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Effect of charge state and stoichiometry on the structure and reactivity of nickel oxide clusters with CO

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ABSTRACT

The collision induced fragmentation and reactivity of cationic and anionic nickel oxide clusters with carbon monoxide were studied experimentally using guided-ion-beam mass spectrometry. Anionic clusters with a stoichiometry containing one more oxygen atom than nickel atom (NiO_2^- , Ni_2O_3^- , Ni_3O_4^- and Ni_4O_5^-) were found to exhibit dominant products resulting from the transfer of a single oxygen atom to CO, suggesting the formation of CO_2 . Of these four species, Ni_2O_3^- and Ni_4O_5^- were observed to be the most reactive having oxygen transfer products accounting for approximately 5% and 10% of the total ion intensity at a maximum pressure of 15 mTorr of CO. Our findings, therefore, indicate that anionic nickel oxide clusters containing an even number of nickel atoms and an odd number of oxygen atoms are more reactive than those with an odd number of nickel atoms and an even number of oxygen atoms. The majority of cationic nickel oxides, in contrast to anionic species, reacted preferentially through the adsorption of CO onto the cluster accompanied by the loss of either molecular O_2 or nickel oxide units. The adsorption of CO onto positively charged nickel oxides, therefore, is exothermic enough to break apart the gas-phase clusters. Collision induced dissociation experiments, employing inert xenon gas, were also conducted to gain insight into the structural properties of nickel oxide clusters. The fragmentation products were found to vary considerably with size and stoichiometry as well as ionic charge state. In general, cationic clusters favored the collisional loss of molecular O_2 while anionic clusters fragmented through the loss of both atomic oxygen and nickel oxide units. Our results provide insight into the effect of ionic charge state on the structure of nickel oxide clusters. Furthermore, we establish how the size and stoichiometry of nickel oxide clusters influences their ability to oxidize CO, an important reaction for environmental pollution abatement.

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1. Introduction

Heterogeneous catalysts significantly reduce the energy requirements and waste disposal associated with the vast majority of industrial chemical processes [1]. However, despite their widespread economic importance, the current approach to designing bulk-phase catalysts is largely combinatorial in nature whereby a variety of different catalyst materials are prepared and exposed to a reactant stream. The product yield is then monitored as a function of various parameters such as temperature and pressure. This methodology has been effective in producing a multitude of catalysts that are currently employed in industry, but from a conceptual point of view, such techniques yield little insight into why one particular catalyst formulation is better than another. Other than general trends established through a huge number of empiri-

cal observations, there is little information to guide the intelligent design of future catalysts. Recently, it has become increasingly well recognized that the directed design of future catalysts with improved activity and selectivity depends on a molecular level understanding of catalytic reactions [1].

Transition metal oxides are widely used as both catalysts and catalyst-support materials for a variety of commercially relevant reactions [2,3]. Nickel based catalysts, in particular, have been employed to promote methanation [4,5] and cracking reactions [4], the reduction of nitrogen oxides [6,7], and the oxidation of volatile organic compounds (VOC) and carbon monoxide (CO) [8]. While these bulk-phase studies provide insight into the effectiveness of different catalyst formulations, the specific active sites responsible for promoting a given reaction often remain undetermined.

Gas-phase cluster experiments enable the investigation of the fundamental physical and chemical behavior of catalyst materials, such as nickel oxide, in the absence of factors which complicate condensed phase research [9]. By avoiding the discrepancies resulting

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from different catalyst preparation methods it is possible to investigate, with atomic level precision, the influence of factors such as size, stoichiometry, and ionic charge state on cluster reactivity [10]. This is particularly important in nanocatalysis where the properties of clusters have been found to change dramatically with the addition or removal of single atoms [11]. Moreover, through a comparison of the reactivity of cationic and anionic clusters it is possible to gain insight into how charging effects at catalytic surfaces influence reactivity [12]. Employing photoelectron spectroscopy (PES), the electronic structure of the nickel atom bound to both one and two oxygen atoms was investigated in a previous study [13]. A large increase in electron affinity (EA) was observed with higher oxygen saturation, consistent with the ionic bonding expected in these species [13]. Furthermore, the NiO_2 cluster was found to have a second isomer with a molecularly bound O_2 unit and a much smaller EA [13]. Another combined experimental and theoretical study provided evidence for the enhanced abundance and stability of the Ni_9O_6 cluster [14]. The reactions of cationic nickel clusters with oxygen in an FT-ICR mass spectrometer were also shown to result in the preferential formation of $\text{Ni}_{13}\text{O}_8^+$ and $\text{Ni}_{16}\text{O}_{10}^+$ which were found to be inert to further oxidation by O_2 [15]. In a guided-ion-beam study, nickel oxide and dioxide bond energies were measured for clusters containing between two and eighteen nickel atoms, revealing small variations with increasing cluster size [16]. The rate of chemisorption and the saturation limits for CO adsorption onto anionic [17] and cationic [18] clusters were also studied in a flow tube reactor, revealing that a larger maximum number of CO molecules bind to Ni compared to the other group 10 elements (Pd and Pt) [17]. Furthermore, it was shown that cationic nickel clusters adsorb more CO molecules than anionic clusters of the same size [17,18]. A series of flow-tube experiments in our laboratory investigated the reactivity of anionic nickel oxide clusters with nitric oxide (NO) [19] revealing the exothermic formation of NO_2 accompanied by the loss of nickel units from the cluster. In a subsequent paper, evidence was presented for a complex mechanism involving first the oxidation of the anionic nickel oxide clusters through reduction of NO followed by the formation of NO_2 and NO_3 which were then released from the cluster as anions [20]. The reactivity of cationic nickel oxides with NO was also studied showing several competing processes including oxidation, addition of NO to the cluster, and replacement of oxygen by NO [21]. Finally, the reactivity of nickel and nickel oxide clusters with NO_2 was examined revealing primarily the oxidation of pure nickel clusters and the adsorption of NO_2 onto nickel oxide clusters [22]. Based on these previous findings it is reasonable to propose that specific nickel oxide clusters may exhibit enhanced reactivity for the oxidation of simple molecules such as CO.

