

# Stability and reactivity patterns of medium-sized vanadium oxide cluster cations $V_xO_y^+$ ( $4 \leq x \leq 14$ )

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Gas-phase vanadium oxide clusters  $V_xO_y^+$  in the size range  $4 \leq x \leq 14$  have been produced *via* laser vaporisation in a continuous flow of He/O<sub>2</sub> carrier gas. The cluster distributions were subsequently characterised by their scattering behaviour at low-density gas targets ( $10^{-4} - 2 \times 10^{-3}$  mbar). The experimental scattering cross sections were used to study differences in the interactions with rare gases, hydrocarbons (alkanes: methane, propane, n-butane and alkenes: ethene, propene, but-1-ene) and also small inorganic molecules (N<sub>2</sub>, O<sub>2</sub>, CO, NO, SO<sub>2</sub>). The compositions of the dominant oxide clusters reveal the predominance of vanadium atoms in the formal oxidation states +4 and +5. The interaction patterns of these oxide clusters with rare gases show no indications for fragmentation at collision energies corresponding to a cluster beam velocity of 900 ms<sup>-1</sup>. Clusters with a composition of  $(V_2O_5)_n^+$  have increased cross sections for the interaction with alkanes and alkenes. Indeed, for the alkenes stable adducts have been detected under the applied scattering conditions. The increased cross sections have been interpreted in terms of a strong reactivity towards hydrocarbons, which is in agreement with previous results on smaller vanadium oxide clusters (R. C. Bell, K. A. Zemski, K. P. Kerns, H. T. Deng and A. W. Castleman, Jr., *J. Phys. Chem. A*, 1998, **102**, 1733).

## Introduction

Vanadium oxides are widely used as components of technical oxidation catalysts. One of the most important processes involving vanadium(v) oxide is the catalytic oxidation of sulfur dioxide to the trioxide in the contact process for industrial sulfuric acid production. The oxidation of aromatic hydrocarbons on vanadium oxide catalysts yields the key chemicals maleic or phthalic anhydride. Interestingly, with mixed vanadium–phosphorus oxides (VPO) it is also possible to oxidise rather inert saturated hydrocarbons *e.g.* n-butane or propane to maleic anhydride or acrylic acid, respectively.<sup>1</sup>

Based on the technical interests in understanding and controlling the mechanisms of these oxidation reactions numerous experimental investigations on the reactivity of isolated gas phase vanadium oxides have been carried out. Previously, the oxidation properties of VO<sub>2</sub><sup>+</sup> towards hydrocarbons<sup>2</sup> as well as the reactions of V<sub>x</sub>O<sub>y</sub><sup>+</sup> ( $x \leq 4$ ) and VO<sup>+</sup> with methyl methacrylates<sup>3,4</sup> have been intensively studied using FT- ion cyclotron resonance (ICR) mass spectrometry. Neutral vanadium oxide clusters containing up to about 40 vanadium atoms have been produced first by Riley and co-workers *via* the reaction of pre-formed metal clusters with molecular oxygen in a flow-tube reactor.<sup>5</sup> The analysis of the corresponding cationic oxide distributions generated by multi-photon laser ionisation yields an average ratio of oxygen to vanadium of between 1.4 and 1.5. This would imply the preferential appearance of the vanadium in a +3 oxidation state in the V<sub>x</sub>O<sub>y</sub><sup>+</sup> clusters. The cations are thought to be formed *via* cluster heating by multi-photon absorption and following thermionic emission of an electron as well as simultaneous loss of oxygen and

hence, the primary neutral oxide clusters are assumed to contain significantly more oxygen than the detected cations.

Castleman and co-workers have done extensive research on small polynuclear vanadium oxide clusters resulting in a rather good understanding of the stability and reactivity of cationic<sup>6–10</sup> and anionic<sup>11</sup> vanadium oxide clusters containing up to 7 vanadium atoms. The most dominant cationic oxides is described in terms of the formula  $(VO_2)_m(V_2O_5)_n(O_2)_o^+$ . The formula reveals that (i) the preferred oxide clusters contain vanadium in the +4 or +5 oxidation states and (ii) extra molecular oxygen can be bound to these oxide clusters. According to Castleman's results, the weakly bound molecular oxygen can be released as a result of collision-induced dissociation (CID), photofragmentation or “ligand exchange” due to a reaction with hydrocarbons. The CID experiments show that at least two different species of extra oxygen are present. Oxide clusters with molecularly adsorbed di-oxygen lose these molecules near thermal energies, while other clusters, in particular the anionic oxides, lose atomic oxygen at collision energies below 2 eV. Unfortunately, quantitative bond dissociation thresholds have not yet been measured. On the other hand, for the mononuclear species VO<sup>+</sup>, VO<sub>2</sub><sup>+</sup> and VO<sub>3</sub><sup>+</sup> the energy dependence of the cross sections for CID have been measured very recently also by the Castleman group,<sup>11</sup> but it is questionable to apply the resulting dissociation energies to larger oxide clusters.

In order to study the size-dependent reactivity of the vanadium oxide clusters we applied a scattering technique to investigate clusters of a larger size-distribution. This work presents the results of our oxide cluster scattering experiments for cluster cations up to V<sub>14</sub>O<sub>31</sub><sup>+</sup> and an analysis of the collision induced reaction processes. It will be shown, that the cluster beam scattering technique gives an effective method of characterising clusters of a large distribution simultaneously and

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identifying clusters with special interactions towards the target molecules.

