Oxidation of CO by Aluminum Oxide Cluster Ions in the Gas Phase

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Small aluminum oxide cluster cations and anions, produced by laser vaporization, were investigated regarding their reactivity toward CO and N_2O employing guided-ion-beam mass spectrometry. Clusters with the same stoichiometry as bulk alumina, Al_2O_3, exhibited atomic oxygen transfer products when reacted with CO, suggesting the formation of CO_2. Anionic clusters were less reactive than cations but showed higher selectivity towards the transfer of only a single oxygen atom. Cationic clusters, in contrast, exhibited additional products corresponding to the sequential transfer of two oxygen atoms and the loss of an aluminum atom. To determine if these stoichiometric clusters could be generated from oxygen-deficient species, clusters having a stoichiometry with one less oxygen atom than bulk alumina, Al_2O_2, were reacted with N_2O. Cationic clusters were found to be selectively oxidized to $Al_2O_3^+$, while anionic clusters added both one and two oxygen atoms forming $Al_2O_3^-$ and $Al_2O_4^-$. The oxygen-rich $Al_2O_4^-$ cluster exhibited comparable reactivity to $Al_2O_3^-$ when reacted with CO.

Introduction

Heterogeneous catalysts are widely employed in industry for both chemical production and the abatement of harmful atmospheric pollutants.[1] These materials typically consist of a fine dispersion of metal particles, the active phase, over a metal oxide support material, the carrier.[2,3] Aluminum oxide (alumina) finds extensive use as a catalyst support material due to its high mechanical strength and resistance to thermal degradation.[4] Its influence on the reactive behavior of certain systems also plays a role in the choice of Al_2O_3 as a support. Indeed, recent findings have demonstrated that Au particles supported on γ-alumina exhibit enhanced catalytic activity for the oxidation of CO to CO_2.[5] Bulk-phase catalysis studies have also revealed that support materials exert a significant influence on the activity of catalyst particles.[6] In particular, it has been suggested that there are two types of support materials for heterogeneous oxidation catalysis which exhibit widely different activity.[7] One variety, the reducible supports, have the capability to adsorb and transfer large quantities of O_2 molecules to the catalyst particle and, consequently, exhibit higher turn-over frequencies (TOF). Irreducible supports, in contrast, do not adsorb significant amounts of O_2. The supply of oxygen to the active centers, therefore, must come from direct adsorption of O_2 onto the catalyst particle rather than the support, and the TOF are, consequently, lower. Aluminum oxide, due to its strong ionic bonding,[4] has historically been regarded as an irreducible support that does not participate directly in heterogeneous oxidation catalysis. Recent studies, however, revealed a transfer of charge to gold particles supported on γ-Al_2O_3 that may be responsible for the enhanced CO oxidation activity of this catalyst.[5] Therefore, fundamental questions can be raised as to whether aluminum oxides are reactive with CO and how an accumulation or deficiency of electron density influences their reactivity.

Gas-phase cluster experiments enable the study of catalyst and catalyst-support materials, such as aluminum oxide, in the absence of factors that complicate condensed-phase research.[8] By avoiding discrepancies resulting from different catalyst preparation methods, gas-phase experiments allow the fundamental physical and chemical behavior of catalytic materials to be investigated with atomic-level precision.[9] Previous studies, employing photoelectron spectroscopy (PES), examined the structure and bonding of $Al_xO_y^-$ ($x = 1$–2, $y = 1-5$)[10] and the metal-to-oxide transformation in Al_3O_y ($y = 0$–5)[11] clusters. Species containing two aluminum atoms were found to have rhombus-like structures with bridging oxygen atoms between the aluminum atoms. Al_2O_3 and Al_2O_4 were calculated to have atomically bound terminal oxygen atoms outside of the Al_2O_2 ring.[10] The PES spectra revealed significant increases in electron affinity (EA) with higher oxygen coverage consistent with the ionic bonding expected for these species.[11] Larger aluminum oxide clusters, examined by infrared photoionization,[12,13] were shown to have structures comparable to bulk γ-Al_2O_3. The electronic and geometric structures of oxide clusters containing one[14] and three[14–18] aluminum atoms were also calculated, revealing a preference toward planar structures for anions, and three-dimensional structures for uncharged clusters.[17]

