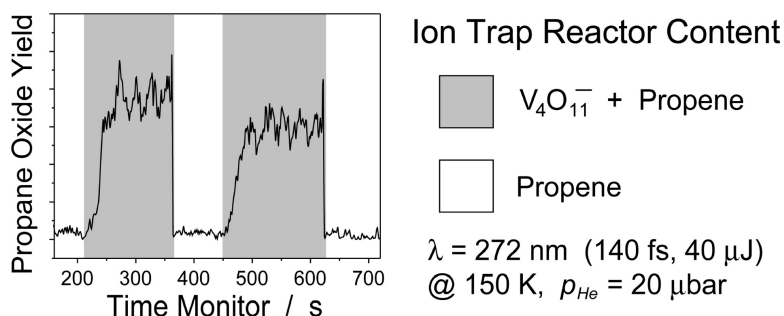## Communication

A Complete Reactant#Product Analysis of the Oxygen Transfer Reaction in [VO·CH]: A Cluster Complex for Modeling Surface Activation and Reactivity

Shaohui Li, Aldo Mirabal, Juri Demuth, Ludger Wo#ste, and Torsten Siebert

Ion Trap Reactor Content

$V_4O_{11}^-$ + Propene

Propene

λ = 272 nm (140 fs, 40 μJ)
@ 150 K, p_{He} = 20 μbar

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A Complete Reactant−Product Analysis of the Oxygen Transfer Reaction in [V$_4$O$_{11}$·C$_3$H$_6$]$^-$: A Cluster Complex for Modeling Surface Activation and Reactivity

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In the context of metal oxide-based heterogeneous catalysis, vanadium oxide surfaces and supports have found numerous industrial applications, and extensive research activities within metal oxide-based systems have been devoted to this catalytic material.[1] Insight to the molecular scale mechanism of catalytic processes can often be attained by employing gas-phase clusters as model systems of active-site surface morphology.[2−4] In the context of this general approach toward cluster-based reactivity, a methodology is presented in this work for a systematic, highly selective, and comprehensive characterization of model active-site cluster systems. The method is based within the instrumentation of tandem mass spectrometry and ion-trap reactors, where cluster species with varying size, geometry, and charge state can be synthesized, selected, and brought to reaction with reactants under defined reaction conditions.[2−4]

While this methodology generally allows for a highly versatile and controlled approach, it has so far been limited to selecting and observing the species of a particular charge state involved in a cluster reaction, without an access to the neutral participants.[3,4] To fill this gap in the analysis of cluster reactivity, high intensity ultraviolet femtosecond radiation is employed for multiphoton ionization (MPI) of neutral reactants and products, giving a comprehensive picture of the reaction under investigation. Furthermore, the reactions characterized in ion traps as well as flow tube reactors have so far been of a thermal and therefore statistical nature, where the starting point of the reaction as well as the structure of the activated complex is undefined beause of variance in the geometry of the collision complex and the energies involved.[3,4] In the approach presented here, the reaction is initiated out of a well-defined, stable aggregate complex of the model active-site cluster and respective reactant. Initiation of the reaction is achieved by photoinduced modifications of charge distribution and structure, leading to the activation of the aggregate complex under fully defined starting conditions.

This comprehensive approach is demonstrated for the case of the photoinduced oxygen transfer reaction of propene, aggregated with the anionic V$_4$O$_{11}$ cluster system in an ion trap reactor. The experimental strategy to these means is shown in Scheme 1 and follows the following route: V$_n$O$_m$$^{-/0/+}$ clusters are synthesized through laser ablation of vanadium bulk, with oxidation as well as transportation out of the plasma region by means of a 2% O$_2$/He gas pulse. Initial thermalization and focusing of the ion beam is preformed in a rf-decapole under 10^{-4} mbar He pressure. Charge and mass selection for V$_4$O$_{11}$$^-$ is carried out in a first rf-quadrupole mass filter. The cluster is guided into a cryostat-controlled hexa-decapole ion trap. The trap contains a C$_3$H$_6$/He gas mixture with partial pressure of $p_{C3H6} < 1$ μbar and $p_{He} = 20$ μbar, respectively, which allows for further thermalization to 150−300 K and formation of the aggregate complex [V$_4$O$_{11}$·C$_3$H$_6$]$^-$ under multi-collision conditions. The initiation of the reaction and MPI of the neutral products is achieved by irradiation with ultraviolet femto-second pulses (10−160 μJ, $\lambda_{center} = 272$ nm, $\Delta\lambda = 1.9$ nm FWHM; $\tau = 140$ fs FWHM 1 kHz). Within the storage time of 500 ms, multiple sequences of photoreaction and MPI take place and analysis of the reaction species is achieved by subsequent extraction, mass screening with a second rf-quadrupole filter, and channeltron detection.