In the present study, we demonstrate that anionic nickel oxide clusters with a stoichiometry containing one more oxygen atom than nickel atom (NiO_2^- , Ni_2O_3^- , Ni_3O_4^- and Ni_4O_5^-) are active towards the transfer of a single oxygen atom to CO, indicating the formation of CO_2 . Furthermore, we establish that the Ni_2O_3^- and Ni_4O_5^- clusters exhibit enhanced oxidation reactivity, thereby demonstrating that anionic clusters with an even number of nickel atoms and an odd number of oxygen atoms are more reactive than those with an odd number of nickel atoms and an even number of oxygen atoms. Cationic nickel oxides, in comparison, are shown to react predominantly through the adsorption of CO onto the cluster accompanied by the loss of either molecular O_2 or nickel oxide units. Finally, we present the results of collision induced dissociation experiments which reveal that cationic clusters fragment preferentially through the loss of molecular O_2 units while anionic clusters typically lose either atomic oxygen or nickel oxide units. The results presented herein, therefore, illustrate how size, stoichiometry and ionic charge state influence the structural and

reactive properties of nickel oxide clusters in the size regime in which each atoms counts.

2. Experimental methods

The reactivity of anionic and cationic nickel oxide clusters with CO was studied using a guided-ion-beam mass spectrometer described in detail in a previous publication [23]. Briefly, nickel oxide clusters were produced in a laser vaporization (LaVa) cluster source by pulsing oxygen seeded in helium (10%) into the plasma formed by ablating a nickel rod with the second harmonic (532 nm) of a Nd:YAG laser. The clusters exit the source region through a 27 mm long conical expansion nozzle and are cooled via supersonic expansion into vacuum. During supersonic expansion the high pressure (13.2 atm) expansion gas mixture passes through a narrow diameter nozzle into vacuum. The random thermal energy of the clusters is thereby converted into directed kinetic energy of the molecular beam. Consequently, the internal vibrational and rotational energy of the clusters is lowered through collisions with the He carrier gas. After exiting the source region the clusters pass through a 3 mm skimmer forming a collimated molecular beam and are then directed into a quadrupole mass filter employing a set of electrostatic lenses. The quadrupole mass filter isolates clusters of a desired mass which are then passed into an octopole collision cell.

Employing a retarding potential analysis, the average kinetic energy of the cluster ions in the octopole collision cell was determined previously [23] to be approximately 1 eV in the laboratory energy frame (E_{LAB}). Ideally, all clusters exiting the supersonic expansion source have the same initial kinetic energy. Therefore, using equation (1),

$$E_{\text{CM}} = E_{\text{LAB}} \frac{\text{Mass}[\text{CO}]}{\text{Mass}[\text{cluster}] + \text{Mass}[\text{CO}]} \quad (1)$$

the initial center-of-mass collision energy (E_{CM}) was calculated for NiO_2 , Ni_2O_4 , Ni_3O_3 , and Ni_4O_4 to be approximately 0.24 eV, 0.13 eV, and 0.11 eV and 0.09 eV with CO. 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. Using equation (2),

$$\sigma_{\text{L}} = \frac{e}{4\epsilon_0} \left(\frac{2\alpha}{E_{\text{CM}}} \right)^{1/2} \quad (2)$$

the Langevin cross section for ion-molecule reactions [25] was calculated to be 48 \AA^2 , 64 \AA^2 , 70 \AA^2 , and 80 \AA^2 for $\text{NiO}_2^{-/+}$, $\text{Ni}_2\text{O}_4^{-/+}$, $\text{Ni}_3\text{O}_3^{-/+}$ and $\text{Ni}_4\text{O}_4^{-/+}$, respectively. In equation (2), e is the charge of the ion, ϵ_0 is the vacuum permittivity, α is the polarizability of CO, and E_{CM} is the center of mass collision energy between the cluster ions and CO. Based on the Langevin cross sections, the pressure of CO gas in the reaction cell at 298 K, the length of the collision cell (12.9 cm) and the velocity of the cluster ions, it was determined that an average of approximately 55, 102, 125, and 164 collisions occur between NiO_2 , Ni_2O_4 , Ni_3O_3 and Ni_4O_4 clusters and CO, respectively, at the maximum CO pressure of 15 mTorr. As subsequent collisions with CO are expected to dissipate the initial kinetic energy of a given cluster the E_{CM} values reported above serve to establish an upper limit on the energy of the reactive collisions.

