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Citation: The Journal of Chemical Physics 139, 194313 (2013); doi: 10.1063/1.4830406
View online: http://dx.doi.org/10.1063/1.4830406
View Table of Contents: http://aip.scitation.org/toc/jcp/139/19
Published by the American Institute of Physics
Generation and reactivity of putative support systems, Ce-Al neutral binary oxide nanoclusters: CO oxidation and C–H bond activation

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(Received 4 September 2013; accepted 30 October 2013; published online 21 November 2013)

Both ceria (CeO2) and alumina (Al2O3) are very important catalyst support materials. Neutral binary oxide nanoclusters (NBONCs), Ce2Al2O5, are generated and detected in the gas phase and their reactivity with carbon monoxide (CO) and butane (C4H10) is studied. The very active species CeAlO4• can react with CO and butane via O atom transfer (OAT) and H atom transfer (HAT), respectively. Other Ce2Al2O5 NBONCs do not show reactivities toward CO and C4H10. The structures, as well as the reactivities, of Ce2Al2O5 NBONCs are studied theoretically employing density functional theory (DFT) calculations. The ground state CeAlO4• NBONC possesses a kite-shaped structure with an O3CeO6bAlO configuration (Ot, terminal oxygen; Ob, bridging oxygen). An unpaired electron is localized on the Ot atom of the AlO moiety rather than the CeO moiety; this Ot centered radical moiety plays a very important role for the reactivity of the CeAlO4• NBONC. The reactivities of Ce2O4, CeAlO4•, and Al2O3 toward CO are compared, emphasizing the importance of a spin-localized terminal oxygen for these reactions. Intramolecular charge distributions do not appear to play a role in the reactivities of these neutral clusters, but could be important for charged isoelectronic BONCs. DFT studies show that the reaction of CeAlO4• with C4H10 to form the CeAlO4H•C4H9• encounter complex is barrierless. While HAT processes have been previously characterized for cationic and anionic oxide clusters, the reported study is the first observation of a HAT process supported by a ground state neutral oxide cluster. Mechanisms for catalytic oxidation of CO over surfaces of Al2O3/MnOx or MnOx/Al2O3 materials are proposed consistent with the presented experimental and theoretical results. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4830406]

I. INTRODUCTION

Ceria (CeO2) is one of the most abundant rare earth oxides and has been extensively studied over the past decades.1–4 Ceria is mostly used as a catalyst support material: it helps to improve mechanical and thermal stability, as well as activity and selectivity of transition, noble, and rare earth metal oxide catalysts.5,6 For example, ceria containing catalysts have been used in “three-way” catalytic converters,7,8 solid oxide fuel cells,8–11 and water splitting processes for hydrogen production.12–14 These catalysts exhibit electrical conductivity and induce the formation of small polarons on the surfaces.15–18 Aluminum oxides are also often used as supporting materials: they serve as a catalyst support for many industrial catalysts, such as those used in hydrodesulfurization, as well as other applications.19–22 Al2O3 is also one of the most active catalysts for D/H exchange in mixtures of D2/CH4 and CH4/CD4; various aspects of C–H bond activation processes have been extensively studied for γ-Al2O3.23–26 Quite recently, the reactive sites of γ-Al2O3 have been identified in a combined experimental/computational study, which has found that the presence of a moderate coverage with water increases the number of reactive nonadjacent Al–O Lewis acid base pairs.24,25

More recent studies focus on preparing nanomaterials of ceria and alumina to improve catalytic performance by increasing the distribution of surface defects, vacancies, or “active sites.”27–35 New applications are being explored by employing nanotechnology; e.g., vacancy engineered ceria nanostructures for protection from radiation-induced cellular damage and the neuro-protection offered by the auto-catalytic ceria nanoparticles.29,31,36 The concept of preparing nanomaterials is to increase the surface to volume ratio and thereby increase the “active sites”; however, existing information on the precise nature and detailed operation of the active sites is still rather limited for many catalytic systems, even on the nanoscale.37–39