The aggregate complex [V$_4$O$_{11}$·C$_3$H$_6$]$^-$ is chosen for simulating surface activation of molecular oxygen and atomic oxygen transfer to a coadsorbed unsaturated hydrocarbon due to the particular geometric and electronic structural attributes of the anionic V$_4$O$_{11}$ cluster system as well as its specific charge state reactivity.[2−4] Infrared photodissociation (IRPD) experiments together with theoretical analysis have shown the anionic V$_4$O$_{10}$ cluster system to have the highly symmetric T_d structure with four terminal vanadyl and six bridging oxygen atoms. This can serve to approximate bulk vanadium oxide surface structure. On the other hand, the two lowest energy-bridged peroxo- and dioxo- structures of anionic V$_4$O$_{11}$ are obtained through replacement of oxygen in one of the V−O−V bond positions in V$_4$O$_{10}$$^-$ with a displaced μ-(η^2- η^2) peroxo- or open dioxo- unit, respectively.[2] This structural motive in V$_4$O$_{11}$$^-$ together with collision induced dissociation (CID)[4c] and IRPD analysis,[2] that demonstrate the loss of atomic oxygen and formation of V$_4$O$_{10}$$^-$ as one of the primary dissociation channels, makes this cluster system an excellent model for the activation of surface adsorbed molecular oxygen. With respect to the electronic structure, the lowering of symmetry in V$_4$O$_{11}$$^-$ leads to localization of the unpaired electron on a single vanadium atom for the dioxo case. In both isomers, a defined photoinduced charge-transfer can be realized in analogy to the photoactivation of vanadium oxide surfaces.[5] Furthermore, choosing the anionic rather than the cationic system reduces the reactivity toward hydrocarbons to the point that a stable aggregate complex with propene can be formed.[3,4] Together with the bridged peroxo- or dioxo- structure, complexes of this type are well-suited to structurally model surface coadsorbed, activated reactants on a defined active-site cluster structure of low dimensionality.

The mechanism of the photoactivated oxidation reaction of propene aggregated with the V$_4$O$_{11}$$^-$ system is shown in Scheme 1, displaying the mass spectrum from the anionic as well as ionized neutral species taking part in the reaction. Since the obtained anionic and cationic mass spectra are fully complementary, a detailed picture of the reaction can be obtained from the identification of the participant masses. The anionic mass spectrum shows the aggregate complex [V$_4$O$_{11}$·C$_3$H$_6$]$^-$ (422 amu), the V$_4$O$_{11}$$^-$ (380 amu), and V$_4$O$_{10}$$^-$ (364 amu) cluster systems, the V$_4$O$_6$$^-$ (300 amu) and V$_3$O$_8$$^-$ (281 amu) fragments as well as the small shoulder peak of the [V$_4$O$_{10}$·H$_2$]$^-$ complex (366 amu). In the cationic reactant and product spectrum, the MPI-peak structure of propene and the respective oxide product species can be seen around 37−42 amu and 53−56 amu.

