

Catalytic Redox Reactions in the CO/N₂O System Mediated by the Bimetallic Oxide-Cluster Couple AlVO₃⁺/AlVO₄⁺**

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

Vanadium species supported on alumina (VO_x/Al₂O₃) have attracted significant interest in recent years owing to their excellent catalytic performance in many redox reactions, such as selective reduction of N₂O 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 N₂O to the acceptor CO [Eq. (1)]; this reactivity is generally mediated by an isolated ionic species Z^{+/-}^[3g,4] as demonstrated for the first time by Kappes and Staley with atomic Fe⁺ as catalyst.^[4d]



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 PtO₂⁺/PtO⁺/Pt revealing a very high turnover number.^[4c]

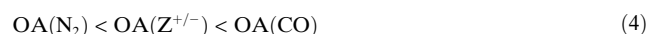
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Furthermore, cationic Pt_x⁺ (x = 6–8)^[6] as well as anionic clusters Pt_x⁻ (x = 3–6)^[4g,h,7] permit efficient catalytic cycles. The energetic requirement for this kind of O-atom transport is defined by the O-atom affinities (OAs) of the three species given in Equations (2) and (3), that must fulfill the requirement given in Equation (4).^[3g]



Recent studies have shown that stoichiometric metal-oxide clusters containing radical oxygen centers M-O_i[•] (M = metal; O_i = 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 Al₂O₃⁺ with CO to form Al⁺ or Al₂O₂⁺ 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_i[•] centers, are reactive towards CO; as the ionic products can be regenerated by treating oxygen-deficient zirconium-oxide clusters with N₂O, a full catalytic cycle exists.^[4a,b] Furthermore, based on a theoretical study, they proposed that by doping neutral stoichiometric zirconium-oxide clusters Zr₂O₄ and Zr₂O₅ with a metal, containing one valence electron more or less (i.e., Y or Sc), the generation of neutral bimetallic oxide cluster containing M-O_i[•] centers should be feasible.^[9] In addition, the experimental observation and theoretical investigation of a neutral VO₃ radical bearing a V-O_i[•] 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_i[•] centers;^[11] one interesting example concerns the thermal activation of methane by AlVO₄⁺ as proposed by Wang et al.^[11b] Surprisingly, the M-O_i[•] center of AlVO₄⁺ 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_i[•] moiety.^[11b]

Herein, we report the first example of a catalytic redox cycle for the oxidation of CO by N₂O mediated by a heteronuclear (bimetallic) couple, that is AlVO₃⁺/AlVO₄⁺. Figure 1a shows the Fourier-transform ion-cyclotron reso-