DOI: 10.1002/chem.200902810

Generation of Gas-Phase Nanosized Vanadium Oxide Clusters from a Mononuclear Precursor by Solution Nucleation and Electrospray Ionization

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Dedicated to Professor Helmut Ringsdorf on the occasion of his 80th birthday

Early transition-metal oxides are well-known for their numerous applications in heterogeneous catalysis, electronics and materials science.[1] For example, hafnium oxide-based gates have been introduced to replace conventional silicon oxides in the latest Intel microprocessor,[2] and vanadium oxides are among the most important and versatile transition-metal catalysts used in chemical technology.[3] The industrial productions of SO_3 from SO_2, dehydrogenation of propane and of ethyl benzene, or the large-scale synthesis of maleic anhydride from butane may serve as examples.[4] However, many of the mechanistic details of oxidation processes occurring on metal-oxide surfaces or the microscopic steps by which metal oxide thin films are formed are far from being fully understood. As a consequence, the rational design of functional materials or of better catalysts still belongs to the realm of "dream chemistry". As to catalysis, although it is quite likely that oxygen vacancies or islands of clusters are present on surfaces, their precise catalytic function in the active site remains to be elucidated.[5]

In this context, gas-phase studies with isolated, mass-selected reactants (atoms or clusters) can provide direct insight into the intrinsic features of the systems of interest and may deepen the understanding of the reaction mechanism that are operative at a strictly molecular level.[6] In fact, experiments with clusters have proven quite useful, as they have turned out to serve as interesting models of their condensed phase analogues.[6]

In the last decade, laser evaporation of an appropriate metal in the presence of oxygen emerged as an excellent method to generate various metal-oxide cluster ions in the gas phase.[7] However, the clusters formed in this way are not always structurally uniform; rather, occasionally they correspond to a mixture of geometric isomers. For example, tetravanadium decaoxide $[V_4O_{10}]^+$, bears an isomeric dioxygen complex $[V_4O_8(O_2)]^+$, which is co-generated upon laser desorption in the presence of O_2.[8] As an alternative means of gas-phase cluster generation, electrospray ionization mass spectrometry (ESI-MS)[9] has opened up new horizons,[10] and when appropriate precursors were employed, ESI provided access to vanadium-oxide cluster cations of the type $[V_mO_n]^+$ ($m=1$–4; $n=1$–10).[11] However, this approach not only requires an additional synthesis step to prepare the inorganic polynuclear clusters, for example, the hexanuclear precursor $V_6O_7(OCH_3)_{12}$.[12] Moreover, a principal limitation of this route concerns the upper cluster ion-size which is determined by the size of the precursor molecule.

Here we report a different strategy for an efficient and convenient production of large-sized vanadium-oxide cluster ions from the easily accessible mononuclear precursor vanadyl isopropoxide, $VO(OiPr)_3$ ($Pr=C_3H_7$). It is well-known that metal alkoxides $M(OR)_m$ serve as ideal precursors for producing large-sized metal oxides by sol–gel processing.[13] Thus, under appropriate conditions metal oxide or metal oxo hydroxide clusters are expected to be accessible in solution through a series of hydrolysis and poly-condensation according to Equation (1). ESI may also assist in the cluster growth, owing to a decrease of the droplet size and solvent evaporation, both increasing the concentration and thus enhancing cluster assembly. In addition, under ESI condition the dehydration and degradation of these clusters in the process of vaporization and ionization may occur to eventually generate gas-phase cluster ions of the generic type $[V_mO_n]^+$ and $[V_oO_pH]^+$, respectively.[14]

$$VO(OiPr)_3 \xrightarrow{H_2O} [V_xO_{y-x}(OH)_{2z}] \xrightarrow{ESI} [V_mO_n]^+ + [V_oO_pH]^+ \quad (1)$$

The ESI-mass spectra of $VO(OiPr)_3$, dissolved in CH_3CN/H_2O (3:1), are shown in Figure 1 for different cone voltages

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902810.