Gas phase nanoclusters in an “isolated” environment are ideal model systems with which to simulate real surface reactions and to discover surface reaction mechanisms.37,39,40 Many excellent studies have been reported in the last decade with regard to the structure and reactivities of gas phase cationic37,38,41–63 and anionic42,64–79 oxide nanoclusters. Recently, He et al. reported systematic studies on the reactions of CeB2O2m+ and CeB2m+ clusters with CO and small hydrocarbons: they found very significant and interesting size-dependent reactivities under near room-temperature conditions.80–82 The groups of Wang and Jarrold performed detailed spectroscopic studies on aluminum oxide clusters.76,83–87 Rather interesting reactivity trends are reported by the Schwarz and Castleman groups for oxidation

[Image 485x760 to 535x781]
reactions generated by Al₂O₃⁺,¹⁵¹,⁸⁸,⁸⁹ and methane activation by the oxygen-rich Al₂O₃⁺ cluster suggests the importance and influence of chemically absorbed O₂ for the C–H bond activation reaction.¹⁵² Other studies of gas phase cerium and aluminum oxide ionic clusters can be found in Refs. ⁹⁰ and ⁹¹.

A number of studies of neutral oxide nanoclusters (NONCs) in both matrix⁹²–⁹⁵ and in the gas phase⁹⁶–⁹⁹–¹¹⁶ have also appeared. Employing neutral oxide nanoclusters for the study of catalytic processes is advantageous, as it minimizes the effect of cluster charge, which has been considered to be significant with regard to cluster reactivity.⁵⁰,¹¹⁷,¹¹⁸ On the other hand, NONCs often have high vertical ionization energies (>8 eV) and multiphoton ionization with a 10 ns Nd³⁺/YAG laser pulse can cause significant cluster fragmentation so as to confuse the mass spectra for reactant and product identification.¹¹⁵,¹¹⁹ Recently, our group has developed a novel 118 nm, single-photon ionization (SPI) technique, which has proved to be reliable for detecting the distribution and reactivity of NONCs without dissociation.¹¹²,¹¹⁶ Many gas phase NONCs and their reactivities have been studied in recent years (e.g., reactions of vanadium, cobalt, iron, manganese, and tantalum containing NONCs with CO¹⁰⁰,¹⁰⁵,₉⁷,₁₀⁴,₁⁰⁶ ethyne,¹⁰⁸ butane,⁹⁷₈ sulfur dioxide,¹⁰⁷ ammonia,⁹⁹,¹⁰² and methane¹⁰³). These cluster studies yield an understanding of the corresponding real catalytic systems and enable one to propose a full catalytic cycle at the molecular level for the bulk catalytic system.

In the last few years, the study of binary oxide nanoclusters (BONCs) has been reported for ionic systems. These cluster systems can serve as a more detailed molecular approach for the understanding of the active sites in catalytic supports and modified catalytic systems.⁴⁶,⁴⁸,⁴⁹,⁶⁵,¹¹⁷,¹²⁰–¹²⁶ The first example of generating, as well as studying, the reactivity of BONCs is reported by He and co-workers: they proposed that the novel AlVO₄⁺ cluster can activate CH₄ oxidation at room temperature.⁴⁹ Additionally, Schwarz and co-workers and He and co-workers report that CH₄ is activated by V₂PO₁₀⁺.¹²¹,¹²⁴ The Schwarz group also illustrated the first complete gas phase catalytic cycle conducted by the AlVO₃⁺/AlVO₄⁺ BONC couple through both experimental and theoretical studies.⁴⁸ Sauer, Asmis, and co-workers studied the infrared spectroscopy of CeVO₄⁺, Ce₂V₂O₇⁺, and Ce₂VO₅⁺ BONCs for the first time, indicating interesting structures parallel to the condensed phase VO₃/VO₂ supported materials.⁴⁶ They also reported enhanced SO₂ chemical absorption abilities via doping V₂O₁₀⁺ cluster with Ti: the enhanced reactivity of V₂TiO₁₀⁺ is attributed to charge localization on the outer oxygen atom that binds with the titanium atom. The presence of a free Ti=O⁺ (O⁺: terminal oxygen) radical in V₂TiO₁₀⁺ allows binding of a second SO₂.¹²⁷ The initial studies of the photoelectron spectroscopy of anionic BONCs are reported by Jarrold and co-workers, whose group investigated the electronic structures of the MoWO₃⁻ BONCs as well as other Mo or Al related BONCs.¹²⁸–¹³⁵ Zheng et al. reported the photoelectron spectroscopy of MAIO₃⁻ and M₂AlO₂⁻ (M = Ti or V; x = 1, 2, or 3) BONCs.⁶⁵,¹²⁵ Studies of BONC ions are becoming increasingly widespread: e.g., AuNbO₄⁺,¹³⁶ V₂Ag₂O₆⁺ (x = 1–4, y = 1–4, z = 3–11),¹³⁷ Al₂V₀₁₀⁻,¹²₃ V₂,Y₂O₇⁺,¹³⁷ V₂P₂O₇⁺,¹³⁸–¹⁴⁰ and AlVO₃⁺.⁸⁹,¹⁴¹ All the above systems are charged BONCs. Our group has extended BONC studies to neutral systems: in particular, neutral V₃Co₃O₁₀ BONCs are generated in the gas phase and their reactivity toward CO is determined.¹⁰⁰

