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## MoVTenbO M1 Phase Catalyzes Olefin Isomerization

Kazuhiko Amakawa,<sup>[a]</sup> Yury V. Kolen'ko,<sup>[a, b]</sup> Robert Schlögl<sup>[a]</sup> and Annette Trunschke<sup>\*[a]</sup>

Dedication ((optional))

Crystalline MoVTenbO materials containing orthorhombic M1 phase (ICSD no. 55097)<sup>[1]</sup> as a major component represent most active and selective catalysts for direct oxidation of light alkanes.<sup>[2,3]</sup> The M1 phase alone is able to accomplish direct oxidation of propane to acrylic acid which involves abstraction of four hydrogen, addition of two oxygen and exchange of eight electrons.<sup>[2,4,5]</sup> Multiple catalytic function of the M1 phase capable to activate various functional groups (e.g. alkane, alkene, alcohol, aldehyde) is considered as a key aspect enabling the direct formation of acrylic acid in high selectivity.<sup>[6,7]</sup> Structural assignment of catalytic functions is not straightforward, as the catalytic functions of M1 are closely related to dynamics of the M1 surface changes in response to the reaction atmosphere (e.g. gas composition, temperature).<sup>[8,9]</sup> It is likely that the gradient of the gas composition within the catalyst bed influences the catalytic property of M1. Especially, reaction conditions with a regulated oxygen partial pressure are often applied in propane oxidation to maximize the yield of desired products.<sup>[10]</sup> The formation of "oxygen deficient zone" inside the catalyst bed becomes plausible under such conditions, leading to an extended modification of the catalyst surface that potentially impacts the catalytic performance.<sup>[11]</sup> In this context, we explored propene conversion over M1 phase in the absence of oxygen. Surprisingly, we discovered that MoVTenbO M1 phase performs propene isomerization into ethene and butenes at low 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), suggesting the occurrence of propene metathesis activity. The ethene/butenes ratio remained approximately 1 with increasing temperature up to 573 K, indicating that the olefin conversion is predominantly due to propene self-metathesis yielding ethene and 2-butenes. In addition to the metathesis reaction, subsequent rearrangements of 2-butenes into 1-butene and isobutene were suggested (Figure 2b). The selectivity profile in Figure 2a reveals the formation of minor amount of 1-butene, and the significant increase of isobutene selectivity at elevated temperature. Accordingly, it is suggested that the M1 phase

exhibits a multifunctional catalysis performing olefin metathesis (propene to ethene and 2-butene), shift of olefinic bond (2-butenes to 1-butene) and skeletal isomerization (n-butenes to isobutene).

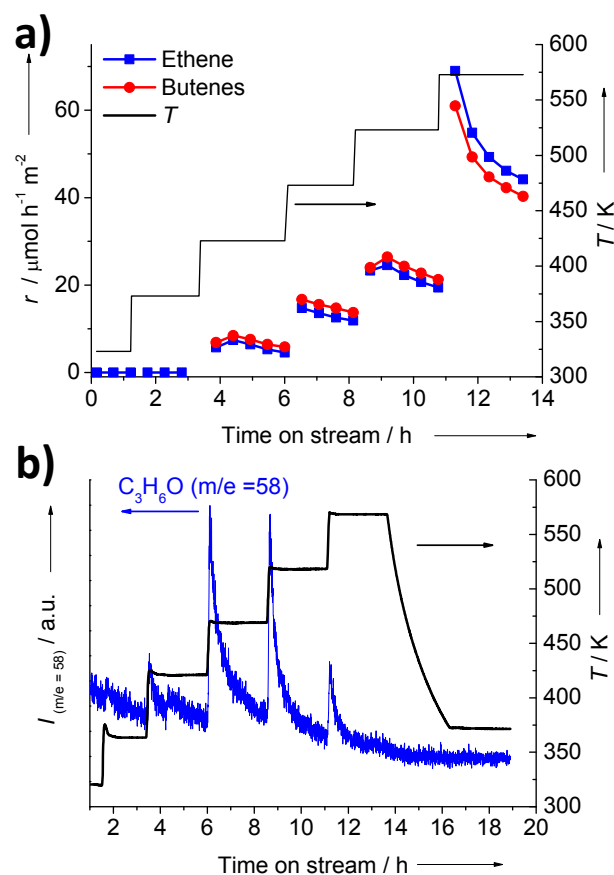


Figure 1. Propene reaction over a MoVTenbO M1 catalyst at 323–573 K.: a) formation rate of ethene and butenes, b) formation of  $\text{C}_3\text{H}_6\text{O}$  ( $m/e = 58$ ) monitored by a mass spectrometer.

