

# Effects of Anion Substitution in (Mo,V)<sub>5</sub>O<sub>14</sub> on Catalytic Performance in Selective Propene Oxidation to Acrolein

S. Kühn, D. Weber, M. Lerch, and T. Ressler\*<sup>[a]</sup>

Molybdenum-based mixed oxides represent well-known model catalysts for the selective oxidation of light alkenes. Here, the anion lattice of  $(Mo,V)_5O_{14}$  was for the first time modified by substituting oxygen ions with nitrogen ions. Investigations by XRD analysis, X-ray absorption spectroscopy, and FTIR spectroscopy revealed that the incorporation of nitrogen in the structure of  $Mo_5O_{14}$  proceeded without changing the average valence of metal centers. Additionally, impedance spectroscopy confirmed the formation of oxygen vacancies. Significant

changes in conductivities remained after the removal of nitrogen. Temperature-programmed reduction measurements were performed to investigate oxygen mobility. The enhanced reducibility of oxide nitrides correlated with the increased conductivity. Catalytic performance in selective propene oxidation was determined by online mass spectrometry und gas chromatography at different temperatures. Selectivity towards acrolein increased with increasing conductivity whereas the formation of total oxidation products  $CO_x$  decreased.

## Introduction

Molybdenum oxide based catalysts are active for selective oxidation reactions of light alkanes and alkenes, for example, propene.<sup>[1-3]</sup> It is assumed that these reactions proceed according to a redox mechanism ("Mars van Krevelen mechanism").<sup>[4]</sup> In a first step propene is chemisorbed at the surface of the catalyst forming an allylic species. Subsequently, the allylic species is oxidized by lattice oxygen from the metal oxide catalyst followed by reoxidation of the catalyst with gas-phase oxygen.<sup>[5]</sup> The reduced chemical and structural complexity of binary oxides like  $\alpha$ -MoO<sub>3</sub> makes it the most simple model system for elucidating structure-activity correlations. Former studies of  $\alpha$ -MoO<sub>3</sub> showed that lattice oxygen is involved in selective oxidation of propene to acrolein.<sup>[6,7]</sup> Further investigations of the defect structure of  $\alpha$ -MoO<sub>3</sub> under propene oxidation conditions revealed a slightly decreased average Mo valence, which might be attributed to the formation of share-structural defects.<sup>[8,9]</sup> Additionally, after selective oxidation of the reactant with nucleophilic lattice oxygen the resulting oxygen vacancy might not be reoxidized immediately at the active site of the catalyst.<sup>[6]</sup> Hence, diffusion of oxygen vacancies and mobility of lattice oxygen is expected to play an important role for catalytic performance. With respect to suitable model systems for elucidating the effect of oxygen mobility on catalytic performance it is desirable to preserve the crystallographic structure of the catalyst. Additionally, the density of vacancies and diffusibility of oxygen ions has to be varied. Cation substitution is an effective method for generating oxygen vacancies. Addition of

 [a] S. Kühn, Dr. D. Weber, Prof. M. Lerch, Prof. T. Ressler Department of Chemistry Technische Universität Berlin Strasse des 17. Juni 135, 10623 Berlin (Germany) E-mail: Thorsten.ressler@tu-berlin.de

ORCID(s) from the author(s) for this article is/are available on the WWW under http://dx.doi.org/10.1002/cctc.201501076.

other transition metals like W, Nb, or V can lead to promoting effects on activity or selectivity in the selective oxidation reaction of light alkenes.<sup>[10–12]</sup> However, promoting Mo-oxide based catalysts with additional metal centers often results in the formation of various crystal structures. Therefore, modification of the cation lattice to modify oxygen mobility seems to be less suited.

Recent studies have shown that nitrogen can be incorporated in the anion lattice of  $\alpha\text{-MoO}_3$  without changing the crystallographic structure. Resulting oxide nitrides represent suitable model system for studying correlations between oxygen mobility and catalytic performance.<sup>[13]</sup> The corresponding oxide nitrides of  $\alpha$ -MoO<sub>3</sub> exhibited an enhanced electronic conductivity.<sup>[14]</sup> In addition, mild ammonolysis resulted in a much improved reducibility, which can be attributed to increased oxygen mobility. Correlations between catalytic performance and electrical properties could not be elucidated because of the low thermal stability of the corresponding oxide nitrides.<sup>[13]</sup> However, MoO<sub>3</sub> is not the most relevant system for studies on selective oxidation of propene. Consequently, the range of oxide nitrides should be extended to more relevant structures in propene oxidation. Model catalysts with the Mo<sub>5</sub>O<sub>14</sub> structure constitute a more complex system compared to that of MoO<sub>3</sub>. Additionally, structural motives of Mo<sub>5</sub>O<sub>14</sub> were found to be more relevant for selective oxidation of propene.<sup>[15, 16]</sup> In this work preparation and structural characterization of (MoV) oxide nitrides with  $\mathsf{Mo}_5\mathsf{O}_{14}$  structure are presented. Furthermore, the effects of ammonolysis of mixed molybdenum oxides on oxygen mobility and catalytic performance in selective oxidation of propene were studied.