Concerning the reactivity of aluminum oxides, the addition of H_2O and CH_3OH to $Al_3O_3^-$ has been studied by a combination of PES and quantum chemical calculations indicating the formation of hydroxide and methoxide products.[19,20] These reactions, as well as the addition of NH_3 to $Al_3O_3^-$, were also examined computationally revealing that dissociative adsorption of H_2O and CH_3OH are highly exothermic, while the barriers for NH_3 dissociation on the cluster are high.[21] Adsorption of H_2O onto the central aluminum atom of $Al_5O_4^-$, accompanied by H migration to a neighboring O atom, was also calculated to be energetically favorable.[22] More recent theoretical work, in combination with IR-REMPI experiments, discovered unique structures for $(Al_2O_3)_4^+$ and $(Al_2O_3)_4$ clusters that have not been observed for bulk alumina.[23] This study also uncovered that the cationic $(Al_2O_3)_4^+$ cluster has a structure with a singly coordi-

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nated radical oxygen center (Al−O•).[23] By comparison, reactivity studies of vanadium oxides conducted in our laboratory and by others have demonstrated that radical oxygen centers with elongated vanadium−oxygen bonds facilitate enhanced reactivity for the oxidation of ethylene[24,25] and activation of methane[26] at thermal energies. On the basis of these findings, it is reasonable to conclude that aluminum oxide clusters with a $(Al_2O_3)_n^+$ stoichiometry may also be active for the oxidation of simple molecules such as CO.

In the present study, we demonstrate that aluminum oxide cluster cations and anions, having the same stoichiometry as bulk alumina, Al_2O_3, are capable of oxidizing CO to CO_2 at thermal energies. The anionic clusters are shown to be less reactive than the cations but highly selective towards the transfer of a single oxygen atom. The cationic clusters, in contrast, are far more reactive exhibiting sequential oxygen transfer products and the loss of an Al atom. Furthermore, oxygen-deficient clusters having a stoichiometry with one oxygen atom less than bulk alumina, Al_2O_2, when reacted with N_2O, exhibit oxygen atom addition products forming both stoichiometric and oxygen-rich species. These findings provide new insight into the supply of reactive oxygen in alumina-supported heterogeneous catalysts.

Experimental Methods

The reactivity of aluminum oxide cations and anions with CO was studied using a guided-ion-beam mass spectrometer described in detail in a previous publication.[27] Briefly, aluminum oxide clusters were produced in a laser vaporization (LaVa) cluster source by pulsing oxygen seeded in helium (1% for cations and 10% for anions) into the plasma formed by ablating an aluminum 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 through supersonic expansion into vacuum. The clusters pass through a 3 mm skimmer forming a collimated molecular beam and are directed into a quadrupole mass filter employing a set of electrostatic lenses. The quadrupole mass filter isolates clusters of a desired stoichiometry, which are then passed into an octopole collision cell. Variable pressures of CO or N_2O 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 mutichannel scalar card. The experimental branching ratios presented in the results section illustrate the change in normalized ion intensity with increasing pressures of CO or N_2O reactant gas. At higher gas pressures, therefore, 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 N_2 to verify that the products observed with CO and N_2O are the result of a chemical reaction and not the products of collisional fragmentation.

Results and Discussion

The relative intensity of $Al_2O_3^+$ with increasing pressure of CO reactant gas is displayed in Figure 1a. The reactant ion, $Al_2O_3^+$, decreases in intensity with increasing CO pressure, while the product ions, $Al_2O_2^+$, Al_2O^+, and Al^+ become more pronounced. The most intense product ion is Al^+, accounting for approximately 45% of the total ion signal at 10 mTorr of CO. Transfer of a single oxygen atom, forming $Al_2O_2^+$, is the second major reaction channel. A minor peak corresponding to Al_2O^+ is also observed. The Al^+ product results from the exothermic adsorption of CO onto $Al_2O_3^+$ that causes loss of the aluminum atom cation according to eq 1.