## Experimental

Details of the molecular beam machine and the laser vaporisation cluster source used in this study have been reported elsewhere.<sup>12,13</sup> Briefly, the clusters are produced by evaporating material from a vanadium rod with a focussed laser beam in a continuous flow of a 0.1% mixture of oxygen in helium as the carrier gas. The vaporisation plasma cools by interaction with the helium in a source channel 105 mm long and oxide clusters are formed. The beam expands at the end of the channel through a 2 mm nozzle. The total pressure in the source is typically 10–25 mbar. After the beam is skimmed, it passes a scattering cell, which is a stainless steel tube of 30 mm diameter and 100 mm length delimited by two plates with central bores of 3 mm diameter. The density of the gas fill is adjusted by a variable leak (Granville-Phillips, series 203) and controlled by a capacitance pressure sensor (MKS Baratron 626A,  $10^{-4}$ –1 mbar). Under working conditions, the pressure in the surrounding vacuum chamber is typically less than  $10^{-5}$  mbar. For measuring the cross sections, the pressure in the cell is tuned to  $10^{-4}$ – $2 \times 10^{-3}$  mbar and the cluster intensity variations are recorded with a perpendicularly extracting Wiley–McLaren time-of-flight mass spectrometer. The distance between the scattering cell and the entrance slit of the mass spectrometer is 200 mm. The time-of-flight mass spectra are averaged over 1000 single shots with a digital oscilloscope (LeCroy 9350 CM) and transferred to a computer for further processing.

## Results

### Vanadium oxide cluster compositions

The vanadium shows a strong affinity to oxygen, so already traces of oxygen in the “pure” carrier gas helium lead to the formation of vanadium oxide cluster cations containing one or two oxygen atoms. At an increased but still low oxygen concentration (0.1%) the oxide distribution changes completely. The smaller clusters containing up to 4 vanadium atoms are strongly depleted and analysis of the cluster compositions reveals the favoured formation of highly oxygenated clusters. The compositions of the most intense oxide clusters are plotted in Fig. 1. The slope of the compositions for clusters up to  $V_{11}O_y^+$  corresponds to the vanadium pentoxide and drops slightly for larger clusters. Assuming that oxygen adopts the  $-2$  oxidation state and the oxide clusters do not contain peroxidic or physisorbed oxygen, the average oxidation state of the vanadium atoms would be  $+5$  or slightly less.

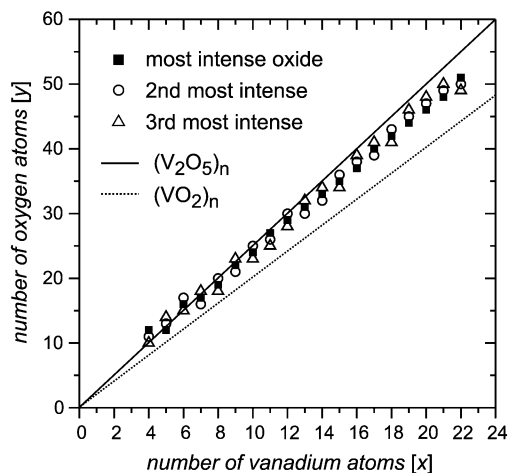
### Scattering with rare gases

The oxide clusters have been probed with respect to their fragmentation behaviour by investigating their interaction with rare gases. These measurements were carried out at room temperature (25 °C). The cluster’s translational energy is given by the molecular beam velocity of about  $900 \text{ m s}^{-1}$  and the clusters were not additionally accelerated. The beam velocity was determined by measuring the time of arrival for the cluster bunch at different positions along the molecular beam axis.

The experimental cross sections for the interaction were calculated from the depletion of cluster signal intensities at increasing target gas densities. The cross sections  $\sigma$  are defined by the exponential law:

$$I = I_0 e^{-\sigma n_B L}$$

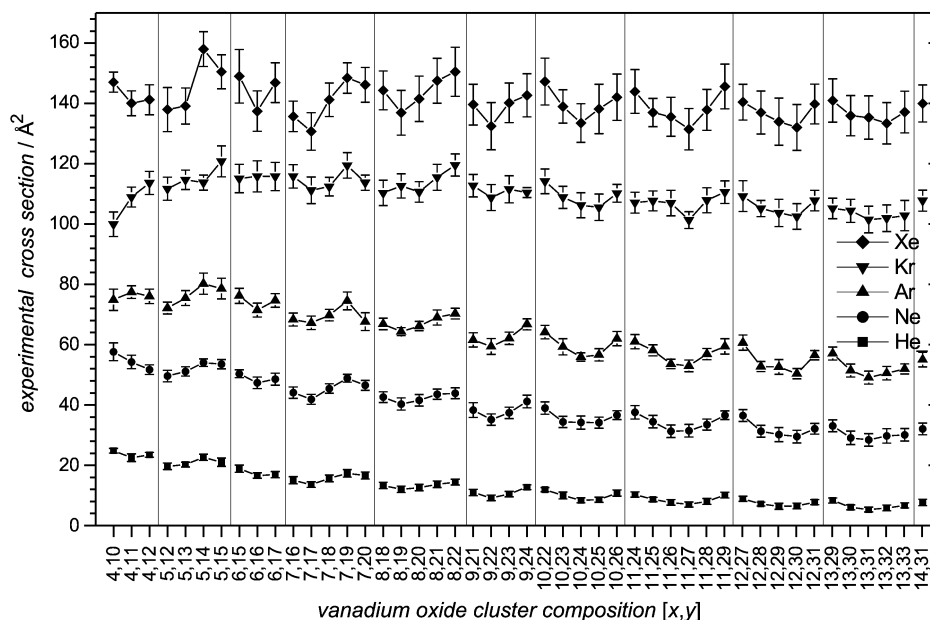
where  $I_0$  and  $I$  are the clusters’ intensities before and after



