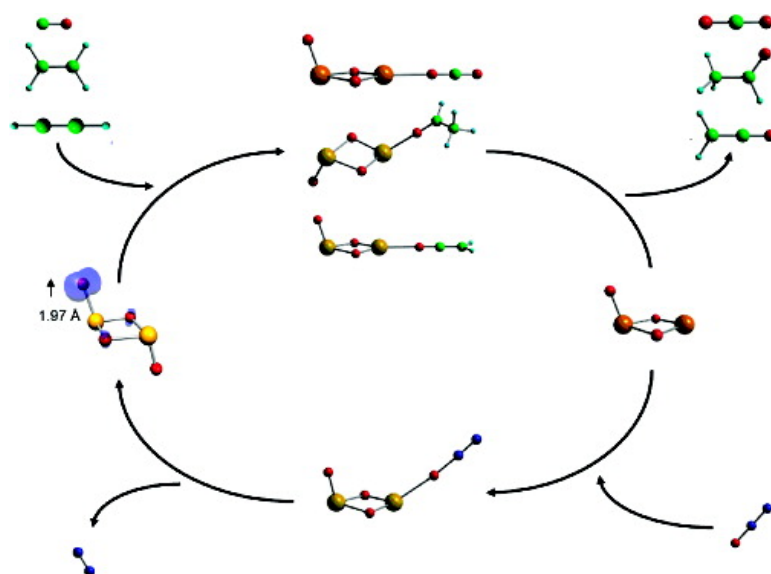


Stoichiometric Zirconium Oxide Cations as Potential Building Blocks for Cluster Assembled Catalysts

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Stoichiometric Zirconium Oxide Cations as Potential Building Blocks for Cluster Assembled Catalysts

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Abstract: Employing guided-ion-beam mass spectrometry, we identified a series of positively charged stoichiometric zirconium oxide clusters that exhibit enhanced activity and selectivity for three oxidation reactions of widespread chemical importance. Density functional theory calculations reveal that these clusters all contain the same active site consisting of a radical oxygen center with an elongated zirconium–oxygen bond. Calculated energy profiles demonstrate that each oxidation reaction is highly favorable energetically and involves easily surmountable barriers. Furthermore, the active stoichiometric clusters may be regenerated by reacting oxygen-deficient clusters with a strong oxidizer. This indicates that these species may promote multiple cycles of oxidation reactions and, therefore, exhibit true catalytic behavior. The stoichiometric clusters, having structures that resemble specific sites in bulk zirconia, are promising candidates for potential incorporation into a cluster assembled catalyst material.

Introduction

A promising prospect in the field of nanoscale research is the use of selected clusters as building blocks to assemble tailored materials with desirable properties.^{1–4} The structural and electronic characteristics of small clusters can be altered considerably by the incorporation or removal of single atoms.⁵ Therefore, in this size regime, in which each atom counts, it is possible to achieve significant changes in chemical reactivity by varying the size and stoichiometry of small clusters. These nanoscale clusters, furthermore, often possess unique structural and electronic features that are not accessible in the corresponding bulk-phase material.⁶ Recently, research has been undertaken to identify and characterize clusters with enhanced stability^{7–9} and desirable electronic,^{10,11} magnetic,¹² and reactive¹³ proper-

ties. Moreover, several examples of cluster assembled materials have been successfully synthesized,^{6,14–16} demonstrating the increasing importance of the cluster-based approach to nanoscale engineering.

A potentially fruitful application of cluster assembly may be the creation of heterogeneous catalysts with improved activity and selectivity for a desired reaction. Bulk-phase catalysts typically contain a wide variety of reactive sites that lower the selectivity for a particular product and often result in the creation of unwanted byproducts.¹⁷ This necessitates the use of more starting materials to manufacture a given amount of product and also increases the energy requirements and waste disposal associated with industrial chemical production. Through assembly of selected clusters that are relatively thermodynamically stable and contain only one type of active site, it may be possible to create a highly active catalyst with near perfect selectivity for one specific product.

Studies of gas-phase clusters have revealed that cationic species of a particular size and stoichiometry often exhibit greatly enhanced activity and selectivity for specific reactions.^{13,18} Furthermore, in several instances, full catalytic cycles have been

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observed in the gas phase, thereby providing insight into the elementary mechanisms of catalytic reactions.^{19–26} Cationic clusters are good models of the positively charged active sites on bulk-phase catalytic surfaces that result from partial electron transfer from a catalyst particle to a support material with greater electron affinity.²⁷ Moreover, cationic clusters generally exhibit significantly higher reactivity than neutral species, making them more tractable model systems for gaining insight into catalytic processes. We extensively investigated the reactivity of cationic oxides of the group V transition metals (vanadium, niobium, and tantalum),¹³ as have other researchers.^{28–31} In a recent publication, we demonstrated, through a combination of experiment and theory, that $(V_2O_5)_{1,2}^+$ clusters promote the selective oxidation of ethylene to acetaldehyde and that the reaction occurs according to a general radical cation mechanism.^{32,33} Findings by Schwarz and co-workers revealed that, while low-valent vanadium oxide cations are active toward methanol dehydrogenation, higher valent oxides favor hydrogen abstraction and oxygen transfer.³⁴ Additional studies by this group found that $V_2O_2^+$ and $V_4O_{10}^+$ were the only vanadium oxide cations that dehydrogenate small alkanes³⁵ and that $V_4O_{10}^+$ was the only species to abstract hydrogen from CH_4 .³⁶ Active sites consisting of radical oxygen centers were also found in cationic main group metal oxide clusters. In two recent studies, radical oxygen centers in both $(Al_2O_3)_x^+$ ($x = 3, 4, 5$) and $(MgO)_x^+$ ($x = 1, 2$) clusters were found to abstract hydrogen from CH_4 at thermal energies.^{37,38} Given the selective nature of these reactions and that they are observed only for specific clusters, we conclude that metal oxide clusters may be tuned, through changes in electronic structure, charge state, size, and stoichi-

ometry, and potentially assembled into highly active catalytic materials that would selectively promote desired reactions.