Both ceria and alumina are very important catalyst support materials. The gas-phase ionic Ce- or Al-relating oxide nanoclusters have been extensively studied. In the current work, we generate and detect Ce₃Al₂O₇ neutral binary oxide nanoclusters (NBONCs) in the gas phase, and explored their reactivity with CO and butane. The very active NBONC species CeAlO₄⁺* can react with CO and butane via O atom transfer (OAT) and H atom transfer (HAT) reactions, respectively. Structures, as well as the reactivities, of the Ce₃Al₂O₇ NBONCs are studied theoretically employing density functional theory (DFT) calculations. The influence of spin distribution and charge effect is considered for the reactivities. An ideal reaction mechanism on the solid surface of supported (e.g., CeO₂) aluminum oxide, and aluminum oxide containing other oxide catalytic materials, is proposed according to the presented experimental and theoretical results.

II. EXPERIMENTAL AND THEORETICAL METHODS

The experimental setup for laser ablation coupled with a fast flow reactor employed in this work has been described previously in detail:⁹⁹,¹⁰¹–¹⁰⁶,¹⁰⁸,¹¹⁴,¹¹⁶,¹⁴²,¹⁴³ only a brief outline of the apparatus is given below. Ce₃Al₂O₇ clusters are generated by laser ablation of either a mixed metal target in the presence of ~1% O₂ seeded in a pure helium carrier gas (99.99%, General Air). The target is a pressed mixture of Ce (99%, Sigma Aldrich) and Al (99.0+%, Sigma Aldrich) powders (molar ratio = 1:1). A 10 Hz, focused, 532 nm Nd³⁺/YAG laser (Nd³⁺: yttrium aluminum garnet) with 10 mJ/pulse energy is used for the laser ablation. The expansion gas is pulsed into the vacuum by a supersonic nozzle (R. M. Jordan, Co.) with a backing pressure of typically 75 psi. Generated oxide clusters react with reactants in a fast flow reactor, which is directly coupled to the cluster generation channel. The reactant gases, CO (99.9% Sigma Aldrich), butane (99.0% Sigma Aldrich), and D-labeled butane (C₄D₁₀, 99.0% Sigma Aldrich) are used as purchased, at a 15 psi backing pressure, and injected into the reactor by a pulsed General Valve (Parker, Serial 9). The reactants and products are estimated to be thermalized to 300–400 K by collisions in the generation channel and the reaction cell. An electric field is placed downstream of the reactor in order to remove any residual ions from the molecular beam. The beam of neutral reactants and products is skimmed into a differentially pumped chamber and ionized by a separated VUV laser beam (118 nm, 10.5 eV/photon). The 118 nm laser light is generated by focusing the third harmonic (355 nm, ~30 mJ) of a Nd³⁺/YAG laser in a tripling cell that contains about a 250 Torr argon/xenon (10/1) gas mixture. A MgF₂ prism (Crystaltechno LTD, Russia, 6° apex angle) is placed in the laser beam to enhance separation of the generated 118 nm laser beam from the defocused 355 nm input laser beam.
After the near threshold ionization, photoions are detected by a time of flight mass spectrometer (TOFMS).