Scheme 1[a]
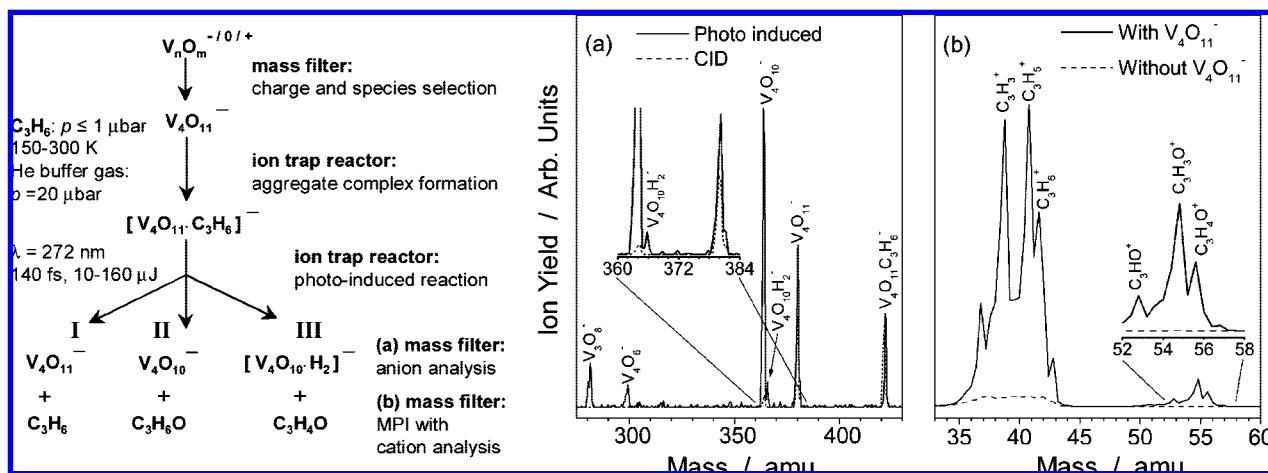
[a] (Left) Experimental procedure for the photoinduced reaction in the $[V_4O_{11} \cdot C_3H_6]^-$ complex with (I) dissociation of the complex, (II) oxygen transfer and dissociation, (III) oxygen transfer, dehydrogenation, and dissociation. (Right) Fully complementary anionic and cationic MPI mass spectra of the photo-induced reaction: (a) anionic mass spectrum taken after 500 ms reaction time at 40 μJ/pulse with broken lines showing the CID background; (b) cationic MPI mass spectrum of neutral reactants and products with broken lines showing the background MPI without $V_4O_{11}^-$ in the ion trap.

Importantly, the MPI cationic spectrum without $V_4O_{11}^-$ in the ion trap reactor (broken line) yields no bands at the position of the oxide product, clearly attributing the oxidation to the photoreaction from $[V_4O_{11} \cdot C_3H_6]^-$ and in comparison, an enhanced ionization of propene from the presence of $V_4O_{11}^-$ in the ion trap can be seen. Additionally, the difference in the CID background (broken line) and photoinduced reaction in the anionic mass spectrum show that a substantial amount of $V_4O_{11}^-$ and $V_4O_{10}^-$ are produced from the photoreaction of $[V_4O_{11} \cdot C_3H_6]^-$. These species directly correlate to the MPI cationic spectrum with the photoinduced dissociation product to propene (complementary to the bare $V_4O_{11}^-$ cluster band in the anionic mass spectrum, channel I in Scheme 1) and the oxide product from the photoinduced oxygen transfer (complementary to the $V_4O_{10}^-$ cluster band in the anionic mass spectrum, channel II in Scheme 1).[3,4] Interestingly, the small shoulder peak shifted 2 amu from the $V_4O_{10}^-$ signal attributed to $[V_4O_{10} \cdot H_2]^-$ shows a third reaction channel characterized by a simultaneous oxygen transfer and dehydrogenation process (channel III in Scheme 1).[3] Intensity dependent MPI control measurements of propene and the oxide product show that this probe process is generally accompanied by fragmentation under the loss of primarily 1 to 3 and 2 to 5 hydrogen atoms in both species, respectively, yet the shift of 2 amu shows the strongest peaks of the oxide product ($C_3H_6O^+$ to $C_3H_4O^+$ and $C_3H_3O^+$ to $C_3H_1O^+$), which supports the mechanism of simultaneous dehydrogenation in the oxygen transfer giving $[V_4O_{10} \cdot H_2]^-$. The $V_3O_8^-$ and $V_4O_6^-$ species are assigned to sequential photofragmentation from $V_4O_{11}^-$ and $V_4O_{10}^-$.[4c]

In summary, it could be demonstrated that the $[V_4O_{11} \cdot C_3H_6]^-$ aggregate complex is an excellent model system for the activation of molecular oxygen and the coadsorption of propene on a vanadium oxide active site structure with a high efficiency of photoinduced atomic oxygen transfer. The detection of neutral participants has allowed for an unambiguous identification of the reaction channels involved. Previous studies on ion–molecule reactions have utilized infrared, laser induced fluorescence and soft X-ray ionization detection schemes in the framework of flow tube reactors as well as neutralization–reionization (NRMS) and charge reversal techniques for this purpose.[6,7] The experimental methodology presented here demonstrates the first fully complementary analysis of anionic and cationic mass spectra detection under MPI of neutral reactants and products in the context of the highly controlled reaction conditions associated with tandem mass-spectrometry and ion trap reactors. In future work, a comparison between the MPI fragmentation pattern in Scheme 1b with all possible product isomers will allow for the propane oxide species to be identified and the selectivity of the reaction to be characterized. Further work will focus on time resolution within a pump–probe charge reversal scenario and controlling the different reaction channels with modulated femtosecond pulses.[7]

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