Zirconium, in comparison to vanadium, has an electronic configuration with one less d electron (Zr: $5s^24d^2$, V: $4s^23d^3$) in its valence shell, resulting in a more oxygen-deficient bulk-phase stoichiometry (Zr: Zr_2O_4 , V: V_2O_5). Furthermore, zirconium has a somewhat larger atomic radius ($\sim 15\%$)³⁹ and ionic radius ($\sim 26\%$)³⁹ than vanadium, which may result in different binding energies of reactant molecules. Moreover, because of its exceptional stability over a wide temperature range and its resistance to poisoning, bulk-phase zirconia (ZrO_2) is employed as both a catalyst and catalyst–support⁴⁰ material for a variety of industrially relevant processes. For example, bulk-phase studies revealed zirconia to be an effective catalytic material for the oxidation of CH_4 ^{41,42} and CO ⁴³ and the epoxidation of propylene.⁴⁴ Because of the larger proportion of exposed potential active sites and the long-range ion-induced dipole interaction between positively charged clusters and polarizable reactant molecules,³³ we expected that cationic zirconium oxide clusters would be far more reactive than neutral zirconia nanoparticles. Furthermore, an understanding of the molecular level interaction of CO and both double- (C_2H_4) and triple- (C_2H_2) bonded hydrocarbons with specific zirconium oxide clusters aids in identifying species with enhanced activity and selectivity for the oxidation of these molecules.

Herein, we discuss the potential of using cationic stoichiometric zirconium oxides in cluster assembled catalysts that would efficiently promote three separate industrially relevant oxidation reactions with a high degree of selectivity. Evidence, obtained by guided-ion-beam mass spectrometry experiments and density functional theory (DFT) calculations, is presented demonstrating the enhanced activity and selectivity of stoichiometric $(ZrO_2)_x^+$ ($x = 1–4$) zirconium oxide clusters for the strongly exothermic oxidation of carbon monoxide to carbon dioxide, ethylene to acetaldehyde, and acetylene to ethenone. These reactions are relevant to the abatement of harmful environmental CO, the large-scale industrial production of acetaldehyde, and the manufacture of higher alkynes, respectively. The enhanced reactivity of the stoichiometric clusters is attributed, on the basis of theory, to the presence of a radical oxygen center with an elongated zirconium–oxygen bond. We propose general mechanisms for the oxidation of CO, C_2H_4 , and C_2H_2 , which show that each process is highly thermodynamically favorable and involves easily surmountable energy barriers. In addition, the active stoichiometric clusters may be regenerated easily from oxygen-deficient species through reaction with N_2O . Because of their exceptional activity in comparison to other zirconium oxides, and the fact that they have structural characteristics that resemble specific sites in bulk zirconia, we conclude that the stoichiometric series of zirconium

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oxide cation clusters are potential candidates for incorporation into a cluster assembled catalyst.

Experimental Methods

The reactivity of zirconium oxide cations with CO, C₂H₄, C₂H₂, or N₂O was studied using a guided-ion-beam mass spectrometer described in detail in a previous publication.⁴⁵ Briefly, zirconium oxide clusters were produced in a laser vaporization cluster source by pulsing oxygen seeded in helium (10%) into the plasma formed by ablating a zirconium rod with the second harmonic (532 nm) of a Nd:YAG laser. To prevent the undesired formation of hydroxo species, ultrahigh purity helium and oxygen were used to create the expansion gas mixture. Furthermore, all of the gas transfer lines, which are constructed of stainless steel, were heated while under vacuum to desorb any residual water. The zirconium oxide clusters exit the source region and are cooled through supersonic expansion into vacuum. During supersonic expansion, the high-pressure (13.2 atm) expansion gas mixture passed through a narrow diameter nozzle into vacuum. The random thermal energy of the clusters was thereby converted into directed kinetic energy of the molecular beam. Consequently, the internal vibrational and rotational energy of the clusters was lowered through collisions with the He carrier gas. The working pressure in the field-free region of the source was between 5 to 9×10^{-5} Torr, depending on the length of time that the pulse valve was open per pulse.⁴⁵ The kinetic energy imparted to the cluster ions by the supersonic expansion was determined previously, employing a retarding potential analysis,⁴⁵ to be approximately 1 eV in the laboratory energy frame (E_{LAB}). Ideally, all clusters exiting the supersonic expansion source had the same initial kinetic energy. The initial center-of-mass collision energy (E_{CM}) was calculated for ZrO₂⁺, Zr₂O₄⁺, Zr₃O₆⁺, and Zr₄O₈⁺ to be approximately 0.19, 0.10, 0.07, and 0.05 eV for CO, C₂H₄, and C₂H₂. As subsequent collisions are expected to dissipate the initial energy of a given cluster, the values reported above serve to establish an upper limit on the kinetic energy of the reactive collisions.

After exiting the source region, the clusters passed through a 3-mm skimmer forming a collimated molecular beam and were then directed into a quadrupole mass filter employing a set of electrostatic lenses. The quadrupole mass filter isolated clusters of a desired mass, which were then passed into an octopole collision cell. To maximize the intensity of a mass-selected cluster, the resolution of the first quadrupole mass filter was adjusted to discriminate completely between adjacent zirconium oxides in the cluster distribution. Therefore, although care was taken to prevent the formation of zirconium hydroxides in the laser vaporization source, as mentioned above, we cannot exclude that a small percentage of the mass-selected ions may consist of these species. Variable pressures of CO, C₂H₄, C₂H₂, or N₂O were introduced into the octopole collision cell employing a low-flow leak valve. The gas pressure was monitored using an MKS Baratron capacitance manometer. During reactivity experiments, the source region was grounded as was the electrostatic lens at the entrance to the octopole collision cell and the octopole rods, thereby ensuring that no additional kinetic energy was imparted to the cluster ions in excess of that resulting from the supersonic expansion ($E_{\text{LAB}} \approx 1$ eV). Product ions formed in the collision cell were mass analyzed by a second quadrupole mass spectrometer. Again, to maximize the intensity of the product ions the resolution of the second quadrupole mass spectrometer was adjusted to discriminate completely between oxygen transfer products, which are the focus of this publication. Because of the isotope distribution of zirconium, and the resolution settings employed, we did not experimentally identify any hydrogen abstraction products. Finally, the ions were detected with a channeltron electron multiplier connected to a multichannel scalar card. The experimental branching ratios presented in the Results

and Discussion illustrate the change in normalized ion intensity with increasing pressures of reactant gas. At higher gas pressures, therefore, the ratio of reactant ion intensity to total ion intensity became smaller while the ratio of product ion intensity to total ion intensity became larger. We present the experimental data as pressure dependent normalized ion intensities for the primary reaction channels because the absolute intensities of different mass-selected reactant ions vary substantially between species. Product mass spectra at a specific reactant gas pressure would indicate the absolute intensity of both reactant and product ions for a given reaction but would not allow for a comparison of the relative reactivity of different cluster ions. Separate experiments were also conducted with inert Xe to verify that the products observed with CO, C₂H₄, or C₂H₂ are the result of a chemical reaction and not the products of collisional fragmentation.