[a] Dr. K. Amakawa, Dr. Y. V. Kolen'ko, Prof. Dr. R. Schlögl, Dr. A. Trunschke  
Department of Inorganic Chemistry  
Fritz-Haber-Institut der Max-Planck-Gesellschaft  
Faradayweg 4-6, 14195 Berlin (Germany)  
Fax: (+) 49 30 8413 4405  
E-mail: [trunschke@fhi-berlin.mpg.de](mailto:trunschke@fhi-berlin.mpg.de)

[b] Present address: International Iberian Nanotechnology Laboratory, Braga 4715-330, Portugal

Mo—carbene species ( $\text{Mo}=\text{CHR}$ ) are known as active sites for olefin metathesis.<sup>[12]</sup> The occurrence of metathesis activity over M1 suggests generation of Mo—carbene species on the M1 surface through the reaction between the M1 surface and propene under anaerobic conditions. The development of the catalytic activity above 423 K (Figure 1a) is accompanied by the temporal formation of  $\text{C}_3\text{H}_6\text{O}$  (Figure 1b; acetone and/or propanal), suggesting that the reduction of the catalyst surface by propene (i.e. formation of  $\text{C}_3\text{H}_6\text{O}$ ) is connected to the occurrence

of the catalytic activity. Most likely, Mo(IV) species formed by the oxygenation of propene act as precursor of Mo-carbene species (Scheme 1), as coordinatively unsaturated Mo(IV) species formed by surface reduction are known as a good precursor of Mo-carbene species.<sup>[13–15]</sup> As vanadium is considered to be essential for oxidation activity of M1,<sup>[2,8]</sup> it is speculated that the formation of Mo(IV) involves first propene oxygenation at vanadium centers and subsequent charge transfer to molybdenum centers that leads to the formation of Mo(IV) centers.

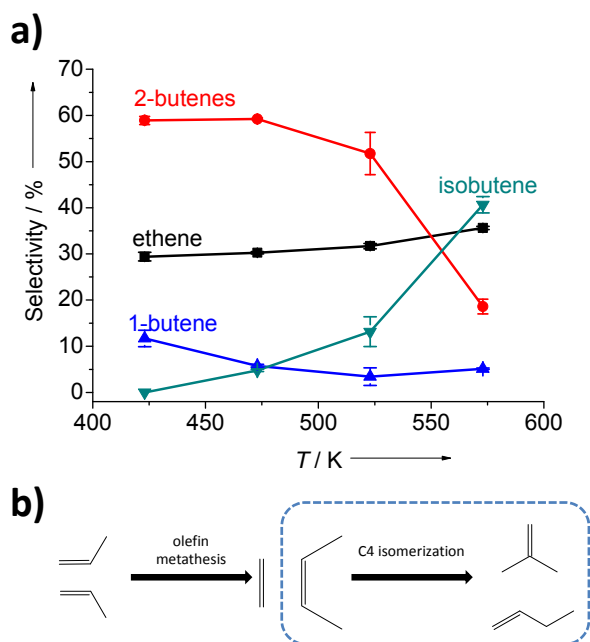
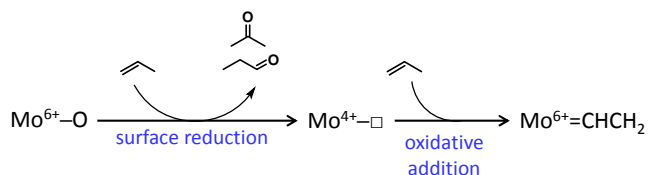


Figure 2. Product distribution of propene reaction over MoVTeNbO M1 catalyst at 323–573 K (a), and suggested reaction scheme of propene conversion (b).