Wiley Online Library



## **Results and Discussion**

#### Ammonolysis of (Mo,V)<sub>5</sub>O<sub>14</sub>

 $(Mo,V)_5O_{14}$  was ammonolyzed at various temperatures between 498 and 573 K. A surface area  $A_{BET}$  of approximately 4 gm<sup>-2</sup> was determined for all samples by N<sub>2</sub> physisorption. The phase composition of various ammonolysis products was investigated by XRD technique. The diffraction patterns of the samples ammonolyzed at 498 K and 523 K showed the same phase composition as that of the starting material (Mo,V)<sub>5</sub>O<sub>14</sub> (Figure 1). At higher temperatures (Mo,V)<sub>5</sub>O<sub>14</sub> was partially re-



**Figure 1.** XRD powder patterns of the products obtained by ammonolysis of  $(Mo,V)_5O_{14}$  at different temperatures. Identified phases are marked by symbols ( $\Box Mo_5O_{14\prime} \diamond Mo_9O_{26\prime} \diamond Mo_3N_2$ ).

duced to  $Mo_9O_{25}$  by  $H_2$  formed during decomposition of gaseous  $NH_3$ .<sup>[20]</sup> The ammonolysis product at 573 K revealed the structure of  $Mo_3N_2$ .<sup>[21]</sup> Elemental analysis provided information about the nitrogen content in the prepared samples. The nitrogen content could be adjusted by varying the ammonia flow rate and the reaction time. Hence, oxide nitrides with  $Mo_5O_{14}$  structure and 1, 1.3, and 1.5 wt% nitrogen were prepared for detailed investigations. The  $Mo_5O_{14}$ -type oxide nitrides with 1 and 1.3 wt% nitrogen were prepared at 498 K with 5 or  $10 Lh^{-1}$  ammonia. The temperature was increased to 523 K for preparing oxide nitride with 1.5 wt% nitrogen adjusting an ammonia gas flow of  $5 Lh^{-1}$ . Metal contents were not affected by ammonolysis.

#### Structural effects of nitrogen incorporation

A Rietveld refinement of the  $Mo_5O_{14}$  crystal structure to XRD patterns of  $(Mo,V)_5O_{14}$  and its corresponding oxide nitrides with 1, 1.3, and 1.5 wt% nitrogen was performed. A pseudo-Voigt function convoluted with an axial divergence asymmetry function was used for Rietveld refinement (Figure 2, ICSD 27202).<sup>[22,23]</sup> The asymmetry function was necessary to account for peak asymmetry at low diffraction angels resulting from instrumental effects. Results obtained from XRD refinement are listed in Table 1. The good agreement of the experimental and theoretical data showed that other crystalline phases were not detected. The formation of significant amounts of amorphous phases during ammonolysis was excluded by analyzing the



**CHEMCATCHEM** 

**Full Papers** 

**Figure 2.** Rietveld refinements of  $(Mo,V)_5O_{14}$  crystal structure to XRD powder patterns of  $(Mo,V)_5O_{14}$  and its corresponding oxides nitrides with different nitrogen contents. Difference curves are shown below each refinement. The resulting fit parameters are given in Table 1.

Table 1. Analysis of lattice parameter a and c, unit cell volume V from

Rietveld refinement (goodness of fit GOF and Chi<sup>2</sup> are listed) and William-

nitrides with different nitrogen contents.						
	Oxide	Oxide nitride 1 wt % N	Oxide nitride 1.3 wt% N	Oxide nitride 1.5 wt % N		
a [Å] c [Å] V [Å <sup>3</sup> ] ε D [nm] GOF Chi <sup>2</sup>	$\begin{array}{c} 22.8666(4) \\ 4.0027(9) \\ 2092.9 \\ 0.061 \\ (57 \pm 2) \\ 1.3 \\ 1.8 \end{array}$	22.8969(8) 3.9939(2) 2093.2 0.095 $(56 \pm 2)$ 1.3 1.6	$\begin{array}{c} 22.9302(8)\\ 3.9950(2)\\ 2100.6\\ 0.148\\ (54\pm2)\\ 2.1\\ 1.5\end{array}$	22.9491(8) 3.9936(2) 2103.3 0.171 (57±2) 1.9 1.4		

XRD powder pattern of a mixture of 50 wt% of the sample and 50 wt% of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as described in the literature.<sup>[24]</sup> The *a* and *b* parameters of the oxide nitrides were slightly increased compared to those of the oxide whereas no significant change in *c* parameter was observed. Consequently, the cell volume was also increased after ammonolysis. The increase of cell parameters might be explained by incorporation of nitrogen in the anion lattice of (Mo,V)<sub>5</sub>O<sub>14</sub>.<sup>[25]</sup> Logvinovich et al. reported a similar behavior of strontium–molybdenum oxide nitrides owing to the larger effective ionic radius of N<sup>3–</sup> (1.32 Å) than that of O<sup>2–</sup> (1.26 Å).<sup>[26]</sup>

A line broadening of the X-ray diffraction peaks after ammonolysis was observed. The full width at half maximum (FWHM) of the most intensive line at  $2\theta = 22.4^{\circ} 2\theta$  increased from 0.14°  $2\theta$  to 0.23°  $2\theta$  after ammonolysis. The line broadening can be



attributed to a decrease in particle size or an increase in lattice strain. For a detailed analysis of the line broadening a size-strain analysis by the Williamson-Hall method was performed.<sup>[27]</sup> The Williamson-Hall analysis assumes that XRD line broadening is represented by the sum of the contributions of particle size and lattice strain. Particle size *D* and lattice strain  $\varepsilon$  could be determined by plotting ( $\beta_{hkl}\cos\theta$ )/ $\lambda$  versus sin $\theta$  according to the Williamson-Hall equation:<sup>[28]</sup>

$$\frac{\beta_{hkl}}{\lambda}\cos\theta = \frac{k}{D} + \frac{4\varepsilon}{\lambda}\sin\theta \tag{1}$$

Integral breadth of LaB6 660a was used as XRD standard to correct the measured integral breadth for instrumental effects. The corrected integral breadth  $\beta_{hkl}$  was estimated by the following expression.<sup>[29]</sup>

$$\beta_{hkl} = ((\beta_{hkl})^2_{\text{measured}} - (\beta_{hkl})^2_{\text{instrumental}})^{(1/2)}$$
(2)

The Williamson-Hall plots for all samples resulted in a straight line over a wide angle range (Figure 3). Integral



Figure 3. Size and strain analysis of all samples by the Williamson–Hall method using a set of reflections of all crystallographic directions.

breadth of selected reflections with varying *hkl* was determined by single line fitting. A linear evolution of Williamson– Hall plots indicated a homogenous distribution of particle size and lattice strain in the samples. The average particle size could be calculated from the intercept with the axis and the lattice strain was obtained from the slope. The intercept with the axis revealed the average particle size of about 56 nm for all samples (Table 1). Conversely, the lattice strain changed significantly from 0.061 to 0.171 after ammonolysis of (Mo,V)<sub>5</sub>O<sub>14</sub>.

