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O-atom transport catalysis by neutral manganese oxide clusters in the gas phase: Reactions with CO, C$_2$H$_4$, NO$_2$, and O$_2$

Shi Yin, Zhechen Wang, and Elliot R. Bernstein$^a$
Department of Chemistry, NSF ERC for Extreme Ultraviolet Science and Technology, Colorado State University, Fort Collins, Colorado 80523, USA

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Reactions of CO, C$_2$H$_4$, NO$_2$, and O$_2$ with neutral Mn$_n$O$_x$ clusters in a fast flow reactor are investigated both experimentally and theoretically. Single photon ionization at 118 nm is used to detect neutral cluster distributions through time of flight mass spectrometry. Mn$_n$O$_x$ clusters are generated through laser ablation of a manganese target in the presence of 5% O$_2$/He carrier gas. A strong size dependent reactivity of Mn$_n$O$_x$ clusters is characterized. Reactions Mn$_2$O$_5$/Mn$_3$O$_7$ + CO $\rightarrow$ Mn$_2$O$_4$/Mn$_3$O$_6$ + CO$_2$ are found for CO oxidation by Mn$_n$O$_x$ clusters, while only association products Mn$_2$O$_5$+C$_2$H$_4$ and Mn$_3$O$_6$+C$_2$H$_4$ are observed for reactions of C$_2$H$_4$ with small Mn$_n$O$_x$ clusters. Reactions of Mn$_n$O$_x$ clusters with NO$_2$ and O$_2$ are also investigated, and the small Mn$_2$O$_n$ clusters are easily oxidized by NO$_2$. This activation suggests that a catalytic cycle can be generated for the Mn$_2$O$_3$ cluster: Mn$_2$O$_5$ + CO + NO$_2$ $\rightarrow$ Mn$_2$O$_4$ + CO$_2$ + NO$_2$ $\rightarrow$ Mn$_2$O$_3$ + CO$_2$ + NO. Density functional theory (DFT) calculations are performed to explore the potential energy surfaces for the reactions Mn$_2$O$_3$/Mn$_3$O$_7$ + CO $\rightarrow$ Mn$_2$O$_4$+Mn$_3$O$_6$ + CO$_2$, Mn$_2$O$_5$ + C$_2$H$_4$ $\rightarrow$ Mn$_2$O$_4$ + CH$_2$CHO, and Mn$_3$O$_4$ + NO$_2$ $\rightarrow$ Mn$_2$O$_3$ + NO. Barrierless and thermodynamically favorable pathways are obtained for Mn$_2$O$_5$/Mn$_3$O$_7$ + CO and Mn$_2$O$_4$ + NO$_2$ reactions. A catalytic cycle for CO oxidation by NO$_2$ over a manganese oxide surface is proposed based on our experimental and theoretical investigations. The various atom related reaction mechanisms explored by DFT are in good agreement with the experimental results. Condensed phase manganese oxide is suggested to be a good catalyst for low temperature CO oxidation by NO$_2$, especially for an oxygen rich sample.

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I. INTRODUCTION

Catalytic conversion of harmful gases, produced in fossil fuel combustion, such as carbon monoxide and the oxides of nitrogen, is of utmost importance both environmentally and economically. NO$_2$ is a very corrosive nitrogen oxide and is one of the most dangerous gases related to health and environmental damage. Depending on temperature, NO$_2$ can attack metal and especially polymer parts in exhaust systems.

Reactions of NO$_x$ + CO are interesting in several areas, including atmospheric chemistry and surface chemistry. While these redox reactions are exothermic (e.g., $\Delta_r H = -228$ kJ mol$^{-1}$ for the process NO$_2$ + CO $\rightarrow$ NO + CO$_2$), they do not occur directly to any measurable extent at either room or elevated temperatures due to activation barriers (e.g., 114 kJ mol$^{-1}$ for the NO$_2$/CO couple). Catalysts are required to reduce these barriers; the specific role played by transition metal complexes in promoting the oxidation of CO by NO$_2$ was first reported by Feltham and Kriege as early as 1979.

Catalytic oxidation of CO has been studied on various supported$^{5,7}$ and unsupported$^{8-12}$ MnO$_x$ catalysts, due to their superior ability to activate and supply oxygen. These catalysts attract considerable attentions from both academia and industry due to their low cost and environmental compatibility, in contrast to the expensive noble metal (Pt, Rh, and Pd) catalysts generally used for the removal of exhaust gas from internal combustion engines. Most of the studies of CO oxidation are performed with stoichiometric manganese oxides. In early works, Klier and Kuchynka$^{13}$ and Kanungo$^{14}$ found high catalytic activity over bulk MnO$_2$ at 293 K and 353 K for the reaction CO to CO$_2$. Liang et al.$^{15}$ synthesized MnO$_2$ catalysts with nanorod morphology and found their catalytic activity to change according to $\alpha - \delta > \gamma > \beta$-MnO$_2$ phase.

Variations of catalytic activity with sample polymorphism for otherwise identical bulk compositions can only be explained by assuming that the specific surface termination, Mn–O bond strength, and surface stoichiometry are determining factors. For commercially available manganese oxides the following trends of CO oxidation activity (at 523 K) are reported by Ramesh et al.$^{16}$ and Wang et al.$^{17}$: MnO $<$ Mn$_2$O$_3$ $<$ Mn$_2$O$_5$.

