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Exploring the Interactions of Atomic Oxygen on Silver Clusters with Hydrogen†

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The interactions between Agₜₚ O⁻ (n=1–8) and H₂ (or D₂) were explored by combination of the mass spectroscopy experiments and density function theory (DFT) calculations. The experiments found that all oxygen atoms in Agₜₚ O⁻ (n=1–8) are inert in the interactions with H₂ or D₂ at the low temperature of 150 K, which is in contrast to their high reactivity with CO under the same condition. These observations are parallel with the preferential oxidation (PROX) of CO in excess hydrogen catalyzed by dispersed silver species in the condensed phase. Possible reaction paths between Agₜₚ O⁻ (n=1–8) and H₂ were explored using DFT calculations. The results indicated that adsorption of H₂ on any site of Agₜₚ O⁻ (n=1–8) is extremely weak, and oxidation of H₂ by any kind of oxygen in Agₜₚ O⁻ (n=1–8) has an apparent barrier strongly dependent on the adsorption style of the “O”. These experiments and theoretical results about cluster reactions provided molecule-level insights into the activity of atomic oxygen on real silver catalysts.

Key words: Silver clusters, Atomic oxygen, Hydrogen, Mass spectroscopy, Density function theory calculations

I. INTRODUCTION

The reactivity of oxygen species on silver is a very import topic in the surface science, because it is closely relevant to many industrially or environmentally important oxidation processes catalyzed by silver, such as the partial oxidation of ethylene or propylene [1], and selective oxidation of CO from hydrogen-rich gas used in fuel cells [2, 3]. Extensive studies were carried out on the structures and properties of oxygen species on bulk silver or dispersed silver particles, showing that they have quite a few various molecular and atomic states [4, 5]. The atomic oxygen on silver was classified to three types, Oα (the weakly adsorbed oxygen atoms on surfaces), Oβ (the atomic oxygen inside bulks), and Oγ (the strongly adsorbed atomic oxygen in crevices or embedded in sub surfaces). They generally have different performances in surface reactions, and this classification was widely used to analyze the catalytic mechanisms on silver [6–8]. With developments of modern surface techniques, more details of the atomic oxygen on silver were resolved [9, 10]. Nevertheless, because of the intrinsic complexities of the solids, there are still many challenges to locate the exact positions of various oxygen atoms on silver, to determine their bonding patterns, and to elucidate their structure-property relations at molecule level.

Silver clusters are ideal models for the active sites of heterogeneous silver catalysts, and many of them were studied using gas phase experiments and density function theory calculations [11–23]. The structures and properties of these small species have many distinctive characters. For example, some small clusters have kind of global or local five-fold symmetry [17, 18], which can not exist in crystals. The adsorption, activation and reactions of O₂ on Agₜₚ were explored by many groups [24–30], and clusters’ spins and electron bonding energies were shown to dominate the reactions. Our recent study showed that this tendency is still true for the clusters with sizes up to 1 nm [31]. Except the reactions with O₂, there were also lots of studies about the reactions of silver clusters with other molecules, like ethylene, CO, NOₓ, etc. [32–36]. However, there were few studies involving chemical properties of adsorbed heterogeneous atoms (including the important atomic oxygen) on silver clusters, even though they are as well directly relevant to real catalytic processes.

In our recent study [37], we generated cluster series Agₜₚ O⁻ (n=1–8), and explored their reactions with CO. In this work, we explored the interactions between Agₜₚ O⁻ (n=1–8) and H₂ or D₂. We also studied the reactions of Agₜₚ O⁻ with CO mixed in the D₂. In these experiments, H₂ and D₂ do not react with Agₜₚ O⁻, Agₜₚ⁻ and other products from CO reactions. The DFT cal-

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culations predicted the adsorption energies of H$_2$ on the above clusters and the possible reaction paths between Ag$_n$O$^-$ ($n=1−8$) and H$_2$. The theoretical results well interpreted the experimental observations. The experiments and the theoretical calculations of these cluster species can be used to understand the processes happening on the active sites of real silver catalysts.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Measurements on clusters’ reactions

The measurements on clusters’ reactions were carried out on an instrument composed of a magnetron sputter cluster source, a flow reactor, and a time-of-flight (TOF) mass spectrometer, whose details were described elsewhere [31, 38, 39]. Briefly, the cluster source generated the Ag$_n$O$^-$ ($n=1−8$) series by mixing trace amount of oxygen (at a ppm level) inside the helium buffer gas, in which the O$_2$ molecules dissociated and combined with silver species around the sputtering region. Together with the buffer gas (110 sccm helium) and the sputtering gas (14 sccm Ar), all clusters from the cluster source entered a continuous flow reactor running at 150 K. They firstly went through a thermalization area, and then entered the reaction area, where the reactant was introduced at a defined flow rate. Since the oxygen mixed inside the buffer gases was at ppm levels, its effect on the subsequent reactions in the reactor was negligible. The parent and product clusters were sampled by a skimmer at the end of the reactor and were directed to the TOF mass spectrometer to be analyzed.