**Fig. 1** Correlation diagram for the compositions of  $V_xO_y^+$ , which are extracted from the time-of-flight mass spectra. The number of oxygen atoms  $y$  is plotted against the number of vanadium atoms  $x$  for the three most intense oxide clusters cations containing the same  $x$ . The two lines represent the compositions of the stable bulk oxides containing vanadium(v) or vanadium(iv).

depletion, respectively,  $n_B$  is the particle density of the gas target, and  $L$  is the length of the target. The plot of the cross sections for the vanadium oxides and the rare gases is shown in Fig. 2. These experimental cross sections for the rare gas interaction are clearly much smaller than theoretically expected. For instance, the hard sphere collision cross section for a spherical  $V_8O_{20}^+$  and Ar would be *ca.*  $120 \text{ \AA}^2$ , assuming the density of bulk  $V_2O_5$  for the cluster ( $3.35 \text{ g cm}^{-3}$ ,<sup>14</sup>  $r_{Ar, 273 \text{ K}} = 3.66 \text{ \AA}$ <sup>15</sup>). At a laboratory energy of 3 eV for  $V_8O_{20}^+$  ( $900 \text{ m s}^{-1}$ ) the Langevin cross section with argon ( $\alpha = 1.64 \times 10^{-24} \text{ cm}^3$ )<sup>14</sup> is of the same order of magnitude as  $160 \text{ \AA}^2$ . For clusters with 4 or 5 vanadium atoms and the rare gases, it is probable that the differences in the relative order of the cross sections (*e.g.* for  $V_4O_{10}^+$  with Ne and Ar) are not real. The intensities of these clusters are low and relatively small fluctuations during the experiments affect the values of the cross sections more strongly than those of clusters with higher intensities. For larger clusters a tendency to smaller cross sections  $\sigma$  has been observed, but using a simple hard sphere model, one should expect an increase in  $\sigma$ . This effect is counter-intuitive, but mainly caused by the experimental arrangement. Heavier clusters are generally deflected through a smaller angle than the lighter ones (“momentum transfer effect”). Then it is probable to detect these deflected clusters, because of the geometry of the entrance slit of the mass spectrometer, which is 1 mm in height, but 20 mm in width. A reduction in the size of the slit is unfavourable because that would lead to a cluster intensity decrease in the ToF-MS.

Due to the low angular resolution of the experimental setup, the measured experimental cross sections are not the exact total values and they are only suitable for comparison of the scattering behaviour of clusters with similar size and mass. Additionally, the cross sections are modulated by a cluster signal intensity effect. This is illustrated in Fig. 3, where we compare the cluster signal intensities before depletion  $I_0$  (on a logarithmic scale!) and the cross sections. Minima in the cross section curve often correspond to clusters with high intensity and *vice versa*. We assume that this modulation is mainly caused by a mass spectral signal overlap that has a stronger effect for the heavier clusters, due to a limited mass resolution. Possibly, a deviation in linearity of the ion detection system also contributes to the modulation, but on the present experimental basis, we cannot entirely exclude a real physical cause of the modulation effect. Nevertheless, the cross section patterns allow us to identify clusters with special interactions



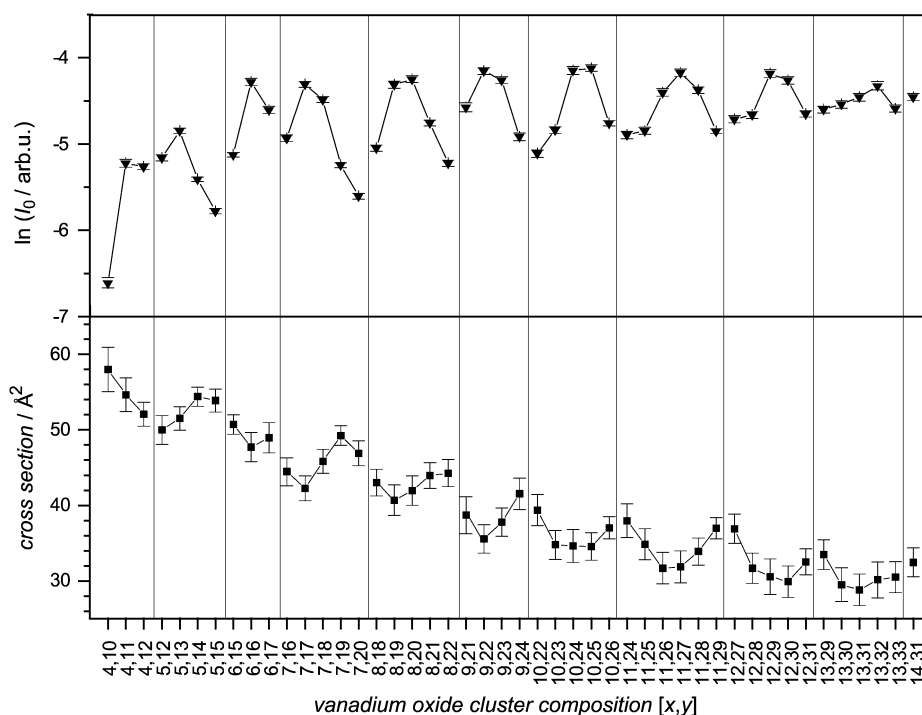
**Fig. 2** Experimental cross sections for the interaction of vanadium oxide cluster cations with rare gases. Vertical lines are used to separate clusters with different numbers of vanadium atoms. The error bars express only the standard deviation coming from the regression procedure, but in addition, the course of the cross sections is modulated by a cluster intensity effect.

*e.g.* collision induced fragmentation or other reactions (see Figs. 4 and 5).

