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Review (Special Issue on Gold Catalysis)

Theoretical investigations on CO oxidation reaction catalyzed by gold nanoparticles

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ABSTRACT

It is crucial to understand the mechanism of low temperature CO oxidation reaction catalyzed by gold nanoparticles so as to find out the origin of the high catalytic reactivity and extend the industrialization applications of nano gold catalysts. In this work, some theoretical works on CO adsorption, O₂ adsorption, atomic oxygen adsorption, formation of surface gold oxide films, reaction mechanisms of CO oxidation involving O₂ reaction with CO and O₂ dissociation before reacting with CO on gold surfaces and Au/metal oxide were summarized, and the influences of coordination number, charge transfer and relativity of gold on CO oxidation reaction were briefly reviewed. It was found that CO reaction mechanism depended on the systems with or without oxide and the strong relativistic effects might play an important role in CO oxidation reaction on gold catalysts. In particular, the relativistic effects are related to the unique behaviors of CO adsorption, O adsorption, O₂ activation on gold surfaces, effects of coordination number and the wide gap between the chemical inertness of bulk gold and high catalytic activity of nano gold. The present work helps us to understand the CO oxidation reaction mechanism on gold catalysts and the influence of relativistic effects on gold catalysis.

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1. Introduction

Gold has been regarded as the most inert metal for a very long time, until the pioneer of Haruta [1,2] found that the gold nanoparticles supported on some metal oxides showed surprisingly high catalytic activity for CO oxidation reaction at low temperature. Since then, the nano gold catalysis has attracted growing attention in the field of heterogeneous catalysis [3–5]. Technologically, numerous potential industrialization applications of nano gold catalysts were developed, such as synthesis of fine chemicals [6,7], selective hydrogenations [8,9], water gas shift reaction [10], carbon–carbon bond forming reaction

[11], oxidation of organic compounds with molecular O₂ [12,13], pollution and emission control [14] and fuel cell applications [15] etc. Some of them have been commercially used, for instance, air purifier in various moto vehicles [16]. Scientifically, a huge number of theoretical and experimental studies have been devoted to understand the wide gap between the chemical inertness of bulk gold and high catalytic activity of nano gold [17–21].

The ability to catalyze CO oxidation reaction at low temperature is one of the unique properties of gold catalysts, and a dramatic increase in the number of studies has been performed to analyze the origin of the high catalytic activity and selectivity

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[6,22–24]. Even so, it remains many puzzles about the simple CO oxidation reaction on gold catalysts. Experimentally, the account of surface active oxygen species is only 1%, thus it is very difficult to be characterized [25]. In addition, the activity and structures of gold nanoparticles strongly depend on the preparation methods, sizes of gold nanoparticles, and supports etc., which makes it very hard to identify the real active centers. Therefore, the importance of theoretical calculations is increasing for the elucidation of the nature of active centers in gold catalysts [4].

In the past two decades, the power of computational hardware, software gradually increased and therefore theoretical calculations became more and more popular and important to investigate structures, stabilities and activities of catalysts. Density functional theory (DFT) calculation relies only on the electron density, which significantly decreases the computational complexities. It becomes an increasingly powerful and useful tool to evaluate various systems, predict catalytic activities, and provide sufficient accuracy to be compared to experimental data [26]. So far, DFT calculation was widely used to investigate the mechanism of gold catalysis and provide fundamental physical insights into gold catalysis [17,27,28].

In this work, we will give a brief review of theoretical investigations on CO oxidation reaction catalyzed by gold nanoparticles, since most of the reviews focused on experimental results and the reviews of theoretical work were relatively rare [29,30]. It should be noted that this work focused on gold nanoparticles and large gold clusters instead of small gold clusters consisting of only few gold atoms. Therefore, it was not concerned about some important effects such as some charge effects [31,32] and even-odd effects [33] on gold etc., which are predominated on small gold clusters and vanish rapidly by increasing the cluster size [34]. In particular, special attention will be paid to the relativistic effects on gold catalysts in this work, since the relativistic effects strongly affect the color of gold, Au–Au bond strength, Au–Au bond lengths [35] and should play an important role for CO oxidation reaction.