DFT calculations are done using the Gaussian 09 program,\textsuperscript{144} employing the hybrid B3LYP exchange-correlation functional\textsuperscript{145–147} with the unrestricted Kohn–Sham solution.\textsuperscript{148} The triple-zeta basis sets with Stuttgart/Dresden relativistic effective core potentials, 28 electrons in the core, denoted as SDD\textsuperscript{149–152} in Gaussian 09 are adopted for Ce and the TZVP basis sets\textsuperscript{153} for other atoms. For the optimization of transition structures (TS), we employed either the Benny algorithm\textsuperscript{154} or the synchronous transit guided quasi-Newton (STQN) method.\textsuperscript{155} For most cases, initial approximate structures of the transition structures are obtained by relaxed potential energy surface (PES) scans using an appropriate internal coordinate. Vibrational frequencies are calculated to characterize the nature of the stationary points as minima or transition structures; the relative energies (given in eV) are corrected for zero point energy (ZPE) contributions. Intrinsic reaction coordinate (IRC) calculations\textsuperscript{156–158} are also performed to connect transition states (TS) with local minima. Test calculations indicate that basis set superposition error (BSSE) is negligible for these systems and thus it is not taken into account in this study.

III. RESULTS AND DISCUSSION

Figure 1 shows the distribution of Ce-Al NBONCs within the mass range of 150 < m/z < 670, detected by 118 nm SPI time of flight mass spectrometry (TOFMS). The distribution is generated by laser ablation of a pressed Ce/Al metal disk with 0.5% O\textsubscript{2} seeded in helium carrier gas. The series Ce\textsubscript{x}Al\textsubscript{y}O\textsubscript{z}, e.g., CeAl\textsubscript{3}O\textsubscript{4}, CeAl\textsubscript{2}O\textsubscript{6}, CeAl\textsubscript{3}O\textsubscript{6}, Ce\textsubscript{2}Al\textsubscript{3}O\textsubscript{7}, Ce\textsubscript{2}Al\textsubscript{2}O\textsubscript{6}, Ce\textsubscript{2}Al\textsubscript{3}O\textsubscript{7}, Ce\textsubscript{2}Al\textsubscript{2}O\textsubscript{7}, Ce\textsubscript{2}Al\textsubscript{4}O\textsubscript{10}, and Ce\textsubscript{2}Al\textsubscript{5}O\textsubscript{9} can be observed. The efficiencies of ionization for observed clusters under 118 nm VUV laser are estimated to be roughly the same.

The reaction of Ce-Al NBONCs with CO is shown in Figure 2. The intensity of the signal for CeAl\textsubscript{4} increases and that for CeAl\textsubscript{2} increases, if CO is added to the fast flow reaction cell, due to the reaction

\[
\text{CeAl}_{2}\text{O}_{4} + \text{CO} \rightarrow \text{CeAl}_{2}\text{O}_{4}^{+} + \text{CO}_{2} \Delta E = -1.35 \text{ eV.} \tag{1}
\]

This reaction is exothermic according to DFT calculations (\(\Delta E\), zero-point energy corrected reaction enthalpy at 0 K). The first order rate constant (\(k\)) in the fast flow reactor can be estimated by using the following equation:\textsuperscript{9,105}

\[
I = I_{0} \exp(-k\rho l/v), \tag{2}
\]

in which \(I\) and \(I_{0}\) are signal magnitudes for the clusters in the presence and absence of reactant gas, respectively; \(\rho\) is the molecular density of reactant gas; \(l\) is the effective path length of the reactor; and \(v\) is the cluster beam velocity. The estimated rate constant for reaction (1) is on the order of $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ according to our experimental results, with the estimated reaction-collisional efficiency of 4% (±50% uncertainty).

The other nanoclusters, such as homonuclear CeO, CeO$_2$, Ce$_2$O$_4$, Al$_4$O$_6$ or heteronuclear NBONCs, such as CeAl$_3$O$_5$, do not show evidence reactions with CO, which means that their reaction rate constants are lower than the observation limit of $10^{-13}$ cm$^3$ molecul$^{-1}$ s$^{-1}$. As for most catalysts, only certain localized sites (often thought as defects in surface structure) are considered to be active catalytic species. We proffer that CeAl$_4$ is one such site, if not the only one: while others may exist, they are not amongst the observed unreactive species found in these experiments. Active catalytic surface sites should have structures, both electronic and geometric, similar to that found for CeAl$_4$.