In addition to XRD investigations X-ray absorption spectroscopy was performed to analyze the influence of nitrogen incorporation on the short-range structure of the MoV oxide nitrides with 1 and 1.5 wt% N. The  $Mo_5O_{14}$  structure contains six metal sites. Thus, the refinement strategy was adapted to simulate an averaged spectrum of the  $Mo_5O_{14}$  structure. Averaging distances can be used for analyzing complex structures such as  $(Mo,V)_5O_{14}$ .<sup>[30,31]</sup> The metal–oxygen and metal–metal distances based on the XRD Rietveld refinements were averaged and grouped into three types of distances. This structure model was refined to experimental data in two steps. One overall  $E_o$  shift and respective Debye–Waller factors for all distances were refined in the first step with average distances kept invariant. Afterwards, free-ranged averaged distances were added to the refinement procedure. The final results of all refinements are shown in Table 2. The significance of the fitted parameters was

**Table 2.** Type, number (*N*), and XAFS disorder parameter ( $\sigma^2$ ) of atoms at a distance *R* from the Mo atoms in (Mo,V)<sub>5</sub>O<sub>14</sub> and oxide nitrides with different nitrogen contents. Experimental distances and disorder parameters were obtained from refinement of a model of averaged distances (*k* range from 3 to 14 Å<sup>-1</sup>, R range from 0.9 to 3.96 Å, *N<sub>ind</sub>* = 23, *N<sub>free</sub>* = 5–11). Subscript c indicates parameters that were correlated in the refinement and subscript f indicates fixed parameters.

Туре	Ν	Oxide		Oxide nitride 1 wt% N		Oxide nitride 1.5 wt % N	
		R [Å]	σ² [Ų]	R [Å]	$\sigma^2  [\text{\AA}^2]$	R [Å]	$\sigma^2$ [Å <sup>2</sup> ]
Mo–O "short"	1.6 <sub>f</sub>	1.74	0.0012 <sub>c</sub>	1.74	0.0013 <sub>c</sub>	1.74	0.0016 <sub>c</sub>
Mo–O "middle"	3.8 <sub>f</sub>	2.00	0.014	2.00	0.014	2.00	0.014
Mo–O "long"	0.7 <sub>f</sub>	2.36	0.0012 <sub>c</sub>	2.36	0.0013 <sub>c</sub>	2.37	0.0016 <sub>c</sub>
Mo–Mo "short"	1.3 <sub>f</sub>	3.32	0.0058	3.33	0.0055	3.33	0.0057
Mo–Mo "middle"	2.3 <sub>f</sub>	3.80	0.0036 <sub>c</sub>	3.80	0.0033 <sub>c</sub>	3.81	0.0034 <sub>c</sub>
Mo–Mo "long"	1 <sub>f</sub>	4.09	0.0036 <sub>c</sub>	4.06	0.0033 <sub>c</sub>	4.06	0.0034 <sub>c</sub>
R		10.5		8.5		9.2	
E <sub>0</sub> [eV]		-	1.78	ç	9.08	7	.88

determined by calculating confidence limits and statistical *F* parameters. The X-ray absorption fine structure (XAFS) spectra of  $(Mo,V)_5O_{14}$  and its corresponding oxide nitrides could be well described with three Mo–O and three Mo–Mo distances. The disorder parameter,  $\sigma^2$ , of the shortest Mo–O distance increased with increasing nitrogen content whereas  $\sigma^2$  of the second Mo–O distance was not affected by the ammonolysis (Figure 4). The formation of structural defects such as oxygen vacancies or incorporated ions might cause structural disorder. The analysis of the local structure around absorbing Mo atoms revealed a modification of the anion lattice. Ammonolysis of (Mo,V)<sub>5</sub>O<sub>14</sub> did not significantly affect the cation lattice. The XRD technique represents a complementary method to XAS technique by providing information about the long-range structure. Combining these two methods, a detailed characteri-



Figure 4. Evolution of the disorder parameter  $\sigma^2$  of two Mo–O distances obtained by EXAFS refinements as a function of nitrogen content.

ChemCatChem **2016**, 8, 758 – 766

www.chemcatchem.org



zation of the structural influences of ammonolysis of  $(Mo,V)_5O_{14}$  could be performed. The increasing lattice strain obtained by XRD confirmed the increasing structural disorder in the local structure of the anion lattice.

FTIR spectra were recorded to compare characteristic vibrational modes before and after ammonolysis (Figure 5). Refining



Figure 5. FTIR spectra of  $(Mo,V)_5O_{14}$  and its corresponding oxide nitrides with different nitrogen contents.

of Gaussian functions to the spectra resulted in maximum peak positions which are summarized in Table 3. The spectra showed the symmetric stretching vibrations of the Mo=O group in a wavenumber range from 900 to 1000 cm<sup>-1</sup>. The bands at lower wavenumbers are assigned to asymmetric vibrations of Mo–O–Me (Me = Mo, V) bridging bonds.<sup>[32-34]</sup> After ammonolysis the same bands could be identified. Additionally, a slight shift of Mo–O–Me and Mo–O bands to lower wavenumbers was revealed by analysis of band positions in the FTIR spectra of Mo<sub>5</sub>O<sub>14</sub>-type oxide nitrides. Gallego reported a similar behavior for the characterization of LaFeO<sub>3-x</sub>N<sub>x</sub> and attributed this shift to an incorporation of nitrogen in ironoxygen octahedral.<sup>[25]</sup> The band shift to lower wavenumbers corresponds to a weakening of bond strength. Hence, decreasing metal–oxygen bond strength may lead to increased