The mechanism for CO oxidation on Mn$_n$O$_x$ surface is still unknown. Determination of the Mn$_n$O$_x$ active phase for CO oxidation is a great challenge. Currently, two mechanisms, the Mars-van-Krevelen mechanism (MvK) (e.g., CO adsorbs on surface, picks up a surface O, leaves the surface, and O is replaced by gas phase O$_2$) and the Langmuir-Hinshelwood (LH) mechanism (e.g., both CO and O$_2$ adsorb on the surface, react as adsorbates, and leave the surface), are generally proposed to be responsible for the CO oxidation on an Mn$_n$O$_x$ catalysts.$^{10,12,18}$ An Eley-Rideal mechanism is also predicted in which the CO adsorbs to the Mn$_n$O$_x$ surface and reacts with a gas phase O$_2$ molecule: such macroscopic mechanisms are

$^a$Author to whom correspondence should be addressed. Electronic mail: erb@lamar.colostate.edu.
not easily distinguished, and it is challenging to determine which (if any) of the three mechanisms is dominant in the reaction. The relevant mechanism for this reaction system has thus been debated for decades. 

Low-temperature, low-cost, and efficient CO oxidation (removal) can solve serious environmental problems caused by CO emission from automobiles, industrial processing, and even cigarette burning. CO oxidation is also important in other areas such as respiratory protection and fuel gas (e.g., C\textsubscript{2}H\textsubscript{4} and H\textsubscript{2}) cleanup. Reforming of hydrocarbons is one of the most attractive approaches to produce hydrogen fuel for polymer electrolyte membrane fuel cells (PEMFC); however, the presence of 1 vol.% CO in the hydrogen stream will poison the Pt anode of a fuel cell, thus removal of CO from the reformate stream for PEMFC applications is essential.

Recently, atomic/molecular level mechanisms for condensed phase catalytic reactions have been suggested to be accurately modeled and understood through the study of gas phase cluster reactions.\textsuperscript{20-22} Reactions of CO and/or NO\textsubscript{2} with various metal oxide clusters (e.g., Ce\textsubscript{m}O\textsubscript{n}+\textsubscript{−}, Al\textsubscript{m}O\textsubscript{n}+\textsubscript{−}, Fe\textsubscript{n}O\textsubscript{y}\textsubscript{+}/0\textsubscript{−}, and V\textsubscript{n}Co\textsubscript{y}O\textsubscript{z}\textsubscript{+}/0\textsubscript{−}) have been reported and related to condensed phase behavior. The high CO oxidation activity of CO\textsubscript{3}O\textsubscript{4}, which is one of the most thoroughly studied 3D metal oxides, is frequently related to the simultaneous presence of tetrahedral Co\textsuperscript{2+} and octahedral Co\textsuperscript{3+} sites.\textsuperscript{31-34} Similarly, high activity has also been observed for Mn oxides; however, the catalytic oxidation of CO by NO\textsubscript{2} supported by manganese oxide clusters has not been reported to the best of our knowledge, and no such site requirement has ever been claimed to exist for these oxides. This is probably due to the structural flexibility of Mn oxides, which exist in a number of different stoichiometries (as MnO\textsubscript{x}, Mn\textsubscript{2}O\textsubscript{3}, Mn\textsubscript{3}O\textsubscript{4}, Mn\textsubscript{5}O\textsubscript{8}, and MnO\textsubscript{2} along with their polymorphs) and non-stoichiometric phases, with the Mn valence varying smoothly between +4, as in MnO\textsubscript{2}, and +2, as in MnO.\textsuperscript{10}

In this paper, we present the first study of CO catalytic oxidation by NO\textsubscript{2} over neutral Mn\textsubscript{n}O\textsubscript{m} clusters. Density functional theory (DFT) calculations and single photon ionization (SPI) techniques are used to investigate the catalytic activity of Mn\textsubscript{n}O\textsubscript{m} clusters toward oxidation of CO by NO\textsubscript{2}. The experimental results are well interpreted by the calculations. Catalytically active sites and details of the gas phase reaction mechanism are obtained, and related condensed phase catalytic processes for CO oxidation by NO\textsubscript{2} over manganese oxides at a molecular level are proposed. Mn\textsubscript{n}O\textsubscript{m} clusters are also studied with regard to their oxidation of unsaturated hydrocarbons (e.g., C\textsubscript{2}H\textsubscript{4}): only adsorption products Mn\textsubscript{n}O\textsubscript{m}(C\textsubscript{2}H\textsubscript{4}) are observed and calculated.