B. Density functional theory (DFT) calculations

The clusters’ reaction paths were investigated using DFT calculations. The B3LYP hybrid functional was used [40–42], which makes use of the Hartree-Fock exact exchange and Becke’s exchange functional and the Lee-Yang-Parr correlation functional. The structural candidates of the reactants, the intermediates, the products, and the transition states were initially optimized with the Lanl2dz basis sets for all elements. The lower lying ones from these preliminary calculations were further optimized using a more sophisticated method, in which the aug-cc-pVTZ-pp basis set was selected for Ag, and the 6-311G$^*$ basis sets for C and O [43]. Scalar and spin-orbital relativistic effects of Ag were taken into account via the energy consistent relativistic pseudopotentials. The predicted structures for the minimum points and the transition states were confirmed by analyzing their vibration modes, which have no and only one imaginary frequency, respectively. Using the intrinsic reaction coordinate (IRC) algorithm, we traced the reaction paths from transition states to the corresponding reactants and products to reconfirm the proposed reaction mechanism. All calculations were accomplished using Gaussian 09 program [44].

III. RESULTS AND DISCUSSION

A. Measurements on interactions of Ag$_n$O$^-$ ($n=1−8$) with H$_2$ (D$_2$) or CO mixed in D$_2$

FIG. 1 shows the mass spectra of anionic clusters sampled at the end of the reactor with no reactants, with 0.20 sccm H$_2$, and with 0.20 sccm D$_2$, respectively. Because the mass resolution ($\Delta m/m$) of these spectra is around 500, the experiments would clearly distinguish the adsorption products of H$_2$ or D$_2$ on Ag$_n$O$^-$ ($n=1−8$) and Ag$_{8n}$O$^-$ ($n=1−11$) if they were ever generated. Nevertheless, the mass spectrum shown in FIG. 1(b) or (c), with high flow of H$_2$ or D$_2$ introduced, is nearly identical to that of FIG. 1(a). That is to say, neither addition of H$_2$ or D$_2$ on Ag$_{8n}$O$^-$ and Ag$_{8n}$O$^-$, nor reduction of Ag$_n$O$^-$ to Ag$_{8n}$O$^-$ happened under the present low temperature condition. FIG. 2 shows the mass spectra of anionic clusters sampled at the end of the reactor without reactants, with pure 0.05 sccm CO, with 0.05 sccm CO mixed in 0.10 sccm D$_2$, and with 0.10 sccm CO mixed in 0.20 sccm D$_2$, respectively.

FIG. 1 Mass spectra showing the cluster series of Ag$_n$O$^-$ ($n=1−8$) and Ag$_{8n}$O$^-$ ($n=1−11$) with (a) no reactant, (b) 0.20 sccm H$_2$ and (c) 0.20 sccm D$_2$ introduced into the reactor at 150 K. The peaks of Ag$_{8n}$O$^-$ ($n=1−8$) were indicated with vertical dashed lines; the peaks of Ag$_n$O$^-$ series were indicated using “+O$^-$. DOI:10.1063/1674-0068/cjcp1710193 ©2017 Chinese Physical Society
mass spectrum in FIG. 2(c), showing the products of cluster reactions with CO mixed in D2, is nearly identical to that in FIG. 2(b), for which only same amount of CO was introduced. The only difference is that the small impurity cluster peaks for AgOH− in FIG. 2(b) (actually also exists without any reactants in FIG. 1(a) and FIG. 2(a)) changed to AgOD−/AgOD−. This indicates that the presence of D2 did not affect the reaction kinetics of AgₙO− (n=1–8) with CO at all. As shown in FIG. 2(d), when the flow of the reactants CO and D₂ doubled in the reactor compared with that of FIG. 2(c), the reactions from AgₙO− (n=1, 2, 5–8) to Agₙ−, and from Ag₃,4O− to Ag₃,4CO₂− were driven to 100% completion. The intensity of AgOD− did not increase, indicating that this cluster was not generated in the reactor. In both FIG. 2 (c) and (d), no addition products of D₂ were observed on Agₙ−, AgₙO−, or the formed AgₙCO₂−; no reduction reactions from AgₙO− to Agₙ− were observed either.

B. Theoretical calculations on proposed reactions between AgₙO− and H₂

The lowest structures of AgₙO− (n=1–8) and their reactions with CO were previously explored [37]. In this work, we explored the possible reaction paths of previous determined structures of AgₙO− (n=1–8) with H₂ using DFT calculations, even though no reactions were observed under the present low temperature. The predicted reaction paths were listed in FIG. 3, including the structures and the relative energies of the involved reactants, the intermediates, the final products, and the transition states.