Figure 3 shows the generation and reaction of gas phase Ce-Al NBONCs with butane (\(\text{C}_4\text{H}_{10}\)) and D-labeled butane (\(\text{C}_4\text{D}_{10}\)). Of the clusters generated employing a Ce/Al mixed target, again CeAl$_4$ is the only species observed to react with \(\text{C}_4\text{H}_{10}\) to generate the HAT products CeAl$_4$H and \(\text{C}_4\text{H}_6\) (Figure 3(b)),

\[
\text{CeAl}_{2}\text{O}_{4} + \text{C}_4\text{H}_{10} \rightarrow \text{CeAl}_{2}\text{O}_{4}\text{H} + \text{C}_4\text{H}_6. \tag{3}
\]
Reaction (3) is further demonstrated if C$_4$D$_{10}$ is employed for the reaction, in which case the product CeAlO$_4$$^•$ is observed (Figure 3(c)). The mass spectrum is very sensitive to experimental conditions, and the three spectra in Figure 3 are recorded at well controlled “identical” conditions except for the introduction of reactant gas for the lower two spectra. The experimental results shown in Figure 3 are highly repeatable. A HAT product is not observed for CH$_4$ or C$_2$H$_6$ introduced into the reaction cell as the reactant gas.

DFT optimized low energy isomers of CeAlO$_3$$^•$ and CeAlO$_4$$^•$ are shown in Figure 4. The diameters of the isomers are estimated to be around 0.5 nm. The lowest energy CeAlO$_3$$^•$ (1) is in a doublet state with Cs point group symmetry and a kite-shaped O$_t$Ce(O$_b$)$_2$Al structure (O$_t$, terminal oxygen; O$_b$, bridging oxygen). This structure is similar to that for neutral V$_2$O$_3$ or CoVO$_3$$^•$ clusters, substituting Al for V or Co at the two oxygen coordinated position and Ce for V at the three oxygen coordinated position, respectively. The CeAlO$_3$$^•$ (2) isomer with the Ce(O$_b$)$_2$AlO$_t$ structure is only about 0.25 eV higher in energy. The energies of other CeAlO$_3$$^•$ isomers are much higher than O$_t$Ce(O$_b$)$_2$AlO$_t$ (1). For example, the energies of O$_t$Ce(O$_b$)$_2$AlO$_t$ (3) and Ce(O$_b$)$_3$AlO$_t$ (4) isomers are 0.85 and 0.92 eV higher than ground state structure, respectively (see Figure 4 for details). Among isomers of CeAlO$_4$$^•$, the one with one Ce = O$_t$ and one Al–O$_t$ terminal bond is identified to be the ground state CeAlO$_4$$^•$ (5). The energies of other CeAlO$_4$$^•$ isomers are much higher than that of the ground state CeAlO$_4$$^•$ (5). Note that the unpaired electron is localized not on the rare earth metal centered Ce = O$_t$, but on the main-group metal centered Al-O$_t$ oxygen, as shown in Figure 5. Former studies of charged nanoclusters such as VAIO$_5$$^{+•}$, ScAlO$_3$$^{+•}$, and VAIO$_5$$^{-•}$ show that the Al-O$_t$ moiety can act as the active site in cationic or anionic BONCs containing transition metals. Here our DFT studies show that the Al-O$_t$ moiety could also be the...
functional site in neutral nanoclusters such as CeAlO₄⁺. This result is in contrast with the traditional concept that both ceria and alumina are mainly used as non-active “supports” for the real catalytic transition metal species.

Ground state CeAlO₄⁺ possesses an unpaired electron spin localized at the terminal Al-O⁻ moiety (Figure 5). DFT calculations are performed for the ion/molecule reactions of CeAlO₄⁺ with C₄H₁₀ on the doublet ground state potential energy surface (PES). Figure 6 shows that the approaching of C₄H₁₀ to the O⁻ site of the Al-O⁻ moiety in CeAlO₄⁺ leads to the smooth HAT associated with a significant gain of energy (−1.13 eV). The DFT optimization process shows direct formation of the intermediate CeAlO₄H•C₄H₉⁻(10), which suggests that the key HAT steps in this reaction proceeds without a noticeable reaction barrier.