2. Adsorption

2.1. CO adsorption on gold surface

In the CO oxidation reaction, the adsorption process of CO from the gas phase onto the gold surface is generally regarded as a key initial step of CO oxidation process. The adsorption of CO on all kinds of gold surfaces was well studied by DFT calculations. Mavrikakis et al. [36] found that the binding of CO on the flat Au(111) surface was very weak, but it became relatively strong at the step sites. Liu et al. [37] investigated CO adsorption on several gold surfaces and also found that the CO adsorption on Au(111) surface was very weak and the adsorption of CO increased considerably on surface defects. Fajín et al. [38] found that CO preferential adsorbed above the outermost surface atom at the edges of the (111) terraces in C-down fashion. The CO adsorption on bridge or hollow sites nearby the step was more favorable than that on top of gold atoms in the middle of the terraces, and the bridge sites along the step were also

very stable for CO adsorption.

Barmparis et al. [39] presented a computational study of CO adsorption on gold nanoparticles and found that CO adsorption energy had a weak dependence on slab thickness but strongly depended on the exchange-correlation functional. Hussain et al. [40] investigated CO and NO adsorption on Au(111), Au(100), Au(110) and Au(310) surfaces, and found that the adsorption energy increased with the increasing degree of coordinative unsaturation of the gold atoms.

Some theoretical results showed that the calculated adsorption energies of CO on gold surfaces increased approximately linearly with decreasing coordination number (CN) of Au [41], regardless of the different functionals [42]. Furthermore, it was also found that the adsorption of NO, O₂ and atomic oxygen increased with the decreasing Au CN [41,43]. Based on this, some researcher proposed that the low-coordinated sites of gold atoms were active sites and thus gold nanoparticles with large amounts of low-coordinated sites showed high catalytic activity [18,37].

We also observed the near-linear relationship between the CO adsorption energy and Au CN based on the DFT calculation results on Au(321), Au(711), Au(100) and Au(111), as shown in Fig. 1(a) [44]. However, we found that the linear relationship did not work anymore for CO adsorption on Au(100)–hex(1×5) surface. In the Au(100)–hex(1×5) structure, the top layer of Au(100) structure is reconstructed to an Au(111) structure, and the relative positions of surface Au(*n*) (*n* = 1–6) atoms after relaxation are shown in Fig. 1(b). It is obvious that the CO adsorption energies on Au(3) and Au(4) of Au(100)–hex(1×5) surface deviate dramatically from the linear relationship, as shown in Fig. 1(a).

Fig. 1. The calculated adsorption energies of CO on gold surfaces with different coordination number of gold (a) and the top view of the relaxed structure of Au(100)–hex(1×5) surface (b). The golden and red balls are gold atoms in the surface and subsurface, respectively. The distances between the neighboring gold atoms are shown in the unit of Å.

To trace the essential reason that the near-linear relationship between CO adsorption energy and the Au CN works well on some gold surfaces but not on the Au(100)–hex(1×5) surface, we investigated thoroughly the CO adsorption on gold surfaces by Hückel theory and DFT calculations [44]. It was found that only the neighboring gold atoms locating at the down area of Au–CO could strengthen CO adsorption, whereas the neighboring gold atoms locating at the side area of Au–CO weakened CO adsorption. It indicates that the CO adsorption is not only dependent on the Au CN, but also relies on the location of the neighboring gold atoms. The extended researches indicated that the strong relativistic effects of gold strengthened the influence from the neighboring gold atoms, because of the wide spatial extension of *d* orbitals of gold [28].

2.2. O₂ adsorption on gold and Au/metal oxide

To gain detailed information about the O₂ adsorption is a relevant issue in order to arrive at a deeper understanding of the CO oxidation reaction. The DFT results from Nørskov et al. [36] showed that the O₂ adsorption was extremely weak on Au(111) surface and gold clusters. Mills et al. [45] found that O₂ did not bind to a planar gold cluster and only bound to gold clusters deposited on an Au(111) surface, which indicated that the surface roughness was an essential factor for O₂ adsorption. Molina et al. [30] found that O₂ adsorption on Au₃₄ cluster and Au/MgO was very weak. The adsorption of molecular oxygen on the Au(321) surface was calculated by Fajín et al. [46], and it was found that the interaction between O₂ and gold was very weak, and the structure with the O–O axis planar to the surface terraces was more favorable.

The calculation results of Gong et al. [47] showed that O₂ could hardly adsorb on flat and stepped gold thin films, but wire-structured gold could adsorb both CO and O₂ rather strongly. They proposed a generalized structural model based on the wired-structured film for active gold. Günay et al. [48] investigated O₂ adsorption on a gold cluster, and found that the stable O₂ adsorption required the presence of an unpaired electron on gold cluster. Lee et al. [49] calculated O₂ and O adsorption on Au₃₈, and found that the most stable sites for O₂ and O adsorption were bridge and hexagonal sites with the adsorption energies of –0.99 and –3.93 eV, respectively. In total, most theoretical work showed that the adsorption of O₂ molecule on gold surfaces was relatively weak except for the wire-structured gold or some special gold clusters.