#### Interaction with hydrocarbons

The cross sections for the interactions of  $V_xO_y^+$  with ethene are shown in Fig. 4. These data are normalised by the cross sections for argon to reduce the intensity modulation effect. In our experience, it is useful to choose argon for the normalisation procedure to almost eliminate the modulation effect. Additionally, the momentum transfer effect (discussed in the Results section) that leads to decreasing cross sections for increasing cluster size is reduced by the normalisation procedure.

The standard deviation of the experimental cross sections (before normalisation) is typically 10–20%, although there is a strong dependence of the cross sections on the cluster composition. Especially for members of the series  $(V_2O_5)_n^+$  ( $n = 3–6$ ) the cross sections are significantly increased by 20% in comparison with other oxide clusters. For the clusters  $(V_2O_5)_nVO_2^+$ ,  $n = 2$  or 3, which also contain  $V^{+v}$ , only a slight increase was observed. The cross section patterns are the same for ethene and the deuterated ethene, but the cross sections for the deuterated species are 10–30% larger. Due to the heavier mass of d4-ethene, the centre of mass energies for collisions of  $V_xO_y^+$  with d4-ethene are *ca.* 15% higher than for normal ethene. Consequently, we assume that the larger experimental



**Fig. 3** Intensity modulation effect for neon. Details of this effect affecting the course of the cross sections are discussed in the results section.

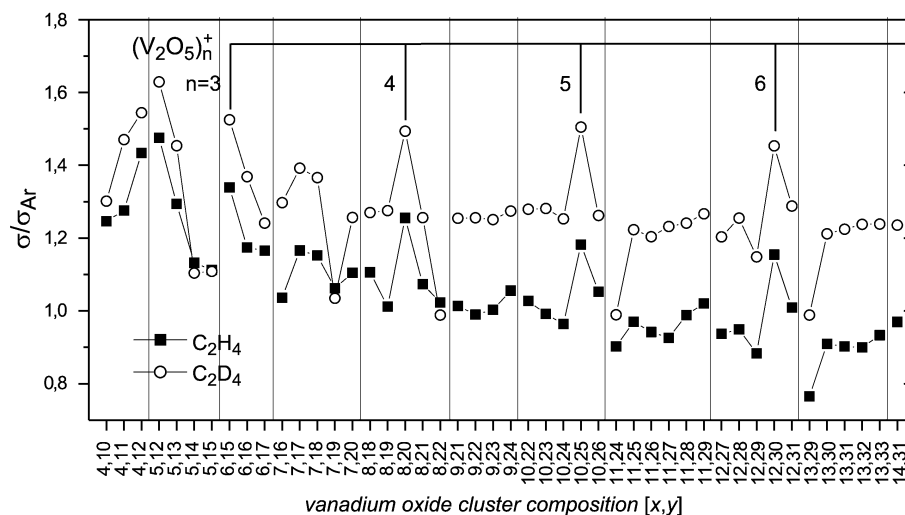


Fig. 4 Normalised experimental cross sections for the interaction of  $V_xO_y^+$  with ethene and deuterated ethene.

cross sections for d4-ethene are not caused by the geometric cross section that is expected to be nearly equal for  $C_2H_4$  and  $C_2D_4$ , but are due to the momentum transfer effect described earlier, that leads to a stronger cluster deflection for the heavier isotopomer. Additionally, mass spectral signals for cluster-ethene adducts  $(V_2O_5)_n C_2H_4^+$  ( $n = 3-6$ ) can be detected. These signals overlap partly with existing signals of pure oxide clusters. Due to this overlap and growing adduct intensities with increasing alkene pressure, the signal intensities of the pure oxide clusters seem to be depleted to a lesser extent, which leads to a decrease in the experimental cross sections. For example,  $V_{13}O_{29}^+$  (1127 u) has a lowered experimental cross section due to signal overlap with the formed adduct  $V_{12}O_{31}(C_2H_4)^+$  (1136 u).

The cross sections for the larger alkenes propene and but-1-ene (Fig. 5) exhibit similar behaviour to ethene: for  $(V_2O_5)_n^+$  ( $n = 4, 5$ , and 6) they are clearly increased. Additionally, the cross sections for propane and n-butane show the same patterns. The absolute  $\sigma$  values are similar for the alkenes and alkanes with the same number of C-atoms, but for an "active" oxide cluster  $(V_2O_5)_n^+$ ,  $\sigma$  is more increased for the alkene.

Furthermore, a remarkable feature is the decrease in cross sections for clusters  $(V_2O_5)_{n-1}(V_2O_4)^+$  having one O atom less than the active ones. This could be caused by the formation of those clusters during the oxide cluster-hydrocarbon interaction. Only methane is rather inert towards all vanadium oxide clusters, resulting in a nearly smooth line of the cross sections.

#### Inorganic gases

The vanadium oxide cluster cations have also been probed with respect to their interaction with  $N_2$ ,  $O_2$ ,  $CO$ ,  $NO$ , and  $SO_2$ . For all of these gases no special interaction patterns with vanadium oxide clusters were found. In contrast to the interactions with hydrocarbons, the cross sections show no specific deviations for a given cluster series. The absolute  $\sigma$  values are in the order,  $SO_2 \gg O_2 > NO > N_2 > CO$ , as one would expect from the size and mass of the gas molecules. Since the diameters of the diatomics are very similar, the differences in the momentum transfer have more dominant influences, e.g. a collision with an  $O_2$  molecule leads to a stronger deflection of a cluster than a collision with the lighter  $CO$ . Fig. 6 shows