The reaction of CeAlO₄⁺ with CO is also studied employing DFT calculations. Reaction (1) involves an OAT from CeAlO₄⁺ to CO. The calculated potential energy surface for this process, as shown in Figure 7(b), reveals that the favorable oxidation proceeds by an initial bonding of the carbon atom of CO on the Al side of the OᵦAlO• moiety to form the OᵦCe(Oᵦ)₂Al(CO)O⁻* encounter complex, intermediate 17. Al binding to the C atom of CO rather than the O atom is typically rationalized by a mechanism that suggests electron donation from the HOMO of CO (σ *) to an empty metal d orbital of Al and electron back donation from the filled metal d orbital of Al to the CO (π *) LUMO. The initial process releases 0.59 eV binding energy, which provides enough energy for the following process of CO₂ moiety formation (17 → 17/18 → 18). Next the C-atom attacks the O⁻ atom of the (Oᵦ)₂AlO• moiety (transition state 17/18, −0.25 eV), resulting in a rather stable intermediate 18 (−1.68 eV) with a nonlinear CO₂ moiety. The elongation of Al–O bond takes place easily to form the finally products CO₂ and CeAlO₄⁺. Note that the nonlinear CO₂ unit is fully located at the Al site rather than the Ce site in intermediate 18.

For comparison, reactions of the homonuclear neutral clusters Ce₂O₄ and Al₂O₄ with CO are also studied employing the DFT calculation (Figures 7(a) and 7(c)), at the same level. The ground state of the neutral Ce₂O₄ is a closed-shell singlet OᵦCe(Oᵦ)₂CeO₂ structure without an unpaired, unequal spin distribution of the mixed clusters. The reaction of Ce₂O₄ with CO is endothermic

\[
\text{Ce}_2\text{O}_4 + \text{CO} \rightarrow \text{Ce}_2\text{O}_3 + \text{CO}_2 \Delta E = 1.48 \text{ eV. (4)}
\]

The approaching of CO to the Ce site of the Ce₂O₄ cluster leads to the formation of the OᵦCe(Oᵦ)₂Ce(CO)O⁻(13) encounter complex. The energy gained by forming the intermediate 13 (−0.53 eV) from the entrance channel of reaction (4) is similar to that for forming the intermediate OᵦCe(Oᵦ)₂Al(CO)O⁻(17, −0.59 eV) from reaction (1); however, a barrier (transition state 13/14, 0.35 eV) occurs as the
C atom of the CO moiety attacks the O\textsubscript{t} atom of the CeO\textsubscript{t} moiety on the same site or side of the Ce\textsubscript{2}O\textsubscript{4}(CO) cluster. The intermediate O\textsubscript{t}Ce(O\textsubscript{b})\textsubscript{2}CeCO\textsubscript{2} (14) is formed from the transition state 13/14. The energy of 14 is 0.21 eV higher than that of the Ce\textsubscript{2}O\textsubscript{4} + CO entrance channel. The dissociation of the CO\textsubscript{2} moiety from 14 leads to the formation of the products Ce\textsubscript{2}O\textsubscript{3} + CO\textsubscript{2}. Comparing the reaction PESs of Figures 7(a) with 7(b), one can easily find that the large differences start from the C atom of the CO attacking the O\textsubscript{t} atom of the (O\textsubscript{b})\textsubscript{2}MO\textsubscript{t} (M = Al or Ce) moieties. With the unpaired electron (spin) density localized on the O\textsubscript{t}• atom, interaction of the C atom with the O\textsubscript{t} atom to form the CO\textsubscript{2} moiety requires very little energy (Figure 7(b), 17 \rightarrow 17/18, the energy difference is only 0.07 eV). On the other hand, with no unpaired electron (spin) density involved in the interaction, the required energy for the CO bond formation can increase to as much as 0.88 eV for the barrier to form a CO\textsubscript{2} moiety (Figure 7(a), 13 \rightarrow 13/14).