Theoretical Calculations

The structural properties of the cationic (ZrO₂)_x⁺ ($x = 1-4$) clusters and their reactivity toward CO, C₂H₄, C₂H₂, and N₂O were studied using the DFT method with the hybrid B3LYP functional.⁴⁶⁻⁴⁸ For the zirconium atoms, a triple- ζ valence plus polarization (TZVP) atomic basis set combined with the Stuttgart group 12 electron relativistic effective core potential (12e-RECP) was employed.^{49,50} For the carbon, oxygen, and hydrogen atoms, the TZVP basis sets were used. Our previous studies of the reactivity of transition-metal oxides showed that such a combination of hybrid density functionals with triple- ζ quality basis sets allow the accurate prediction of the reaction energetics and mechanisms. All structures presented were fully optimized using gradient minimization techniques, and stationary points were characterized as minima or transition states by calculating the frequencies. The basis set superposition error corrections for binding energies were calculated and have values that are below 0.1 eV, which lies within the accuracy of the DFT method. Moreover, the reaction mechanisms were determined by calculating the energy profiles based on electronic energies of the DFT calculations. This is justified since the GIB experiments were performed under microcanonical conditions at relatively low pressures. The proposed reaction mechanisms were also confirmed by performing ab initio molecular dynamics (MD) simulations “on the fly” based on the DFT method. Newton’s equations of motion were solved using the Verlet algorithm with time steps of 0.5 fs, and the forces were calculated employing the analytical energy gradients in the framework of the TURBOMOLE program.⁵¹ The MD simulations performed at constant energy allowed the rearrangements of bonds along the reaction pathways to be followed. To improve efficiency, the resolution of identity (RI)-DFT procedure^{52,53} was employed involving the Perdew–Burke–Ernzerhof⁵⁴ functional with the 12e-RECPs for zirconium combined with Gaussian basis sets of triple- ζ quality for all atoms.⁴⁹

Results and Discussion

Each cluster in the overall distribution of zirconium oxide cations was reacted individually with CO, C₂H₄, or C₂H₂. For these reactant molecules, it was determined that the stoichio-

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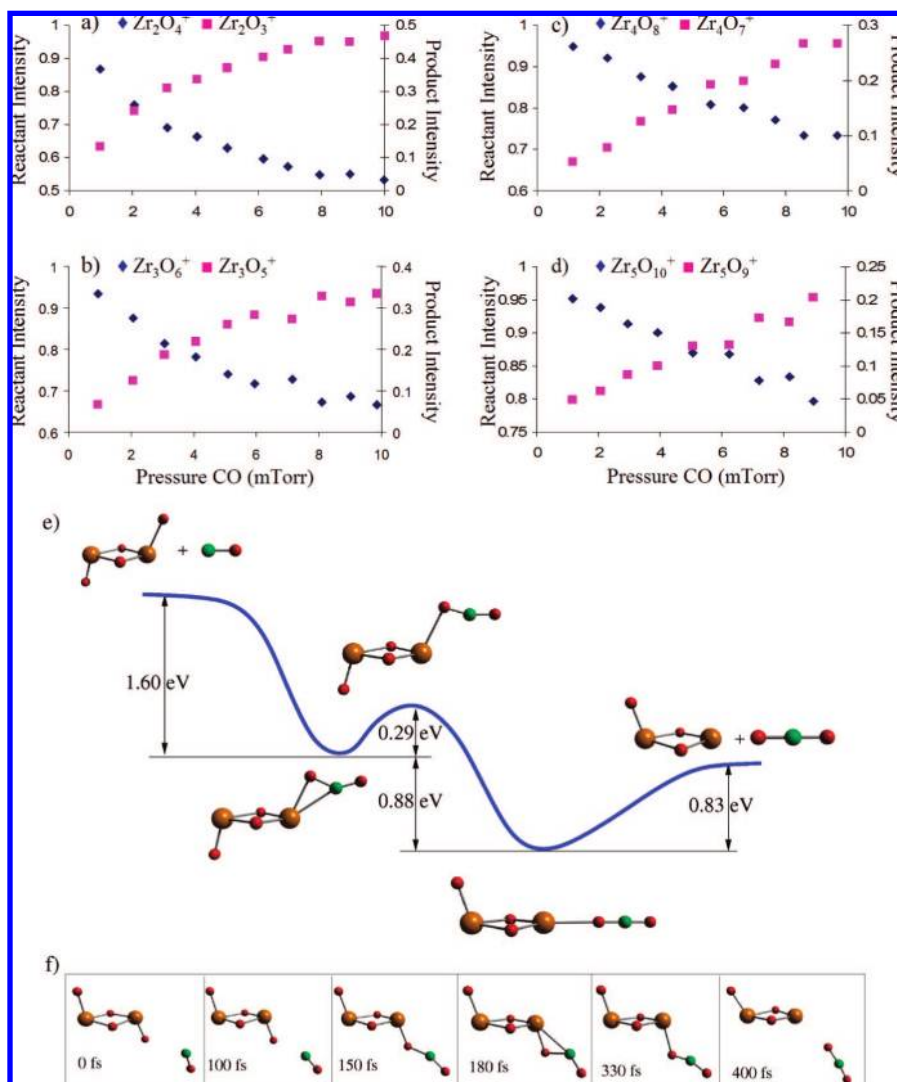


Figure 1. Normalized ion intensities of (a) $Zr_2O_4^+$, (b) $Zr_3O_6^+$, (c) $Zr_4O_8^+$, and (d) $Zr_5O_{10}^+$ with increasing pressure of CO. (e) Calculated energy profile for the reaction of $Zr_2O_4^+$ with CO. (f) Snapshots from MD simulations of the reaction of $Zr_2O_4^+$ with CO.

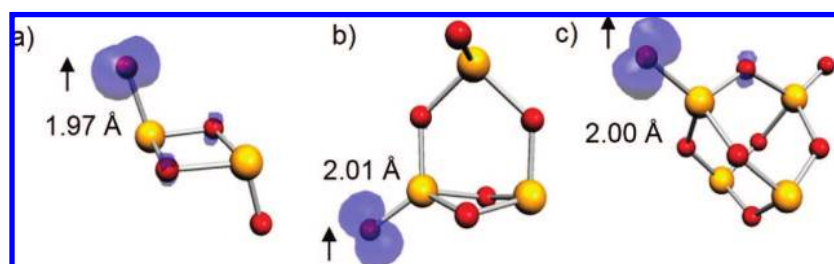
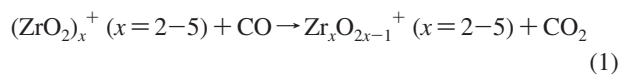


Figure 2. Calculated lowest energy structures for (a) $Zr_2O_4^+$, (b) $Zr_3O_6^+$, and (c) $Zr_4O_8^+$. The radical oxygen centers are indicated by an arrow. The blue isosurface indicates the localized spin density.

metric series of zirconium oxide clusters, $(ZrO_2)_x^+$ ($x = 1-4$), was the most active and selective toward the transfer of a single oxygen atom, suggesting the formation of CO_2 , C_2H_4O , and C_2H_2O , respectively.