<b>Table 3.</b> Positions and assigned vibrational modes from FTIR refinements of $(Mo,V)_5O_{14}$ and oxide nitrides with different nitrogen contents. <sup>[14, 32-34, 37]</sup>						
Oxide	Oxide nitride 1 wt % N	Oxide nitride 1.3 wt % N	Oxide nitride 1.5 wt % N	Vibrational mode		
569	565	564	559	Mo-O-M		
592	589	589	585	V–O–Mo		
628	632	632	631	Mo-O-M		
731	728	732	731	Mo-O-M		
814	810	813	813	Mo-O-M		
865	861	865	861	Mo-O-M		
909	904	907	895	Mo-O		
980	976	976	955	symmetric stretching Mo–O symmetric stretching		
-	1055	1057	1057	Mo-N stretching		
-	-	1405	1409	N–H bending		

oxygen mobility and altered redox properties for the selective oxidation of propene.  $^{\scriptscriptstyle [35,36]}$ 

With respect to the IR spectrum of  $(Mo,V)_5O_{14}$ , an additional band at 1055 cm<sup>-1</sup> appeared in the spectrum of all oxide nitrides. This band could be assigned to the stretching mode of Mo–N bonds.<sup>[37]</sup> Detecting a Mo–N stretching mode indicated the incorporation of nitrogen atoms in the anion lattice of  $(Mo,V)_5O_{14}$ . Additionally, oxide nitrides with 1.3 and 1.5 wt% nitrogen showed a N–H bending mode at 1405 cm<sup>-1</sup>.<sup>[14]</sup> N–H stretching modes at higher wavenumbers were not detectable in the used setup. Hence, intensified treatment of  $(Mo,V)_5O_{14}$  with ammonia resulted in the formation of incorporated  $(NH)^{2-}$ .

## Compensation of additional negative charge

Substitution of oxygen ions O<sup>2-</sup> by nitrogen ions N<sup>3-</sup> in the anion lattice of  $(Mo,V)_5O_{14}$  leads to an additional negative charge, which must be compensated. Charge compensation processes include: (i) oxidation of one type of metal center (Mo or V), (ii) additional incorporation of positive charges like H<sup>+</sup>, for example, in the form of  $(NH)^{2-}$ , or (iii) generation of anion vacancies, for example:<sup>[38]</sup>

$$2NH_3 + 3O_0^{\chi} = 2N_0 + V_0^{\cdot} + 3H_2O$$
(3)

X-ray absorption near edge spectroscopy (XANES) was used to determine the oxidation state of the Mo and V metal centers. Analyzing characteristic maxima in the Mo XANES spectra revealed the average valence of molybdenum metal centers.<sup>[9]</sup> Various molybdenum oxides were used as references for a correlation between average valence and energy of the Mo Kedge (Figure 6). Analysis of Mo XANES spectra revealed an average molybdenum valence of 5.66 for the oxide and 5.61 for the oxide nitride with 1.0 and 1.5 wt % nitrogen.

A refinement of three Gaussian functions and an arctangent function to simulate the absorption edge jump resulted in a good agreement with V XANES spectra.<sup>[39]</sup> The centroid of the arctangent function represented the position of the ab-

sorption edge. Fitting XANES spectra of a set of vanadium oxide references ( $V_2O_3$ ,  $V_6O_{13}$ , and  $V_7O_{13}$ ) yielded a linear correlation between adsorption edge energy and average vanadium valance. Applying this fitting method resulted in an average vanadium valence of 4.50 for the oxide and 4.40 for the oxide nitrides.

In summary, oxidation of Mo or V metal centers for charge compensation could be excluded by XAS measurements. An additional incorporation of positive charge by H<sup>+</sup> was only detectable for samples with 1.3 and 1.5 wt% nitrogen. Elemental analysis of oxide nitrides confirmed the absence of hydrogen at 1.0 wt% nitrogen. It might be possible that formation of  $(NH)^{2-}$  is a parallel process by intensified treatment of  $(Mo,V)_5O_{14}$ . Apparently, at low nitrogen contents the additional negative charge was compensated by the formation of oxygen vacancies.

www.chemcatchem.org





**Figure 6.** Determination of average valences of molybdenum and vanadium. The calibration was performed by a set of references of each element (squares).

#### **Electronic properties**

Substitution of anions associated with the formation of oxygen vacancies should strongly influence the electronic properties of the oxide nitrides. Electrical properties were measured by impedance spectroscopy. Nyquist plots (negative imaginary part of impedance Z'' vs. real part of impedance Z'' are shown in Figure 7. The spectrum of each sample consisted of slightly



Figure 7. Nyquist presentation of impedance measurements of  $(Mo,V)_5O_{14}$  and its corresponding oxide nitrides with different nitrogen contents at 298 K.

depressed semicircles. The ohmic resistances were determined by refining a calculated equivalent circuit to the experimental spectra. A parallel connection of an ohmic resistor *R* and a constant phase element (*CPE*) was used as equivalent circuit.<sup>[40]</sup> Using a *CPE* described the deformed semicircles in the experimental data and represents a widely used empirical model. The refinement resulted in an increased conductivity with higher nitrogen contents. Bulk conductivities exhibited an exponential dependence on nitrogen content. The increase of electrical conductivity with higher substitution degree might be due to the formation of oxygen vacancies.<sup>[41]</sup> Formation of oxygen vacancies can also influence the mobility of lattice oxygen.<sup>[42,43]</sup>

Conductivities of  $(Mo,V)_5O_{14}$  and oxide nitrides with different nitrogen contents as a function of temperature are shown in





**Figure 8.** Evolution of conductivity during thermal treatment (330–650 K) of  $(Mo,V)_5O_{14}$  and its corresponding oxide nitrides with different nitrogen contents in air and ion current m/Z 28 (nitrogen, green line).