Variable pressures of CO, N_2 or Xe are introduced into the octopole collision cell employing a low flow leak valve. The gas pressure is monitored using a MKS Baratron capacitance manometer. Product ions formed in the collision cell are mass analyzed by a second quadrupole mass spectrometer. Finally, the ions are detected

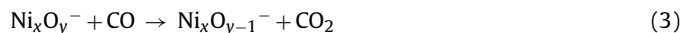
with a channeltron electron multiplier connected to a multichannel scalar card. The experimental branching ratios presented in the results section illustrate the change in normalized ion intensity with increasing pressures of CO reactant gas. At higher gas pressures the ratio of reactant ion intensity to total ion intensity becomes smaller while the ratio of product ion intensity to total ion intensity becomes larger. Experiments were also conducted with inert N₂ to verify that the products observed with CO are the result of a chemical reaction and not the products of collisional fragmentation. In addition, collision induced dissociation experiments were conducted employing inert Xe gas at three pressures, 0.08 mTorr, 0.12 mTorr, and 0.22 mTorr. During these experiments the kinetic energy of the cluster ions was increased by applying an accelerating DC potential to the octopole rods. The fragmentation products were, thereby, observed according to the energy required to generate them.

3. Results and discussion

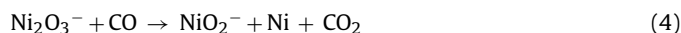
Fig. 1 displays a typical distribution of anionic and cationic nickel oxide clusters obtained by laser vaporization. Anionic clusters containing between one and four nickel atoms and two to five oxygen atoms were reacted with CO to determine the influence of size and stoichiometry on cluster reactivity. Cationic clusters containing one and two nickel atoms and between one and four oxygen atoms were also studied. One important feature that is apparent in Fig. 1 is that oxide clusters containing both an even and odd number of oxygen atoms are created in the laser vaporization source. This enables the reactivity of nickel clusters containing both molecular and atomic oxygen to be studied.

The products observed from the chemical reaction of anionic and cationic nickel oxide clusters with CO are listed in Table 1. The

fragmentation products resulting from the collision induced dissociation of the clusters with both N₂ and Xe are also provided for comparison. Nickel oxide clusters that exhibit atomic oxygen transfer products when reacted with CO are active for the oxidation of CO to CO₂. Species that display atomic oxygen loss channels with N₂ are unreactive as the products result from collisional fragmentation and not chemical reaction. Inspection of Table 1 reveals that anionic clusters with the stoichiometries NiO₂[−], NiO₃[−], Ni₂O₃[−], Ni₃O₄[−] and Ni₄O₅[−] all exhibit dominant atomic oxygen transfer products when reacted with CO but not when exposed to an equal pressure of N₂. Each of these clusters, therefore, is active towards the oxidation of CO according to equation (3).



The normalized ion intensities of each of these clusters with increasing pressures of CO reactant gas are shown in Fig. 2. For each cluster it is observed that the normalized reactant ion intensity decreases with increasing pressure of CO while the atomic oxygen transfer product becomes more pronounced. The Ni₂O₃[−] cluster also showed a minor product resulting from the loss of Ni forming NiO₂[−] according to equation (4).



As shown in Fig. 2c, the NiO₂[−] product does not become pronounced until a reactant gas pressure of around 12 mTorr of CO. This suggests that generation of the NiO₂[−] product from Ni₂O₃[−] depends on multiple collisions with CO. It is reasonable that the more oxygen rich NiO₂[−] product retains the extra electron of the anion as NiO₂ has an electron affinity of 3.05 eV while that of Ni is 1.16 eV [13]. As this minor product was not observed in separate studies with N₂, it results from the exothermic oxidation of CO by Ni₂O₃[−]. Indeed, the NiO₂[−] fragment was also observed at an *E*_{CM} of 0.3 eV in collision induced dissociation experiments with Xe indicating that additional energy, either in the form of kinetic energy or chemical heat of reaction is necessary to dissociate Ni₂O₃[−]. A minor product resulting from the loss of molecular O₂ from Ni₄O₅[−] was also seen but not included in Fig. 2e for the sake of clarity. This O₂ loss product was found during separate studies with N₂ and Xe confirming that it is the result of collisional fragmentation according to equation (5).



Out of the five anionic nickel oxide clusters found to be reactive for CO oxidation, Ni₂O₃[−] and Ni₄O₅[−] appeared to show enhanced reactivity, having oxygen transfer products accounting for approximately 5% and 10% of the total ion intensity, respectively, at 15 mTorr of CO.

To further analyze the influence of cluster size on oxidation reactivity for NiO₂[−], Ni₂O₃[−], Ni₃O₄[−] and Ni₄O₅[−] the phenomenological rate constant at the average lab frame energy of 1 eV was calculated for each cluster assuming pseudo-first order kinetics according to equation (6).

$$\ln \left[\frac{I_r}{I_0} \right] = -k[R]t \quad (6)$$

In equation (6), *I_r* is the reactant ion intensity with the addition of CO, *I₀* is the reactant ion intensity without CO, *k* is the rate constant, *R* is the concentration of CO 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 based on the length of the reaction cell which was determined using a trapezoidal pressure falloff approximation to be 12.9 cm [23] and the velocity of the ions resulting from the supersonic expansion which was calculated using the equations of Anderson and Fenn [24,25]. The same initial kinetic energy of 1 eV in the laboratory frame

