VIP Gas-Phase Reactions

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Catalytic Redox Reactions in the CO/N_2O System Mediated by the Bimetallic Oxide-Cluster Couple $AlVO_3^+/AlVO_4^+$**

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Dedicated to Professor K. Barry Sharpless on the occasion of his 70th birthday

Vanadium species supported on alumina (VO_x/Al_2O_3) have attracted significant interest in recent years owing to their excellent catalytic performance in many redox reactions, such as selective reduction of N_2O and NO_x ($x=1,2$), oxidation of CO, and oxidative dehydrogenation of alkanes to industrially more-valuable products.[1] However, probing and understanding at a strictly molecular level the "active sites" on the surface of the VO_x/support catalysts is still a challenge, despite of the many surface-characterization methods being used.[2]

An ideal arena for probing the energetics and kinetics of a chemical process in an unperturbed environment is provided by gas-phase studies on "isolated" reactants.[3] Also, many catalytic cycles have been reported involving, for example, oxygen-atom transfer from the donor N_2O to the acceptor CO [Eq. (1)]; this reactivity is generelly mediated by an isolated ionic species $Z^{+/-}$[3g,4] as demonstrated for the first time by Kappes and Staley with atomic Fe^+ as catalyst.[4i]

$$CO + N_2O \rightarrow CO_2 + N_2 \quad (1)$$

Systematic studies have been performed on this reaction and out of the 26 fourth to sixth row atomic cations investigated only 10, namely Ca^+, Fe^+, Ge^+, Sr^+, Ba^+, Os^+, Ir^+, Pt^+, Eu^+, and Y^+ exhibit catalytic activity.[3g,4d,5] Another interesting example concerns the catalytic conversion by $PtO_2^+/PtO^+/Pt$ revealing a very high turnover number.[4e] Furthermore, cationic Pt_x^+ ($x=6$–8)[6] as well as anionic clusters Pt_x^- ($x=3$–6)[4g,h,7] permit efficient catalytic cycles. The energetic requirement for this kind of O-atom transport is defined by the O-atom affinities (OAs) of the three species given in Equations (2) and (3), that must fulfill the requirement given in Equation (4).[3g]

$$N_2O + Z^{+/-} \rightarrow N_2 + ZO^{+/-} \quad (2)$$

$$ZO^{+/-} + CO \rightarrow Z^{+/-} + CO_2 \quad (3)$$

$$OA(N_2) < OA(Z^{+/-}) < OA(CO) \quad (4)$$

Recent studies have shown that stoichiometric metal-oxide clusters containing radical oxygen centers M-$O_t^{\bullet}$ (M = metal; O_t = terminal oxygen atom) are active towards the selective oxidation of CO and small hydrocarbons.[3a,e,4a,8] Castleman and co-workers provided experimental evidence for the reaction of the aluminum-oxide cluster $Al_2O_3^+$ with CO to form Al^+ or $Al_2O_2^+$ through two separate reaction channels.[8f] They also showed that stoichiometric zirconium-oxide clusters $Zr_xO_{2x}^+$ and $Zr_xO_{2x+1}^-$ ($x=1$–4), which contain M-$O_t^{\bullet}$ centers, are reactive towards CO; as the ionic products can be regenerated by treating oxygen-deficient zirconium-oxide clusters with N_2O, a full catalytic cycle exists.[4a,b] Furthermore, based on a theoretical study, they proposed that by doping neutral stoichiometric zirconium-oxide clusters Zr_2O_4 and Zr_2O_5 with a metal, containig one valence electron more or less (i.e., Y or Sc), the generation of neutral bimetallic oxide cluster containing M-$O_t^{\bullet}$ centers should be feasible.[9] In addition, the experimental observation and theoretical investigation of a neutral VO_3 radical bearing a V-$O_t^{\bullet}$ center have been reported by Bernstein and co-workers.[10] More recently, the groups of Schwarz and He described the efficient, thermal activation of methane by various stoichiometric binary oxide clusters containing M-$O_t^{\bullet}$ centers;[11] one interesting example concerns the thermal activation of methane by $AlVO_4^+$ as proposed by Wang et al.[11b] Surprisingly, the M-$O_t^{\bullet}$ center of $AlVO_4^+$ is located on the main-group metal Al but not on the transition-metal V. The thermodynamic and kinetic driving force of methane activation is indeed related to the properties of the Al-$O_t^{\bullet}$ moiety.[11b]

Herein, we report the first example of a catalytic redox cycle for the oxidation of CO by N_2O mediated by a heteronuclear (bimetallic) couple, that is $AlVO_3^+/AlVO_4^+$. Figure 1a shows the Fourier-transform ion-cyclotron reso-

