Radical Clusters

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Generation of Oxygen Radical Centers in Binary Neutral Metal Oxide Clusters for Catalytic Oxidation Reactions**

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Designing catalysts with a high degree of selectivity or high turnover rates is a subject of considerable current interest, with extensive effort being devoted to elucidating the fundamentals influencing these factors.[1–5] In the above-mentioned contexts, emphasis is placed on highly dispersed nanoscale materials, with special attention paid to metal oxide species for oxidation reactions.[6] A promising approach to designing appropriate systems is the use of clusters[7] to unravel fundamental mechanisms with attention to size, composition, oxidation state, and charge state.[8–17]

During recent years we[9–11,16,17] and others[13–15,18–21] have devoted considerable effort to shedding light on the mechanisms of oxygen transfer from transition-metal oxide species to a number of molecules, including CO and a variety of small organic species. Particularly revealing have been recent findings pertaining to reactions of anionic and cationic zirconium oxide clusters derived from collaboratory theoretical and experimental studies of the Bonačić-Koutecký and Castleman groups.[8,16,17] Results that provided evidence of the role of radical oxygen centers in governing the reactivity of selected systems were especially significant. Specifically, findings obtained from guided-ion-beam mass spectrometry experiments and density functional theory (DFT) calculations show that cationic zirconium oxide clusters of stoichiometric composition possess radical oxygen centers with lengthened metal–oxygen bonds.[16] Furthermore, by adding one oxygen atom with a full octet of valence electrons (O^{2-}) to stoichiometric cationic zirconium oxide clusters $(ZrO_2)_x^+$ ($x = 1$–4), a series of anionic clusters $(Zr_xO_{2x+1})^-$ ($x = 1$–4) can be formed that also contain radical oxygen centers with elongated metal–oxygen bonds (Figure 1 a, b).[17] The anionic clusters were found to oxidize carbon monoxide, strongly associate acetylene, and weakly associate ethylene, in contrast to the cationic species, which were found to be highly active towards the oxidation of all three molecules. Interestingly, theoretical investigations indicate that a critical hydrogen transfer step necessary for the oxidation of ethylene and acetylene at metal oxide clusters containing radical oxygen centers is energetically favorable for cationic clusters but unfavorable for the corresponding anionic species.[16,17]

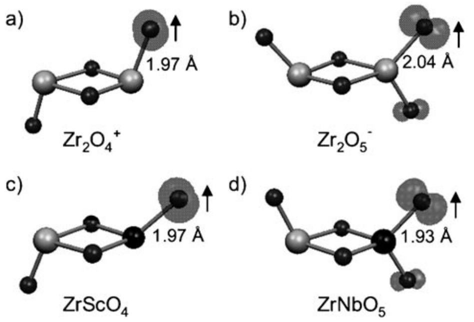

Figure 1. Calculated lowest-energy structures for a) $Zr_2O_4^+$, b) $Zr_2O_5^-$, c) $ZrScO_4$, and d) $ZrNbO_5$. The radical oxygen centers are indicated by an arrow. The gray isosurfaces indicate localized spin density.

Prompted by the important role of radical oxygen centers in influencing the reactivity of charged systems, we began exploring ways in which such centers could be effected for neutral cluster systems as well. Realizing that radical centers might be formed in certain systems with the same total valence electron count (termed isoelectronic in the following), we conducted calculations using DFT, thus establishing that replacing a zirconium atom in a cluster with an atom that has one more or one less electron (in this case niobium and scandium, respectively) might accomplish our objective. For similar reactivity to be obtained in the case of isoelectronic systems, the electronic character and location of the radical oxygen center must be effectively equivalent. In this context, $ZrScO_4$ (Figure 1 c) is seen to be isoelectronic with $Zr_2O_4^+$ (Figure 1 a), and $ZrNbO_5$ (Figure 1 d) is isoelectronic with $Zr_2O_5^-$ (Figure 1 b); importantly, the structural features and locations of the radical centers are effectively the same.