(Figure 8). All samples exhibited a semiconducting behavior corresponding to an increasing conductivity with temperature. In contrast to (Mo,V)<sub>5</sub>O<sub>14</sub> the conductivities of all oxide nitrides decreased slightly in a temperature range of 550 to 620 K. Analyzing the evolved gas phase by mass spectrometer revealed a release of nitrogen (m/e 28) in the same temperature range. After release of nitrogen the conductivities increased again. Elemental analysis of treated samples revealed complete removal of nitrogen. Comparable studies on MoO<sub>3</sub>-type oxide nitrides showed that conductivities after nitrogen removal were the same as that for  $\alpha$ -MoO<sub>3</sub>.<sup>[13]</sup> Conversely, conductivities of Mo<sub>5</sub>O<sub>14</sub>-type oxide nitrides exhibited a dependence on nitrogen content above 620 K. Apparently, structural defects caused by anion substitution in (Mo,V)<sub>5</sub>O<sub>14</sub> were preserved after nitrogen removal in the temperature range of selective propene oxidation.

From an Arrhenius-type presentation of conductivities of all samples up to 500 K activation energies for extrinsic conduction were calculated (Figure 9). Owing to nitrogen removal from 550 to 620 K and phase transformation above 673 K in air no reliable activation energies could be obtained at higher temperatures. The activation energies for extrinsic conduction decreased with higher degree of substitution from 0.44 to 0.35 eV. The decreasing activation energies corroborated the



**Figure 9.** Arrhenius type presentation of conductivities (330–500 K) of  $(Mo,V)_5O_{14}$  and its corresponding oxides nitrides. Activation energies of extrinsic conduction process are indicated.

formation of structural defects. Apparently, the formation of oxygen vacancies led to changes in band structure. Consequently, electron transition from valence band to conduction band was facilitated.

## Reducibility

According to the redox mechanism for the selective oxidation of propene, the availability of lattice oxygen plays an important role. Temperature-programmed reduction experiments (TPR) are commonly used to elucidate the availability of lattice oxygen of catalysts in selective oxidation reactions.<sup>[44,45]</sup> Here, reducibility of (Mo,V)5O14 and the corresponding oxide nitrides was investigated by using in situ XAS during TPR in 5% propene in helium up to 763 K. The reduction of (Mo,V)<sub>5</sub>O<sub>14</sub> proceeded in a one-step reaction to MoO<sub>2</sub> without any detectable intermediate phases.<sup>[10]</sup> The measured XANES spectra were fitted with a linear combination (LC) of (Mo,V)<sub>5</sub>O<sub>14</sub> and MoO<sub>2</sub> reference spectra to determine the phase composition during TPR (Figure 10). Results of LC XANES fits revealed a strong dependence of the onset of reduction on nitrogen content. The onset temperature was lowered from 700 to 650 K by incorporation of nitrogen. With regard to the similar long-range structure and crystallinity, the improved reducibility of the oxide nitrides can be attributed to an increased availability of lattice oxygen. This increased oxygen availability correlated with an increased density of oxygen vacancies. A linear correlation could be established between temperature of extent of reduc-



**Figure 10.** Top: Evolution of phase composition during TPR in 5 % propene up to 763 K of (Mo,V)<sub>5</sub>O<sub>14</sub> and its oxide nitrides with 1.0 and 1.5 wt % N. Bottom: Conductivities of impedance measurements as a function of temperatures at a conversion degree  $\alpha = 0.5$  during TPR indicated a correlation between conductivity and oxygen availability.

tion  $\alpha = 0.5$  (phase ratio Mo<sub>5</sub>O<sub>14</sub>/MoO<sub>2</sub>=1) and conductivity. This relation corroborated that the increasing conductivity was associated with increasing oxygen availability.

## Catalytic behavior in selective propene oxidation

Reaction rates for propene conversion and acrolein formation at different temperatures are shown in Figure 11. Only the



Figure 11. Reaction rates for propene conversion (bottom) and acrolein formation (top) based on the catalyst's initial weight at 648, 673, and 698 K in 5% propene and 5% oxygen.

rates of the sample with the highest nitrogen content were slightly increased at 698 K. Propene conversion and acrolein formation exhibited a similar evolution after nitrogen substitution. Selectivities towards acrolein were determined for each sample at different temperatures and similar propene conversions as well as similar time on stream (Figure 12). The selectivities towards acrolein increased with higher nitrogen contents of the samples at every temperature while the fraction of total oxidation products  $CO_x$  decreased. The increase of selectivity for the oxide nitride with 1.0 wt% nitrogen was independent of temperature. Selectivities of oxide nitrides with 1.3 and 1.5 wt% nitrogen were dependent on temperature. The change of selectivity with increasing nitrogen content was more distinct at low temperatures. At 698 K the increase of selectivity could be described by a linear regression over the



Figure 12. Dependency of selectivity towards acrolein on nitrogen contents at 648 K, 673 K and 698 K in 5% propene and 5% oxygen.

ChemCatChem **2016**, 8, 758–766



whole range of nitrogen contents. FTIR measurements indicated the formation of N–H bonds in the samples with 1.3 and 1.5 wt% nitrogen. Hence, the formation of N–H groups might cause an additional effect on selectivity. An elemental analysis of samples treated at 698 K yielded the remaining nitrogen content of the samples (0.25 wt%). The dependence of selectivities of oxide nitrides with 1.3 and 1.5 wt% nitrogen on temperature might result from the partial removal of nitrogen. XRD analysis of these samples showed that the  $Mo_5O_{14}$  structure was preserved during catalytic treatment. This was corroborated by in situ XRD and XAS experiments.