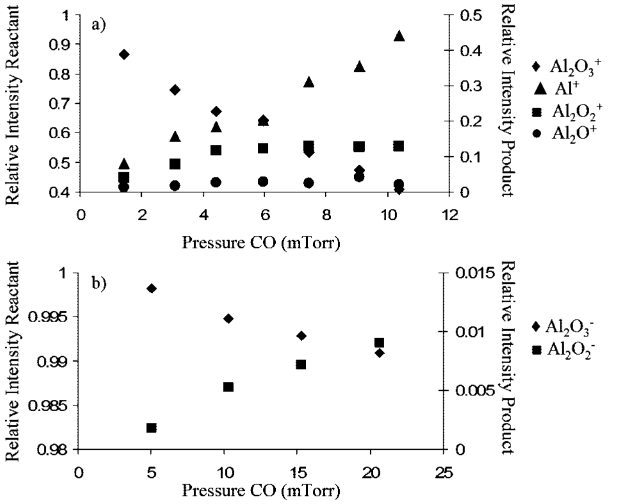

Figure 1. Relative ion intensities of (a) $Al_2O_3^+$, (b) $Al_2O_3^-$ and reaction products with increasing pressure of CO. Notice the decrease in the reactant ion intensity and the concomitant increase in the O-atom transfer products. The reactant ion intensity is plotted on the left axis and the product is on the right.

$$Al_2O_3^+ + CO \rightarrow AlO_3CO + Al^+ \tag{1}$$

Previous studies have shown that CO binds strongly to positively charged metal centers,[28] and because all of the adsorption energy is retained by the gas-phase cluster, it is reasonable that loss of Al^+ would occur. Indeed, studies of the reactivity of Al_n^+ clusters with O_2 have observed the exothermic loss of Al_2O molecules.[29] In addition, the cationic charge stays with the Al atom because the more oxygen-rich AlO_3CO product probably has a larger ionization potential.[10,11] The oxygen-deficient products, $Al_2O_2^+$ and Al_2O^+, result from an oxygen atom transfer to CO forming neutral CO_2 according to eq 2 and 3.

$$Al_2O_3^+ + CO \rightarrow Al_2O_2^+ + CO_2 \tag{2}$$

$$Al_2O_2^+ + CO \rightarrow Al_2O^+ + CO_2 \tag{3}$$

The significantly lower intensity of the Al_2O^+ product is attributed to the sequential oxidation of two CO molecules by $Al_2O_3^+$. At 10 mTorr of CO the intensity of the $Al_2O_2^+$ intermediate accounts for approximately 10% of the total ion signal. Approximately 10% of the $Al_2O_2^+$ clusters are then reduced to Al_2O^+ accounting for the 1% relative intensity of this species. On the basis of the structures of the Al_2O_{2-3} neutral clusters calculated previously,[10] the reactivity of the $Al_2O_3^+$ cluster with CO is proposed to be higher than that of $Al_2O_2^+$ because the reactive center is probably an atomically bound oxygen atom outside of the Al_2O_2 ring. As mentioned previously, larger $(Al_2O_3)_4^+$ clusters were calculated to have an atomically bound oxygen with strong radical (Al−O•) character.[23] This same type of center, if present on the $Al_2O_3^+$ cluster, would facilitate higher reactivity with CO. $Al_2O_2^+$, in contrast, probably has a ring structure similar to the neutral cluster[10] with the oxygen atoms bound in a bridging configuration between the aluminum atoms. These doubly coordinated oxygen atoms typically exhibit lower oxidation reactivity because they are more strongly bound.[30] The products observed for the reaction between $Al_2O_3^+$ and CO were not observed in separate