II. METHODS

A. Experimental procedures

The experimental setup for laser ablation coupled with a fast flow reactor employed in this work has been described previously in detail.\textsuperscript{35-39} Only a brief outline of the apparatus is given below. Mn\textsubscript{n}O\textsubscript{m} clusters are generated in a laser ablation source: manganese plasma, ablated from a manganese foil disk, reacts with oxygen seeded in helium (5% O\textsubscript{2}/He) expansion gas. A 10 Hz, focused, 532 nm Nd\textsuperscript{3+}:YAG laser (Nd\textsuperscript{3+}: yttrium aluminum garnet) with \textasciitilde6 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 Mn\textsubscript{n}O\textsubscript{m} clusters react with reactants in a fast flow reactor (i.d. 6.3 mm \times 76 mm), which is directly coupled to the cluster generation channel (i.d. 1.8 mm \times 19 mm). The reactant gases (CO, C\textsubscript{2}H\textsubscript{4}, O\textsubscript{2}, and NO\textsubscript{2}), with a 10 psi backing pressure, are injected into the reactor by a pulsed general valve (Parker, Series 9). Timing between the Jordan valve and the general valve opening is optimized for the best product yields. The pressure in the fast flow reactor can be estimated \textasciitilde14 Torr for the reaction.\textsuperscript{28} Reactants and products are thermalized to 300–400 K by collision during the reaction.\textsuperscript{40} 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 vacuum ultraviolet (UV) laser beam (118 nm, 10.5 eV/photon). The 118 nm laser light is generated by focusing the third harmonic (355 nm, \textasciitilde30 mJ) of a Nd\textsuperscript{3+}:YAG laser in a tripling cell that contains about a 250 Torr argon/xenon (10/1) gas mixture. An MgF\textsubscript{2} prism (Crystaltechno LTD, Russia, 6° apex angle) is placed into the laser beam to enhance separation of the generated 118 nm laser beam from the 355 nm input laser beam. After the near threshold ionization, photolions are detected by a time of flight mass spectrometer (TOFMS).

B. Calculational procedures

Calculations of the structural parameters for neutral Mn\textsubscript{n}O\textsubscript{m} clusters and the reactions of CO, C\textsubscript{2}H\textsubscript{4}, and NO\textsubscript{2} with Mn\textsubscript{2}O\textsubscript{3.5} and Mn\textsubscript{3}O\textsubscript{7} clusters are performed employing density functional theory. The hybrid B3LYP exchange-correlation functional\textsuperscript{41-44} and a 6-311+G\textsuperscript{*} basis set\textsuperscript{44-46} are used. This choice of the B3LYP/6-311+G\textsuperscript{*} method with moderate computational cost has been tested to provide reasonable results in previous studies on manganese oxide clusters.\textsuperscript{47,48} This approach yields good results in the interpretation of vibrational spectra of manganese oxides.\textsuperscript{39,50} The adopted DFT method also reproduces the experimental bond dissociation enthalpies of OC–O, ON–O, and Mn–O species. The experimental bond dissociation enthalpies of CO\textsubscript{2}, NO\textsubscript{2}, and MnO are 5.52, 3.16, and 4.17 \textdegree\textsubscript{C}, respectively,\textsuperscript{51-53} and the DFT calculated values for B3LYP/6-311+G\textsuperscript{*} are 5.54, 3.17, and 4.00 \textdegree\textsubscript{C}, respectively. Binding energies between neutral Mn\textsubscript{n}O\textsubscript{m} and reactants are calculated at different typical association geometries to obtain the lowest energy structures. The calculations for the potential energy surfaces (PESs) of the reactions of CO, C\textsubscript{2}H\textsubscript{4}, and NO\textsubscript{2} with various Mn\textsubscript{n}O\textsubscript{m} clusters involve geometry optimizations of the reactants, intermediates, transition states, and products. Vibrational frequency calculations are further performed to confirm the global minima ground states and transition states, which have zero and one imaginary frequency, respectively. Additionally, intrinsic reaction coordinate (IRC) calculations are carried out to determine that an estimated transition state connects two
appropriate local minima along the reaction pathway. Binding energies are calculated for a few species employing the Basis Set Superposition Error (BSSE) counterpoise correction; these corrections are found to be insignificant at the present level of theory.

III. RESULTS

A. Experimental

Figure 1 presents a typical TOF mass spectrum of neutral manganese oxide \( \text{Mn}_m \text{O}_n \) \((m = 2–13, n = 1–21)\) clusters generated by laser ablation of a manganese foil into 5% \( \text{O}_2/\text{He} \) carrier gas, and ionized by 118 nm laser radiation. The intense mass peaks for the manganese oxide series are \( \text{Mn}_m \text{O}_n \) \((m, n) = (2, 5; 3, 6–8; 4, 7–9; 5, 9–10; 6, 10–12; 7, 10–12; 8, 11–13; 9, 13–15; 10, 15; 11, 16–17; 12, 17–19)\). The relatively high \( \text{Mn}_m \text{O}_n \) signal intensities are at \( n = 2m + 1 \) \((m = 2, 3)\), \( n = 2m \) \((m = 4–6)\), \( n = 2m - 3 \) \((m = 7–9)\), and \( n = 2m - 5 \) \((m = 10–12)\). Mass spectra are similar to the one shown in Figure 1 for \( \text{O}_2 \) concentrations in the range 1%–10%.