Oxygen transfer products, which are proposed to result from the oxidation of CO to CO_2 according to eq 1,



were observed for stoichiometric zirconium oxide cations containing between two and five zirconium atoms. The results

of the reactivity experiments, displayed in Figure 1a–d, illustrate a decrease in the stoichiometric reactant ion intensity, $(ZrO_2)_x^+$ ($x = 2-5$), and a concomitant increase in the intensity of an oxygen transfer product $(Zr_xO_{2x-1})^+$ ($x = 2-5$) with higher concentrations of CO. While other zirconium oxide clusters revealed small oxygen transfer products with CO (approximately 0.03% of the total ion intensity at the maximum pressure of 10 mTorr of CO), it was only the cluster series with a $(ZrO_2)_x^+$ ($x = 2-5$) stoichiometry that exhibited enhanced oxidation reactivity (products equal to 20–50% of the total ion intensity at the maximum pressure of 10 mTorr of CO). The $Zr_2O_4^+$

cluster was found to have the most intense oxygen transfer product, accounting for approximately 50% of the total ion intensity at the maximum pressure of 10 mTorr of CO. The oxygen transfer products for the Zr_3O_6^+ , Zr_4O_8^+ , and $\text{Zr}_5\text{O}_{10}^+$ clusters were found to be roughly equivalent, accounting for around 25–30% of the total ion intensity at 10 mTorr of CO. No atomic oxygen loss products were observed for the $(\text{ZrO}_2)_x^+$ ($x = 2-5$) series of clusters in separate experiments with Xe, confirming that the $\text{Zr}_x\text{O}_{2x-1}^+$ products result from chemical reaction with CO and not collisional fragmentation. Minor products resulting from the association of CO onto the $(\text{ZrO}_2)_x^+$ ($x = 2-5$) reactant ions and charge transfer from the cationic clusters to CO were also observed but are not included in Figure 1a–d because of their negligible intensity compared to the primary oxygen transfer channel. To facilitate a qualitative comparison of the relative reactivity of Zr_2O_4^+ , Zr_3O_6^+ , Zr_4O_8^+ , and $\text{Zr}_5\text{O}_{10}^+$, the phenomenological rate constant at the average laboratory frame energy of 1 eV was calculated for each cluster assuming pseudo-first-order kinetics according to eq 2.

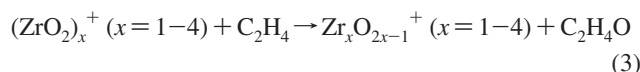
$$\ln\left[\frac{I_r}{I_0}\right] = -k[R]t \quad (2)$$

In eq 2, I_r is the reactant ion intensity with the addition of reactant gas, I_0 is the reactant ion intensity without reactant gas, k is the rate constant, R is the concentration of reactant gas, and t is the time it takes the reactant ion to pass through the octopole reaction cell. The reaction time may be calculated on the basis of the length of the reaction cell, which was determined using a trapezoidal pressure falloff approximation⁴⁵ to be 12.9 cm, and the velocity of the ions resulting from the supersonic expansion, which was determined using the equations of Anderson and Fenn.^{33,55} Therefore, the rate constant takes into account the larger amount of time spent in the reaction cell by heavier clusters because of their lower velocity. Previous studies in our laboratory showed that the pseudo-first-order rate constants obtained using eq 2 agree well with the phenomenological rate constants calculated from zero pressure cross section data.³³ Assuming pseudo-first-order kinetics, the slopes of the plots of $\ln[I_r/I_0]$ vs reactant gas concentration are equal to $-kt$. The values of the slopes, when divided by reaction time, reveal rate constants on the order of $2.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for Zr_2O_4^+ , $1.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for Zr_3O_6^+ , $1.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for Zr_4O_8^+ , and $6.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for $\text{Zr}_5\text{O}_{10}^+$. The phenomenological rate constants allow a better qualitative comparison of the relative reactivity of the different clusters than can be obtained from the normalized ion intensities in Figure 1a–d. The kinetic analysis confirms that Zr_2O_4^+ is the most reactive species and that the relative reactivity of the clusters decreases with increasing size from Zr_2O_4^+ to $\text{Zr}_5\text{O}_{10}^+$.

The calculated ground-state geometries of these clusters reveal the presence of a single radical oxygen center for Zr_2O_4^+ , Zr_3O_6^+ , and Zr_4O_8^+ , as depicted in Figure 2. Snapshots from the molecular dynamics simulations, shown in Figure 1f for Zr_2O_4^+ , illustrate that the oxidation reaction proceeds according to a general mechanism involving the initial binding of the carbon atom of CO to the radical oxygen where the zirconium–oxygen bond is elongated (1.97 Å). The calculated energy profile for the reaction, displayed in Figure 1e, shows that a $\text{Zr}_2\text{O}_4\text{CO}^+$ complex forms that is 1.60 eV lower in energy than the separated reactants. This complex, consisting of a CO molecule bound to the radical oxygen atom and the adjacent zirconium atom of the

cluster, then proceeds through a transition state that is 0.29 eV higher in energy. This transition state involves cleavage of the carbon–zirconium bond and formation of a weakly bound linear CO_2 subunit that is 2.48 eV lower in energy than the reactants. Cleavage of the zirconium–oxygen bond to form the products, Zr_2O_3^+ and CO_2 , requires 0.83 eV of energy. The calculated energy profile for the reaction demonstrates that the overall process is exothermic by 1.65 eV and that the barrier to oxidation is significantly lower in energy than the reactants. This general mechanism for the oxidation of CO applies for the entire series of stoichiometric clusters $(\text{ZrO}_2)_x^+$ ($x = 2-5$) because of the presence of a radical oxygen center in each of these species. The ground-state geometries of these clusters coincide with specific sites in the monoclinic phase of bulk zirconia. In particular, the Zr_2O_4^+ cluster has a very similar structure to a site in the monoclinic phase containing the same number of atoms. Consequently, our findings suggest that oxygen centers with radical character may be responsible for the oxidation of CO over bulk zirconia and, furthermore, indicate that a material assembled to contain such sites may result in a catalyst with greatly enhanced CO oxidation reactivity.