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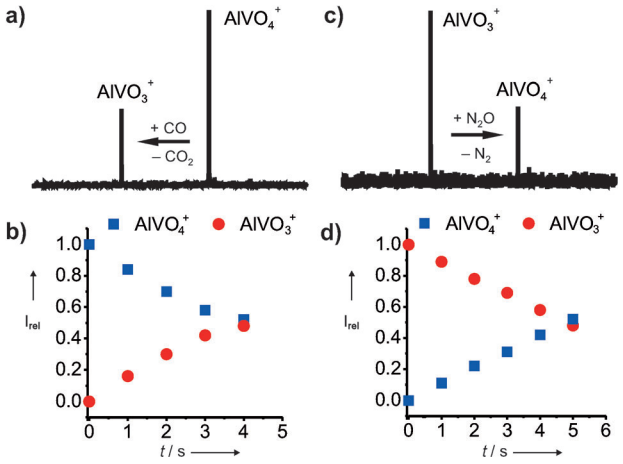

Figure 1. Fourier-transform ion-cyclotron resonance (FT-ICR) mass spectra showing the thermal reactions of a) $AlVO_4^+$ cluster with CO ($t = 3$ s) and c) $AlVO_3^+$ cluster with N_2O ($t = 2$ s); the pressures of CO and N_2O in each case are 8×10^{-9} mbar. The relative intensities of $AlVO_4^+$ and $AlVO_3^+$ with increasing reaction times are shown in (b) and (d), respectively.

nance (FT-ICR) mass spectrum, showing the reaction of thermalized, mass-selected $AlVO_4^+$ with CO. The intensity of the signal for the $AlVO_4^+$ cluster decreases with increasing reaction time, whereas the oxygen-loss product $AlVO_3^+$ becomes more pronounced (Figure 1b). According to density functional theory (DFT) calculations, the reaction in Equation (5) is rather exothermic (ΔE is the zero-point energy corrected reaction enthalpy).

$$AlVO_4^+ + CO \rightarrow AlVO_3^+ + CO_2 \qquad \Delta E = -177\ \text{kJ mol}^{-1} \qquad (5)$$

The rate constant for Reaction (5), $k(5)$ is 4.1×10^{-10} cm^3 molecule^{-1} s^{-1}, corresponding to a collision efficiency (ϕ) of 59 %.[12] The regeneration of $AlVO_4^+$ is achieved by treating $AlVO_3^+$ with N_2O [Eq. (6); Figure 1c,d]; the rate constant amounts to $k(6) = 4.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; this corresponds to $\phi = 65$ %.

$$AlVO_3^+ + N_2O \rightarrow AlVO_4^+ + N_2 \qquad \Delta E = -184\ \text{kJ mol}^{-1} \qquad (6)$$

Reactions (5) and (6) are very clean, no by-products or the encounter complexes, that means $[AlVO_x(N_2O)]^+$ and $[AlVO_x(CO)]^+$ ($x = 3,4$) are observed. Thus, the turnover number of the catalytic cycle is principally infinite but in reality limited by side reactions with background impurities; a typical side product is $AlVO_4H^+$, which results from the hydrogen-atom transfer from any residual organic substrate or from water to $AlVO_4^+$ during the catalytic cycle.[11b] The combination of Reactions (5) and (6) results in the overall Reaction (1), in which the gaseous couple $AlVO_3^+/AlVO_4^+$ effectively catalyzes the oxidation of CO by N_2O. Although this reaction is thermodynamically favored with an exothermicity of -361 kJ mol^{-1}, the process is kinetically hindered by a substantial barrier and does not proceed at all at ambient or elevated temperatures without a suitable catalyst.

The potential-energy surface (PES) calculated for the oxidation of CO by N_2O and catalyzed by the $AlVO_3^+/AlVO_4^+$ couple according to the Reactions (1), (5), and (6) is shown in Figure 2. All the intermediates and transition