Mass spectra generated from the reaction of small neutral manganese oxide \((\text{Mn}_{2,3}\text{O}_n)\) clusters with \( \text{CO} \) and \( \text{C}_2\text{H}_4 \) in a fast flow reactor are presented in Figures 2(b) and 2(c), respectively. By way of comparison, Figure 2(a) shows the TOFMS for \( \text{Mn}_{2,3}\text{O}_n \) clusters reacting with pure \( \text{He} \) in the reaction cell. If pure \( \text{He} \) gas is added to the reactor cell, all cluster signals decrease in roughly the same proportion due to scattering by the inert gas in the reactor (Figure 2(a)). The mass signal of \( \text{Mn}_2\text{O}_5 \) decreases about 85% after it reacts with \( \text{CO} \), and a comparable signal increase for \( \text{Mn}_2\text{O}_4 \) is observed, whereas no apparent signal depletion is observed for \( \text{Mn}_2\text{O}_2,3 \) under the same conditions. Significant signal depletion of \( \text{Mn}_3\text{O}_7 \) and increase of \( \text{Mn}_3\text{O}_6 \) are also observed after the reaction with \( \text{CO} \). These observations suggest the likely reactions, \( \text{Mn}_2\text{O}_5 + \text{CO} \rightarrow \text{Mn}_2\text{O}_4 + \text{CO}_2 \) and \( \text{Mn}_3\text{O}_7 + \text{CO} \rightarrow \text{Mn}_3\text{O}_6 + \text{CO}_2 \). The pseudo first order rate constants \( (k) \) for the \( \text{Mn}_m\text{O}_n + \text{CO} \) reaction in the fast flow reactor can be estimated as previously described, by using the equation \( k = \ln(I_0/I)/\rho \times \Delta t \), in which \( I \) and \( I_0 \) are signal magnitudes of the clusters in the presence and absence of \( \text{H}_2 \) reagent gas, respectively, \( \rho \) is the reactant molecular density, and \( \Delta t \) is the reaction time (\( \sim 50 \mu s \)) in the fast flow reactor. The rate constants \( k(\text{Mn}_2\text{O}_5 + \text{CO}) \) and \( k(\text{Mn}_3\text{O}_7 + \text{CO}) \) values are estimated to be \( 6.5 \times 10^{-13} \) and \( 1.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), respectively. The absolute error in the values of the rate constants is ca. 30% based on an estimation of \( \rho \) and \( \Delta t \) in...
The reactivity of neutral manganese oxide clusters (Mn₂O₅ and Mn₃O₇) toward unsaturated hydrocarbons is investigated. The reaction selectivity of small neutral manganese oxide clusters in the presence of NO₂ and O₂ in a fast flow reactor is explored. Reactions of Mn₂,3O₆ with (a) He, (b) NO₂, and (c) O₂ in a fast flow reactor are studied. Different reaction mechanisms of Mn₂O₄,5 and Mn₃O₇ clusters with NO₂ and O₂ are observed in the flow tube reactor. Different reaction mechanisms of Mn₂O₄,5 and Mn₃O₇ clusters with NO₂ and O₂ are observed. Significant overall reaction barriers (ORB) of 0.54 eV, 0.33 eV, 0.78 eV, 1.23 eV, and 1.34 eV are determined for the reactions paths 2 to 6 for reaction of Mn₂O₅ with CO, respectively. For reaction path 1, the result in Figure 4 shows that no ORB (or negative ORB of ~0.11 eV) exists for CO reacting with Mn₃O₇ in the ground state. The negative ORB for the Mn₂O₅ + CO reaction coordinate is consistent with the system high reactivity (Figure 2(b)). Note that, the crossing of spin triplet (path 2) and quintet (path 1) potential energy surfaces (spin conversion) is obtained: this surface path crossing suggests that the initial reactants ³Mn₂O₅ + CO can also form intermediate In1 through the spin conversion point (CP) in Figure 4.

### B. Theoretical

Figures 4–6 plot the DFT calculated reaction pathways for CO oxidation by Mn₂O₅, Mn₃O₇, and Mn₂O₄, respectively. Mn₂O₅ has a quintet ground state, and the triplet state is above the quintet by 0.55 eV. The Mn₂O₅ cluster contains two bridge-bonded (O₃) and three terminally bonded (O₅) oxygen atoms, and two manganese atoms Mn₁, which bonds with one O₅ and Mn₅, which bonds with two O₅. Potential energy profiles for ³Mn₂O₅ + CO are determined for CO attaching to the different possible sites on the Mn₂O₅ cluster. CO can bond to Mn₉ (paths 1 and 2 of Figure 4), O₅ on Mn₁ (paths 3 and 5 of Figure 4), or O₅ on Mn₅ (paths 4 and 6 of Figure 4). Significant overall reaction barriers (ORB) of 0.54 eV, 0.33 eV, 0.78 eV, 1.23 eV, and 1.34 eV are determined for the reaction paths 2 to 6 for reaction of Mn₂O₅ with CO, respectively. For reaction path 1, the result in Figure 4 shows that no ORB (or negative ORB of ~0.11 eV) exists for CO reacting with Mn₃O₇ in the ground state. The negative ORB for the Mn₂O₅ + CO reaction coordinate is consistent with the system high reactivity (Figure 2(b)). Note that, the crossing of spin triplet (path 2) and quintet (path 1) potential energy surfaces (spin conversion) is obtained: this surface path crossing suggests that the initial reactants ³Mn₂O₅ + CO can also form intermediate In1 through the spin conversion point (CP) in Figure 4.