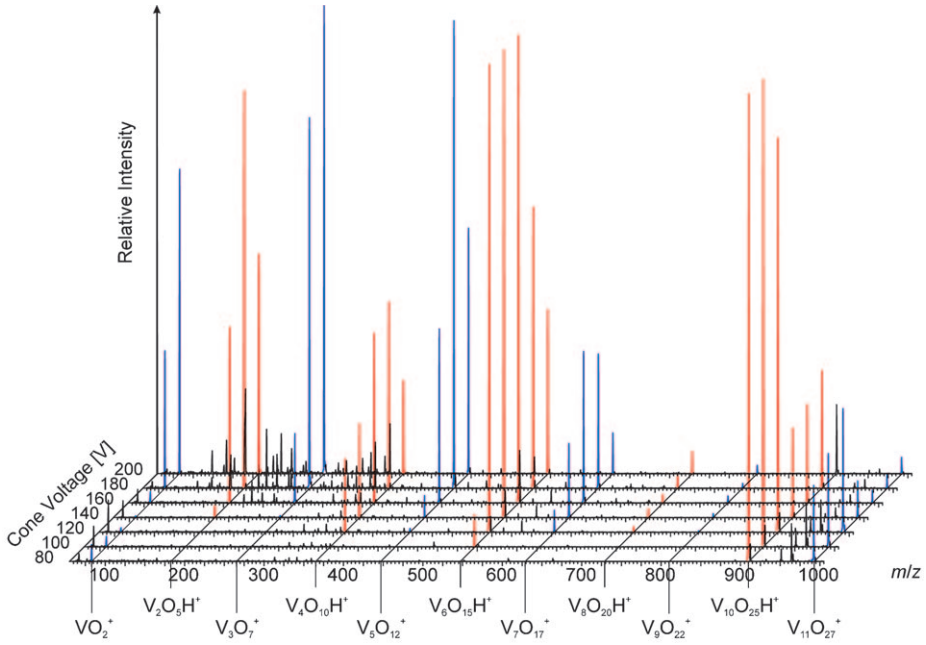

Figure 1. ESI Mass spectra of $VO(OiPr)_3$ in CH_3CN/H_2O (3:1) at cone voltages of 80–200 V.

(U_c). The latter determines the degree of collisional activation of the incident ions in the transfer from the ESI source to the mass spectrometer and thus controls the degree of cluster degradation.[15]

The main peaks in Figure 1 are assigned to two groups of cluster ions, that is, $[(V_2O_5)_nVO_2]^+$ and $[(V_2O_5)_nH]^+$. Common to both families is that vanadium retains the formal oxidation state V^{+5}, which is the most important state in bulk vanadium oxide catalysts.[16] As to the formation of these clusters, we propose the following scenario: Hydrolysis and poly-condensation of the mononuclear precursor in solution constitute the initial steps;[13] next, in the ESI source dehydration as well as cluster fragmentation are brought about by collisions with the inert drying gas N_2.[11,15] At cone voltages $U_c \geq 80$ V we observe a maximum of ion yield. Upon further increase of U_c degradation of the larger clusters to smaller ones takes place, thus giving rise to the terminal formation of $[V_3O_7]^+$ and $[VO_2]^+$ as the most abundant cluster ions. We note that the cluster distribution shown in Figure 1 differs from the one obtained in laser vaporization experiments.[7] In the latter studies, the intensity of the $[V_mO_n]^+$ series decays with increasing cluster size, and features of "magic number" clusters, which indicate particularly stable species, were not observed. In contrast, clusters generated by our protocol exhibit the presence of magic numbers corresponding to $[V_{11}O_{27}]^+$, $[V_{10}O_{25}H]^+$, $[V_6O_{15}H]^+$, $[V_5O_{12}]^+$, $[V_3O_7]^+$ and $[V_2O_5H]^+$. Cluster ions of the compositions $[V_8O_{20}H]^+$ or $[V_9O_{22}]^+$ are much less pronounced irrespective of the ionization conditions chosen. This finding suggests that in the cluster growth process in solutions and in the gas-phase degradation of the initially formed clusters certain molecular units act as building blocks or are eliminated as neutral fragments. In this respect one wonders how large can these clusters grow? In Figure 2 we reproduce the ESI mass spectrum for the m/z range 950–2000. Although the abundance of the larger cluster ions is reduced compared to that of the smaller ones (Figure 1), one nevertheless obtains decent signal intensities and, more importantly, for the two families of clusters, once more, magic numbers are observed. For example, the cluster ions $[V_{11}O_{27}]^+$, $[V_{13}O_{32}]^+$, $[V_{15}O_{37}]^+$, and $[V_{21}O_{52}]^+$ are particularly prominent, whereas others, for example, $[V_{19}O_{47}]^+$, are negligible. Similarly, the hydrogen-containing series exhibits strong signals for the cluster compositions $[V_{12}O_{30}H]^+$, $[V_{14}O_{35}H]^+$ and $[V_{20}O_{50}H]^+$, respectively. In the upper mass range $1950 < m/z < 3000$, only a signal at m/z 2728 is prominent having the elemental composition $[V_{30}O_{75}H]^+$; the stoichiometries of these clusters point to a building principle that employs $V_{10}O_{25}$ as a unit (see Figure S1 in the Supporting Information). Furthermore, it looks like some of these clusters are connected by well defined differences in stoichiometry. For example, a $V_{10}O_{25}$ unit connects $[VO_2]^+$ with $[V_{11}O_{27}]^+$, the latter is linked with $[V_{21}O_{52}]^+$, $[V_3O_7]^+$ with $[V_{13}O_{32}]^+$, and $[V_5O_{12}]^+$ with $[V_{15}O_{37}]^+$, respectively. The same "Aufbauprinzip" (construction principal) holds true for the hydrogen-containing cluster ions $[(V_2O_5)_nH]^+$. We note in passing that owing to the absence of a hydrogen source, none of these "hydrogen-