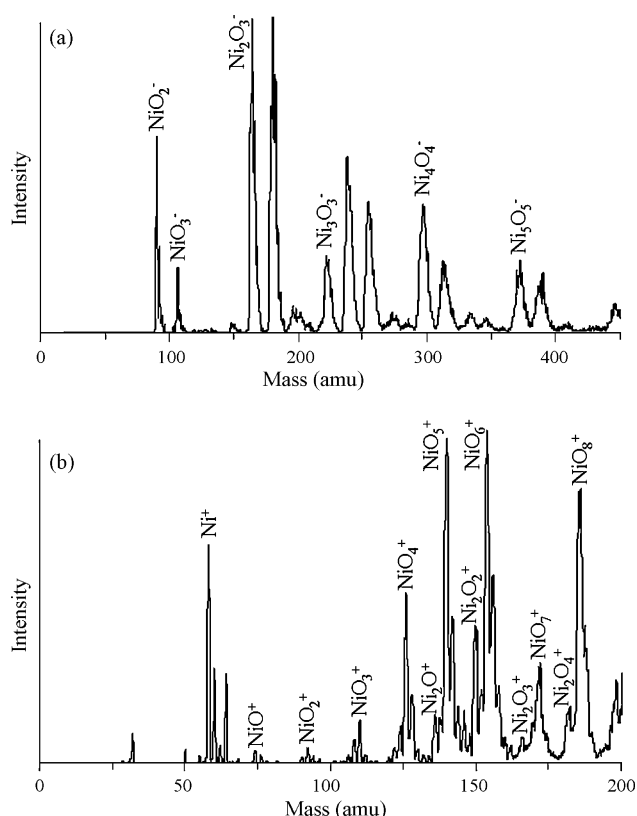


Fig. 1. A typical mass distribution of (a) anionic and (b) cationic nickel oxide clusters produced by laser vaporization.

Table 1
List of products resulting from the chemical reactions between mass selected anionic and cationic nickel oxide clusters and carbon monoxide. Fragmentation products resulting from collision induced dissociation with inert N₂ and Xe are also shown for comparison.

Nickel oxide anions				
Ni _x O _y [−] (x, y)	Products with CO	Products with N ₂	Products with Xe	Neutral(s) lost with Xe
1, 2	NiO [−]	None	1, 1	0, 1
1, 3	NiO ₂ [−]	None	1, 1 1, 2	0, 2 0, 1
2, 3	Ni ₂ O ₂ [−] NiO ₂ [−]	None	1, 2 2, 2	1, 1 0, 1
2, 4	Ni ₂ O ₃ [−] Ni ₂ O ₂ [−]	2, 3	1, 2 2, 3 2, 2 1, 3	1, 2 0, 1 0, 2 1, 1
3, 3	No reaction		2, 3	1, 0
3, 4	Ni ₃ O ₃ [−]	None	3, 3 2, 3	0, 1 1, 1
3, 5	Ni ₃ O ₃ [−] Ni ₃ O ₄ [−]	3, 3 3, 4	3, 3 3, 4 2, 3	0, 2 ^b 0, 1 1, 2
4, 4	No reaction		4, 2 3, 3	0, 2 1, 1
4, 5	Ni ₄ O ₄ [−] Ni ₄ O ₃ [−]	4, 3 4, 4	4, 3 4, 4 2, 3	0, 2 0, 1 2, 2
Nickel oxide cations				
Ni _x O _y ⁺ (x, y)	Products with CO	Products with N ₂	Products with Xe	Neutral(s) lost with Xe
1, 1	Ni ⁺	1, 0	1, 0	0, 1
1, 2	NiCO ⁺ NiO ⁺	1, 1 1, 0	1, 0 1, 1	0, 2 0, 1
1, 3	NiOCO ⁺ Ni ⁺ NiO ₂ ⁺ NiCO ⁺ NiO ⁺	1, 1	1, 1 1, 2	0, 2 0, 1
1, 4	NiCO ⁺ NiO ₂ ⁺ NiO ₂ CO ⁺ NiO ⁺ Ni ⁺		1, 2 1, 3	0, 2 0, 1
2, 1	NiOCO ⁺			
2, 2	Ni(CO) ₂ ⁺ NiO ₂ CO ⁺ NiCO ⁺	2, 0	2, 0 1, 3 1, 2	0, 2 ^b 1, 1 1, 0
2, 3	Ni ₂ O ⁺ Ni ₂ OCO ⁺ NiO(CO) ₂ ⁺ Ni ₂ O ₂ ⁺ Ni(CO) ₂ ⁺ NiOCO ⁺ NiCO ⁺	2, 1	2, 1	0, 2 ^b
2, 4	Ni ₂ O ₂ ⁺ Ni(CO) ₂ ⁺ NiO ₂ CO ⁺ Ni ₂ O ₂ CO ⁺ [*] NiCO ⁺ [*] NiOCO ⁺		2, 2 2, 0	0, 2 ^b 0, 4

^{*} Denotes a minor product channel whose relative intensity is less than 1% and not shown in the branching ratios for clarity.