Products that are proposed to result from the transfer of oxygen to ethylene, according to eq 3,



were also observed for the stoichiometric $(\text{ZrO}_2)_x^+$ ($x = 1-4$) clusters as shown in Figure 3a–d. The reactivity experiments revealed a pronounced decrease in the stoichiometric reactant ion intensity accompanied by a significant increase in the oxygen transfer product with higher pressures of C_2H_4 . A channel corresponding to the association of ethylene onto each stoichiometric cluster was also observed. Minor products resulting from charge-transfer interactions with C_2H_4 were also observed but are not included in Figure 3a–d because of their negligible intensity compared to the primary oxygen transfer channel. The ZrO_2^+ , Zr_2O_4^+ , and Zr_4O_8^+ clusters were found to have oxygen transfer products accounting for approximately 25% of the total ion intensity at the maximum pressure of 10 mTorr of C_2H_4 . In contrast, the stoichiometric Zr_3O_6^+ cluster was observed to have an oxygen transfer product accounting for only 8% of the total ion intensity at the maximum pressure of 10 mTorr of C_2H_4 . A larger product channel corresponding to the association of C_2H_4 onto this cluster was also observed. To enable a qualitative comparison of the relative C_2H_4 oxidation reactivity of the $(\text{ZrO}_2)_x^+$ ($x = 1-4$) clusters, the phenomenological rate constants were calculated as described above for CO. The rate constants were determined to be on the order of $1.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for ZrO_2^+ and Zr_2O_4^+ , $3.1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for Zr_3O_6^+ , and $9.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for Zr_4O_8^+ . These results confirm that Zr_3O_6^+ is relatively less reactive toward the oxidation of C_2H_4 and that ZrO_2^+ , Zr_2O_4^+ , and Zr_4O_8^+ have comparable reactivity.

Theoretical investigations were undertaken to identify the oxygen transfer product ($\text{C}_2\text{H}_4\text{O}$), which could correspond to acetaldehyde, vinyl alcohol, or oxirane. The calculated energy profile and snapshots from molecular dynamics simulations, shown in Figure 3e,f, reveal that the oxidation reaction proceeds by the initial binding of the carbon atom of ethylene to the radical oxygen atom of Zr_2O_4^+ , resulting in an initial encounter complex that is 1.90 eV more stable than the separated reactants. Subsequently, a hydrogen atom is transferred from the oxygen

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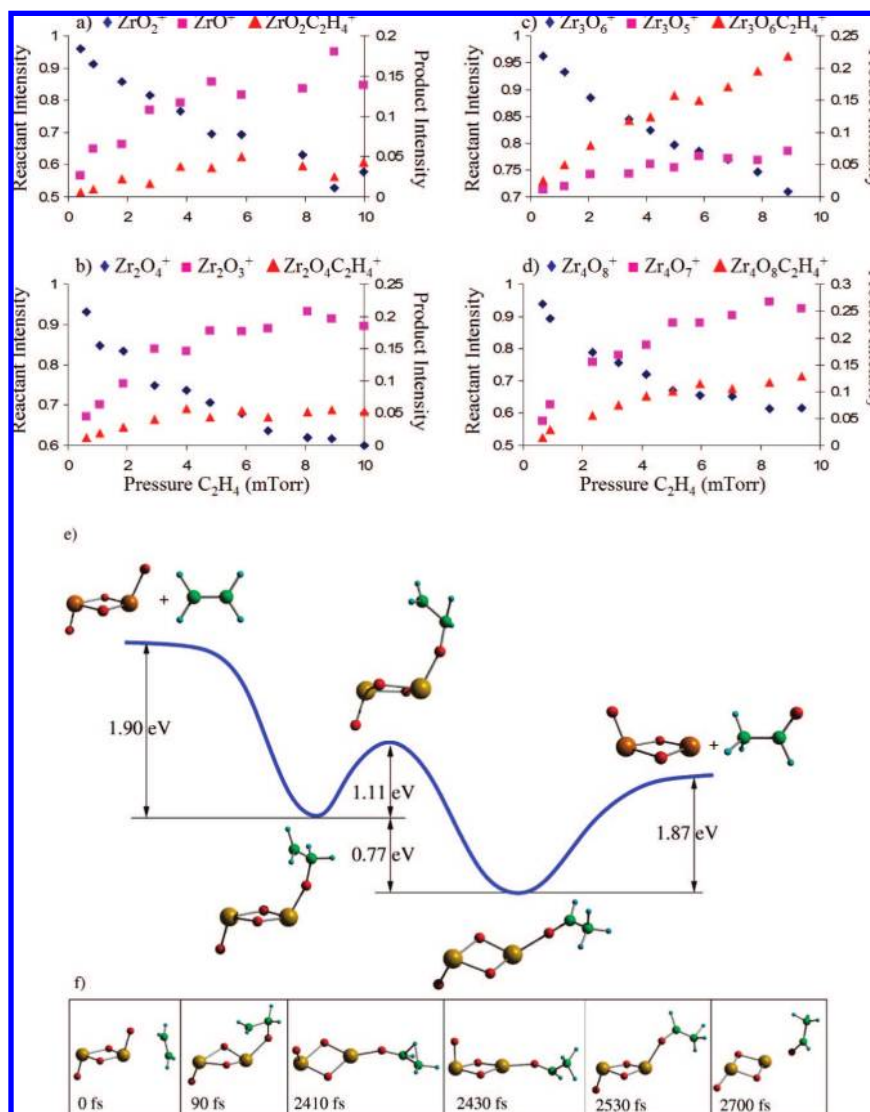
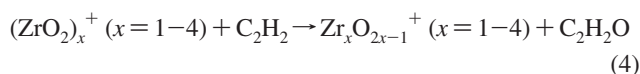


Figure 3. Normalized ion intensities of (a) ZrO_2^+ , (b) Zr_2O_4^+ , (c) Zr_3O_6^+ , and (d) Zr_4O_8^+ with increasing pressure of C_2H_4 . (e) Calculated energy profile for the reaction of Zr_2O_4^+ with C_2H_4 . (f) Snapshots from MD simulations of the reaction of Zr_2O_4^+ with C_2H_4 .

bound carbon atom to the other carbon atom of ethylene. This hydrogen transfer step involves a transition state that is higher in energy than the initial encounter complex by 1.11 eV and results in a species with an acetaldehyde molecule bound to the cluster that is 2.67 eV more stable than the reactants. Cleavage of the zirconium–oxygen bond resulting in the Zr_2O_3^+ cluster and acetaldehyde requires 1.87 eV of energy. The overall process, therefore, is calculated to be exothermic by 0.80 eV. These findings concerning ethylene suggest that radical oxygen centers may promote the oxidation of doubly bonded hydrocarbons on zirconium-based catalysts. Moreover, an assembly of clusters containing these sites may result in a catalyst with extremely high selectivity toward the production of acetaldehyde, which is energetically the most favorable oxidation channel. In a bulk catalytic material, however, further oxidation of acetaldehyde to CO or CO_2 at an adjacent radical oxygen center may occur, thereby reducing the overall selectivity.