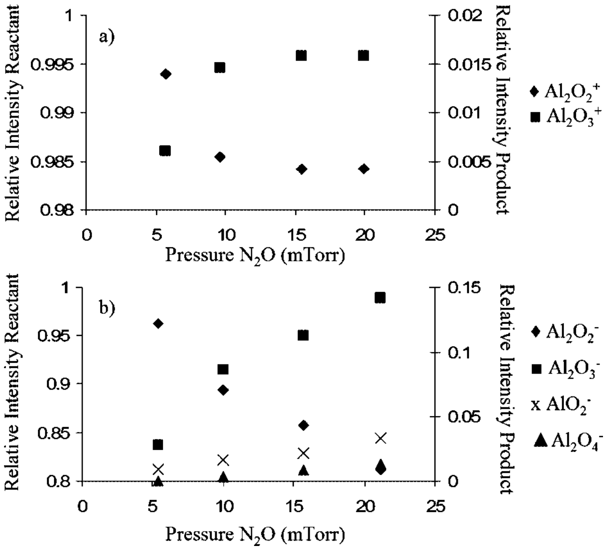

Figure 2. Relative ion intensities of (a) $Al_2O_2^+$, (b) $Al_2O_2^-$ and reaction products with increasing pressure of N_2O. Notice the decrease in the reactant ion intensity and the concomitant increase in the O-atom addition products. The reactant ion intensity is plotted on the left axis and the products are on the right.

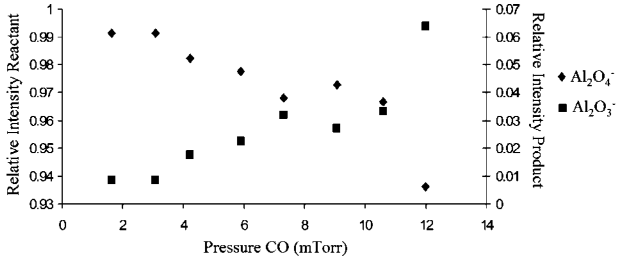

Figure 3. Relative ion intensities of $Al_2O_4^-$ and reaction products with increasing pressure of CO. Notice the decrease in the reactant ion intensity and the concomitant increase in the O-atom transfer product. The reactant ion intensity is plotted on the left axis and the product is on the right.

experiments employing N_2, indicating that these species are the result of a chemical reaction between $Al_2O_3^+$ and CO and not the products of collisional fragmentation.

The reactivity of $Al_2O_3^-$ with CO is displayed in Figure 1b. In comparison to the behavior observed for the cationic cluster two major differences are apparent. First, the reactivity of the anionic cluster is significantly lower than the cationic cluster. While the maximum pressure of CO in the anion reaction is double that for the cation, the product intensity is an order of magnitude lower. Second, the anionic cluster is extremely selective toward the transfer of only one oxygen atom. No aluminum atom loss products were observed for the anionic cluster. This is because the negative charge density present on the anionic cluster causes a repulsive interaction with the lone pair of electrons on CO, and therefore, lowers the CO binding energy.[30] Therefore, insufficient energy is present to cause the loss of an Al atom from the anionic cluster.

These gas-phase findings indicate that aluminum oxide clusters, having the same stoichiometry as bulk alumina, are moderately reactive for the oxidation of CO to CO_2. Furthermore, the ionic charge state of the cluster is shown to exert a significant influence on the activity and selectivity of the reaction. While cationic clusters are far more reactive, anionic clusters are highly selective towards the transfer of only a single oxygen atom.

