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Gold catalysts: A new insight into the molecular adsorption and CO oxidation

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ABSTRACT

The molecular adsorption and CO oxidation on a gold-deposited TiO_2 catalyst were investigated by means of molecular dynamics simulation. The results indicate that the molecules (i.e., O_2, CO, and H_2O) are selectively adsorbed on the specific locations such as gold particle, gold-support perimeter interface, and support surface. The adsorption and dissociation of H_2O molecules at the perimeter interface enhance the supply of oxygen, thus promoting the oxidation of CO on the Au/TiO_2 catalyst. However, the presence of Cl^- ions could significantly impede CO oxidation due to their competition with O_2, CO, and H_2O for the adsorption sites. A reaction mechanism of CO oxidation is postulated on this basis. The findings are useful in developing a comprehensive picture about CO oxidation on gold-deposited TiO_2 and in the design of new gold catalysts with high catalytic activity.

Gold has traditionally been regarded to be inactive as a catalyst. However, when gold is deposited as nanoparticles on metal oxide substrates (e.g., TiO_2, Fe_2O_3, Co_3O_4, Al_2O_3, and SiO_2), it exhibits surprisingly high catalytic activity towards many chemical reactions, such as CO oxidation, propene epoxidation, hydrogenation, and NO reduction [1]. This finding has evoked great research interest in gold catalysts. In recent years, many efforts have been made to develop new methods for preparing gold catalysts with controlled shape and size of gold nanoparticles, and expand their applications to pollution control, chemical processing, sensors and fuel cell technology [2,3]. It is generally accepted that the catalytic activity of gold catalysts depends on the fabrication methods, the nature of gold nanoparticles, and the type and characteristics (e.g., phase structure, crystal size, surface and textural properties) of metal oxide supports [4–8]. In particular, the perimeter interface around gold nanoparticles is believed to contribute significantly to the catalytic activities.

To identify the active sites, density functional theory (DFT) has been used to study the adsorption of individual molecules on either defect-free or defected gold surfaces [9–11]. Such theoretical work has provided some important evidences for the possible reaction routes around gold particles. However, few studies have been made on the adsorption of a mixture of molecules at the perimeter interface of gold-support [10]. This is largely because of the current limitations of computer capability which does not allow us to apply DFT calculation to such complicated gold-deposited catalysts to generate a full picture for the catalytic reaction. Despite the aforementioned theoretical efforts, some questions have yet to be addressed. For example, where and to what extent is each type of reactant molecules adsorbed on different locations, including the surface of metal oxide support, the surface of gold nanoparticles, and the perimeter interface of gold-support? To address these issues, molecular dynamics (MD) simulation is a more attractive option.

CO oxidation is a typical reaction for which catalysts with gold nanoparticles of 2–4 nm show extraordinary active at a temperature as low as 200 K and also much more active than other noble metal catalysts [4,12–14]. Among various metal oxides (e.g., TiO_2, Al_2O_3, Fe_2O_3, and NiO), gold-deposited TiO_2 receives the most intensive studies because neither gold nor TiO_2 alone is active for CO oxidation whilst their combination creates surprisingly high catalytic activity. So, many efforts have been made to understand the mechanisms underlying CO oxidation, including the effects of TiO_2 support characteristics and pretreatment of Au/TiO_2 catalysts, the active state of gold and gold-support interface, oxygen activation, and the possible reaction pathways [7–11,15]. Nevertheless, the mechanism of CO oxidation on Au/TiO_2 catalysts is still controversial [9]. Some investigators believe that the deposited gold particles themselves are active sites where O_2 molecules adsorb, dissociate, and interact with CO molecules [16,17]. Others suggest that the metal oxide support is responsible for O_2 adsorption and dissociation, and believe that O_2 molecules adsorb on the defect sites of metal oxides and then dissociate into O atoms to react with the adsorbed CO molecules [18,19]. So far, there is no direct experimental evidence on whether O_2 molecules are dissociately or non-dissociately adsorbed and where they are adsorbed.