**FIG. 4.** A potential energy surface profile for the reaction Mn₂O₅ + CO → Mn₂O₄ + CO₂. Energies are in eV and relative to the initial reactants energy of ³Mn₂O₅ + CO. Energy levels are calculated by B3LYP/6-311+G*. The spin multiplicity (M) is listed as ³Mn₂O₅5. “CP” denotes a possible spin conversion point for reaction paths 1 and 2. See text for details.
FIG. 5. A potential energy surface profile for the reaction \( \text{Mn}_3\text{O}_7 + \text{CO} \rightarrow \text{Mn}_3\text{O}_6 + \text{CO}_2 \). Energies are in eV and relative to the initial reactant energy of \( 8\text{Mn}_3\text{O}_7 + \text{CO} \). Energy levels are calculated by B3LYP/6-311+G*. The spin multiplicity \( (M) \) is listed as \( \text{Mn}_3\text{O}_6,7 \). See text for details.

The DFT calculation summarized in Figure 5 predicts that the Mn\(_3\)O\(_7\) has an octet ground state and a sextet state above it at 0.36 eV. A positive ORB of 0.16 eV is present for CO approaching sextet Mn\(_3\)O\(_7\) (on MnI), whereas the ORB is negative (−0.13 eV) for CO approaching octet Mn\(_3\)O\(_7\) (on MnI). The reaction pathway shown in Figure 6 predicts that the oxidation of CO by the ground and low-lying excited states of Mn\(_2\)O\(_4\) is subject to significant ORBs 0.60 eV and 0.24 eV (even considering a spin inversion mechanism\(^{55}\)). These DFT results can be used to explain the observed reactivity of Mn\(_2\)O\(_5\), Mn\(_3\)O\(_7\), and Mn\(_2\)O\(_4\) clusters.

The PESs and the optimized geometries of reaction intermediates and transition states calculated by DFT for the reaction \( 5\text{Mn}_2\text{O}_5 + \text{C}_2\text{H}_4 \rightarrow 5\text{Mn}_2\text{O}_4 + \text{CH}_3\text{CHO} \) (oxidation of an unsaturated hydrocarbon) are presented in Figure 7. The most stable adsorption structure (In18) is for one C atom of C\(_2\)H\(_4\) bonded to manganese atom MnI and the other C atom bonded to the oxygen atom O\(_t\) of MnI in the Mn\(_2\)O\(_5\) cluster. A positive ORB of 0.31 eV is present for a hydrogen transfer from the CH\(_2\) moiety bonded to O\(_t\) to the other carbon via TS13. The positive ORB and stable association intermediate In18 (−1.13 eV) of the \( 5\text{Mn}_2\text{O}_5 + \text{C}_2\text{H}_4 \) system are consistent with the adsorptive but non-oxidative reactivity of Mn\(_2\)O\(_5\) toward C\(_2\)H\(_4\) presented in Figure 2(c).

In order to study the regeneration mechanism for the manganese oxide cluster Mn\(_2\)O\(_5\) by oxidant NO\(_2\), DFT calculations are performed for the reaction \( \text{Mn}_2\text{O}_4 + \text{NO}_2 \rightarrow \text{Mn}_2\text{O}_5 + \text{NO} \). Cluster \( 5\text{Mn}_2\text{O}_4 \), which is a product of the barrierless reaction path 1 obtained from the calculation results presented in Figure 4 (\( \text{O}_2\text{Mn}_1\text{O}_2\text{Mn}_2\text{zero}, \text{Mn}_2\text{zero}: \text{without O}_t \)), and \( 2\text{NO}_2 \) are adopted as initial reactants. Figure 8 presents the reaction pathway for \( 5\text{Mn}_2\text{O}_4 \) oxidized by NO\(_2\). NO\(_2\) bonds to the Mn\(_{\text{zero}}\) atom of Mn\(_2\)O\(_4\) to form intermediate I\(_21\), and the NO moiety transfers to Mn\(_{\text{zero}}\) via transition state TS14 (−1.04 eV) to yield In22: this structure has an Mn\(_2\)O\(_5\)(NO) geometry with an Mn\(_{\text{zero}}\)NO attachment. The release of NO from the Mn\(_2\)O\(_5\) cluster requires 0.18 eV, and then Mn\(_2\)O\(_5\) is regenerated from Mn\(_2\)O\(_4\) oxidation by NO\(_2\).

Thus, good agreement between DFT calculations and the experimental observations has been achieved through the above collective mechanism. This agreement between theory and experiment enables us to draw qualitative conclusions concerning the mechanisms of CO oxidation by NO\(_2\) on Mn\(_n\)O\(_m\) clusters based on the DFT results.

IV. DISCUSSION

A. Mechanisms of CO oxidation by manganese oxide clusters

Special size dependent behavior is identified for the reaction of Mn\(_n\)O\(_m\) clusters with CO both in experiments and calculations, as presented in Figure 2 and Figures 4–6, respectively. Clusters Mn\(_2\)O\(_5\) and Mn\(_3\)O\(_7\) are found to have
in these reactions involves CO adsorption onto the clusters by carbon-manganese interaction to form species $O_nMn_{m-1}Mn–CO$. Oxygen manganese interactions ($O_nMn_{m-1}Mn–OC$) are also explored: species formed in this way are usually unstable or very high in energy. Direct CO$_2$ formation (carbon oxygen interaction such as $O_2Mn_2O–CO$ shown in reaction paths 3–6 in Figure 4) is also tested. The reaction barriers are much higher than the one presented for path 1 (Figure 4). These results suggest that the CO molecule will adsorb on the Mn site.