### Correlation of conductivity and selectivity

Characterization of  $(Mo,V)_5O_{14}$  and the corresponding oxide nitrides revealed a significant correlation between conductivity, selectivity, and the nitrogen content in the samples. The plot in Figure 13 shows the selectivity towards acrolein and  $CO_x$  as



**Figure 13.** Selectivity towards acrolein and  $CO_x$  as a function of conductivities indicating the oxygen availability at 648 K.

a function of conductivity at 648 K. Selectivity towards acrolein increased linearly with increasing conductivity. As discussed above conductivity represented a measure of mobility of lattice oxygen. Consequently, increasing oxygen mobility led to an increased selectivity towards acrolein and a decreased formation of  $CO_x$ . According to the redox mechanism nucleophilic lattice oxygen of the bulk is inserted in the adsorbed allylic species to form acrolein. Conversely, electrophilic species are more likely to form total oxidation products.<sup>[46]</sup> According to Grasselli the resulting anion vacancy migrates to another site and is replaced by adjacent lattice oxygen.<sup>[6]</sup> Gaseous oxygen is adsorbed at another site on the surface and replenishes the anion vacancies.<sup>[47]</sup>

$$O_{2,ads} + e^{-} \rightleftharpoons O_{2}^{-} + e^{-} \rightleftharpoons O_{2}^{2-} \rightleftharpoons 2O^{-} + 2e^{-} \rightleftharpoons 2O^{2-}$$
(4)

The required electrons are transported in the bulk sample. Investigations of conductivities of the samples revealed an increased electron transport in the bulk sample and electrons might be readily available to form nucleophilic lattice oxygen  $O^{2^{-}}$ .

Several examples from the literature show that supported and highly dispersed transition metal oxides species are also active in selective propene oxidation.[48,49] Hence, migration of anion vacancy in the bulk may not be mandatory for catalytic activity. However, the reoxidation of supported catalysts is also associated with a transfer of electrons to adsorbed oxygen species on M-O-M units. Isolated monomeric species on support material showed very low catalytic activity owing to the missing transfer of electrons.<sup>[50]</sup> However, the role of electron transport is difficult to access because conductivity represents a bulk characteristic. Consequently, the influence of conductivity can best be investigated by using bulk model systems. Here, the correlation between oxygen mobility and selectivity towards acrolein could be demonstrated for the first time without changing the crystal structure of the catalyst or addition of promoting cations.

## Conclusions

Oxygen ions of  $(Mo,V)_5O_{14}$  were substituted by nitrogen ions through ammonolysis to prepare mixed molybdenum oxide nitride. Compared to previous studies on  $MoO_3$ -type oxide nitrides this approach could be successfully applied to a more relevant system for studies in the selective oxidation of propene. In addition, the stability of oxide nitrides was enhanced. Investigations on the ammonolysis of  $(Mo,V)_5O_{14}$  resulted in oxide nitrides with a preserved crystal structure and an invariant cation composition. However, modification of the anion lattice led to a significantly varied conductivity and reducibility.

The formation of oxygen vacancies compensated the additional negative charge of nitrogen ions compared to that of oxygen ions. Samples with higher nitrogen content showed an additional formation of (NH)<sup>2–</sup>. Ammonolysis led to a weakening of metal–oxygen bond strength as well as increased bulk conductivity. Moreover, the resulting enhanced conductivity correlated with an increased selectivity towards acrolein in selective oxidation of propene. Apparently, Mo<sub>5</sub>O<sub>14</sub> oxide nitrides represent a suitable model system for studying correlations between conductivity, oxygen availability, and catalytic performance.

## **Experimental Section**

#### **Catalyst preparation**

The  $(Mo,V)_5O_{14}$  precursor was prepared as described elsewhere.<sup>[10]</sup> An aqueous solution of vanadyl oxalate was obtained by adding oxalic acid (180 mg) to a suspension of V<sub>2</sub>O<sub>5</sub> (109.2 mg) in bidestilled water (50 mL) at 353 K. The resulting blue solution was mixed with a solution of ammonia heptamolybdate (AHM, 3 g) in bidestilled water (20 mL). After stirring the solution for 1 h at 353 K the MoV oxide precursor was crystallized at 338 K. The MoV oxide precursor was treated in helium at 773 K for 4 h followed by dissolution of impurities in 1 m ammonia solution. Finally, the  $(Mo,V)_5O_{14}$ model catalyst was obtained by an additional treatment in helium at 773 K for 4 h. The metal content in the  $(Mo,V)_5O_{14}$  phase was 93 mol% Mo and 7 mol% V.



According to previous work, a furnace with a silica tube and a direct gas supply was used to produce the corresponding oxide nitrides.<sup>[13]</sup> Preparation conditions (temperature and ammonia flow rate) were varied to preserve the  $Mo_sO_{14}$  structure and optimize the incorporation of nitrogen. Gas flows were adjusted by mass flow controllers (Bronkhorst). Ammonolysis was performed in a temperature range from 498 K to 573 K and the ammonia gas flow was varied between 5 and 20 Lh<sup>-1</sup>.

#### **Characterization methods**

XRD patterns were recorded on an X'Pert PRO MPD diffractometer (Panalytical) in  $\theta$ – $\theta$  geometry using Cu<sub>Ka</sub> radiation and a solid-state multichannel PIXcel detector. Measurements were performed in reflection mode in a range of 5 to 80° 2 $\theta$  in steps of 0.013° 2 $\theta$  with a silicon sample holder. Rietveld refinements were performed by using the FullPROF program.<sup>[17]</sup>

A Magna System 750 (Nicolet) was used to measure IR spectra of the samples in a wavenumber range of  $400-4000 \text{ cm}^{-1}$ . Samples were diluted with CsI (1:300) pressed into pellets of 13 mm in diameter.

Elemental contents of C, H, and N were determined by using an analyzer (FlashEA 1112 NC, ThermoFinnigan/ThermoElectron) with CHNS-O configuration. Measurements were performed to determine nitrogen contents after ammonolysis of  $(Mo,V)_5O_{14}$ .