The importance of spin localized terminal oxygen for this kind of reaction is further elucidated for homonuclear Al\textsubscript{2}O\textsubscript{4} as the reactant to interact with CO,

$$\text{Al}_2\text{O}_4 + \text{CO} \rightarrow \text{Al}_2\text{O}_3 + \text{CO}_2 \Delta E = -1.35 \text{ eV.} \quad (5)$$

According to DFT calculations, the ground state Al\textsubscript{2}O\textsubscript{4} has a triplet diradical electronic distribution with a kite-shaped structure, in agreement with former experimental and theoretical studies.\textsuperscript{139} The Mulliken atomic spin distribution (MASD) indicates that the two unpaired electrons are located on the two terminal oxygens of the Al\textsubscript{2}O\textsubscript{4} cluster. Figure 7(c) shows that the reaction of Al\textsubscript{2}O\textsubscript{4} with CO is similar to that for CeAlO\textsubscript{4}• with CO, emphasizing the dominant role of the spin localized O\textsubscript{t}• as the active site.

The above discussion of electron distribution makes clear that the unpaired electron density on the terminal Al – attached O atom, O\textsubscript{t}, plays a major role in the active site for OAT and HAT reactions for both CeAlO\textsubscript{4}• and Al\textsubscript{2}O\textsubscript{4} NBONC. Additionally, however, we have noted that charged BONCs can also be active for such reactions, as well. One can also explore the effect of internal charge distribution on the OAT and HAT reactivity of neutral and charged BONCs: even for the cationic nanoclusters, the partial electrostatic charge difference can affect the reactivities.\textsuperscript{50,160,161} The MASD as well as the electrostatic potential (ESP) distributions of Ce\textsubscript{2}O\textsubscript{4}, CeAlO\textsubscript{4}•, and Al\textsubscript{2}O\textsubscript{4} are shown in Figure 8. ESP distributions for these three clusters are very similar, which emphasizes once again that the spin localized O\textsubscript{t}• dominates the reaction of these three clusters for OAT and HAT reactions.

Charged clusters have also demonstrated activity with regard to OAT and HAT reactions. An isoelectronic system containing three nanoclusters with different charge states can be constructed and explored by similar DFT calculations: three such clusters are cationic VAIO\textsubscript{4}••, neutral TiAlO\textsubscript{4}•, and anionic ScAlO\textsubscript{4}−• (see Figure 9).

The ground states of these three clusters possess the similar (O\textsubscript{b})\textsubscript{2}AlO\textsubscript{t}• moieties as that of the neutral CeAlO\textsubscript{4}• nanocluster, while their ESP distributions are significantly different (see Figure 9 for details). The reactivity of cationic VAIO\textsubscript{4}•• has been studied previously by both experimental and theoretical studies.\textsuperscript{48,49} Methane activation can be achieved by VAIO\textsubscript{4}•• at room temperature and a HAT process shows no observable barrier.\textsuperscript{49} The nanocluster VAIO\textsubscript{4}•• is also very reactive toward CO.\textsuperscript{48} The spin and electrostatic charge distributions of neutral TiAlO\textsubscript{4}• on the (O\textsubscript{b})\textsubscript{2}AlO\textsubscript{t}• moiety are similar to those of NBONC CeAlO\textsubscript{4}•: the latter reacts with C\textsubscript{4}H\textsubscript{10} via HAT but does not react with CH\textsubscript{4}. The ground state structure of ScAlO\textsubscript{4}−• is similar to that of...
Al$_2$O$_4^-$, which is covalently isoelectronic to ScAlO$_4^-$.

Further, recent studies show that Al$_2$O$_4^-$ is an active species since it can react with both CO and C$_4$H$_{10}$.

The reactions of methane with VAIO$_4^+\cdot$, TiAlO$_4^\cdot$, and ScAlO$_4^-$ are selected as a typical comparison system for elucidating the charge effect (Figure 10) on the reactivity of these clusters. All three reactions are exothermic:

$$VAI_O^+\cdot + CH_4 \rightarrow VAI_O^+H^+ + CH^+_3 \Delta E = -1.10 \text{ eV}, \quad (6)$$

$$TiAlO^\cdot + CH_4 \rightarrow TiAlO^+H + CH^+_3 \Delta E = -0.74 \text{ eV}, \quad (7)$$

$$ScAlO^-\cdot + CH_4 \rightarrow ScAlO^-H^- + CH^+_3 \Delta E = -0.34 \text{ eV}.$$  

(8)

Reaction (6) is barrierless even at room temperature and the formation of the VAIO$_4^+\cdot$CH$_3^+$ ($26\cdot$) intermediate is straightforward without any barrier (Figure 10(a)). The counter complex VAIO$_4^+\cdot$CH$_3^+$ ($25\cdot$) and the following transition state VAIO$_4^+\cdot$HCH$_3^+$ ($25/26\cdot$) cannot be located.