In this letter, we presented a molecular study of the reaction mechanism of CO oxidation on Au/TiO_2 catalyst. Specifically, we employed MD simulation to: (i) identify the adsorption sites (e.g., gold particle, gold-support interfacial perimeter, and support sur-

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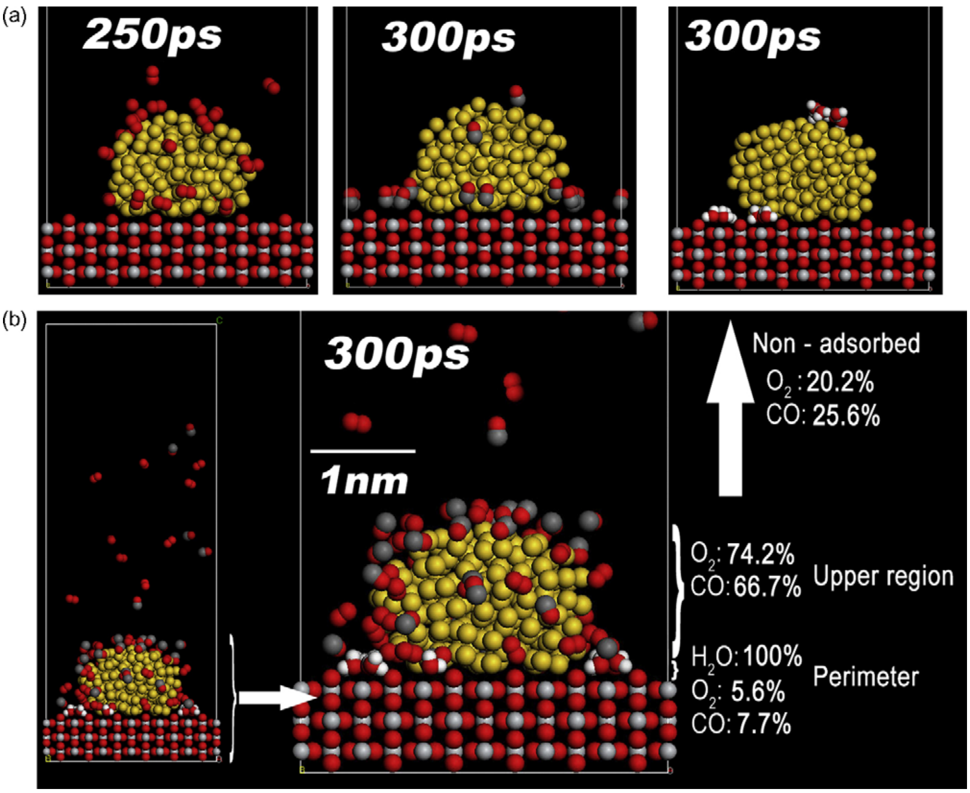

Fig. 1. Molecular distributions of the individuals (top) and mixture (bottom) of CO (grey and red), O_2 (red) and H_2O (white and red) molecules at different locations on Au/TiO_2 (1 1 0) surface at 298 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

face) for reactant molecules; (ii) quantify the amount of molecules (i.e., CO, O_2 and H_2O) adsorbed on these sites; (iii) examine the effects of Cl^- ions; and finally (iv) postulate, in conjunction with the existing DFT calculation and experimental facts in the literature, the possible reaction mechanism for CO oxidation.

Our molecular models of Au/TiO_2 catalyst systems consist of a rutile TiO_2 (1 1 0) surface, a single gold nanocluster, and a certain number of either individual species (i.e., O_2, CO, H_2O and Cl^- ion) or their mixtures. These species commonly exist in CO oxidation reactions. The MD cell has a dimension of $26.63 \times 38.98 \times (30-100)\,Å^3$ and $\alpha = \beta = \gamma = 90°$. All MD simulations were performed under canonical (nvt) ensembles at 298 K by using Discover Module of Material Studio V3.2 package for 250–450 ps. The force field of condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) was employed. Recently, we have successfully applied COMPASS force field to study the deposition of gold nanocluster on TiO_2 surface [6]. Its reliability to other TiO_2 systems has also been verified in the studies of molecular adsorption (e.g., water and organic molecules) on TiO_2 surface [20,21]. Before MD simulation, energy minimization was performed to relax the model system and achieve a relatively stable state judged from the deviation of the total energy from its average. Quantitative analysis was carried out in terms of the atomic density profile of adsorbed species in the upper region of gold nanocluster and at the perimeter interface.