Impedance spectra of mixed molybdenum oxides and oxide nitrides were obtained by measuring the magnitude |Z| and the phase  $\phi$  of an alternating current as a response of an applied alternating potential (impedance analyzer N4L: IAI + PSM1735). The real part Z' and the imaginary part Z'' of the impedance were calculated from these results. The impedance was measured as a function of frequency (1 Hz–10 MHz) and temperature. Oxides and oxide nitride samples were pressed to pellets with a diameter of 5 mm (initial weight 50 mg, 750 MPa pressure) and placed between two Au disc electrodes for impedance measurements.

Transmission XAS experiments were conducted at Mo K-edge (20.0 keV) and V K-edge (5.465 keV) at beamline X1 and C at the Hamburg Synchrotron Radiation Laboratory, HASYLAB, respectively. For ex situ measurements samples were diluted with wax (Hoechst wax C micropowder, Merck) and pressed into self-supporting pellets with a diameter of 13 mm. Boron nitride (hexagonal, Alfa Aesar, 99.5%) was used as diluent for in situ measurements using self-supporting pellets with a diameter of 5 mm. Sample masses were calculated to result in an edge jump around  $\Delta \mu(d) = 1.5$  at the Mo K edge and  $\Delta \mu(d) = 0.3$  at the V K edge.

In situ XAS experiments were performed in transmission mode in a flow reactor at atmospheric pressure with 5 % propene in helium (~30 mLmin<sup>-1</sup>).<sup>[18]</sup> TPR experiments were performed in a temperature range from 298 to 763 K. The gas-phase composition at the cell outlet was continuously monitored by using a mass spectrometer (Omnistar, Pfeifer).

Data analysis was performed by using the software package WinXAS v3.2.<sup>[19]</sup> Background subtraction and normalization were performed by fitting a linear polynomial and a third-degree polynomial to the pre-edge and post-edge region of an absorption spectrum, respectively. The EXAFS  $\chi(k)$  was extracted by using cubic splines to obtain a smooth atomic background  $\mu_o(k)$ . The *FT*( $\chi(k)\cdot k^3$ ), often referred to a pseudo radial distribution function, was calculated by Fourier transforming the  $k^3$ -weighted experimental  $\chi(k)$  function, multiplied by a Bessel window, in the *R* space.

#### **Catalytic activity**

Catalytic activities were measured in a conventional fixed-bed reactor connected to an online gas chromatography system (CP-3800, Varian). The fixed-bed reactor consisted of a  $SiO_2$  tube (length 30 cm, inner diameter 9 mm) placed vertically in a tube furnace. The sample was placed on a P3 frit in the center of the isothermal zone. The catalyst bed in the reactor was approximately 2 cm in height. To achieve a constant volume in the reactor and to quench thermal effects, catalyst samples (about 50 mg) were diluted with boron nitride (hexagonal, Alfa Aesar, 99.5%) to result in an overall sample mass of 250 mg. To ensure differential reaction conditions, the reactor was operated at propene conversion levels below 10%.

Hydrocarbons and oxygenated reaction products (acetic aldehyde, propionic aldehyde, acetone, acrolein, isopropyl alcohol, n-propanol, allyl alcohol, acetic acid, propanoic acid, acrylic acid, acrylonitrile, acetonitrile, propanenitrile) were by analyzed using a Carbowax 52CB capillary column, connected to an Al<sub>2</sub>O<sub>3</sub>/MAPD capillary column, and a fused silica restriction (25 m·0.32 mm). Each column was connected to a flame ionization detector. Permanent gases (O2, N2, CO2, CO) were separated and analyzed using a Varian CP-3800 permanent gas analyzer connected to a thermal conductivity detector. Reactant gas flow rates of oxygen, propene, and helium were adjusted through separate mass flow controllers (Bronkhorst) to a total flow of 40 mLmin<sup>-1</sup>. A mixture of 5% propene and 5% oxygen in helium was used for catalytic tests in the temperature range of 648-698 K. Additionally, a mass spectrometer (Omnistar, Pfeiffer) was connected to continuously monitor reactant and product gas composition. The experimental error of the given reaction rates was estimated from the relative errors of reactant gas flow rates and catalyst sample masses.

## Acknowledgements

The Hamburg Synchrotron Radiation Laboratory, HASYLAB, is acknowledged for providing beamtime for this work. We are grateful to Dr. J. Scholz, A. Müller, Dr. R. Zubrzycki, and G. Koch for contributing to the characterization of the materials. We also acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG).

**Keywords:** conducting materials • molybdenum • nitrides • oxidation • structure–activity relationships

- [1] B. Grzybowska-Świerkosz, Top. Catal. 2000, 11/12, 23-42.
- [2] J. Haber, E. Lalik, Catal. Today 1997, 33, 119-137.
- [3] R. K. Grasselli, Catal. Today 1999, 49, 141-153.
- [4] P. Mars, D. W. van Krevelen, Chem. Eng. Sci. 1954, 3, 41-59.
- [5] G. W. Keulks, L. D. Krenzke, T. M. Notermann, Adv. Catal. 1979, 27, 183– 225.
- [6] R. K. Grasselli, Top. Catal. 2002, 21, 79-88.
- [7] A. Guerrero-Ruiz, I. Rodriguez-Ramos, P. Ferreira-Aparicio, M. Abon, J. C. Volta, *Catal. Today* **1996**, *32*, 223 – 227.
- [8] T. Ressler, J. Wienold, R. E. Jentoft, F. Girgsdies, Eur. J. Inorg. Chem. 2003, 301–312.
- [9] T. Ressler, J. Catal. 2002, 210, 67-83.
- [10] E. Rödel, O. Timpe, A. Trunschke, G. Zenkovets, G. Kryukova, R. Schlögl, T. Ressler, *Catal. Today* 2007, *126*, 112–118.
- [11] M. O. Guerrero-Pérez, M. A. Bañares, Catal. Today 2009, 142, 245-251.
- [12] X. Li, J. Zhao, W. Ji, Z. Zhang, Y. Chen, C. Au, S. Han, H. Hibst, J. Catal. 2006, 237, 58–66.
   [12] C. L. Li, Z. Li, J. Zhao, W. Ji, Z. Zhang, Y. Chen, C. Au, S. Han, H. Hibst, J. Catal. 2006, 237, 58–66.
- [13] S. Kühn, P. Schmidt-Zhang, A. H. P. Hahn, M. Huber, M. Lerch, T. Ressler, Chem. Cent. J. 2011, 5, 42.