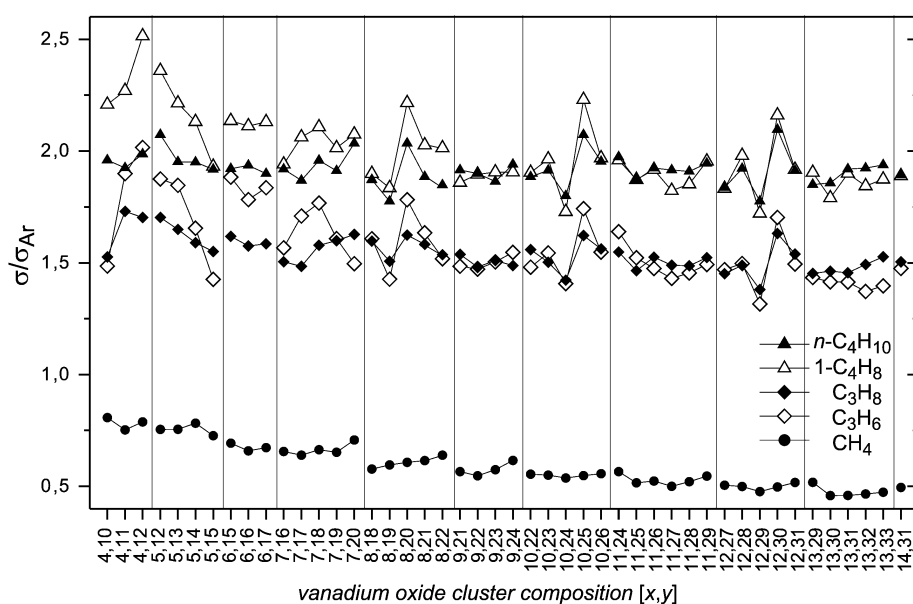


Fig. 5 Normalised experimental cross sections for the interaction of  $V_xO_y^+$  with the alkenes propene and but-1-ene and the alkanes methane, propane, and n-butane.

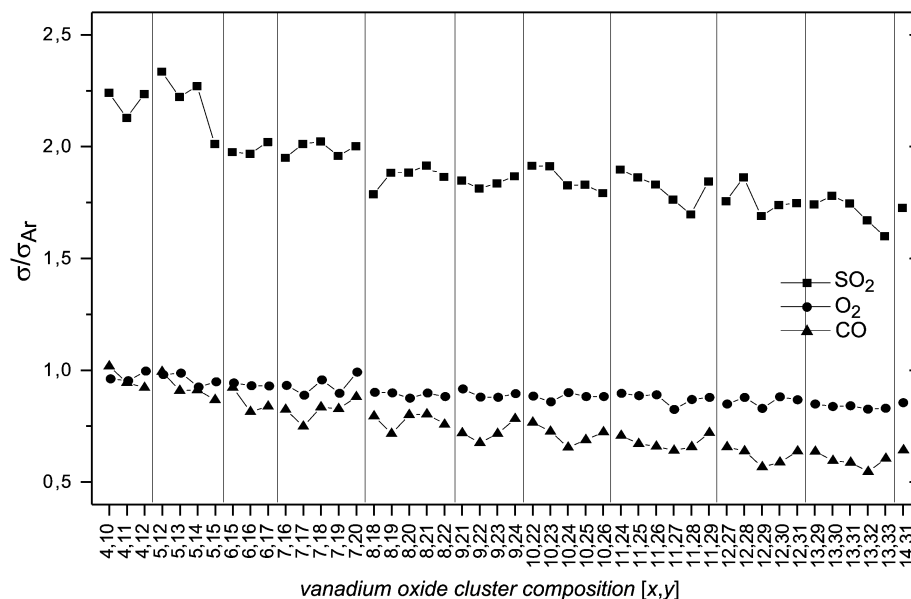


Fig. 6 Normalised experimental cross sections for the interaction of  $V_xO_y^+$  with sulfur dioxide, oxygen and carbon monoxide.

exemplary interaction patterns of  $V_xO_y^+$  and  $O_2$ , CO, and  $SO_2$ .

## Discussion

### Oxide stability vs. collision induced dissociation

The identification of the different oxide species, which are present in an oxide cluster is highly desirable, as they strongly affect the reaction behaviour of the cluster. Starting from the dominant compositions of the vanadium oxide clusters (Fig. 1) it seems to be reasonable to assume that the oxides contain mainly vanadium atoms in the +5 oxidation state. This assumption is confirmed by very recent calculations of Vyboishchikov and Sauer on neutral clusters  $(V_2O_5)_n$  (for  $n$  up to 12).<sup>16</sup> According to these calculations, the  $(V_2O_5)_n$  clusters form polyhedral cage structures, which consist of 4-fold coordinated vanadium(v) and the oxygen atoms are located in vanadyl groups or in a bridging position between the vanadyl groups. Also, in their previous calculations on small neutral and anionic vanadium oxide clusters up to  $V_4O_{11}$  Vyboishchikov and Sauer reveal the presence of a high oxidation state for vanadium rather than peroxide formation.<sup>17</sup> Peroxidic structures have only been found for clusters which would exceed a formal oxidation state of +5 for vanadium.

It should be possible to gain more evidence of the present oxide species by investigating the collision induced dissociation, as has been done by Castleman and co-workers.<sup>6,11</sup> We have recently observed for another metal oxide cluster containing weakly bound molecular oxygen  $[Bi_6O_9 \cdot O_2]^+$ , that the oxygen molecule is released under the scattering conditions, resulting in a stronger depletion of the cluster signal and finally giving an increased cross section.<sup>18</sup> By analysing the temperature dependence of the oxygen adsorption equilibrium in a flow tube reactor we were able to calculate the binding energy of the  $O_2$  as  $0.48 \pm 0.02$  eV. If some of the vanadium oxide clusters discussed here contained oxygen with similar or lower binding energy than the cluster, one should also expect increased cross sections for these cluster species. But this has not been observed.