As a starting point, MD simulations were performed to investigate the adsorption of individual O_2, CO, and H_2O molecules on gold-deposited TiO_2 (1 1 0) surfaces (Fig. 1). It was found that O_2 molecules are mainly attracted to the upper region of gold nanocluster (64.0%) with a small amount present at the gold/TiO_2 perimeter interface and no affinity for the rutile TiO_2 (1 1 0) surface. In contrast, the majority (62.5%) of CO molecules are located around the gold/TiO_2 perimeter interface with a slight affinity for the gold nanocluster. Moreover, CO molecules align themselves in a perpendicular fashion along the normal to the rutile TiO_2 (1 1 0) surface with the carbon atoms toward Ti^{4+} sites. H_2O molecules exhibit equivalent affinity for the Ti^{4+} sites on TiO_2 and the top of gold nanocluster. The H_2O molecules adsorbed on the TiO_2 (1 1 0) surface are oriented in such a way that the oxygen is attracted to the Ti^{4+} sites, whilst hydrogen atoms face upwards from the surface. Therefore, if O_2 molecules come into contact with CO molecules on this location, reaction between them is likely to take place.

In addition to the adsorption behaviors of individual molecules, we also investigated a more realistic system: the adsorption of a mixture of O_2, CO, and H_2O; the latter was included since CO oxidation usually takes place under certain moisture [22]. The interplay between these molecules may affect their adsorption strength and molecular distribution on different locations. To this end, MD simulation was performed for a system consisting of a gold-deposited TiO_2 (1 1 0) surface and a mixture of O_2, CO, and H_2O. The simulation results of the mixture show a distinct behavior in the adsorption as compared to that of individual molecules. H_2O molecules compete with CO molecules for the Ti^{4+} sites and become the major molecules adsorbed on the rutile TiO_2 (1 1 0) surface (Fig. 1). Such competitive adsorption for Ti^{4+} sites significantly reduces the Ti^{4+} sites available for CO molecules. As a result, the adsorption location of CO molecules shifts from perimeter interface to gold nanocluster where competitive adsorption is observed between CO and O_2 molecules. In addition to the adsorption behavior, changes in molecular orientation are observed. CO molecules no longer align themselves in a fashion perpendicular to the rutile TiO_2 (1 1 0) surface but are loosely adsorbed, which allows them to come into contact with O_2. Furthermore, H_2O molecules are oriented in such a way that oxygen atoms are attracted toward Ti^{4+} sites whilst hydrogen atoms face upwards from the surface. Such orientation indicates that CO or O_2 could react with the hydrogen of H_2O.