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

Reduced molybdenum centers formed on the M1 surface under the reaction condition 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,<sup>[16]</sup> where Brønsted acidity has been suggested to play an important role.<sup>[17]</sup> Indeed, we have found that the MoVTeNbO M1 catalyst exhibits Brønsted acidity,<sup>[8]</sup> which may contribute to the C4 isomerization activity.

The reduction of the M1 surface by propene was also supported by temperature programmed reaction with propene (TPR; Figure 3). The broad peak of C<sub>3</sub>H<sub>6</sub>O (*m/e* 58) centered at 470 K is consistent with the temporal formation of C<sub>3</sub>H<sub>6</sub>O detected upon increments of the reaction temperature in the catalytic test (Figure 1b). A large consumption of propene and concurrent formation of oxygenated products were observed at

around 750 K (which is far higher than the temperature range of the catalytic test) in the TPR profile (Figure 3), indicating a bulk reduction of the M1 catalyst by propene that probably yields bulk metal carbide materials.<sup>[18]</sup>

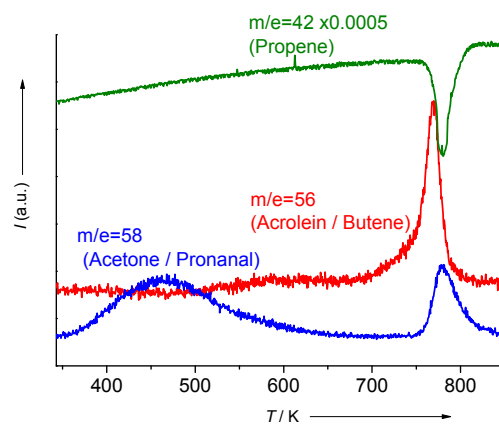


Figure 3. Profile of propene (*m/e* 42) consumption as well as acrolein/butene (*m/e* 56) and acetone/propanal (*m/e* 58) formation traced by mass spectrometry during the temperature programmed reaction of MoVTeNbO M1 in 5%-propene at 2 K min<sup>-1</sup>.

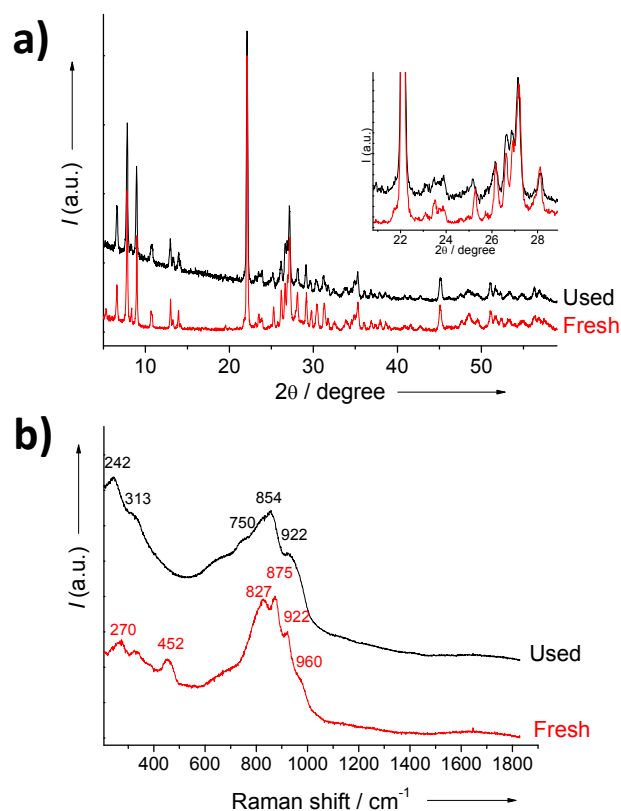


Figure 4. Characterization of MoVTeNbO M1 before and after propene reaction. a): XRD patterns; the inset shows a magnification. b): Raman spectra upon excitation at 633 nm.