The experimental cross section of the weakly bound adduct  $[Bi_6O_9 \cdot O_2]^+$  is 10–20% larger than the neighbouring values. For  $V_xO_y^+$  we cannot detect such deviations of the cross sections, which should be more frequent for oxygen-rich

vanadium oxide clusters. We have observed such oxygen-rich clusters, which must contain peroxidic bound oxygen, but the energy transfer of the collisions seems to be inefficient in inducing fragmentation. However, the clusters with an oxygen content up to a ratio  $O/V = 2.5$  certainly contain real vanadium(v) and not adsorbed oxygen. We believe, that these differences between our findings and the results of the previous dissociation experiments,<sup>6</sup> where an  $O_2$  loss was found near thermal energy, e.g. for  $V_4O_{10}^+$  or  $V_6O_{15}^+$ , are caused by cluster-growth and cluster-temperature effects. Under our experimental conditions the residence time in the source is quite long ( $\sim 500$   $\mu$ s), so there is no kinetic restriction of the oxidation and the clusters have the possibility of becoming thermalised and relaxed in the flow tube. In the pulsed flow cluster sources the reaction time is commonly much lower and the expansion leads to a fast freezing of the system. This stabilises cluster-adsorbate complexes, which are not necessarily the energetically favoured species.

The energy that is available to induce cluster fragmentation can be estimated by using the ‘‘impulsive collision transfer’’ (ICT) theory. This theory is used to calculate the energy uptake for vanadium oxide clusters of the composition  $(V_2O_5)_n$  in collisions with the rare gases Ar, Kr, and Xe (Fig. 7). The ICT theory was originally developed to describe collisions of large organic molecules with rare gas atoms at several hundred eV collisional energy,<sup>19,20</sup> but has already been successfully applied to cluster collisions.<sup>21–23</sup> This theory is based on the idea of describing the cluster-atom collision as an atom(of a cluster)-atom collision process. The translational energy that is transmitted during an elastic atom-atom collision leads to an inelastic process for the entire cluster. Considering the conservation of momentum, energy and angular momentum, the calculation yields the fraction of energy that is transformed from kinetic energy into internal energy of the cluster.

Corresponding to the ICT theory, the maximum energy uptake,  $Q_{\max}$ , for multiple collisions of a cluster with the mass  $m_{Cl}$  is given by:

$$Q_{\max} = \frac{m_t(m_{Cl} - m_a)}{m_t(m_{Cl} - m_a) + m_{Cl}m_a} E.$$

$E$  is the kinetic energy of the cluster ion and the target atom is considered to be at rest. This expression requires that each of the multiple collisions is between a single type of cluster atom

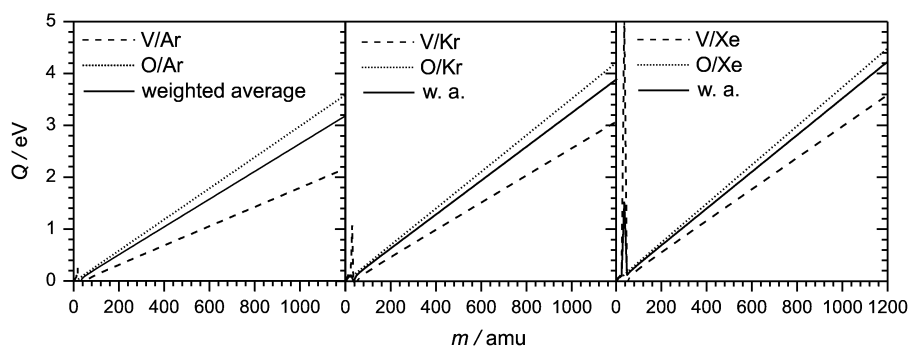


Fig. 7 Internal energy uptake at cluster–rare gas collisions assuming the ICT theory for vanadium oxide clusters with an O/V ratio of 2.5.

with mass  $m_a$  and a target atom with mass  $m_t$ . The composition of the binary cluster and the possibility of hitting either oxygen or vanadium atoms is accounted for here by calculating a weighted average of the energy uptake under the assumption that the collisions are equally distributed to the V and O atoms and the V/O ratio is 2/5.

$$Q_{\text{w.a.}} = \frac{2}{7}Q(\text{V}) + \frac{5}{7}Q(\text{O})$$

In a further development of the ICT theory a substance-specific empirical parameter  $C$  has been introduced that takes into account the binding situation in the cluster.

$$Q' = CQ_{\text{max}}$$

The known  $C$  values for the coinage metal clusters are of the order of about 0.4.<sup>23</sup>  $C$  is omitted here, since it is unknown for the  $V_xO_y$  clusters but it is assumed to be of the order of magnitude of unity. Consequently, the calculated energy uptake is only a rough estimation. The maximum energy uptake of clusters with an oxygen to vanadium ratio of 2.5 and a velocity of  $900 \text{ m s}^{-1}$  in multiple collisions with Ar, Kr or Xe is plotted in Fig. 7. The amount of transferred energy depends on the affected atom and increases almost linearly with the cluster size. The internal energy increase for the oxide clusters is maximal for collisions with the heaviest rare gas Xe. Since we do not observe indications for collision induced fragmentation, the curve for Xe gives an estimation of the lower limits of the fragmentation energies for the observed  $V_xO_y^+$  clusters as a function of cluster mass. Under the assumption that  $C = 1$  (see above), these limits, for instance for the clusters  $(V_2O_5)_n^+$  with  $n = 2, 3$ , and 4, are 1.3, 1.9, and 2.6 eV, respectively.