^b Denotes that fragmentation occurs at near thermal energy.

is imparted to all of the clusters leaving the supersonic expansion. Therefore, more massive clusters will have a lower velocity and, consequently, spend more time in the reaction cell. Previous studies in our laboratory have shown that the pseudo-first

order rate constants obtained using equation (6) agree well with the phenomenological rate constants calculated from zero pressure cross section data [25]. The plots of ln[I_r/I₀] as a function of CO concentration are displayed in Fig. 3. Assuming pseudo-

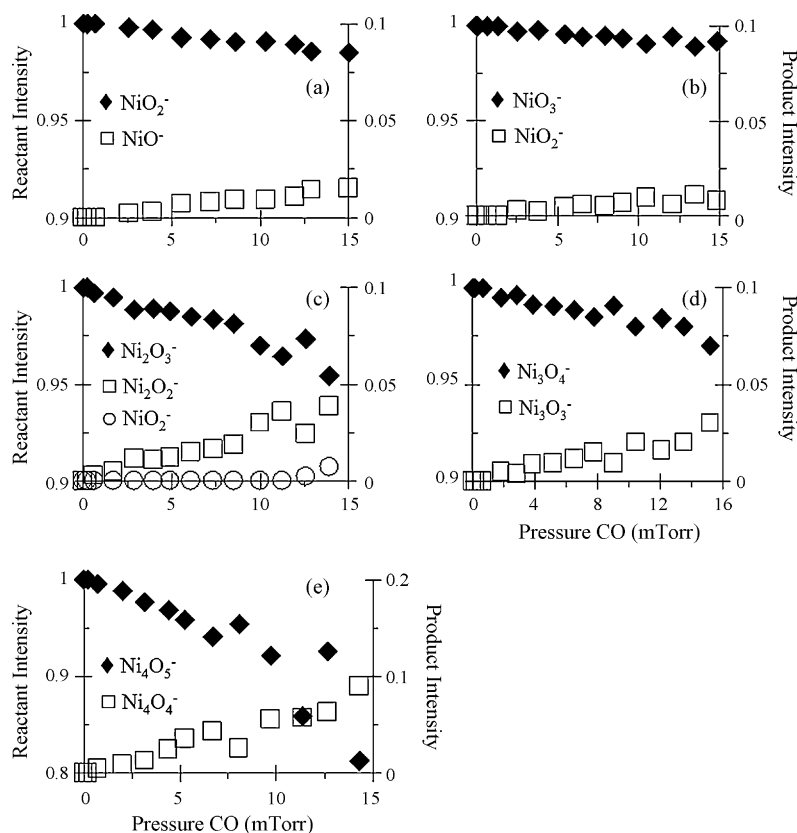


Fig. 2. Normalized intensity of (a) NiO_2^- , (b) NiO_3^- , (c) Ni_2O_3^- , (d) Ni_3O_4^- and (e) Ni_4O_5^- with increasing pressure of CO. Note the decrease in the reactant ion intensity and the increase in the product corresponding to the oxidation of CO. The normalized reactant ion intensity is plotted on the left y-axis and the product ion intensity on the right y-axis.

first order kinetics, the slopes of the plots are equal to $-kt$. The values of the slopes, when divided by the reaction time, reveal rate constants on the order of $9.2 \pm 0.5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ for NiO_2^- , $1.9 \pm 0.1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for Ni_2O_3^- , $9.6 \pm 0.8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ for Ni_3O_4^- and $3.0 \pm 0.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for Ni_4O_5^- . The pseudo-first order rate constants reported herein allow for a better qualitative comparison of the relative reactivity of these clusters with CO, thereby providing insight into how cluster size influences the oxidation reaction. The kinetic analysis confirms that Ni_4O_5^- is the most reactive species, followed by Ni_2O_3^- . Furthermore, it is established that anionic nickel oxide clusters containing an even number of nickel atoms and an odd number of oxygen atoms are more reactive towards the oxidation of CO than clusters with an odd number of nickel atoms and an even number of oxygen atoms. This oscillatory behavior in the rate constants with increasing cluster size is plotted in Fig. 4. The anionic nickel oxide clusters which were not found to be active towards CO oxidation all exhibited collisional atomic or molecular oxygen loss when exposed to N_2 in the reaction cell or, otherwise, were found to be completely inert. The products observed for these clusters are provided in Table 1 for the sake of completeness.

In contrast to the anionic clusters, cationic nickel oxides reacted preferentially through the strong adsorption of CO onto the cluster accompanied by the loss of either molecular O_2 or nickel oxide units as shown in Table 1. These processes correspond to equations (7) and (8), respectively.

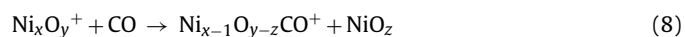
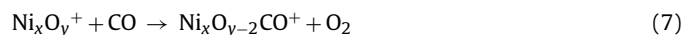
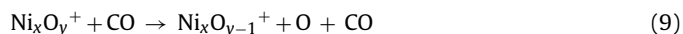


Fig. 5 displays the normalized ion intensities of NiO_2^+ , NiO_3^+ , Ni_2O^+ and Ni_2O_2^+ with increasing pressure of CO. NiO_2^+ and NiO_3^+ both decrease in intensity with increasing CO pressure while the products corresponding to the association of CO and loss of O_2 (NiCO^+ and NiOCO^+) become more pronounced. Minor products resulting from the loss of atomic O according to equation (9) are also observed.