The study of CO oxidation by small iron oxide clusters also finds that the initial intermediate formation involves a carbon iron interaction. For the oxidation of CO by anionic AuO$_n^-$ clusters, the initial complex formation involves a carbon oxygen interaction: the CO molecule is able to bind directly to an oxygen atom of AuO$_n^-$. This could imply an intrinsic mechanism difference for CO oxidation over noble and non-noble metal catalysts.

After the initial intermediate formation through carbon manganese interactions, the second critical step of the reaction involves one terminal Mn–O$_t$ bond activation. This is clearly demonstrated in Figures 4 and 5 in which the activated Mn–O$_t$ bond lengths (in Å in the list below) of the first transition states are significantly longer than those of the initial intermediates: 1.68 versus 1.59 for $5Mn_2O_5$; and 1.68 versus 1.58 for $8Mn_3O_7$. The activation energies, which are 0.25 eV ($5Mn_2O_5 + CO$) and 0.17 eV ($8Mn_3O_7 + CO$) with respect to the initial intermediates, decide the oxidative reactivity of $Mn_2O_4$, although $Mn_2O_4$ clusters contain O$_t$ atoms bonded with Mn(IV) sites. As presented in Figure 9, the HSOMO for the triplet $Mn_2O_4$ (the coupling is antiferromagnetic on two MnI sites) is mainly a d-type orbital localized on one MnI atom. The HSOMO for the quintet $Mn_2O_4$ (one unpaired electron (d$^0$) on the MnII site and three unpaired electrons (d$^3$) on the MnI site), however, is composed of non-bonding orbitals of MnI d atomic orbitals and O$_t$ p atomic orbitals: this $Mn_2O_5$ orbital localizes on MnI.

The CO$_2$ deoxygenation energy (5.54 eV) is higher than that of $Mn_2O_{1.5}$ and $Mn_3O_7$ clusters (3.11–3.88 eV), which implies that the oxygenation of CO by these $Mn_nO_x$ clusters should be thermodynamically available. Nevertheless, in the PES for the reaction of the $Mn_2O_4$ cluster with CO displayed in Figure 6, a high barrier is consistent with the non-oxidative reactivity of $Mn_2O_4$, although $Mn_2O_4$ clusters contain O$_t$ atoms bonded with Mn(IV) sites.

In order to understand the different reactivity of $Mn_nO_x$ clusters, deoxygenation energies for $Mn_2O_{1.5}$ and $Mn_3O_7$ clusters are calculated and compared to the CO$_2$ deoxygenation as given in following equations:

$5Mn_2O_5 \rightarrow 3Mn_2O_4 + 1/2 O_2 \quad \Delta H_{298} = 3.68 \text{ eV,}$

$3Mn_2O_4 \rightarrow 5Mn_2O_3 + 1/2 O_2 \quad \Delta H_{298} = 3.88 \text{ eV,}$

$8Mn_3O_7 \rightarrow 10Mn_3O_6 + 1/2 O_2 \quad \Delta H_{298} = 3.11 \text{ eV,}$

$\text{CO}_2 \rightarrow \text{CO} + 1/2 O_2 \quad \Delta H_{298} = 5.54 \text{ eV.}$
and O\(_t\) (bonded with Mn\(_I\)) atoms. This implies that the O\(_t\) atom (on Mn\(_I\)) of Mn\(_2\)O\(_5\) is easily activated for the interaction of CO with an Mn\(_2\)O\(_5\) cluster. A little longer length of Mn\(_t\)–O\(_t\) bond in the Mn\(_2\)O\(_5\) cluster (1.58 Å compared with 1.55 Å in the Mn\(_2\)O\(_4\)) also enhances its activity with the carbon atom of the adsorbed CO. The low HSOMO distribution on the O\(_t\) atom and a short bond length of the Mn\(_t\)–O\(_t\) bond of the Mn\(_2\)O\(_4\) cluster are both responsible for the high positive ORB of the reaction \(3\)Mn\(_2\)O\(_4\) + CO: the activation energy, 0.65 eV (\(3\)Mn\(_2\)O\(_4\) + CO) with respect to the initial intermediates, is much higher than that for reactions \(3\)Mn\(_2\)O\(_3\) + CO (0.25 eV) and \(3\)Mn\(_1\)O\(_2\) + CO (0.17 eV).

In summary, our calculational and experimental results indicate that Mn\(_I\)(IV) atoms of reactive (catalytic) Mn\(_2\)O\(_5\) and Mn\(_1\)O\(_2\) clusters are the active sites for holding CO molecules during the CO oxidation processes. The next essential step is the Mn\(_I\)(IV)–O\(_t\) bond activation, which then transfers the O\(_t\) atom to the adsorbed CO to yield the intermediate Mn\(_n\)O\(_{n-1}\)CO\(_2\) (\(m, n = 2, 5\) and 3, 7). The catalytic reactivity of Mn\(_n\)O\(_{n-1}\) clusters is found to be associated with the following factors: (1) the presence of a Mn\(_I\)(IV)–O\(_t\) moiety; (2) the HSOMO distribution on the O\(_t\) atom; and (3) the length of the Mn\(_I\)(IV)–O\(_t\) bond.