## Reactivity

In an ideal scattering experiment the geometric cross sections or long-range effects, especially ion–molecule interactions, would mainly influence the cross section patterns. Due to our experimental set-up, it is also possible to detect product channels of cluster ion–molecule reactions. In principle, three types of reactions are possible: (i) electron transfer from the molecule to the cluster cation, (ii) fragmentation of the cluster or (iii) formation of a cluster–molecule adduct eventually followed by a chemical reaction. These separate processes will now be discussed in more detail.

If electron transfer were the important factor for the interaction, the ionisation potentials (IPs) of the active oxide clusters should be clearly higher than those of the inactive ones. It is known that the IP depends on the oxygen content of the cluster and generally, it increases with the formal oxidation state of the vanadium.<sup>10</sup> Nevertheless, it is not to be expected that one missing or one additional oxygen atom would cause strong differences in the IPs of such large oxide clusters. The known IPs for oxygen-rich and multi-nuclear vanadium oxides are quite

high e.g.  $V_4O_{12}$  and  $V_4O_8$  have IPs of 11.8 and 13 eV.<sup>24,25</sup> From the energetic point of view, these values permit the electron abstraction from most hydrocarbons, but hydrocarbon ions or their fragments have never been observed. Hence, simple electron transfer seems to be irrelevant for the cluster–ion interaction process. Furthermore, it has been already shown for rare gases, that the collision induced fragmentation is also unimportant and cannot explain the cross section patterns.

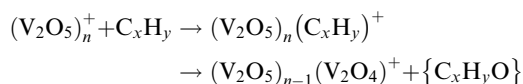
Consequently, we suppose the formation of cluster–hydrocarbon adducts to be the cause of the enhanced signal depletion for  $(V_2O_5)_n^+$ , which results in increased cross sections. We have recently reported a very similar effect for the interaction of bismuth oxide cations with alkenes.<sup>12</sup> In this system, an increased cross section of an oxide cluster is always accompanied by high reactivity, that has been derived from the reaction kinetics.

The rates of the reaction with alkenes have been measured using a flow reactor. For the vanadium oxide cluster cations  $(V_2O_5)_n^+$  and the alkenes ethene and propene stable adducts exist and their signals are abundant in the mass spectra obtained under the scattering conditions. These adducts  $(V_2O_5)_n(\text{alkene})^+$  are the only detectable products which contain hydrocarbons and no other organic fragments could be observed. Since most of the adducts will be deflected, only a small fraction reach the entrance slit of the mass spectrometer. In fact, the possibility of detecting these adducts, which are formed under the scattering conditions, indicates a very strong reactivity of the members of  $(V_2O_5)_n^+$  and at least an intermediate stability of the alkene adduct  $(V_2O_5)_n(\text{alkene})^+$ . From this observation we assume that the strong formation of the adducts is a main reaction channel for the  $(V_2O_5)_n^+$  and causes the increased cross sections. For alkanes, these adducts have apparently only an intermediate stability on our experimental time scale (*ca.* 200  $\mu\text{s}$  time-of-flight) and cannot be detected.

The reactions of smaller vanadium oxide clusters with C4 hydrocarbons (n-butane, but-1-ene and buta-1,3-diene) have been previously reported by Bell *et al.*<sup>6</sup> There, the dominant products for the clusters  $V_4O_{10}^+$  and  $V_6O_{15}^+$  [ $(V_2O_5)_n^+$  ( $n = 2$  and 3)] are the singly deoxygenated clusters  $V_4O_9^+$  and  $V_6O_{14}^+$  and less intense products are the hydrocarbon adducts  $V_4O_{10-k}(C_4H_m)^+$  and  $V_6O_{15-k}(C_4H_m)^+$  ( $k = 0-2$ ,  $m = 6, 8, 10$ ). From the mass spectrometric point of view, the hydrocarbons remain unchanged and no cracked or dehydrogenated products have been identified. It can be assumed, that the partly deoxygenated oxide clusters are products of hydrocarbon oxidation processes, while the neutral oxidation products have not been detected.

We have observed by studying the scattering behaviour, that also larger oxide clusters of the formula  $(V_2O_5)_n^+$  are active towards saturated and unsaturated hydrocarbons and that large differences exist between the reactivity of the members of this series and other oxide clusters with similar compositions. In considering the reactions of small vanadium oxide clusters, the decrease in the cross sections for reduced clusters

with stoichiometries  $(V_2O_5)_{n-1}(V_2O_4)^+$  can be understood if they are formed during the reaction of  $(V_2O_5)_n^+$  with the hydrocarbons. Those reduced clusters cannot be produced by CID at comparable impact energies. The observations can be summarised in a reaction scheme for hydrocarbon oxidation with intermediate formation of an adduct:



This mechanism is in agreement with the results of Bell *et al.*, except that we have no indication of collisional induced dissociation of the oxide clusters.

Despite the similarities of the reactivity scheme for alkanes and alkenes, the mechanisms of oxidation or oxygen transfer are expected to be different. In principle, with bulk  $V_2O_5$  both general oxidation mechanisms, either electrophilic or nucleophilic, are possible.<sup>1</sup> Strong electrophilic reactants are only the oxygen species  $O_2$ ,  $O_2^-$  and  $O^-$ , whereas the oxygen atoms in the clusters with a formal  $-2$  oxidation state are nucleophilic. Saturated alkanes are usually attacked by the nucleophilic  $O^{2-}$  and typical reactions are H-abstractions from the alkanes. This pathway complies with the oxidation of ethane at the monomeric cation  $VO_2^+$  leading to the hydrated cation  $[V_2O_2 \cdot H_2]^+$  and ethene found by Harvey *et al.*<sup>2</sup> The H-abstraction leads to unsaturated compounds which should form stable adducts with the oxide cluster, as *e.g.* the alkenes, but such adducts have not been observed for the alkanes. A second pathway similar to the first is the formation of free hydrocarbon radicals by H-abstraction, but that also could not explain the oxygen loss of the active oxide cluster. A third pathway, the insertion of O in a C–H bond resulting in an alcohol could be an alternative oxidation process. According to calculations of Broclawik *et al.*<sup>26</sup> for the reaction of a binuclear vanadium oxide cluster with methane we expect, that the formation of hydroxy and an alkoxy intermediate located at a bridging oxygen is an intermediate state of the alkane oxidation.