Attaining evidence that utilizing isoelectronic species to mimic charge states would yield similar reactivity for neutral systems is critical and requires information on the reaction profiles of the different systems. Such evidence was attained

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from calculations of energy profiles of the reactions previously considered in detail for anionic and cationic systems. Deduced profiles for mimics of representative cationic systems are presented in Figure 2. Specifically, as determined for cations, the mimic $ZrScO_4$ is also found to undergo a favorable reaction with both CO and C_2H_2. Further evidence of the validity of the isoelectronic mimic concept is obtained for reactions of anion stand-ins with these same molecules. As with the negatively charged clusters, the reactions are favorable for $ZrNbO_5$ with CO but not with C_2H_2 (Figure 3 a, b). Indeed, the findings are in good accord with zirconium oxides of equivalent electronic character.

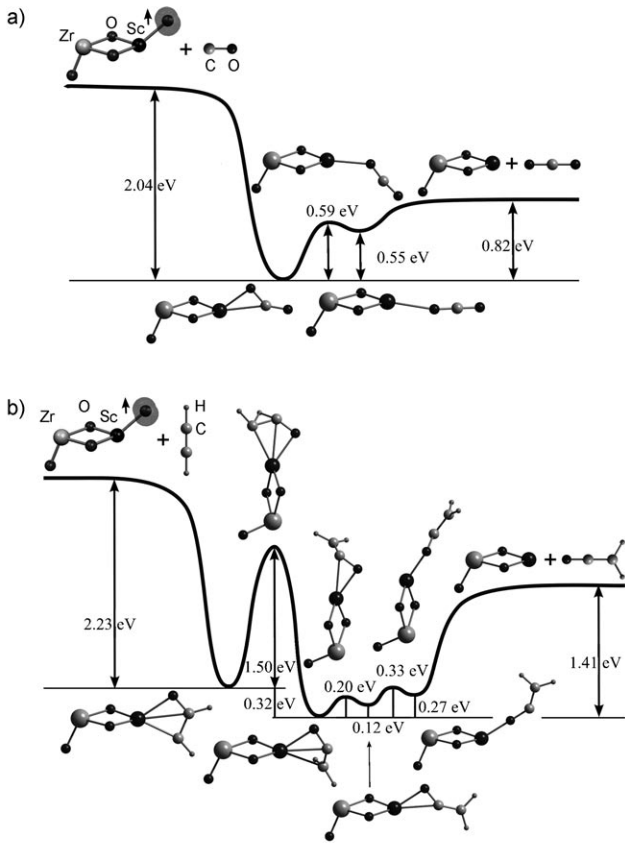

Figure 2. Calculated energy profiles for reactions of a) $ZrScO_4$ with CO and b) $ZrScO_4$ with C_2H_2.

From Figure 2 and Figure 3 the mechanisms for oxidation reactions involving both binary oxide clusters can be revealed. Let us first consider oxidation reactions for $ZrScO_4$, which is isoelectronic with the cationic species $Zr_2O_4^+$ [Eqs. (1,2)]:

$$ZrScO_4 + CO \rightarrow ZrScO_3 + CO_2 \qquad (1)$$

$$ZrScO_4 + C_2H_2 \rightarrow ZrScO_3 + C_2H_2O \qquad (2)$$

The ground-state geometry for $ZrScO_4$ presented in Figure 1 c reveals the presence of a radical oxygen atom associated with the Sc atom, which is characterized by a scandium–oxygen bond that is longer than the other metal–oxygen bonds by about 0.2 Å in analogy to $Zr_2O_4^+$. The calculated energy profile for the oxidation of CO according to Equation (1) (Figure 2 a) shows that a general mechanism involves the initial binding of the carbon atom of CO to the radical oxygen center, in which the scandium–oxygen bond is elongated (1.97 Å). The resulting $ZrScO_4$–CO complex is 2.04 eV lower in energy than the separated reactants. This complex consists of a CO molecule bound to the radical oxygen atom and to the Sc atom; it then proceeds over a transition state that is 0.59 eV higher in energy. This transition state involves cleavage of the Sc−C bond and formation of a weakly bound almost linear CO_2 subunit, which is 1.49 eV lower in energy than the reactants. Cleavage of the scandium–oxygen bond to form products $ZrScO_3$ and CO_2 requires 0.27 eV energy, leading to the overall oxidation reaction, which is exothermic by 1.22 eV.