- [14] X.-J. Wang, R. Nesper, C. Villevieille, P. Novák, *Adv. Energy Mater.* 2013, *3*, 606–614.
- [15] S. Knobl, J. Catal. 2003, 215, 177–187.
- [16] R. Schlögl, A. Knop-Gericke, M. Hävecker, U. Wild, D. Frickel, T. Ressler, R. E. Jentoft, J. Wienold, G. Mestl, A. Blume, O. Timpe, Y. Uchida, *Top. Catal.* 2001, *15*, 219–228.
- [17] J. Rodriguez-Carvajal, Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr 1990, 127.
- [18] T. Ressler, Anal. Bioanal. Chem. 2003, 376, 584-593.
- [19] T. Ressler, J. Synchrotron Radiat. 1998, 5, 118-122.
- [20] F. Portemer, M. Sundberg, L. Kihlborg, M. Figlarz, J. Solid State Chem. 1993, 103, 403-414.
- [21] N. V. Troitskaya, Z. G. Pinsker, Kristallografiya 1959, 4, 33.
- [22] L. W. Finger, D. E. Cox, A. P. Jephcoat, J. Appl. Crystallogr. 1994, 27, 892– 900.
- [23] M. A. G. Aranda, E. R. Losilla, A. Cabeza, S. Bruque, J. Appl. Crystallogr. 1998, 31, 16–21.
- [24] A. G. de La Torre, S. Bruque, M. A. G. Aranda, J. Appl. Crystallogr. 2001, 34, 196–202.
- [25] G. Sierra Gallego, N. Marín Alzate, O. Arnache, J. Alloys Compd. 2013, 549, 163–169.
- [26] D. Logvinovich, R. Aguiar, R. Robert, M. Trottmann, S. Ebbinghaus, A. Reller, A. Weidenkaff, J. Solid State Chem. 2007, 180, 2649-2654.
- [27] G. Williamson, W. Hall, Acta Metall. 1953, 1, 22-31.
- [28] N. Gonçalves, J. Carvalho, Z. Lima, J. Sasaki, Mater. Lett. 2012, 72, 36– 38.
- [29] K. Venkateswarlu, A. Chandra Bose, N. Rameshbabu, Phys. B 2010, 405, 4256–4261.
- [30] T. Y. Kardash, D. I. Kochubei, L. M. Plyasova, V. M. Bondareva, J. Struct. Chem. 2008, 49, 116–123.
- [31] E. Rödel, Dissertation, TU Berlin, Berlin, 2006.

- [32] F. Cariati, J. Bart, A. Sgamellotti, Inorg. Chim. Acta 1981, 48, 97-103.
- [33] S. Ishikawa, T. Murayama, S. Ohmura, M. Sadakane, W. Ueda, Chem. Mater. 2013, 25, 2211-2219.

**CHEMCATCHEM** 

**Full Papers** 

- [34] P. Botella, J. Catal. 2002, 209, 445-455.
- [35] D. Martin, D. Duprez, J. Phys. Chem. 1996, 100, 9429-9438.
- [36] R. B. Watson, U. S. Ozkan, J. Mol. Catal. A 2003, 194, 115-135.
- [37] X. Wang, L. Andrews, R. Lindh, V. Veryazov, B. O. Roos, J. Phys. Chem. A 2008, 112, 8030–8037.
- [38] S. G. Ebbinghaus, H.-P. Abicht, R. Dronskowski, T. Müller, A. Reller, A. Weidenkaff, Prog. Solid State Chem. 2009, 37, 173–205.
- [39] D. Haskel, Z. Islam, J. Lang, C. Kmety, G. Srajer, K. Pokhodnya, A. Epstein, J. Miller, *Phys. Rev. B* 2004, *70*, 054422.
- [40] M. Shoar Abouzari, F. Berkemeier, G. Schmitz, D. Wilmer, Solid State lonics 2009, 180, 922–927.
- [41] A. Pantazidis, A. Auroux, J.-M. Herrmann, C. Mirodatos, *Catal. Today* 1996, 32, 81–88.
- [42] B. Grzybowska-Świerkosz, Top. Catal. 2002, 21, 35–46.
- [43] L. Y. Margolis, A. A. Firsova, Int. Rev. Phys. Chem. 1989, 8, 1-20.
- [44] T. Franzke, F. Rosowski, M. Muhler, Chem. Ing. Tech. 2011, 83, 1705– 1710.
- [45] L. F. Liotta, M. Ousmane, G. Di Carlo, G. Pantaleo, G. Deganello, G. Marcì, L. Retailleau, A. Giroir-Fendler, *Appl. Catal. A* 2008, 347, 81–88.
- [46] J. Haber, W. Turek, J. Catal. 2000, 190, 320-326.
- [47] E. Bordes, C. R. Acad. Sci. Ser. Ilc 2000, 3, 725-733.
- [48] R. Zubrzycki, J. D. Epping, T. Ressler, ChemCatChem 2015, 7, 1112-1121.
- [49] A. N. Desikan, W. M. Zhang, S. T. Oyama, J. Catal. 1995, 157, 740-748.
- [50] J. Scholz, A. Walter, T. Ressler, J. Catal. 2014, 309, 105-114.

Received: October 1, 2015 Published online on January 15, 2016