 423 K (Figure 1a); this suggests the occurrence of propene metathesis



Figure 1. Propene reaction over the MoVTeNbO M1 catalyst at 323–573 K: a) Formation rate of ethene and butenes; b) formation of $C_3H_6O~(m/z=58)$ monitored by mass spectrometry.

activity. The consumption rate of propene over the bulk MoV-TeNbO M1 catalyst, which is characterized by a low specific surface area ($S_{BET} = 7.5 \text{ m}^2 \text{g}^{-1}$), reached a remarkable value of 1 mmol_{propene} $\text{g}_{cat}^{-1} h^{-1}$ at the highest reaction temperature of 573 K. This is close to the temperature range in which the catalyst normally operates in selective oxidation reactions. The activity was, however, lower than the specific activity of molybdenum oxide species anchored on the surface of supports with high specific surface area, which are typically applied in olefin metathesis reactions; these catalysts include MoO_x/SiO₂ (8 mmol_{propene} $\text{g}_{cat}^{-1} h^{-1}$ at 323 K, $S_{BET} = 556 \text{ m}^2 \text{g}^{-1}$)^[13] and MoO_x/SiO₂-Al₂O₃ (30 mmol_{propene} $\text{g}_{cat}^{-1} h^{-1}$ at 313 K, $S_{BET} = 480 \text{ m}^2 \text{g}^{-1}$).^[14] Upon normalizing the rates at 323 K to the sur-

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face area, the activity of the MoVTeNbO M1 catalyst (1 μ mol_{propene} m_{cat}⁻²h⁻¹) is one order of magnitude lower than that of MoO_x/SiO₂ (14 μ mol_{propene} m_{cat}⁻²h⁻¹).^[13] The ethene/butenes ratio remained at approximately 1 with increasing temperatures up to 573 K, and this indicates that olefin conversion is predominantly the result of propene self-metathesis to yield ethene and 2-butenes. In addition to the metathesis reaction, subsequent rearrangement of the 2-butenes into 1-butene and isobutene was suggested (Figure 2). The selectivity profile in



Figure 2. a) Product distribution of the propene reaction over the MoVTe-NbO M1 catalyst at 323–573 K and b) suggested reaction scheme for propene conversion.

Figure 2a reveals the formation of a minor amount of 1butene and a significant increase in isobutene selectivity at elevated temperatures. At the highest reaction temperature of 573 K, the relative ratio of the butenes approaches thermodynamic equilibrium.^[15] Accordingly, it is suggested that the M1 phase exhibits multifunctional catalysis including olefin metathesis (propene to ethene and 2-butenes), shift of the olefinic bond (2-butenes to 1-butene), and skeletal isomerization (*n*butenes to isobutene).

Mo-carbene species (Mo = CHR) are known as active sites for olefin metathesis.^[16] The occurrence of metathesis activity over M1 suggests the generation of Mo-carbene species on the M1 surface through the reaction of the M1 surface and propene under anaerobic conditions. The development of catalytic activity above 423 K (Figure 1a) is accompanied by the temporal formation of C₃H₆O (Figure 1b, acetone and/or propanal), which suggests that the reduction of the catalyst surface by propene (i.e., formation of C_3H_6O) is connected to catalytic activity. Most likely, Mo^{IV} species formed by the oxygenation of propene act as precursors of the Mo-carbene species (Scheme 1), as coordinatively unsaturated Mo[™] species formed by surface reduction are known to be good precursors of Mo-carbene species.^[13, 17, 18] As vanadium is considered to be essential for the oxidation activity of M1,^[2,8] it is speculated that the formation of Mo^{IV} involves, first, propene oxidation at



Scheme 1. Suggested pathway for the formation of active Mo–carbene sites in the propene reaction on the surface of MoVTeNbO M1.

the vanadium centers and, second, charge transfer to the molybdenum centers, which leads to the formation of Mo^{IV} centers. Alternatively, molybdenum oxide sites may be directly involved. Te⁴⁺–O and O=Mo⁶⁺=O centers in close vicinity on the surface of M1 have been considered to be able to perform α -H abstraction from adsorbed propene and O insertion into the resulting π -allylic intermediate, respectively, which lead to Mo⁴⁺ and desorption of acrolein.^[19]

Reduced molybdenum centers formed on the M1 surface under the reaction conditions are likely responsible for the observed C4 isomerization activity (i.e., formation of 1-butene and isobutene). Supported molybdenum oxide catalysts in reduced states are known to be active for C4 isomerization reactions at 623 K,^[20] for which Brønsted acidity has been suggested to play an important role.^[21] Indeed, we found that the MoVTeNbO M1 catalyst exhibits Brønsted acidity,^[8] which may contribute to the C4 isomerization activity.