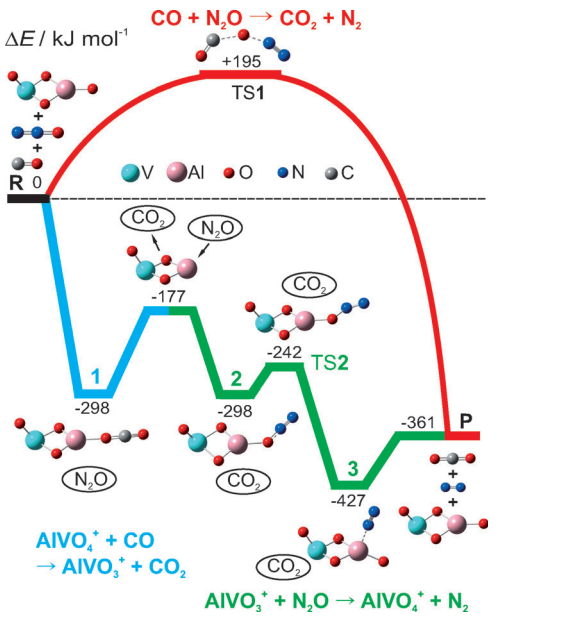

Figure 2. Potential-energy surfaces (B3LYP/TZVP) for the oxidation of CO by N_2O in the absence (red line) and the presence of $AlVO_4^+$ (blue/green line). The relative energies ΔE are given in kJ mol^{-1} and corrected for zero point energy. The blue and green profiles correspond to the reaction of $AlVO_4^+$ with CO and of $AlVO_3^+$ with N_2O, respectively. TS = transition structure; **R** = $CO + N_2O (+AlVO_4^+)$; **P** = $CO_2 + N_2 (+AlVO_4^+)$.

structures are in the doublet electronic states, which are much lower in energy than the corresponding quartet states. The uncatalyzed oxidation (Figure 2, red line) proceeds in one step with a high activation barrier of 195 kJ mol^{-1} (TS**1**); the calculated exothermicity of -361 kJ mol^{-1} is in good agreement with the exothermicity of -369 kJ mol^{-1} based on experimental data.[13]

The first half of the catalytic cycle involves an O-atom transfer from $AlVO_4^+$ to CO. The ground-state geometry of the intermediate $[O_tV(\mu\text{-}O)_2AlOCO]^+$ (**1**) reveals that the oxidation proceeds by an initial binding of the carbon atom of CO to the radical O atom of the Al-$O_t^{\bullet}$ moiety. As shown in Figure 2, intermediate **1**, containing a linear CO_2 subunit, is 298 kJ mol^{-1} lower in energy than the separated reactants. Cleavage of the VO_3Al^+–OCO bond requires 121 kJ mol^{-1} to generate the products $AlVO_3^+$ and CO_2. The calculated PES demonstrates that this step exhibits no reaction barrier in addition to its endothermicity.

Reduction of N_2O by $AlVO_3^+$ constitutes the other half of the catalytic cycle. The theoretical investigations indicate that the O atom of N_2O approaches the less-coordinated Al atom; this is energetically favorable as compared to competing processes such as N-atom transfer. The formation of the encounter complex $[O_tV(\mu\text{-}O)_2Al(ON_2)]^+$ (**2**) is straightforward without a barrier. The energy released during the

combination process is sufficient to surmount the barrier for breaking the weak O-N_2 bond (TS**2**) and to release the N_2 moiety (**3**→**P**). The terminal radical oxygen Al-$O_t^{\bullet}$ moiety is thus regenerated in this step and ready for the next catalytic cycle.[14]

Note that the catalytic cycle cannot be promoted by the non-radical terminal oxygen of the V=O_t moiety, because according to our DFT calculations, the reaction $[O_tV(\mu\text{-}O)_2AlO_t]^+ + CO \rightarrow [V(\mu\text{-}O)_2AlO_t]^+ + CO_2$ is kinetically inhibited and thermochemically much less favorable than the reaction $[O_tV(\mu\text{-}O)_2AlO_t]^+ + CO \rightarrow [O_tV(\mu\text{-}O)_2Al]^+ + CO_2$ (Figure 3).

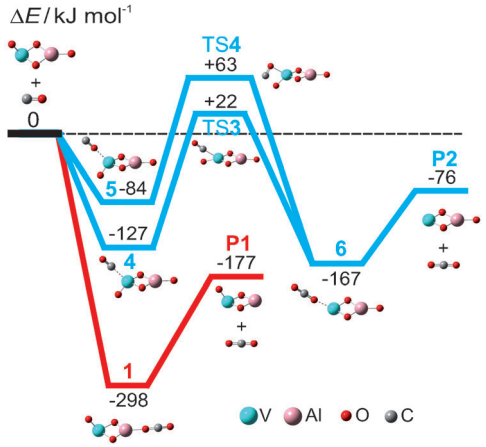

Figure 3. The reaction $[O_tV(\mu\text{-}O)_2AlO_t]^+ + CO \rightarrow [V(\mu\text{-}O)_2AlO_t]^+ + CO_2$ (blue lines) is kinetically inhibited and thermochemically much less favorable than the reaction $[O_tV(\mu\text{-}O)_2AlO_t]^+ + CO \rightarrow [O_tV(\mu\text{-}O)_2Al]^+ + CO_2$ (red line).