The predicted H₂ adsorption energies on any site of Agₙ− (n=1–11), AgₙO− (n=1–8), and AgₙCO₂− (n=3 and 4) are close to zero, and some of them are even slightly negative. The higher energies of the adsorption minima, i.e. the theoretical negative adsorption energies, can be caused by deviations from the intrinsic limitations of DFT methods in predicting the extremely weak nonbonding interactions. However, the results at least showed that the adsorption of H₂ on any of these clusters is very weak, which is consistent with the experimental observations that no H₂ adsorption products presented in the obtained mass spectra. When a H₂ molecule was put around AgₙO− (n=1–8), the theoretical optimization unexceptionally converged to the structures with H₂ staying around the oxygen atom. The most stable product of AgₙO− (n=1, 2, 5–8) and H₂ was predicted to be Agₙ− taking an adsorbed H₂O, in which the two hydrogen atoms were oriented toward the Agₙ−. The relative energies of these products were more than 1.0 eV lower than those of the corresponding reactants, AgₙO−+H₂, and 0.3–0.6 eV lower than those of separate Agₙ− and H₂O. The oxidations of H₂ by the oxygen in the quasi-linear structures of AgₙO− and Ag₄O− were predicted to form AgH₂OAg₂− and Ag₂H₂OAg₂−, respectively. In these two structures, each H₂O unit connected two silver fragments using the oxygen atom and one of its hydrogen atoms. The fragmentation of AgH₂OAg₂− and Ag₂H₂OAg₂− needs at least 1.06 and 0.87 eV, respectively. Their structures and fragmentation are very similar to those of previously observed AgCO₂Ag₂− and Ag₂CO₂Ag₂− [37]. The relative energies of AgH₂OAg₂− and Ag₂H₂OAg₂− are more than 1.0 eV lower than those of their initial reactants, AgₙO−+H₂ and AgₙO−+H₂. FIG. 3 also listed the structures and the energies of the transition states of the proposed reactions between AgₙO− (n=1–8) and H₂. The main barriers in the reactions of AgₙO− and Ag₂O−, which contain terminal oxygen, were estimated to be 0.19 eV; those of Ag₃O− and Ag₄O−, which contain Ag−O−Ag linear structures, were estimated to be 0.47 and 0.28 eV, respectively; those of Ag₅O− (n=5–8), which contain bridge oxygen atoms, were estimated to be 0.6–1.2 eV. These theoretical results are consistent with the experimental observations that all AgₙO− (n=1–8) can not react with H₂ or D₂ at the low temperature.

C. Comparing the gas phase results with surface studies about atomic oxygen in condensed phases

The reactivity of surface oxygen on silver was extensively investigated in condensed phases. It was shown that most atomic oxygen on silver reacts with CO below 200 K [45–48], while activation or reactions of H₂ on these oxygen species generally happen at temperatures higher than 400 K [49–52]. This difference is the
FIG. 3 Theoretical paths for the reactions between $\text{Ag}_n\text{O}^-$ ($n=1$–8) and $\text{H}_2$. The structures and the relative energies of the reactants, the intermediates, the transition states, and the products were included.
fundamental for applications of silver catalysts in selective oxidation of CO from H$_2$-rich gas in fuel cells, where the Pt anodes are easily poisoned by traces of CO. The significant barriers for the reactions with hydrogen revealed in this work and the previously reported barrierless reactions with CO provide the underlying molecule-level interpretation. We also noticed that the barriers in the reactions of Ag$_n$O$^-$ with H$_2$ are strongly dependent on the adsorption structures of atomic oxygen. The terminal oxygen corresponds to the lowest reaction barriers; those of the quasi-linear structures of Ag-O-Ag are slightly higher; those of the bridging ones, especially the ones bridging on two silver atoms, are the highest ones and can be more than 1.0 eV. This implies that those different atomic oxygen tend to activate or react with H$_2$ at different high temperatures. In condensed phases, the pretreatment of silver catalysts at high temperatures with presence of H$_2$ is shown to significantly change their activity and selectivity, and the temperature is usually among the most important parameters [2, 3, 53]. According to the micro figures revealed in this work, different pretreatment temperatures lead to removal of various atomic oxygen. The population of different kinds of atomic oxygen on silver directly determines the subsequent reaction mechanisms in the catalytic processes.

IV. CONCLUSION

We explored the reactions of Ag$_n$O$^-$ with hydrogen (H$_2$ or D$_2$), and CO mixed in D$_2$. It was found that all atomic oxygen in Ag$_n$O$^-$ ($n$=1–8) does not react with H$_2$ or D$_2$ at 150 K, which is in contrast to their high reactivity with CO under the same condition. The theoretical calculations predicted the barriers of the reactions between Ag$_n$O$^-$ and H$_2$, which are strongly dependent on the adsorption structures of the atomic oxygen. These results provide molecule-level understanding on the catalytic process of selective oxidation of CO from H$_2$-rich gas in fuel cells and the pretreatment process of silver catalysts with presence of H$_2$.

V. ACKNOWLEDGMENTS

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