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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.

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 empirical 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 $Ni_{13}O_8{}^+$ and $Ni_{16}O_{10}{}^+$ 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),

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

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),

$$\sigma_L = \frac{e}{4\varepsilon_0}\left(\frac{2\alpha}{E_{CM}}\right)^{1/2} \tag{2}$$

the Langevin cross section for ion-molecule reactions [25] was calculated to be 48 $Å^2$, 64 $Å^2$, 70 $Å^2$, and 80 $Å^2$ for $NiO_2{}^{-/+}$, $Ni_2O_4{}^{-/+}$, $Ni_3O_3{}^{-/+}$ and $Ni_4O_4{}^{-/+}$, respectively. In equation (2), e is the charge of the ion, ε_o 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