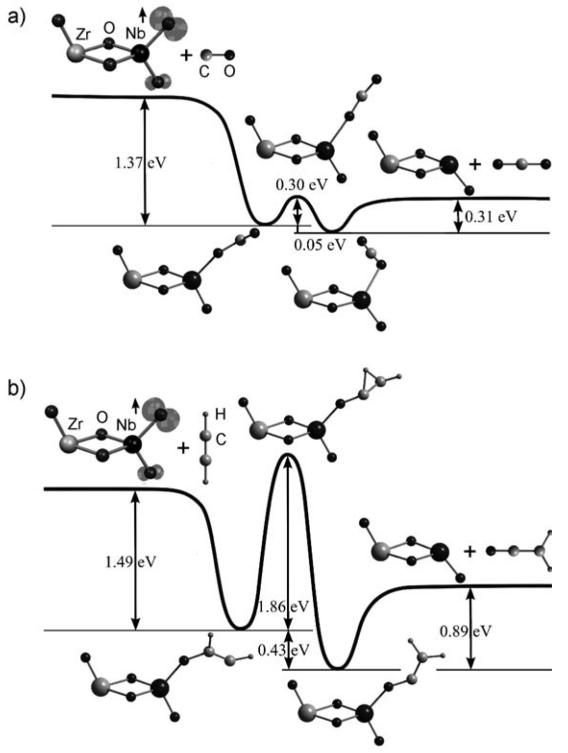

Figure 3. Calculated energy profiles for reactions of a) $ZrNbO_5$ with CO and b) $ZrNbO_5$ with C_2H_2.

The calculated energy profile for oxidation of acetylene according to Equation (2) reveals that the reaction proceeds through the strong binding of one carbon atom to the radical oxygen center and weaker binding of both carbon atoms to the scandium atom (Figure 2 b). The initial encounter complex is 2.23 eV more stable than the separated reactants. In the next step, the hydrogen atom is transferred from the oxygen-bound carbon atom to the other carbon atom of acetylene, involving a transition state which is 1.50 eV higher in energy. The resulting complex after hydrogen transfer is lower in energy by 2.55 eV than the reactants. The barrier for the cleavage of the carbon atom bound to the hydrogen atoms from the scandium atom is 0.20 eV. Finally, the barrier for the cleavage of the second carbon atom from the scandium atom is 0.21 eV, leading to an almost linearly bound ethenone molecule. Finally, the dissociation of the scandium–oxygen bond to form ethenone and $ZrScO_3$ requires 1.14 eV. The overall process is calculated to be exothermic by 1.14 eV.

Altogether, Figure 2 shows that oxidation of CO and of triply bonded hydrocarbons at radical oxygen centers in binary neutral zirconium scandium oxide clusters is favorable, in analogy to cationic stoichiometric zirconium oxide clusters $(ZrO_2)_x^+$ ($x = 1$–4).[16]