For NiO_2^+ this same product was observed in experiments with N_2 suggesting that it is a collisional fragment. However, in CID studies with Xe, NiO_2^+ was observed to lose molecular O_2 as the preferred fragmentation channel followed by atomic oxygen at higher energy. As mentioned in the experimental section, the CO and N_2 experiments were performed at pressures where multiple collisions occur between the cluster ions and the reactant gas molecules. The CID studies with Xe, in comparison, are performed at near single collision conditions. Loss of atomic oxygen from NiO_2^+ , therefore, appears to result from multiple collisions with either CO or N_2 . NiO_3^+ , however, does not lose atomic oxygen when interacted with N_2 . For this reason we cannot exclude that NiO_3^+ may be oxidizing CO to CO_2 . Cationic oxide clusters containing two nickel atoms were found to lose nickel oxide units when reacted with CO. Ni_2O^+ , for example, exhibits a strong product corresponding to the loss of a nickel atom as shown in Fig. 5c. Ni_2O_2^+ was also observed to lose both pure nickel and/or a nickel oxide unit. The adsorption of CO onto positively charged nickel oxides, therefore, is exothermic enough to break apart the gas-phase clusters. The number of different products observed from the reaction of cationic nickel oxides with CO increases substantially with higher oxygen saturation and larger cluster size. Rather than present an exhaustive discussion

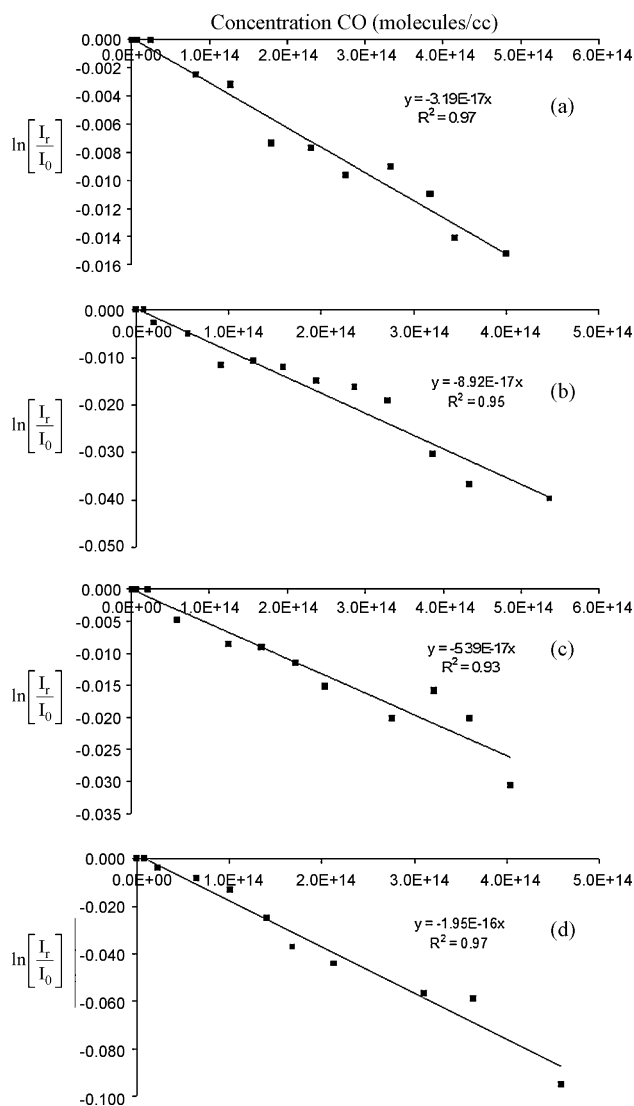


Fig. 3. Plot of the logarithm of the ratio of reactant ion intensity with and without CO reactant gas $\ln(I_r/I_0)$ as a function of the concentration of CO for (a) NiO_2^+ , (b) Ni_2O_3^+ (c) Ni_3O_4^+ and (d) Ni_4O_5^+ . Note the larger value of $-kt$ for Ni_4O_5^+ and Ni_2O_3^+ compared to the other clusters.

of the behavior of each individual cluster we draw attention to two additional general observations. First, at higher oxygen saturation, we found products corresponding to the adsorption of CO accompanied by the loss of two O_2 molecules in accordance with

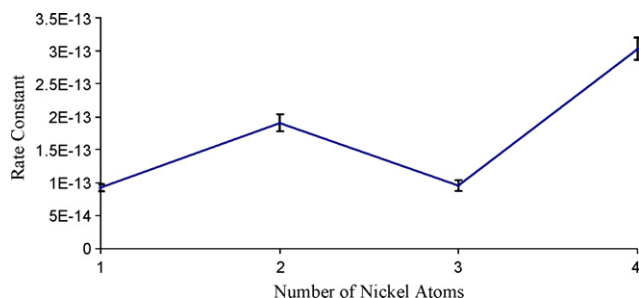
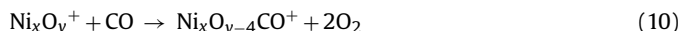


Fig. 4. Plot of the rate constants for the oxidation of CO by $\text{Ni}_x\text{O}_{x+1}^-$ clusters as a function of cluster size. Note the odd–even oscillation in the rate constants with increasing size.

equation (10).



Second, cationic oxide clusters containing two nickel atoms were found to dissociate into nickel atoms with two CO molecules attached (e.g., $\text{Ni}(\text{CO})_2^+$). These products most likely form through the exothermic adsorption of CO onto the cluster accompanied by the loss of a nickel oxide subunit. The NiCO^+ intermediate then associates a second CO molecule forming the dicarbonyl product. Indeed, a small intensity of the proposed NiCO^+ intermediate was observed in the reaction of Ni_2O_2^+ with CO as shown in Fig. 5d. The complete list of products is provided in Table 1 for the interested reader.