The experimental reactivity studies also suggest that the production of $\text{C}_2\text{H}_2\text{O}$ through the oxidation of acetylene according to eq 4



is extremely favorable for the stoichiometric series of clusters as shown in Figure 4a–d. The results show that the oxygen transfer product is very pronounced for each cluster in the series. A minor channel resulting from the association of intact acetylene onto Zr_3O_6^+ and Zr_4O_8^+ was also observed. Significant C_6H_6^+ products resulting from the cyclotrimerization of acetylene into benzene^{56–58} accompanied by a charge-transfer interaction were also observed for ZrO_2^+ and Zr_2O_4^+ . C_6H_6^+ products are not shown in Figure 4a,b as the focus of this publication is on the primary oxygen transfer reactions. This product was much less pronounced for Zr_3O_6^+ and Zr_4O_8^+ . In addition, minor products resulting from charge-transfer interactions with C_2H_2 were found but are not included in Figure 4a–d because of their negligible intensity compared to the primary oxygen-transfer channel. The Zr_4O_8^+ cluster exhibited the largest oxygen-transfer product accounting for around 70% of the total ion intensity at the maximum pressure of 10 mTorr of C_2H_2 . The Zr_2O_4^+ and Zr_3O_6^+ clusters were observed to have

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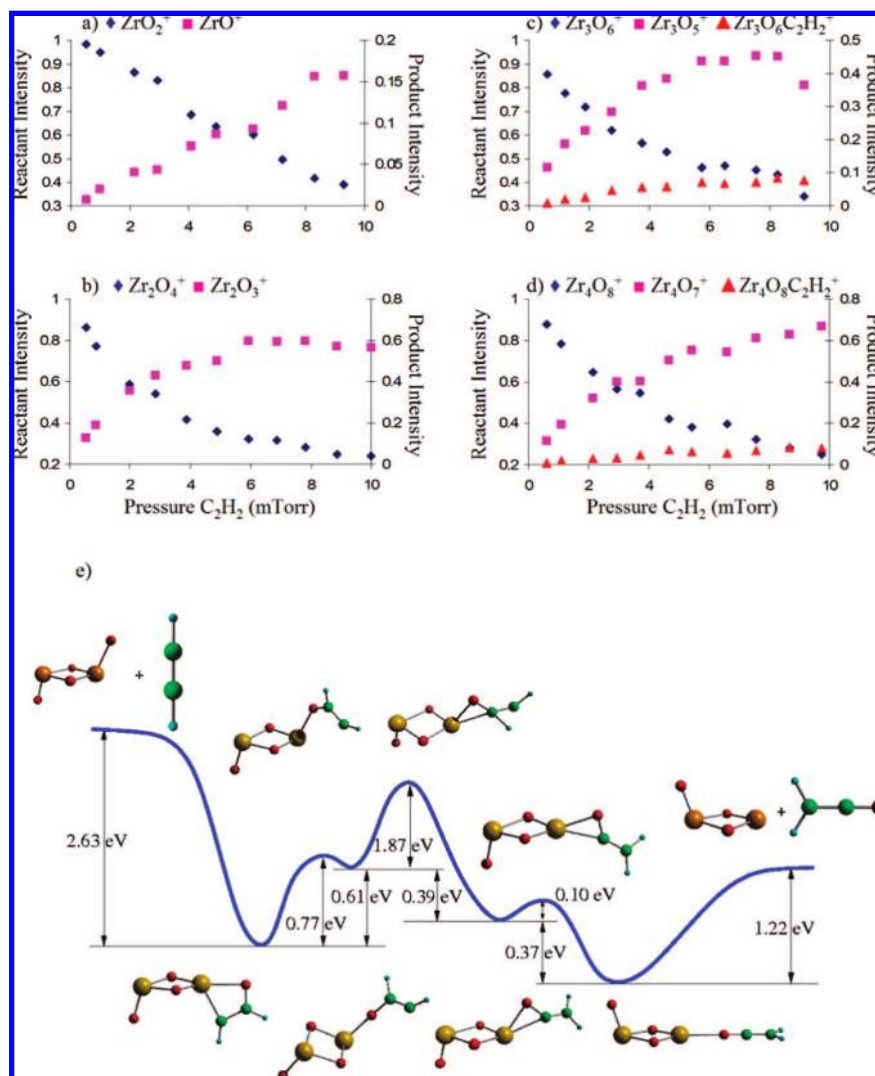


Figure 4. Normalized ion intensities of (a) ZrO_2^+ , (b) $Zr_2O_4^+$, (c) $Zr_3O_6^+$, and (d) $Zr_4O_8^+$ with increasing pressure of C_2H_2 . (e) Calculated energy profile for the reaction of $Zr_2O_4^+$ with C_2H_2 .

comparable oxygen-transfer products, while that for ZrO_2^+ was found to be relatively less intense. Using the pseudo-first-order kinetics method described above for CO, the phenomenological rate constants for the oxidation of C_2H_2 were determined to be approximately $1.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for ZrO_2^+ , $5.9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for $Zr_2O_4^+$, $2.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for $Zr_3O_6^+$, and $4.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for $Zr_4O_8^+$. Therefore, despite the fact that the oxygen-transfer product is more intense for $Zr_4O_8^+$ than for $Zr_2O_4^+$ at the same pressure of C_2H_2 , because $Zr_4O_8^+$ is heavier and spends more time in the octopole reaction cell, the rate constant for $Zr_2O_4^+$ is calculated to be larger. The rate constants also indicate an odd–even oscillation in C_2H_2 oxidation reactivity with increasing cluster size.