Now we consider oxidation reactions for both CO and C_2H_2 involving the $ZrNbO_5$ cluster that is isoelectronic with the anionic species $Zr_2O_5^-$. From the calculated energy profile of Figure 3a we deduce the following mechanism for the CO reaction [Eq. (3)]:

$$ZrNbO_5 + CO \rightarrow ZrNbO_4 + CO_2 \quad (3)$$

The calculated ground-state geometry for $ZrNbO_5$ presented in Figure 1d again reveals the presence of a radical oxygen center, this time associated with the Nb atom. It is characterized by a longer, weaker metal–oxygen bond (by ca. 0.2 Å) in analogy to the anionic $Zr_2O_5^-$ cluster (cf. Figure 1b). The isomer in which the radical oxygen center is associated with the Zr atom is considerably higher in energy. The calculated energy profile (Figure 3a) shows that the initial encounter complex is 1.37 eV more stable than the reactants and contains a slightly bent CO_2 subunit that results from the transfer of charge from cluster to CO. Transfer of charge from CO_2 back to the cluster involves a barrier of 0.3 eV, resulting in a structure with a linearly bound CO_2 subunit that is 1.42 eV more stable than the reactants. Loss of CO_2 from the cluster requires an additional energy of 0.31 eV, and the overall process is exothermic by 1.11 eV, resulting in $ZrNbO_4$ and CO_2 products. The oxidation reaction is similar to that with the anionic $Zr_2O_5^-$ cluster, in which case the reaction is exothermic by 0.87 eV.

In contrast, the energy profiles for the reaction of $ZrNbO_5$ with acetylene show large barriers for the transfer of hydrogen from one carbon atom to the other necessary for the formation of an ethenone subunit. One of the reaction pathways involving attack of acetylene on the oxygen radical center is shown in Figure 3b. The other, involving the formation of a ring configuration between NbO_2 and the C_2H_2 subunit, is also strongly unfavorable (see the Supporting Information). This finding is again in complete analogy to the anionic $Zr_2O_5^-$ species, which is reactive towards oxidation of CO but not towards hydrocarbons.

Altogether, Figure 2 and Figure 3 provide evidence for the isoelectronic mimic concept for binary neutral metal oxide clusters. $ZrScO_4$ mimics cationic $Zr_2O_4^+$, and both undergo favorable reactions with CO and C_2H_2. $ZrNbO_5$ mimics anionic $Zr_2O_5^-$, and both undergo reaction with CO but not with C_2H_2. Moreover, common features are characteristic for the mechanisms responsible for the reactions.

An additional supporting finding for the reactive centers is acquired by considerations of the molecular electrostatic potentials. Considering the single-metal (Zr) clusters, the calculated electrostatic potential of the cluster revealed that in the case of cations, a favorable interaction with nucleophilic molecules takes place over the whole surface of the $(ZrO_2)_x^+$ ($x = 1$–4) clusters, compared to a restricted interaction of ethylene and acetylene with the less-coordinated zirconium atom in the case of the anionic $(Zr_xO_{2x+1})^-$ ($x = 1$–4) species.[17] Therefore, in spite of the common presence of a radical oxygen center in specific anionic and cationic stoichiometries, the extent to which various classes of reactions are promoted is influenced by charge state. This general idea is demonstrated in the case of neutral binary metal systems, where it is largely the total electron number that affects the reactive behavior.

A further noteworthy point pertains to the ability to acquire a full reaction cycle necessary for catalysis. Indeed, we established that a full cycle is attainable in the reactions with CO and C_2H_2 for neutral $ZrScO_4$ (Figure 4) and with CO for neutral $ZrNbO_5$ (see the Supporting Information), in analogy to stoichiometric cationic zirconium oxides $(ZrO_2)_x^+$ and anionic $(Zr_xO_{2x+1})^-$ species, all of which contain radical oxygen centers. As can be recognized from the schematic representation of the catalytic cycle given in Figure 4, the oxygen radical center (left side of Figure 4) reacts with CO or C_2H_2 to form a stable complex (top of Figure 4), which after rearrangement leads to the formation of the oxidation product and a cluster with one less oxygen atom (right side of Figure 4). The initial cluster species can be subsequently regenerated by using strong oxidants such as N_2O (lower part of Figure 4), thus closing the catalytic cycle. This finding also indicates that the neutral mimics may promote multiple cycles for oxidation.