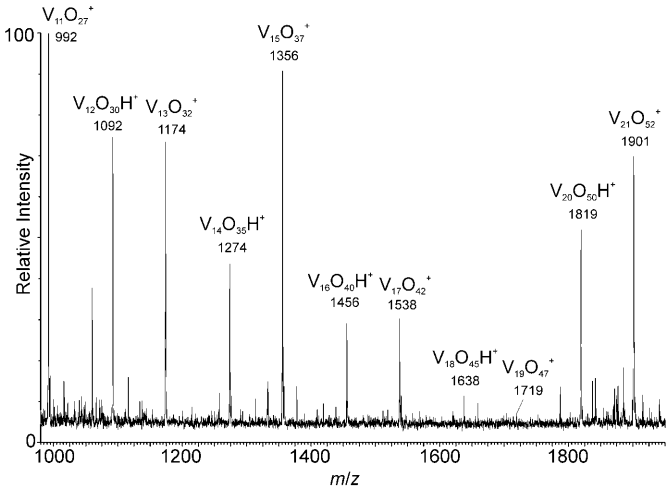

Figure 2. ESI Mass spectrum of $VO(OiPr)_3$ in CH_3CN/H_2O (3:1) at a cone voltage of 180 V.

ated" clusters are accessible by the conventional laser desorption of vanadium in the presence of O_2.

Indications on the origin of the observed cluster-size preferences as well as hints to structural features can be derived from collision-induced dissociation (CID) experiments, in which mass-selected cluster ions are collided with Xenon. Two representative CID spectra for the cluster ions $[V_{10}O_{25}H]^+$ and $[V_{11}O_{27}]^+$ are shown in Figure 3. Quite

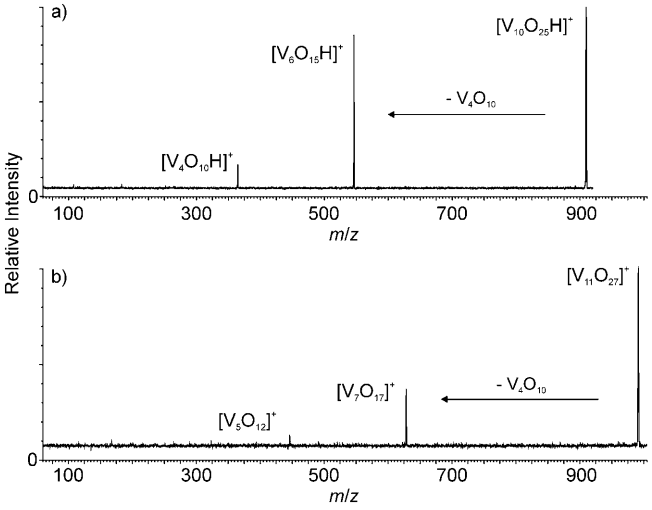

Figure 3. CID mass spectra of a) $[V_{10}O_{25}H]^+$ at $E_{CM}=1.9$ eV; b) $[V_{11}O_{27}]^+$ at $E_{CM}=2.3$ eV.

clearly, at collision energies $E_{CM}\approx 2.0$ eV the dominant fragmentation channel corresponds to the evaporation of V_4O_{10}, and this holds true for all the cluster ions containing 5–15 vanadium atoms (see Figure S2 in the Supporting Information). For larger clusters and at higher collision energies, in addition to the loss of V_4O_{10}, a weak signal assigned to the elimination of V_6O_{15} (or the combined extrusion of V_4O_{10} and V_2O_5) shows up in the spectra. From the absence of signals due to O_2 loss we exclude the presence of weakly bound peroxo or superoxo units as well as isomers that contain molecular O_2 as a building block in the vanadium-oxide clusters generated.

Finally, additional insight into structural aspects is provided by DFT calculations. As the number of conceivable isomers and the complexity of structural motifs increase dramatically with cluster size, on economic grounds we had to introduce some boundary conditions. Based on the present CID experiments and the obvious existence of a common building block unit in both the cluster growth and decomposition processes as well as previous experimental/computational studies,[17] the following assumptions were made: 1) The cluster ions do neither contain V–V nor O–O bonds and 2) the vanadium atoms adopt the formal oxidation state +5 and are tetrahedrally co-coordinated with at most one vanadyl group per vanadium.