The alkenes can also be oxidised with electrophilic or with nucleophilic oxygen species, but the stoichiometry and the proven stability of the oxide clusters rather excludes the presence of the weaker bound electrophiles  $O_2$ ,  $O_2^-$  and  $O^-$ . Harvey *et al.* have shown that the oxidation of ethene with  $VO_2^+$  goes *via* a V–C  $\sigma$ -complex and involves a H-shift leading to the final products acetic aldehyde and  $VO^+$ .<sup>2</sup> Analogously we assume, that alkene oxidation on the vanadium oxide clusters involves an electrophilic attack by the  $V^{+v}$  and subsequent O-insertion in the V–C bond.

Taking into consideration the formal oxidation states of vanadium, the reactive clusters  $(V_2O_5)_n^+$  can be reformulated to be  $V_{2n-1}^{+v}V^{+iv}O_{5n}$ , showing the formal coexistence of vanadium in its oxidation states  $+4$  and  $+5$ . It is proposed, that pairs of associated  $V^{+v}$  and  $V^{+iv}$  atoms are the active centres in catalytic n-butane oxidation on VPO catalysts leading to maleic anhydride. For the VPO catalysts, the butane activation *via* H-abstraction has been assigned to Lewis acid  $V^{+iv}$  sites, whereas  $V^{+v}$  supplies oxygen for further oxidation of the activated hydrocarbon.<sup>27,28</sup> Despite the fact that there are no phosphorus atoms in our clusters, the high activity of the oxide clusters with the stoichiometry  $(V_2O_5)_n^+$  does conform with the assumptions on the nature of the active centres of the VPO catalyst. Possibly, already very small vanadium oxide clusters resemble the structure of these active centres.

For the diatomics  $N_2$ ,  $O_2$ , NO, CO and  $SO_2$  we have no indication for reactive interactions with the vanadium oxide cluster cations. This is not surprising for the rather unreactive  $N_2$ , but, *e.g.* for  $O_2$  in its triplet ground state, several addition reactions, especially to the V-sites, have to be taken into account (formation of peroxy or superoxy species). Similar radical addition or complex formation reactions are also known for the other reactants. A possible reason for the appar-

ent non-reactive interactions under our experimental conditions is the non-existence of channels for the disposal of the reaction energy. The lowest vibrations of the diatomics are of the order of  $1550\text{ cm}^{-1}$  ( $O_2$ ) up to  $2330\text{ cm}^{-1}$  ( $N_2$ ), whereas the vibrational frequencies of the clusters are expected to be much lower (*e.g.* around  $800$  and  $1100\text{ cm}^{-1}$  for tetrahedral  $V_4O_{10}^{14}$ ). Since, under the scattering conditions, the reactions are strictly bimolecular, the energy can only be dissipated by internal vibrational relaxation of the collision complex. A mismatch of the vibrational modes of a cluster and the attached molecule would imply an immediate decomposition of the collision complex and no further reactions can occur.

## Summary and conclusion

The stability and reactivity of vanadium oxide clusters have been investigated using their scattering behaviour to probe the interaction with rare gases, hydrocarbons and small inorganic molecules. The oxide clusters with an average O/V ratio of 2.5 are stable towards collision induced dissociation up to collision energies corresponding to a velocity of about  $900\text{ m s}^{-1}$ . This indicates the presence of strongly bound oxygen species rather than of adsorbed oxygen.

The members of the cluster series  $(V_2O_5)_n^+$  exhibit a distinct interaction with alkenes and alkanes and form intermediate cluster–hydrocarbon adducts, which indeed have been detected for the alkenes. Furthermore, there are indications of the formation of reduced clusters with stoichiometries  $(V_2O_5)_{n-1}(V_2O_4)^+$ . Using the concept of formal oxidation states, the active clusters  $(V_2O_5)_n^+$  can be described by  $V_{2n-1}^{+v}V^{+iv}O_{5n}$  and accordingly, the activity seems to be connected with the coexistence of vanadium in the different oxidation states  $+5$  and  $+4$ . It is assumed, that these  $V^{+v}V^{+iv}$  couples are also the active centres for butane activation and maleic anhydride formation on VPO catalysts.

Interestingly, we could not detect any special interaction between the vanadium oxide clusters and  $SO_2$  or other reducing agents like CO or NO. Finally, the clusters' structure and the nature of the active sites are certainly the key to the reactivity effects. The IR-REMPI technique utilising a free electron laser is capable of obtaining this structural information on metal oxide clusters.<sup>29</sup> It would be useful to study the structures of vanadium oxide clusters and their reaction products using this technique.

## Note added in proof

During the preparation of the final version of this article A. W. Castleman, Jr. and coworkers published new results about reactions of Group 5 transition metal oxide clusters including vanadium oxides with ethane and ethene.<sup>30</sup> They found similar reaction channels for the reactions of small oxide clusters  $(V_2O_5)_n^+$  ( $n = 2, 3$ ) with hydrocarbons as we have suggested for medium sized clusters with the same stoichiometry up to  $n = 6$ . On the basis of both articles we conclude that the reactive position of the vanadium oxide clusters  $(V_2O_5)_n^+$  exists already in very small clusters ( $V_4O_{10}^+$ ) and seems to be preserved also in the larger homologues.

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