Additionally, ethylene is chosen as a prototypical example to consider for the selective oxidative property of Mn\(_n\)O\(_{n-1}\) clusters toward hydrocarbons. Spectra shown in Figure 2(c) make clear that C\(_2\)H\(_4\) cannot be oxidized by Mn\(_2\)O\(_4\) clusters, as only association products Mn\(_2\)O\(_3\)C\(_2\)H\(_4\) and Mn\(_2\)O\(_5\)C\(_2\)H\(_4\) are observed. A positive ORB (0.31 eV) and stable association intermediate In18 (−1.13 eV) of the \(3\)Mn\(_2\)O\(_5\) + C\(_2\)H\(_4\) system are also obtained from DFT calculations (Figure 7): these combined results are consistent with the non-oxidative reactivity of Mn\(_2\)O\(_3\) + C\(_2\)H\(_4\). Taken together with the CO/NO\(_2\) reactions clarified above, these C\(_2\)H\(_4\) results suggest that manganese oxide may be a potential catalyst for CO removal from a hydrocarbon stream, since the selective CO oxidation by the Mn\(_n\)O\(_{n-1}\) cluster is observed both experimentally and theoretically and is more energetically favorable than the hydrocarbon and Mn\(_n\)O\(_{n-1}\) clusters interaction.

**B. The oxidation of Mn\(_m\)O\(_n\) clusters by oxidants**

In the practical catalytic oxidation of CO by oxidants, the catalyst must be involved in a cyclic reaction. Reactions of Mn\(_2\)O\(_4\) clusters with NO\(_2\) and O\(_2\) oxidants are investigated to explore the regeneration of oxidative Mn\(_2\)O\(_3\) and Mn\(_1\)O\(_2\) clusters, and to develop a full catalytic cycle for CO oxidation by oxidants over manganese oxide clusters. As displayed in Figure 3(c), neither association nor reaction between Mn\(_2\)O\(_4\) clusters and O\(_2\) occurs. Since the O–O bond breaking process is subject to a high absolute reaction barrier (∼1.2 eV), based on the study of reactions between small neutral iron oxide clusters and oxygen at low temperature,\(^{28}\) the absence of reaction for O\(_2\) + Mn\(_2\)O\(_4\) is proposed to be due to a high barrier for the O–O bond breaking process at low temperature.

As suggested by the results of reactions of Mn\(_2\)O\(_4\) with NO\(_2\) (Figure 3(b)), the reaction (Mn\(_2\)O\(_4\) + NO\(_2\) → Mn\(_2\)O\(_5\) + NO) is studied by DFT potential energy surface calculations to understand the regeneration of reactive Mn\(_2\)O\(_5\) clusters. The allowed reaction pathway for NO\(_2\) with Mn\(_2\)O\(_4\) cluster indicates that NO\(_2\) is adsorbed on the Mn\(_{zero}\) atom of a Mn\(_2\)O\(_4\) cluster in the first step of the reaction. The lowest energy structure of the association product Mn\(_2\)O\(_4\)(NO\(_2\)) (Figure 8) shows that NO\(_2\) binds with Mn\(_2\)O\(_4\) clusters through forming a Mn\(_2\)O\(_4\)Mn\(_{zero}\)–ONO intermediate. These results suggest that the Mn\(_{zero}\) atom, generated by the CO → CO\(_2\) reaction on Mn\(_2\)O\(_5\), is the active site for the adsorption of NO\(_2\).

The next step for Mn\(_2\)O\(_5\) regeneration is the rupture of O–NO\(_2\) bond and transfer of the NO moiety to Mn\(_{zero}\), forming In22 (Mn\(_2\)O\(_5\)–NO) via a low energy transition state TS14 (−1.04 eV). To generate products, only 0.18 eV is required to release NO from In22 to form Mn\(_2\)O\(_5\) + NO. Based on these DFT calculations, the overall reaction of Mn\(_2\)O\(_4\) + NO\(_2\) → Mn\(_2\)O\(_5\) + NO is barrierless and thermodynamically favorable. The regeneration of Mn\(_2\)O\(_5\) from Mn\(_2\)O\(_4\) oxidation by NO\(_2\) is readily accomplished.