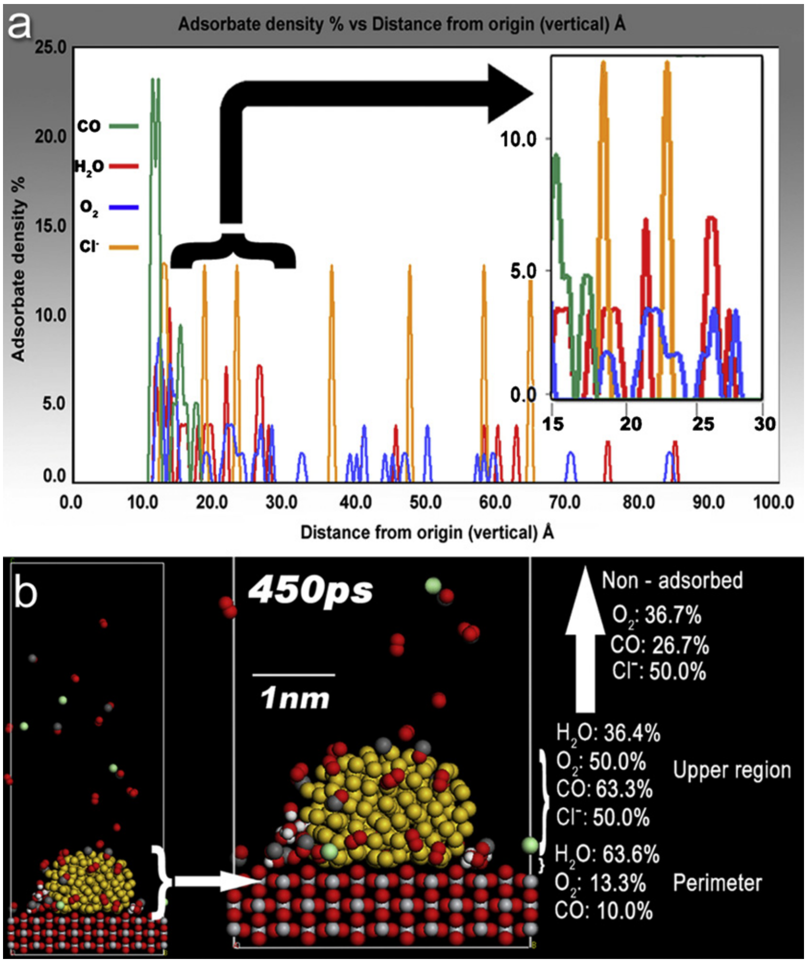

Fig. 2. Atom density profiles (top) and molecular distributions (bottom) of the mixture of CO, O_2, and H_2O in the presence of Cl^- ions on Au/TiO_2 (1 1 0) surface at 450 ps at 298 K. Yellow: Au, red: O, grey: Ti, white: H, black: C, green: Cl^- ion. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Further quantitative analysis was made in terms of atomic density profile, which provides the molecular distribution at various locations. As shown in Fig. 1, the perimeter of gold nanocluster and TiO_2 surface adsorbs 100% H_2O molecules but only 7.7% CO and 5.6% O_2 molecules. The upper region of gold nanocluster adsorbs 66.7% CO and 74.2% O_2 molecules. As a whole, there are in total 74.4% CO and 79.8% O_2 molecules attracted to the Au/TiO_2 surface. And the other CO and O_2 molecules are not adsorbed but are located in the bulk of the system, which is probably because of the saturation of adsorption sites. Such selective adsorption on various locations can explain the mechanism of CO oxidation as discussed further.

During the fabrication of Au/TiO_2 catalysts, chloroauric acid ($HAuCl_4{\cdot}4H_2O$) is usually used as the Au precursor. This leads to the inevitable presence of Cl^- ions in the system. It has been known that Cl^- ions not only promote the aggregation of gold nanoclusters but also block Au active sites [23,24]. As a result, a washing process is always used to remove Cl^- ions. To understand the effect of Cl^- ions, MD simulation consisting of a gold-deposited TiO_2 (1 1 0) surface and a mixture of O_2, CO, H_2O, and Cl^- ions was performed. It was found that Cl^- ions compete with CO and H_2O for the Ti^{4+} sites at the perimeter interface and with CO and O_2 on the gold nanocluster. However, the Cl^- ions are finally rejected from the perimeter interface during such competitive adsorption and are partially adsorbed in the upper region of gold nanoclusters. H_2O molecules were found to be adsorbed not only at the perimeter interface but also in the upper region of gold nanocluster, which is different from the simulation result of a mixture of molecules without Cl^- ions. Moreover, the Cl^- ions impede the adsorption of O_2, CO, and H_2O molecules and thus increase the time for them to reach the adsorption equilibrium. The position of H_2O molecules at the perimeter interface is the same as that in the system without Cl^- ion whilst those in the upper region of gold nanocluster are randomly positioned.

The effect of Cl^- ions on CO oxidation can be reflected from the atom density profile and molecular distribution. Our simulation results (Fig. 2) show that the presence of Cl^- ions significantly reduces the adsorption of O_2 (i.e., from 74.2 to 50%) in the upper region of gold nanocluster and H_2O (i.e., from 100 to 63.6%) at the perimeter interface of the Au/TiO_2 catalyst. This is the result of the competitive adsorption of Cl^- ions for the adsorption sites of O_2, CO, and H_2O molecules. Note that 50% Cl^- ions are located in the upper region of the gold nanocluster. Thus, the presence of Cl^- ions would lead to the poisoning of Au/TiO_2 catalyst and reduce its catalytic properties for CO oxidation. The effect of Cl^- ions on CO and O_2 adsorption can be further seen from their atomic density profiles in the range of 15.0–30.0 Å (the inset in Fig. 2). The presence of Cl^- ions significantly reduces the amount of CO and O_2 molecules adsorbed. When Cl^- ion is at its highest density percentage (12.5%), CO and O_2 are at their lowest density of about 3.3 and 1.7%, respectively.