In order to gain insight into the structural properties of nickel oxide clusters and how an accumulation or deficiency of electron density influences the binding of oxygen to nickel, we conducted a systematic fragmentation study employing Xe gas as the collision partner. The collision induced dissociation products observed for each cluster are listed in Table 1 in order of appearance with increasing collision energy. Concerning anionic clusters containing one nickel atom, NiO_2^- was found to dissociate through the loss of atomic oxygen at an E_{CM} of 3.6 eV consistent with a structure containing atomically rather than molecularly bound O_2 . NiO_3^- , in contrast, first loses a molecular O_2 group at an E_{CM} of 0.4 eV followed by atomic oxygen at 3.1 eV. This suggests that one oxygen atom is bound strongly to the nickel anion while the other two oxygen atoms form a weakly bound molecular O_2 unit. For the two nickel atom clusters, Ni_2O_3^- first loses NiO forming NiO_2^- at an E_{CM} of 0.3 eV. As mentioned previously, this fragment was also observed from the exothermic oxidation of CO by Ni_2O_3^- . The NiO_2^- product indicates that the nickel–nickel bonds in Ni_2O_3^- , if any, are weaker than the nickel–oxygen bonds. Indeed, only at an E_{CM} of 1.5 eV is the loss of atomic oxygen observed from Ni_2O_3^- . Ni_2O_4^- dissociates preferentially through the loss of NiO_2 forming NiO_2^- at an E_{CM} of 0.7 eV. This corresponds to the cluster being split in half with either fragment having an equal probability of retaining the additional electron of the anion. At an E_{CM} of around 2.0 eV the loss of atomic and molecular oxygen from Ni_2O_4^- is observed. Again, the loss of nickel oxide units at low energy suggests that the nickel–nickel bonds in two nickel atom clusters are weaker than the nickel–oxygen bonds. At the highest collision energy of 3.4 eV, a final product corresponding to the loss of NiO forming NiO_3^- is found for Ni_2O_4^- . It is reasonable that the NiO_3^- fragment retains the additional electron as it is more oxygen rich than NiO and, consequently, should have a higher electron affinity. Interesting trends were also observed for the anionic three nickel atom clusters. Ni_3O_3^- loses a nickel atom as its only fragmentation product at an E_{CM} of 0.6 eV. This finding indicates that the oxygen atoms are very strongly bound in Ni_3O_3^- , consistent with the fact that no oxidation product is observed from the reaction of this cluster with CO. Ni_3O_4^- , in contrast, readily loses an oxygen atom at 0.5 eV followed by a NiO unit at 1.0 eV forming Ni_2O_3^- . A weakly bound atomic oxygen is consistent with the fact that an oxidation product is observed from the reaction of Ni_3O_4^- with CO. Ni_3O_5^- loses molecular O_2 at an E_{CM} of 0.2 eV followed by atomic oxygen at 1.0 eV. This indicates that at a saturation of five oxygen atoms, anionic three nickel atom clusters begin to bind oxygen weakly in the molecular form. Molecular O_2 loss is also the first fragmentation product observed for the anionic four nickel atom clusters. At higher collision energies around 1.7 eV the loss of NiO and formation of Ni_3O_3^- is observed for Ni_4O_4^- while Ni_4O_5^- is found to lose Ni_2O_2 forming Ni_2O_3^- at an E_{CM} of 1.2 eV.

The fragmentation properties of the cationic nickel oxide clusters were also examined. Regarding the one nickel atom clusters, NiO_2^+ was found to dissociate molecular O_2 at an E_{CM} of 3.5 eV indi-

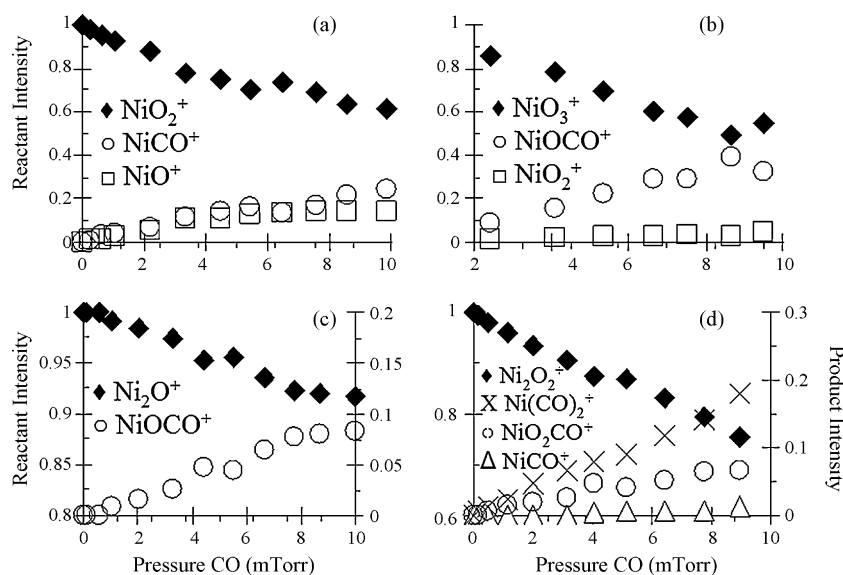


Fig. 5. Normalized intensity of (a) NiO_2^+ , (b) NiO_3^+ , (c) Ni_2O^+ and (d) Ni_2O_2^+ with increasing pressure of CO. Note the decrease in the reactant ion intensity and the increase in the products corresponding to the association of CO accompanied by the loss of either O_2 or NiO_x . The normalized reactant ion intensity is plotted on the left y-axis and the product ion intensity on the right y-axis.