The reduction of the M1 surface by propene was also supported by a temperature-programmed reaction (TPR) with propene (Figure 3). The broad band of C_3H_6O (m/z=58) centered



Figure 3. Profile for the consumption of propene (m/z=42) as well as the profiles for the formation of acrolein/butene (m/z=56) and acetone/propanal (m/z=58) traced by mass spectrometry during the temperature-programmed reaction of MoVTeNbO M1 in 5% propene at 2 Kmin⁻¹.

at 470 K is consistent with the temporal formation of C_3H_6O detected upon increasing the reaction temperature in the catalytic test (Figure 1 b). A large consumption of propene with concurrent formation of oxygenated products was observed at approximately 750 K (which is much higher than the temperature range of the catalytic test) in the TPR profile (Figure 3); this is indicative of bulk reduction of the M1 catalyst by propene, which probably yields bulk metal carbide materials.^[22]

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Structural characterization of the catalyst used in metathesis (Figure 2) indicated that the M1 phase preserved its bulk structure but that it did undergo a minor modification that was much less severe than the reduction of M1 in propane at 673 K.^[10] No essential change was observed in the XRD pattern after the propene reaction (Figure 4a), and this indicates that the bulk structure of the M1 phase was preserved. A whole



Figure 4. Characterization of MoVTeNbO M1 before and after the propene reaction. a) XRD patterns (the inset shows a magnification); b) Raman spectra upon excitation at $\lambda = 633$ nm.

powder pattern fitting indicates a very minor but notable change in the lattice parameters of the *a* and *b* axes, which is reflected in the shift of the (600) reflection at $2\theta = 25-26^{\circ}$ (Figure 4a, inset). The minor change in the lattice parameters is indicative of the reduction of the M1 phase.^[10] In agreement with the XRD results, after the propene reaction the Raman spectrum kept the general features of M1 but lost distinct bands at $\tilde{\nu} = 875$ (M–O stretching) and 450 cm⁻¹. These two Raman bands were identified as indicators of the high crystallinity of the M1 phase, as the bands occurred upon annealing nanocrystalline M1 into microcrystalline M1 at elevated temperatures.^[23] Besides, no sign of coke deposition^[24] at $\tilde{\nu} =$ 1300–1800 cm⁻¹ was observed in the Raman analysis. Summarizing the structural analyses, it is suggested that the M1 catalyst underwent partial reduction of the M1 phase that involved cleavage of the M-O bonds, whereas the bulk crystal structure was preserved. The preservation of the M1 bulk phase is likely important for catalysis, because crystalline MoO₃ showed no propene conversion activity even after reductive pretreatment by hydrogen or propene (data not shown).

Considering the significant activity observed at low temperature (i.e., T = 423-573 K), olefin isomerization catalysis may op-

erate under alkane oxidation conditions (T = 613-693 K),^[2] although the degree of reduction of the M1 surface is very likely lower than that of the present test conditions and, thus, lower olefin isomerization activity is expected. The propene consumption rate reached 130-85 µmolm⁻²h⁻¹ at 573 K, which is comparable to typical propene formation rates in propane oxidation over MoVTeNbO catalysts (e.g., 280 μ mol m⁻² h⁻¹ at 653 K^[5]). Accordingly, a minor amount of olefin isomerization under the oxidation conditions seems plausible. Indeed, we observed the formation of ethene and isobutene as minor products under the propane oxidation conditions.^[10] It is speculated that the major fraction of the C4 olefins formed by the metathesis route under the propane oxidation conditions undergoes further oxidation to yield stable end products (e.g., CO₂, methacrylic acid, maleic anhydride). Though it is not clear how significant olefin isomerization is under propane oxidation conditions, the present findings provide new insight into the complex reaction network of propane oxidation over MoVTe-NbO M1 catalysts and the versatility of the M1 phase in catalysis.

In summary, we discovered propene metathesis and isomerization catalysis over the MoVTeNbO M1 catalyst to yield ethene and butenes. It appears that the reduction of the M1 surface triggers the catalyst's activity for metathesis and the isomerization of olefins. The findings highlight the highly multifunctional nature of M1 and reveal the prominent role of dynamic changes in the surface of the catalyst under the reaction conditions.

Experimental Section

The phase-pure MoVTeNbO M1 catalyst ($S_{BET} = 7.5 \text{ m}^2 \text{g}^{-1}$, internal ID# 6902) was synthesized by spray drying and subsequent purification. Details of the synthesis and characterization are reported elsewhere.^[5] Powder X-ray diffraction (XRD) analysis was performed by using a STOE STADI-P transmission diffractometer equipped with CuK_{a1} radiation. Confocal Raman spectra were collected at room temperature by using a Horiba-Jobin Ybon LabRam instrument equipped with red laser excitation (633 nm/1.96 eV, 1.5 mW at the sample position). Propene conversion activity was tested in a fixed-bed reactor at 323–573 K at a contact time of 0.15 sg mL⁻¹ by using thoroughly dehydrated and deoxygenated neat propene at atmospheric pressure. Inlet and outlet gases were analyzed by an online gas chromatograph equipped with a flame ionization detector. The activity is presented as the formation rates of the products normalized by the specific BET surface area of the catalyst. Selectivity was calculated on the basis of the number of carbon atoms in the products. Temperature-programmed reaction with propene was performed with a fixed-bed reactor equipped with a quadrupole mass spectrometer by using 5% propene in helium at a heating rate of 2 Kmin^{-1} .

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M1 FTW! The MoVTeNbO M1 phase, known as an excellent catalyst for the direct oxidation of propane to acrylic acid, exhibits remarkable catalytic activity in the conversion of propene into ethene and butenes. This activity is attributed to partial reduction of the catalyst surface under the reaction conditions. The multifunctionality of the M1 phase is also reflected in the formation of 1-butene and isobutene owing to C4 isomerization.



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