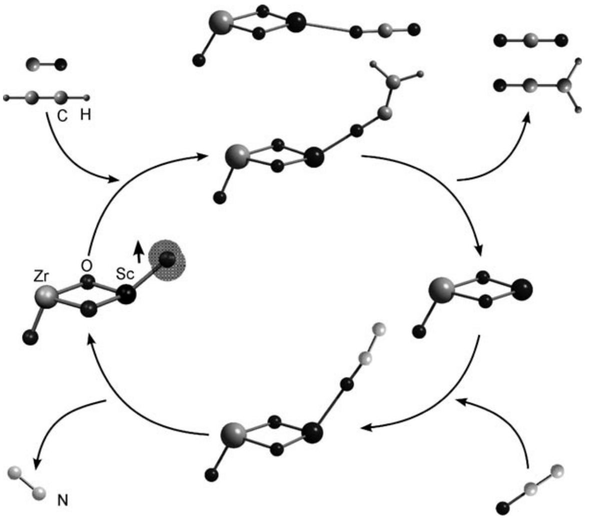

Figure 4. Schematic representation of the full catalytic cycle involved in the oxidation reactions of $ZrScO_4$ with CO and C_2H_2 with subsequent regeneration of the active species with N_2O.

Our findings concerning the influence of charge state on catalytic oxidation reactions at zirconium oxide clusters containing radical oxygen centers have conceptual ramifications for the design of future heterogeneous oxidation catalysts. As shown in our previous two publications devoted to this subject,[16,17] radical oxygen centers are likely to be responsible for the selective oxidation of a variety of industrially relevant molecules. Herein, we provide strong evidence that this idea can be extended to acquiring neutral metal oxide systems with similar reactivity characteristics. Therefore, through controlled deposition of size-selected clusters onto chosen supports, it may be possible to create catalytic materials with a high concentration of oxygen radical centers that would promote various oxidation reactions, a critical step in catalyst design through the concept of cluster assembly. By forming systems containing one less electron (i.e. with Sc), it would be possible to generate neutral zirconium oxide clusters with $Zr_{x-1}ScO_{2x}$ stoichiometry. The hole from the dopant atom should form an oxygen radical center that would be expected to exhibit reactivity similar to the cationic zirconium oxide clusters. At the same time, by forming systems containing one additional valence electron (i.e with Nb), and also exposing them to a strong oxidizer such as N_2O, generation of neutral zirconium oxide clusters with a $Zr_{x-1}NbO_{2x+1}$ stoichiometry would be possible. The one additional oxygen atom and the electron from the dopant atom should form an oxygen radical center that would be expected to exhibit reactivity similar to the anionic zirconium oxide clusters discussed herein. Therefore, p-type doping of zirconium oxides is expected to result in the formation of clusters that efficiently promote the oxidation of CO, C_2H_4, and C_2H_2, while n-type doping would create clusters that promote the oxidation of CO. Based on our findings, we believe the prospects for catalyst design abound.

Experimental Section

The structural properties of the neutral $ZrScO_4$ and $ZrNbO_5$ clusters and their reactivity were studied using the DFT method with the hybrid B3LYP functional.[22–24] For the Zr, Nb, and Sc atoms, a triple-zeta-valence-plus-polarization (TZVP) atomic basis set combined with the Stuttgart group relativistic effective core potential were employed.[25–28] For the C, O, N, and H atoms the TZVP basis sets were used.[29] Our previous studies of the reactivity of transition-metal oxides have shown that such a combination of hybrid density functionals with triple-zeta-quality basis sets allows the accurate prediction of the reaction energetics and mechanisms.[8,10,16,17] All structures presented were fully optimized using gradient minimization techniques, and stationary points were characterized as minima or transition states by calculating the vibrational frequencies. Moreover, the reaction mechanisms were deduced from the energy profiles based on energies obtained from DFT calculations.

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