cating that oxygen is bound in the molecular form at a saturation of two oxygen atoms. This is in contrast to the anionic NiO_2^- cluster where oxygen is bound atomically. NiO_3^+ and NiO_4^+ both lose molecular O_2 at a low energy of around 0.4 eV followed by atomic O at higher energies of approximately 1 eV. Due to the fact that NiO_3^+ contains an odd number of oxygen atoms, the only reasonable structure is one with a strongly bound atomic oxygen and a weakly bound molecular O_2 unit. For NiO_4^+ , however, the atomic oxygen fragment is more difficult to explain. Because loss of molecular O_2 is observed from NiO_2^+ , it is expected that the two additional oxygen atoms in NiO_4^+ would form a second molecular O_2 unit. This indicates that additional energy is needed to rupture the O–O bond in one of these O_2 units resulting in loss of atomic oxygen from NiO_4^+ . Concerning the two nickel atom clusters, Ni_2O_2^+ , Ni_2O_3^+ and Ni_2O_4^+ all lose molecular O_2 as the preferred fragmentation pathway. At higher energies around 2.0 eV the loss of nickel oxide units is also observed. The findings discussed above demonstrate that cationic nickel oxide clusters bind oxygen preferentially in the molecular form while anionic clusters have a higher occurrence of atomically bound oxygen.

3.1. Implications for catalysis

The results presented above have ramifications for nickel oxide based heterogeneous catalysis. We establish, through collision induced dissociation and reactivity studies that negatively charged clusters contain a larger proportion of atomically bound oxygen than positively charged species. The activation of the strong O–O bond in molecular O_2 has been proposed to be the rate limiting step in CO oxidation. Furthermore, it has been shown that in the case of gold particles, a partial negative charging is necessary to activate the O–O bond and facilitate the formation of CO_2 [26,27]. Therefore, specific negatively charged nickel oxides containing atomically bound oxygen, where the activation of the O–O bond is complete, should be active sites for the oxidation of CO. In contrast, positively charged nickel oxide clusters are shown to bind CO much more strongly than negatively charged species. In fact, the heat of adsorption is so exothermic that in many cases it breaks apart the nickel oxide cluster into smaller units. In heterogeneous catalysis, there is typically an optimum binding energy of reac-

tant molecules to the catalyst surface which results in the highest activity [4]. Essentially, the reactant molecules must bind strongly enough to the catalyst to become activated but not so strongly that they poison the surface [4]. Our results show that the presence of molecularly bound oxygen at positively charged nickel centers does not prevent the subsequent adsorption of CO. In contrast, for negatively charged nickel oxides, no products with CO adsorbed on the cluster were observed. This is because CO is a strong nucleophile that binds through donation of its lone pair of electrons into the lowest unoccupied molecular orbital (LUMO) of a cluster. The extra electron present in the anionic clusters typically raises the energies of the LUMO levels resulting in a less favorable bonding interaction with CO in comparison to the cationic species. This suggests that the oxidation of CO by anionic nickel oxides occurs by a gas-phase CO molecule reacting directly with either an atomically bound oxygen atom [28] or a highly activated superoxide unit [29]. CO_2 is then immediately released from the cluster. This Eley–Rideal-like mechanism has been observed previously for the oxidation of CO by anionic gold oxide clusters [28,30]. On an infinite surface, however, it is also possible that sites with a partial positive and a partial negative charge may occur in close proximity to each other. In such a hypothetical situation, it is likely, based on our gas-phase findings that the positively charged sites would serve to bind CO to the catalyst surface and the negative sites would provide the activated oxygen necessary to form CO_2 . As most catalytic reactions are run at elevated temperatures the barrier for diffusion of CO from one site to the other may be easily overcome. This Langmuir–Hinshelwood-like mechanism has also been observed previously in the oxidation of CO by positively charged gold-oxide clusters [30].

4. Conclusions

The findings presented herein demonstrate that anionic nickel oxide clusters with a stoichiometry containing one more oxygen atom than nickel atom are reactive towards the transfer of a single oxygen atom to CO, indicating the formation of CO_2 . Furthermore, it is established that anionic clusters containing an even number of nickel atoms and an odd number of oxygen atoms are more reactive than those with an odd number of nickel atoms and an even

number of oxygen atoms. Cationic nickel oxide clusters, in contrast, are shown to react mainly through the adsorption of CO onto the cluster accompanied by the loss of either molecular O₂ or nickel oxide units. The adsorption of CO onto positively charged nickel oxides, therefore, is exothermic enough to break apart the cluster. Collision induced dissociation studies also reveal that cationic nickel clusters bind oxygen preferentially in the molecular form while anionic clusters contain a higher percentage of atomically bound oxygen. Our results provide insight into the influence of size and ionic charge state on the structure of nickel oxide clusters and their reactivity with carbon monoxide.

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