While the oxidation of CO by aluminum oxide clusters constitutes a novel finding, it only represents half of a complete catalytic cycle. To determine whether or not the oxygen-deficient product clusters, $Al_2O_2^+$, may be oxidized back to the original active stoichiometry, these species were reacted with N_2O, which has a particularly weak N_2-O bond. The reactivity of $Al_2O_2^+$ with N_2O is displayed in Figure 2a. As the pressure of N_2O is increased the intensity of the reactant ion decreases and the oxygen addition product, $Al_2O_3^+$, becomes more pronounced. The cationic cluster, therefore, is highly selective towards the addition of a single oxygen atom according to eq 4.

$$Al_2O_2^+ + N_2O \rightarrow Al_2O_3^+ + N_2 \qquad (4)$$

In comparison, the reactivity of the $Al_2O_2^-$ anion with N_2O, displayed in Figure 2b, reveals three major product channels. The most intense product, $Al_2O_3^-$, results from the addition of a single oxygen atom to $Al_2O_2^-$. Another product, AlO_2^-, is caused by fragmentation induced by the exothermic oxidation of the oxygen-deficient $Al_2O_2^-$ cluster according to eq 5.

$$Al_2O_2^- + N_2O \rightarrow AlO_2^- + AlO + N_2 \qquad (5)$$

The more oxygen-rich AlO_2 fragment retains the extra electron as it has an electron affinity of 4.23 eV,[10] while that of AlO is only 2.60 eV.[10] A minor product corresponding to the addition of two oxygen atoms according to eq 6 was also observed.

$$Al_2O_2^- + 2N_2O \rightarrow Al_2O_4^- + 2N_2 \qquad (6)$$

This relative behavior indicates that anionic aluminum centers can be oxidized beyond the Al_2O_3 stoichiometry of bulk alumina. The oxygen-rich anionic clusters $Al_2O_4^-$ and $Al_2O_5^-$ were observed previously by Desai and co-workers[10] and proposed to have structures with atomically and molecularly bound O_2 units outside of the Al_2O_2 ring, respectively. On the basis of reactivity observed between the stoichiometric cluster, $Al_2O_3^-$, and CO, it is reasonable to expect that the oxygen-rich species, $Al_2O_4^-$, would also exhibit reactivity for the oxidation of CO. The reactivity of $Al_2O_4^-$ is displayed in Figure 3. This cluster is shown to selectively transfer one oxygen atom to CO and to be roughly as reactive as $Al_2O_3^-$. The relative intensity of the $Al_2O_3^-$ product ion increases smoothly with higher pressures of CO except for an abnormal decrease around 9 mTorr of CO. This anomaly is likely the result of an unintentional decrease in CO reactant gas pressure. It was somewhat surprising that two oxygen atom transfer products were not observed for $Al_2O_4^-$ as $Al_2O_3^-$ was also shown to be reactive with CO. We attribute this to the relatively low intensity of the $Al_2O_3^-$ intermediate that would make the additional oxygen transfer product, $Al_2O_2^-$, very difficult to detect experimentally. These results indicate that oxygen-deficient aluminum oxide anion clusters can be oxidized up to and beyond the stoichiometry of bulk alumina through reaction with N_2O. Furthermore, both the stoichiometric and the oxygen-rich species exhibit reactivity for the oxidation of CO to CO_2.

Conclusion

The gas-phase findings presented herein demonstrate that cationic and anionic aluminum oxide clusters having the same stoichiometry as bulk alumina, Al_2O_3, are active for the oxidation of CO to CO_2. Furthermore, it is shown that the ionic charge state has a pronounced effect on the reactivity. Cationic clusters are far more reactive, while anionic clusters are more selective for the transfer of a single oxygen atom. We also establish that oxygen-deficient aluminum oxide clusters can be oxidized up to and beyond the stoichiometry of bulk alumina, and that the oxygen-rich anionic clusters are also active for the oxidation of CO. Our findings provide new insight into the role of aluminum oxide support materials in heterogeneous oxidation catalysis.

Note Added in Proof. During the preparation of this manuscript Feyel and co-workers published the following paper on the activation of methane by oligomeric $(Al_2O_3)_x^+$ ($x = 3, 4, 5$). Feyel, S.; Dobler, J.; Hokendorf, R.; Beyer, M. K.; Sauer, J.; Schwarz, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 1946.

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