The most stable isomers for each set of cluster stoichiometry investigated are given in Figure 4. Acyclic isomers or clusters that contain cage-like sub-units are much higher in energy. In previous experiments, gas-phase IR spectroscopy has been applied to probe experimentally structural aspects of vanadium-oxide clusters,[8a,18] and related future studies are indicated to verify the systems described in this Communication.

In view of the rather straightforward implementation and the broad scope of this protocol to generate metal-oxide clusters, which are otherwise more difficult to access, in future work we intend to probe the gas-phase reactivity of these (and other) clusters in the context of, for example, methanol oxidation[19] or to produce heterometallic oxide clusters; the latter are considered as models to probe the role of support material in heterogeneous catalysis.[20]

Hydrolysis and poly-condensation of a commercially available mononuclear precursor in combination with ESI-induced dehydration permit production of charged metal-oxide clusters in the gas phase in a size regime, which is otherwise more difficult, if not impossible, to access. Major advantages of this new protocol are the significantly enlarged cluster size regime and the formation of structurally more uniform systems. There are experimental indications that the gas-phase cluster distribution reflects the stability of the building block(s) present in the condensed phase and important units, $V_{10}O_{25}$ (or multiples of V_2O_5) have been identified.

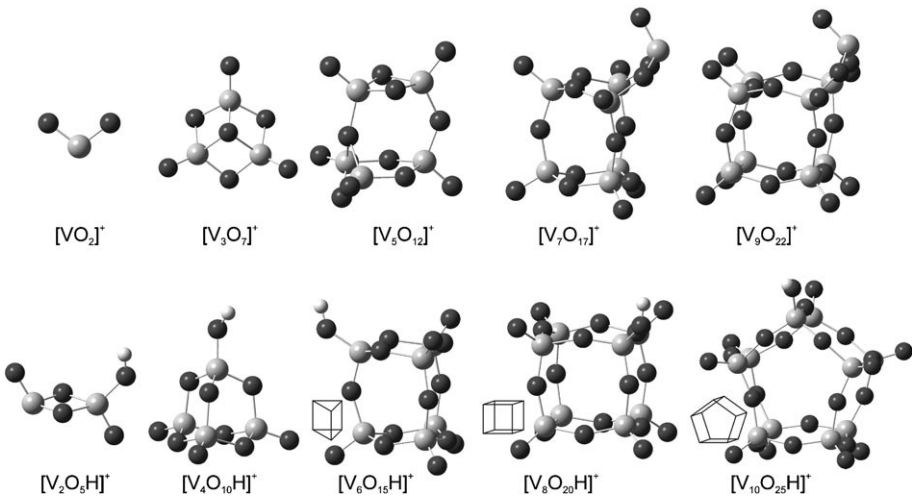

Figure 4. Optimized structures of vanadium oxide and vanadium hydroxide cationic clusters.

Experimental Section

The experiments were performed by using a VG BIO-Q mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole) equipped with an ESI source as described in detail previously.[21] In brief, commercially available (Aldrich) $VO(OiPr)_3$ was dissolved in *iso*-propanol and then diluted with CH_3CN/H_2O (3:1), and millimolar solutions were introduced through a fused-silica capillary to the ESI source via a syringe pump ($\approx 4\,\mu L\,min^{-1}$). Nitrogen was used as a nebulizing and drying gas at a source temperature of 90 °C. Maximum yields of the desired cluster oxides were achieved by adjusting the cone voltage (U_c) around 80–200 V. For CID experiments, the ions of interest were mass-selected using Q1, interacted with Xe as a collision gas (typically $p = 3 \times 10^{-4}$ mbar) at variable collision energies, while scanning Q2 to monitor the ionic products.

In the computational studies, the geometries of all cluster ions were optimized at the B3LYP level of theory[22] as implemented in the Gaussian03 program package[23] using TZVP basis sets of triple ξ-quality.[24] The nature of the stationary points was elucidated by a frequency analysis.

Acknowledgements

Financial support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft "Cluster of Excellence: Unifying Concepts in Catalysis" is acknowledged. X.Z. is grateful to the Alexander von Humboldt-Stiftung for a postdoctoral fellowship, and technical assistance by Dr. Maria Schlangen and Dr. Thomas Weiske is appreciated.

Keywords: density functional calculations · cluster compounds · electrospray ionization · mass spectrometry · vanadium

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Received: October 12, 2009
Published online: December 18, 2009