The calculated energy profile reveals that the reaction proceeds through the strong binding of one carbon atom of acetylene to the radical oxygen center of $Zr_2O_4^+$ and the other carbon to the adjacent zirconium atom, as shown in Figure 4e. The initial encounter complex is 2.63 eV more stable than the separate reactants. Subsequently, the carbon zirconium bond is broken by way of a transition state that is 0.77 eV higher in energy than the initial encounter complex. The resulting complex has a linear zirconium–oxygen–carbon subunit and is 2.02 eV more stable than the reactants. In the next step, a hydrogen atom is transferred from the oxygen-bound carbon atom to the other

carbon atom of acetylene, involving a transition state that is 1.87 eV higher in energy. The ensuing complex, consisting of a bent ethenone molecule bound to the $Zr_2O_3^+$ cluster, is 2.42 eV more stable than the reactants. Following the hydrogen-transfer step, cleavage of the zirconium carbon bond occurs through a transition state that is 0.10 eV higher in energy and results in a complex with a linearly bound ethenone molecule that is 2.79 eV more stable than the reactants. Finally, dissociation of the zirconium oxygen bond to form ethenone and $Zr_2O_3^+$ requires 1.22 eV of energy. The overall process is calculated to be exothermic by 1.57 eV. The oxidation of triply bonded hydrocarbons at radical oxygen centers in zirconium oxides, therefore, is extremely favorable. These findings suggest that a material assembled to contain a large proportion of such sites may be highly active for the oxidation of alkynes.

Experiments were also conducted to determine whether the $(ZrO_2)_x^+$ ($x = 1-4$) series of clusters are capable of transferring an oxygen atom to alkanes as well as alkenes and alkynes. Specifically, the clusters were reacted with methane (CH_4) and ethane (C_2H_6). In both cases, no oxygen transfer products were observed. It is possible that hydrogen abstraction may occur at the radical oxygen centers, as shown previously by Feyel and co-workers^{35,37} for $V_4O_{10}^+$ and oligomers of $Al_2O_3^+$. Unfortunately, because of the isotope distribution of zirconium and

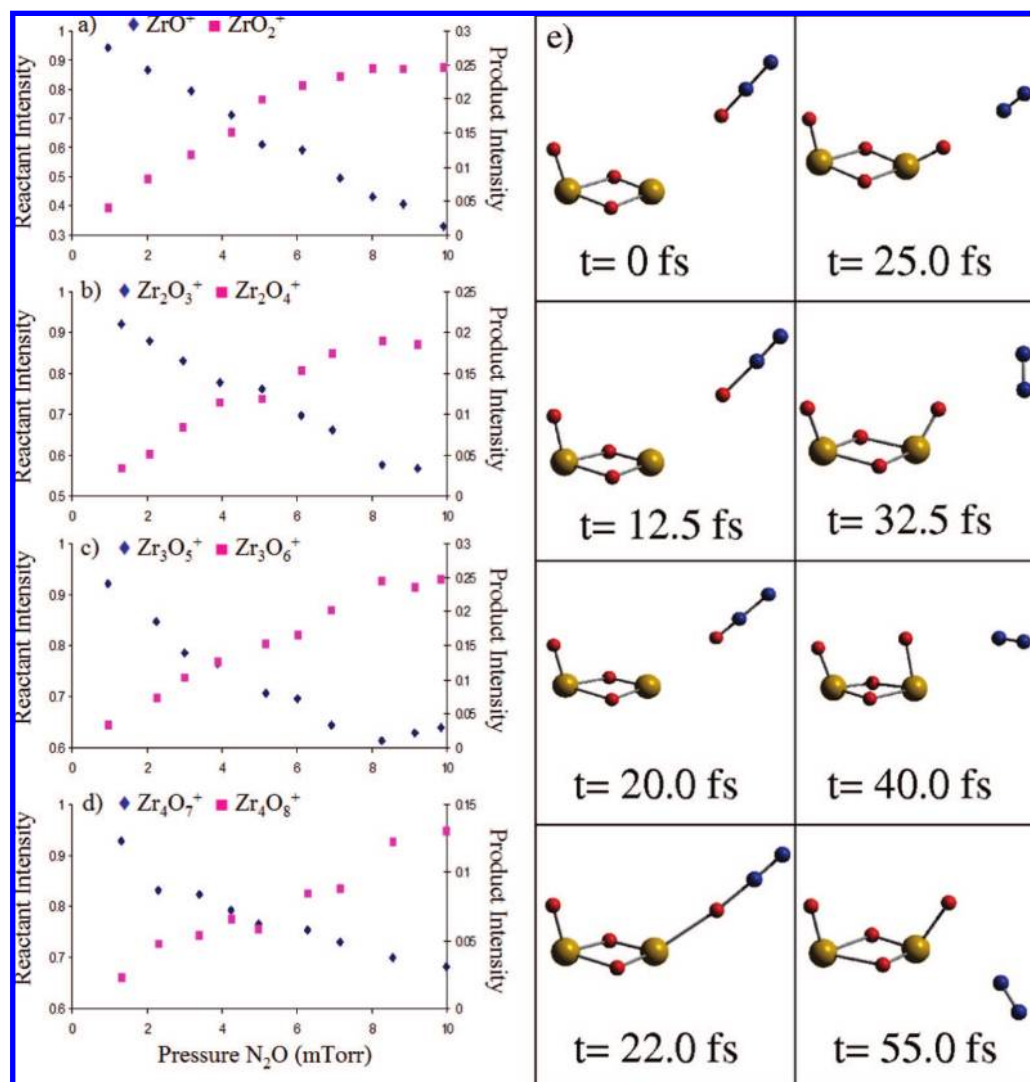
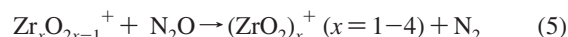


Figure 5. Normalized ion intensities of (a) ZrO^+ , (b) $Zr_2O_3^+$, (c) $Zr_3O_5^+$, and (d) $Zr_4O_7^+$ with increasing pressure of N_2O . (e) Snapshots from MD simulations of the reaction of $Zr_2O_3^+$ with N_2O .

limitations on mass resolution, we were unable to experimentally identify any such reactions. Consequently, theoretical investigations were not undertaken to examine hydrogen abstraction from alkanes for the $(ZrO_2)_x^+$ ($x = 1-4$) series of clusters.