The supply of oxygen is believed to play an important role in initializing and promoting CO oxidation. The oxygen may come from

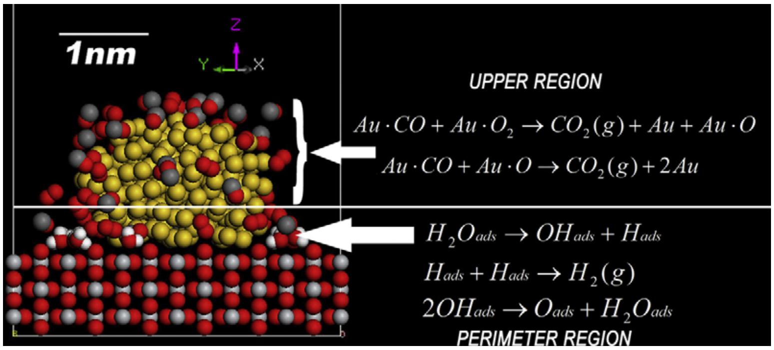

Fig. 3. Proposed CO oxidation mechanisms on gold-deposited TiO_2 (1 1 0) surface, including the reactions at the perimeter interface and in the upper region of gold nanocluster.

the gas phase (O_2) via direct adsorption or OH groups generated from H_2O dissociation [25]. From the above simulation (Fig. 1), the selective adsorption and distribution of molecules (e.g., O_2, CO, and H_2O) can explain the supply of oxygen and thus the high catalytic properties of Au/TiO_2 catalysts. It is believed that H_2O molecules can dissociate into H and OH groups on TiO_2 surface with oxygen vacancies [25]. Therefore, at the perimeter interface the adsorption and dissociation of H_2O molecules would lead to the generation of H_{ads} and OH_{ads} species. Therefore, two dissociated H_{ads} form H_2 (g) and two dissociated OH_{ads} form atomic O_{ads} and H_2O_{ads}. The formed O_{ads} would be adsorbed on the surface of gold nanocluster and thus supply oxygen for CO oxidation. Meanwhile, a previous study showed that O_2 adsorption energy increased considerably with the increase of OH_{ads} species [25]. This means that the formed OH_{ads} can improve the adsorption of O_2 from gas phase on to TiO_2. Such major effects of H_2O molecules on CO oxidation are in agreement with the experimental observations in which the moisture under ordinary experimental conditions were found to enhance the oxidation of CO over Au/TiO_2 [15,24,26]. Moreover, oxygen generated from the adsorption and the reaction at the perimeter interface will ensure the CO oxidation in the upper region of gold nanocluster. Therefore, the mechanism of CO oxidation may be illustrated as follows (Fig. 3): (i) the CO oxidation process begins from the reaction of O_2 and CO, which forms O and CO_2 (gas); (ii) the formed O is then adsorbed on Au surface whilst CO_2 (gas) is desorbed from the Au surface; and (iii) as more O is formed and adsorbed on Au surface, the CO oxidation is preferred, and the reaction rate of CO oxidation increases.

In summary, this work represents our attempt to construct a more comprehensive picture of CO oxidation on Au/TiO_2 catalyst by using MD simulation. Our quantitative analysis indicates that the molecules (i.e., O_2, CO, and H_2O) are selectively adsorbed on various locations of the gold-deposited catalyst: CO and O_2 molecules are mainly adsorbed on gold nanocluster whilst H_2O molecules are exclusively attracted to the perimeter interface. Accordingly, it is clarified that the CO oxidation process begins from the reaction of O_2 and CO in the upper region of gold nanocluster, followed by the reaction between CO and the formed O. The dissociation of H_2O molecules at the perimeter interface further ensures the supply of O for the CO oxidation. Cl^- ions are found to compete with the reactants for the adsorption sites and thus significantly reduce the supply of O, leading to the poisoning of Au/TiO_2 catalyst. The finding demonstrates a new way of examining the reaction mechanisms of gold catalysts and has important implications for the optimization and design of novel efficient gold-deposited metal oxide catalysts.

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