Structural characterization indicates that the M1 phase preserved its bulk structure while undergoing a minor modification. No essential change was observed in the XRD pattern after the

propene reaction (Figure 4a), indicating that the bulk structure of M1 phase was preserved. A whole powder pattern fitting indicates a very minor but notable change in the lattice parameters of a- and b- axes, which is reflected in the shift of (006) reflection at 25-26° (inset in Figure 4a). The minor change in the lattice parameters is indicative for the reduction of the M1 phase. In agreement with the XRD result, the Raman spectrum after the propene reaction kept the general feature of M1 but lost the distinct bands at 875 (M—O stretching) and 450 cm<sup>-1</sup>. These two Raman bands have been identified as indicators for a high crystallinity of M1 phase, as the bands occurred upon an annealing of nano-crystalline M1 into micro-crystalline M1 at elevated temperature.<sup>[19]</sup> Besides, no sign of coke deposition<sup>[20]</sup> at 1300-1800 cm<sup>-1</sup> was observed in the Raman analysis. Summarizing the structural analyses, it is suggested that the M1 catalyst underwent a partial reduction of M1 phase involving a breakage of M—O bonds while preserving yet the bulk crystal structure. The preservation of M1 bulk phase is likely important for the catalysis, because crystalline MoO<sub>3</sub> 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. 423—573 K), the olefin isomerization catalysis may operate in alkane oxidation typically conducted at 613—693 K,<sup>[2]</sup> although the degree of reduction of the M1 surface is very likely lower than the present test condition thus a lower olefin isomerization activity is expected. The propene consumption rate reached at 90—130 mmol h<sup>-1</sup> m<sup>-2</sup> at 573 K, which is comparable to typical propene formation rate in propane oxidation over MoVTeNbO catalysts (e.g. 280 mmol h<sup>-1</sup> m<sup>-2</sup> at 653 K<sup>[5]</sup>). Accordingly, a minor occurrence of the olefin isomerization reactions under oxidation conditions seems a plausible scenario. Indeed, we observed the formation of ethene and isobutene as minor products under propane oxidation conditions. It is speculated that the major fraction of C4 olefins formed via the metathesis route under propane oxidation further undergoes deep oxidation to yield stable end products (e.g. CO<sub>2</sub>, methacrylic acid, maleic anhydride). Though it is not clear how significant the olefin isomerization catalysis in propane oxidation conditions is, the present findings provide new insights into the complex reaction network of propane oxidation over MoVTeNbO M1 catalysts.

In summary, we discovered propene isomerization catalysis over MoVTeNbO M1 catalyst yielding ethene and butenes. It appears that the reduction of the M1 surface triggers the activity of metathesis and isomerization of olefin. The findings highlight highly multifunctional nature of M1 and underlying prominent roles of dynamic changes of the surface under reaction conditions.

## Experimental Section

A phase-pure MoVTeNbO M1 catalyst (BET surface area 7.5 m<sup>2</sup> g<sup>-1</sup>, internal ID# 6902) was synthesized by spray-drying and subsequent purification. The details of synthesis and characterization are reported elsewhere.<sup>[5]</sup> Powder X-ray Diffraction (XRD) analysis was performed using a STOE STADI-P transmission diffractometer equipped with CuK<sub>α1</sub> radiation. Confocal Raman spectra were collected at room temperature using a Horiba-Jobin Yvon LabRam instrument equipped with a 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 - 573K and at contact time of 0.15 s g ml<sup>-1</sup> using thoroughly dehydrated and deoxygenated neat propene at the atmospheric pressure. Inlet and outlet gases were analyzed by an on-line gas chromatograph equipped with a flame ionization detector. The activity is presented as formation rates of products normalized by the specific BET surface area of catalyst. Selectivity was calculated based on the number of carbon atoms in products. Temperature programmed reaction with propene (TPR) was performed on a fixed bed reactor equipped with a quadrupole mass spectrometer using 5% propene in helium at the heating rate of 2 K min<sup>-1</sup>.

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**Keywords:** M1 • olefin • isomerization • metathesis • MoVTeNbO