While the oxidation of CO, C_2H_4 , and C_2H_2 by stoichiometric zirconium oxide cations constitutes a novel finding with ramifications for heterogeneous oxidation catalysis, these reactions only account for half of a complete catalytic cycle. After these stoichiometric clusters have oxidized a particular molecule, it is critical that the active site be regenerated so that a material assembled from these species will have a reasonable catalytic lifetime. To determine whether the oxygen-deficient product clusters, $Zr_xO_{2x-1}^+$ ($x = 1-4$), may be oxidized back to the original active stoichiometry, these clusters were reacted with N_2O , which has a particularly weak N_2-O bond. We selected N_2O , rather than O_2 , because we wanted to investigate whether it was possible to selectively add a single oxygen atom to the $Zr_xO_{2x-1}^+$ ($x = 1-4$) clusters. The reactivity of the oxygen-deficient clusters with N_2O is displayed in Figure 5a–d. As the pressure of N_2O gas is increased, the intensity of the oxygen-deficient clusters decreases and a strong oxygen addition product $(ZrO_2)_x^+$ ($x = 1-4$) is observed. This suggests the production

of the active stoichiometric clusters from oxygen deficient species according to eq 5.



Minor products resulting from the oxidative degradation of the oxygen-deficient clusters into smaller zirconium oxide units were also observed but are not included in Figure 5a–d because of their negligible intensity compared to the dominant oxygen addition product. Again, using the pseudo-first-order kinetics method described above, we calculated the phenomenological rate constants for the oxidation of each oxygen-deficient cluster to the active stoichiometric species. The rate constants were determined to be approximately $2.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for ZrO^+ , $1.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for $Zr_2O_3^+$, $1.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for $Zr_3O_5^+$, and $4.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for $Zr_4O_7^+$. Therefore, the phenomenological rate constants for the regeneration of the oxygen radical centers are comparable to the rate constants for the oxidation of CO, C_2H_4 , and C_2H_2 .

Snapshots from the MD simulation of the oxidation of $Zr_2O_3^+$ to $Zr_2O_4^+$ by N_2O are shown in Figure 5e. The experimental data and theoretical calculations indicate that the oxygen-deficient clusters may be oxidized to the stoichiometric species that show enhanced oxidation reactivity with CO, C_2H_4 , and

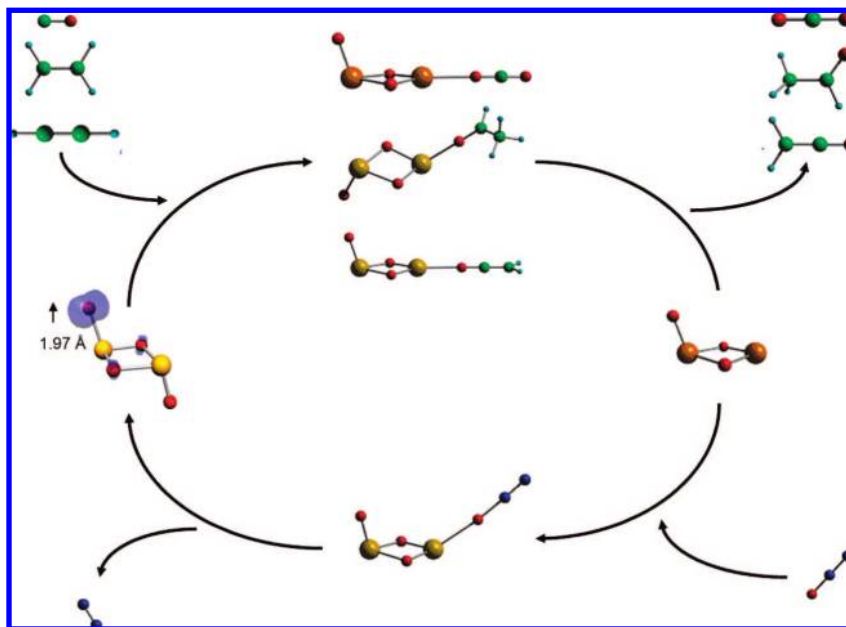


Figure 6. Schematic representation of the full catalytic cycle involved in the oxidation of CO, C₂H₄, and C₂H₂ with subsequent regeneration of the active stoichiometric species with N₂O.

C₂H₂. These findings, therefore, indicate that a material assembled to contain a large concentration of radical oxygen centers may indeed behave like a true catalyst and promote repeated oxidation cycles as shown schematically in Figure 6.

Recent studies showed that it is possible to fabricate cluster assembled materials, including model catalytic systems, through the controlled deposition of size-selected clusters.^{59–61} Employing low-energy deposition techniques, several researchers successfully deposited relatively monodisperse clusters onto surfaces and studied their size and structure-dependent chemical behavior.⁵⁹ Furthermore, through optimization of cluster–cluster and cluster–surface interactions, Tainoff and co-workers recently obtained a well-organized array of platinum clusters on a graphite surface.⁶¹ These developments suggest that with a carefully prepared substrate, ideally an insulator containing surface defects with high electron affinity, it may be possible to deposit gas-phase stoichiometric zirconium oxide clusters and retain the active radical oxygen centers.

Our findings also have conceptual ramifications for bulk-phase heterogeneous oxidation catalysts. Radical oxygen centers have been proposed to be responsible for the selective oxidation of a variety of industrially relevant molecules over bulk-phase molybdena and vanadia catalysts.⁶² Furthermore, it has been shown that, by doping metal oxides such as MgO with an element such as Li that has one less valence electron, it is possible to generate radical oxygen centers in bulk metal oxides.^{63,64} On the basis of these previous findings, we propose

that by doping neutral stoichiometric zirconium oxide clusters (ZrO₂)_x with a metal containing one less valence electron (i.e., Y or Sc) it may be possible to generate neutral metal oxide clusters with localized radical oxygen centers. These clusters would be expected to have catalytic properties closely resembling the cationic stoichiometric zirconium oxide clusters discussed in this publication. Therefore, they may serve as active sites for the selective oxidation of CO to CO₂, ethylene to acetaldehyde, and acetylene to ethenone.

Conclusions

Gas-phase cluster reactivity experiments indicate that a distinct series of stoichiometric cationic zirconium oxide clusters (ZrO₂)_x⁺ ($x = 1–4$) are active toward the transfer of an oxygen atom to CO, C₂H₄, and C₂H₂. Theoretical investigations reveal that the enhanced reactivity of these clusters can be attributed to a radical oxygen center with an elongated zirconium–oxygen bond. The presence of this reactive center, combined with favorable energetics for each reaction, suggests that positively charged, stoichiometric zirconium oxides are potential candidates for incorporation into a cluster assembled material that would be highly active for three industrially important oxidation reactions. Furthermore, because these active stoichiometric species can be regenerated from oxygen-deficient clusters using a suitable oxidizing agent, such a material may potentially promote repeated catalytic cycles. On the basis of these findings, we propose that through an assembly of selected clusters it may be feasible to create a catalytic material with strong activity toward a particular desired product.

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