Unlike the cationic reaction (6), that the encounter complex for neutral reaction (7), TiAlO$_4^\cdot$CH$_3^+$ ($29\cdot$), is easily located and the transition state TiAlO$_4^\cdot$HCOH$_3^+$ ($29/30\cdot$) between TiAlO$_4^\cdot$CH$_3^+$ ($29\cdot$) and TiAlO$_4^+HCH$_3^+$ ($30\cdot$) can also be fully optimized (Figure 10(b)). Although the ZPE corrected energy of transition state $26/27$ ($-0.06 \text{ eV}$) is slightly lower than the entrance channel, taking entropy into consideration, according to a Gibbs free energy calculation, reaction (7) is not favorable at room temperature. The HAT transition state ScAlO$_4^-$\cdot$HCH$_3^+$ ($33/34\cdot$) is the key species in the anionic reaction (8), showing clearly a barrier (0.18 eV) for this anionic reaction (Figure 10(c)). Comparison of reaction (6)–(8) suggests that for a certain structure with identified spin distribution, electrostatic charge modification may be an effective way to adjust the reactivity and selectivity of some catalytic reactions, even though the reaction site is still clearly the Al-O$^-$ moiety of the BONCs.

The gas phase nanocluster CeAlO$_4$ provides a clear and perhaps ideal mechanism for the CO oxidation by a real Ce-Al oxide surface (see Figure 11(a) for details): (1) CO is chemically absorbed on the Al site; (2) CO interacts with O$_t$ atoms bonding to the Al site, forming a nonlinear CO$_2$ unit; and (3) another O atom from O$_2$ or other oxidants can be added to Al site to complete the proposed catalytic cycle. This catalytic cycle suggests a mechanism for a Ce-Al oxide catalyst surface enhancing the CO to CO$_2$ oxidation reaction. Moreover, even taking alumina as a supporting material, the (O$_b$)$_2$AlO$_4^-$ moiety can still play the major role in catalytic reactions (Figure 11(b)). The “supported material” may just be added to “modify” the reactivity of the surface of alumina: this mechanism is not consistent with the traditional concepts that the supported materials are the active species and that the supporting material (such as alumina) is important only to enhance surface area and access, but is otherwise inert.
IV. CONCLUSIONS

Neutral Ce₆Al₂O₉ nanoclusters are generated by laser ablation, and their reactions with CO and CₓHᵧO₂ are studied. The neutral bimetallic nanocluster CeAlO₄• is highly reactive with CO (CeAlO₄• + CO → CeAlO₄ + CO₂), while the pure Ce₂O₄ cluster is not. CeAlO₄• can also perform C–H bond activation via reaction with CₓHᵧO₂ to produce CeAlO₂H and CₓHᵧ•. DFT studies show that the spin localized terminal oxygen at the Al site instead of the Ce site plays a major role in these reactions. The charge distribution over clusters can also affect the reactivities, but are not the main driver of the O- or H-atom transfer reactions. The HAT process for the reaction of CeAlO₄• with CₓHᵧO₂ is barrierless to form the CeAlO₂H•Ce₂Hᵧ• encounter complex. This is the first observation of a HAT process supported by a ground state, neutral oxide cluster. Mechanisms for the catalytic oxidation of CO over surfaces of Al₂O₃/CeₓO₉ or CeₓO₉/Al₂O₃ materials are proposed based on these experimental and theoretical results. This research implies that the Al₂O₃ sites on “Al₂O₃/CeₓO₉ supporting systems” can also be highly reactive. Supporting materials such as Al₂O₃ can be more functional and complex than has been traditionally conceived: they are apparently not simply “inert materials.”

ACKNOWLEDGMENTS

We thank the AFOSR (Grant No. FA9550-10-1-0454), the NSF ERC for EUV Science and Technology (Grant No. 0310717) and XSEDE supercomputer resources provided by SDSC (Grant No. TG-CHE110083) for support of this work.

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