- [1] P. DeSanto, D. Buttrey, R. Grasselli, C. Lugmair, A. Volpe, B. Toby, T. Vogt, *Z. Kristall.* **2004**, *219*, 152–165.
- [2] A. Trunschke, in *RSC Nanoscience & Nanotechnology* (Eds.: C. Hess, R. Schlögl), Royal Society Of Chemistry, Cambridge, **2011**, pp. 56–95.
- [3] R. Grasselli, D. Buttrey, J. Burrington, A. Andersson, J. Holmberg, W. Ueda, J. Kubo, C. Lugmair, A. Volpe, *Top. Catal.* **2006**, *38*, 7–16.
- [4] W. Ueda, D. Vitry, T. Katou, *Catal. Today* **2005**, *99*, 43–49.
- [5] Y. V. Kolen'ko, W. Zhang, R. N. d'Alnoncourt, F. Girgsdies, T. W. Hansen, T. Wolfram, R. Schlögl, A. Trunschke, *ChemCatChem* **2011**, *3*, 1597–1606.
- [6] V. V. Gulians, R. Bhandari, A. R. Hughett, S. Bhatt, B. D. Schuler, H. H. Brongersma, A. Knoester, A. M. Gaffney, S. Han, *J. Phys. Chem. B* **2006**, *110*, 6129–6140.
- [7] K. Amakawa, Y. V. Kolen'ko, A. Villa, M. E. Schuster, L.-I. Csepei, G. Weinberg, S. Wrabetz, R. Naumann d'Alnoncourt, F. Girgsdies, L. Prati, R. Schlögl, A. Trunschke, *ACS Catal.* **2013**, *1103*–1113.
- [8] M. Hävecker, S. Wrabetz, J. Kröhnert, L.-I. Csepei, R. Naumann d'Alnoncourt, Y. V. Kolen'ko, F. Girgsdies, R. Schlögl, A. Trunschke, *J. Catal.* **2012**, *285*, 48–60.
- [9] A. Celaya Sanfiz, T. W. Hansen, D. Teschner, P. Schnörch, F. Girgsdies, A. Trunschke, R. Schlögl, M. H. Looi, S. B. A. Hamid, *J. Phys. Chem. C* **2010**, *114*, 1912–1921.
- [10] O. Ovsitser, R. Schomaecker, E. V. Kondratenko, T. Wolfram, A. Trunschke, *Catal. Today* **2012**, *192*, 16–19.
- [11] R. Schlögl, *Top. Catal.* **2011**, *54*, 627–638.
- [12] Y. Chauvin, *Angew. Chem. Int. Ed.* **2006**, *45*, 3740–3747.
- [13] K. Amakawa, S. Wrabetz, J. Kröhnert, G. Tzolova-Müller, R. Schlögl, A. Trunschke, *J. Am. Chem. Soc.* **2012**, *134*, 11462–11473.
- [14] Y. Iwasawa, H. Ichinose, S. Ogasawara, M. Soma, *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1763–1777.
- [15] B. N. Shelimov, I. V. Elev, V. B. Kazansky, *J. Mol. Catal.* **1988**, *46*, 187–200.
- [16] Z. X. Cheng, V. Ponec, *Catal Lett* **1994**, *25*, 337–349.
- [17] J. Houžvička, V. Ponec, *Catal. Rev. Sci. Technol.* **1997**, *39*, 319–344.
- [18] T. Cotter, B. Frank, W. Zhang, R. Schlögl, A. Trunschke, *Chem. Mater.* **2013**, *25*, 3124–3136.
- [19] M. Sanchez Sanchez, F. Girgsdies, M. Jastak, P. Kube, R. Schlögl, A. Trunschke, *Angew. Chem. Int. Ed.* **2012**, *51*, 7194–7197.
- [20] A. C. Ferrari, J. Robertson, *Phys. Rev. B* **2000**, *61*, 14095–14107.

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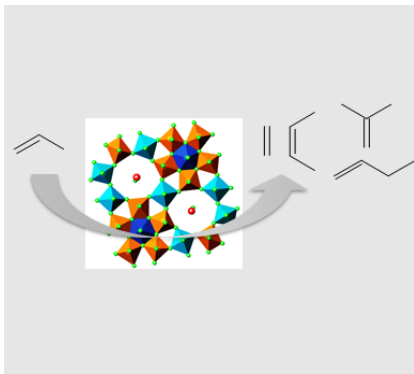
## Entry for the Table of Contents (Please choose one layout only)

Layout 1:

### COMMUNICATION

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MoVTeNbO M1 phase, known as an excellent catalyst for direct oxidation of propane to acrylic acid, exhibits remarkable catalytic activity in propene conversion into ethene and butenes.



*K. Amakawa, Y. V. Kolen'ko, R. Schlögl  
A. Trunschke\**

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