As mentioned above, the reaction of $Al_2O_3^+$ with CO has been reported recently and the most abundant product ion is Al^+, with $Al_2O_2^+$ being the second major product.[8f] Although regeneration of $Al_2O_3^+$ by oxidation of $Al_2O_2^+$ by N_2O occurs, the catalytic selectivity and efficiency of the $Al_2O_2^+/Al_2O_3^+$ couple, due to the formation of Al^+, are much lower than that of the $AlVO_3^+/AlVO_4^+$ couple. The difference between these two couples is apparently caused by the replacement of one Al atom of the $Al_2O_2^+/Al_2O_3^+$ system by the corresponding V=O_t moiety of the $AlVO_3^+/AlVO_4^+$ couple,[15] which totally inhibits the Al^+-generating channel.[16]

In conclusion, for the first time it is demonstrated that $AlVO_3^+/AlVO_4^+$ provides an ideal model for the catalytic oxidation of CO by N_2O. Theoretical investigations reveal that the overall catalytic process is promoted by the radical oxygen center of the Al-$O_t^{\bullet}$ and not the V=O_t moiety. Our findings may shed light on the nature of the active sites on the surface of the supported VO_x/Al_2O_3 catalysts and may prove helpful in the further design of even more efficient catalysts for solving one of the global environmental problems caused by automobile exhaust.[17]

Experimental Section

The ion/molecule reactions were performed with a Spectrospin CMS 47X FTICR mass spectrometer equipped with an external ion source as described elsewhere.[18] In brief, cluster cations $AlVO_x^+$ (x = 3,4) are generated by laser ablation of an aluminum/vanadium target using a Nd:YAG laser operating at 1064 nm in the presence of ca. 1 % O_2 seeded in helium carrier gas. Using a series of potentials and ion lenses, the ions are transferred into the ICR cell which is positioned in the bore of a 7.05 T superconducting magnet. After collisional thermalization by pulses of argon (ca. 2×10^{-6} mbar), $AlVO_x^+$ (x = 3,4) ions are mass-selected and studied with respect to their reaction by introducing the reactants CO and N_2O by a leak-valve at stationary pressures. The experimental second-order rate constants are evaluated assuming the pseudo-first-order kinetic approximation after calibration of the measured pressure and acknowledgment of the ion-gauge sensitivities. The rate constants have an uncertainty of ±30 %.[19] For the thermalized cluster ions a temperature of 298 K is assumed.[19]

The DFT calculations have been carried out using the Gaussian 09 program[20] employing the hybrid B3LYP exchange-correlation functional[21] with the unrestricted Kohn–Sham solution,[22] and TZVP basis sets.[23] The unrestricted B3LYP/TZVP level of theory proved reliable in previous studies of cationic,[24] anionic,[25] and neutral[10] transition-metal oxide clusters, main-group oxide clusters, such as MgO^+,[8g,26] $(Al_2O_3)_x^+$ (x = 3,4,5),[8e] and $P_4O_{10}^+$,[8d] as well as binary clusters, such as $AlVO_4^+$,[11b] $AlVO_5^-$,[27] $V_2SiO_8^-$,[28] $V_2SiO_7^+$,[11d] and $V_3PO_{10}^+$[11a,c] and their gas-phase reactions with small alkanes. For the optimization of transition structures (TS), we employed either the Berny algorithm[29] or the synchronous transit-guided quasi-Newton (STQN) method.[30] For most cases, initial estimated structures of the transition structures were obtained by relaxed potential-energy surface (PES) scans using an appropriate internal coordinate. Vibrational frequencies were calculated to characterize the nature of the stationary points as minima or transition structures; the relative energies (given in kJ mol^{-1}) are corrected for zero-point energy (ZPE) contributions. Intrinsic reaction-coordinate (IRC) calculations[31] were also performed to connect the TS with the local minima.

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[15] Note that, according to our calculations, the ground-state structure of $Al_2O_3^+$ corresponds to $[Al(\mu\text{-}O)_2AlO_t]^+$ with a diamond core. The replacement of the doubly coordinated Al atom by a $V{=}O_t$ moiety results in the ground-state structure of $AlVO_4^+$, that is, $[O_tV(\mu\text{-}O)_2AlO_t]^+$. The same situation holds true for $Al_2O_2^+$ and $AlVO_3^+$.

[16] We have repeated the reaction of $Al_2O_3^+ + CO$ with our FT-ICR MS equipment and only observe the reaction channel to form $Al_2O_2^+$. One possibility is that $Al_2O_3^+$ generated by the Castleman group may rather contain the $[Al(\mu\text{-}O)Al(O_2)]^+$ isomer; the formation of Al^+ could then be due to the following reaction: $[Al(\mu\text{-}O)Al(O_2)]^+ + CO \rightarrow Al^+ + AlCO_2 + O_2$.

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