**C. Understanding the catalytic cycle for CO oxidation by NO\(_2\) over manganese oxide at a molecular/atomic level**

A Langmuir-Hinshelwood type mechanism between molecular CO and atomic oxygen generating carbon dioxide (CO\(_2\)) on the surface of metals or metals supported by oxides is generally accepted, while a Mars-van-Krevelen type mechanism is frequently suggested for pure metal oxides.\(^{10}\) The LH mechanism proposes two surface adsorbed gas phase species (in this case, CO and NO\(_2\)) reacting with one another, and the MVK mechanism proposes one surface adsorbed species (in this case CO) reacting with a gas phase molecule (in this case NO\(_2\)); section of these macroscopic mechanism is applicable to the present reaction. The identified mechanism for CO oxidation by NO\(_2\) on the manganese oxide cluster (surface), however, has not been proposed previously. Studies of CO oxidation by Mn\(_n\)O\(_{n-1}\) clusters and Mn\(_n\)O\(_{n-1}\) clusters oxidation by NO\(_2\) in the gas phase aid in the understanding of the related condensed phase catalysis reaction at an atomic level. Catalytic clusters in the gas phase can be seen as a good model system for the active moieties that exist on a catalyst surface. Thereby, a catalytic cycle for CO oxidation by NO\(_2\) on manganese oxide surfaces can be proposed, and is presented in Figure 10. This proposal is offered based on experimental and calculational results presented in Figures 2–5 and 8.

This suggested mechanism generally parallels that proposed by Luo et al. for the CO oxidation by O\(_2\) at low temperature (<220°C) on the α-Mn\(_2\)O\(_3\) nanocatalyst surface.\(^{18}\) The cluster based mechanism, however, presents additional important information about active sites on the catalyst surface. Our proposed mechanism indicates that the CO molecule adsorbs on the Mn\(_I\)(IV) site, which bonds to only one terminal oxygen atom, and reacts with the active O\(_t\) atom on that Mn\(_I\)(IV) site. The mechanism suggested from condensed phase surface studies does not supply the details of active sites on the catalytic surface.

We conclude that the Mn\(_I\)(IV) surface sites are the active sites for adsorption of a CO molecule. The CO attaches to the Mn\(_I\)(IV) site through its C atom (Mn–C bond formation
V. CONCLUSION

Reactions of neutral manganese oxide clusters $\text{Mn}_n\text{O}_m$ with CO, C$_2$H$_4$, NO$_2$, and O$_2$ are investigated by time of flight mass spectrometry employing 118 nm single photon ionization and DFT calculations. Strong cluster size dependent behavior is observed for the oxidation reactions of CO by $\text{Mn}_m\text{O}_n$ clusters ($m = 2–13$, $n = 1–21$). PESs are calculated for CO oxidation reactions on $\text{Mn}_2\text{O}_{15}$ and $\text{Mn}_2\text{O}_7$ clusters: CO molecules are predicted to be adsorbed on the $\text{Mn}_2(\text{IV})$ site. Reactions for CO to form CO$_2$ on $\text{Mn}_2\text{O}_3$ and $\text{Mn}_2\text{O}_7$ clusters are estimated as overall barrierless and thermodynamically favorable processes. Theoretical calculations suggest that activity of $\text{Mn}_2\text{O}_4$ and $\text{Mn}_2\text{O}_7$ clusters is related to: (1) a $\text{Mn}_2(\text{IV})$–O$_2$ moiety, (2) the HSOMO distribution on the O$_2$ atom, and (3) the bond length of the $\text{Mn}_2(\text{IV})$–O$_2$ bond. Two essential steps are present in the oxidation of CO by $\text{Mn}_m\text{O}_n$ clusters: (1) the initial intermediate formation that involves a carbon-manganese interaction; and (2) the $\text{Mn}_2(\text{IV})$–O$_2$ bond activation that determines the overall reaction barrier. The Mn–O bond activation energy at room temperature varies from $-0.11 \text{ eV} (\text{Mn}_2\text{O}_3)$ to $0.60 \text{ eV} (\text{Mn}_2\text{O}_4)$. For reactions with C$_2$H$_4$, only association products (such as $\text{Mn}_2\text{O}_2$(C$_2$H$_4$) and $\text{Mn}_3\text{O}_2$(C$_2$H$_4$)) are observed, which suggests that $\text{Mn}_2\text{O}_4$ and $\text{Mn}_2\text{O}_7$ clusters, which have high activity for the oxidation of CO, adsorb, but do not oxidize small hydrocarbon compounds. In order to generate a whole catalytic reaction cycle for CO oxidation through commonly used oxidants, reactions of $\text{Mn}_m\text{O}_n$ clusters with NO$_2$ and O$_2$ are also investigated. Small $\text{Mn}_2\text{O}_4$ clusters are easily oxidized by NO$_2$, which suggests that the catalytically reactive $\text{Mn}_2\text{O}_4$ clusters can be regenerated by NO$_2$ after reaction with CO: $\text{Mn}_2\text{O}_4 + \text{CO} + \text{NO}_2 \rightarrow \text{Mn}_2\text{O}_4 + \text{CO}_2 + \text{NO}$. A condensed phase surface catalytic cycle for CO oxidation by NO$_2$ is proposed based on the present gas phase cluster experimental and theoretical studies. The various reaction mechanisms explored by DFT calculations are in good agreement with the experimental results. The exposed $\text{Mn}_2(\text{IV})$ species with only one terminal oxygen on a manganese oxide surface are predicted to be the active catalytic sites for low temperature catalytic oxidation of CO by oxidants like NO$_2$.

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58See supplementary material at http://dx.doi.org/10.1063/1.4819059 for all singly occupied molecular orbitals (SOMOs) of Mn₂O₃⁻⁵ and Mn₃O₆⁻⁷ clusters in Figure S1.