Liu et al. [17] calculated O₂ adsorption on Au/TiO₂(110) and found that O₂ adsorption at the interface was highly favored compared to the adsorption on the gold surfaces. Molina et al. [50] also found that O₂ adsorption at the interface of Au/TiO₂ was reasonably strong. Remediakis et al. [51] reported that the adsorption site for O₂ on Au/TiO₂ was at the interface between gold cluster and Ti^{5c} (surface 5-fold coordinated Ti atoms) on the surface, which was confirmed by Koga et al. [52].

Chen et al. [29] demonstrated that the interface of Au/TiO₂ was far more favorable for O₂ adsorption than low-coordinated gold atoms. The DFT results from Cai et al. [53] proved that O₂ could only be adsorbed at the interfacial sites on Au/TiO₂(110)

surface. These DFT calculation results clearly showed that O₂ preferred to adsorb at the interface between gold and TiO₂ on Au/TiO₂ catalysts. Due to the strong adsorption of O₂ at the perimeter edge of gold oxide contacts, it was proposed that the perimeter sites were the active sites for CO oxidation in some studies [17,50,54].

Gong et al. [55] investigated O₂ adsorption on Au/CeO₂, and found that only the surface Ce of CeO₂(111) could adsorb O₂ with high stability, which showed that the O₂ preferred to be adsorbed on CeO₂ surface than on gold surface. Han et al. [56] investigated CO and O₂ adsorption on gold clusters with a 2D–3D structure on CeO_{2–x}(111), and found that the Au CN and charges of gold atoms dominated the adsorption strength of CO and O₂ and the influence of the interface of Au/CeO₂ was relatively weak.

2.3. O adsorption on gold surfaces

In the last two decades, the O adsorption on gold surface has been investigated by DFT calculations on a variety of gold surfaces including gold single crystal and gold clusters. Nørskov et al. [57] calculated that the dissociative chemisorption energies for O₂ on gold surface was 0.54 eV, which implied that gold did not bind oxygen at all [43]. Shi et al. [58] investigated the adsorption of oxygen on Au(111) surface by DFT calculations, and found that atomic oxygen adsorption was weak compared to molecular oxygen. However, the DFT results from Fajín et al. [46] showed that the dissociation of O₂ on Au(321) surface was exothermic. In addition, O₂ temperature-programmed desorption (TPD) peaks on gold surfaces are higher than 500 K [59], indicating that the atomic oxygen adsorption on gold surface is not so weak.

Liu et al. [37] calculated atomic oxygen adsorption on a series of gold surfaces, and found that the bridge site of monatomic step edge was the most stable site for O adsorption on Au(221) and Au(211) surfaces. The 3-fold hollow site was the most stable site on Au(111) surface, which was confirmed by Zeng et al. [60]. In addition, Liu et al. [37] also found that the adsorption energy on stepped surface increased compared to the flat Au(111) surface. Fajín et al. [46,61] studied atomic oxygen adsorption in stepped Au(321) surface and found that the atomic oxygen preferred to occupy the fcc hollow cavities near the edge of the step connecting (111) terraces.

We investigated atomic oxygen adsorption on gold surfaces by Hückel theory and DFT calculations [62] and found that the atomic oxygen preferred to locate at multifold sites on Au(111), Au(100), Au(110), Au(211) and Au(321) surfaces, which agreed well with the results reported by Fajín et al. [46]. Furthermore, we found that the linear O–Au–O structure was the most stable structure for atomic oxygen adsorption, and the corresponding structure on Au(110) surface is shown in Fig. 2.

Nørskov et al. [41,43] found that the binding energies for oxygen on gold were approximately linearly relationship with Au CN, which means that lower Au CN will induce to the stronger oxygen adsorption. However, Liu et al. [37] found that the oxygen adsorption on Au kink–I and kink–II with lower Au CN did not show stronger adsorption compared to the gold

Fig. 2. Top view (a) and side view (b) of linear O–Au–O structure on Au(110) surface. The golden and red balls are gold atoms and oxygen atoms, respectively.

atoms at the steps, which is quite different from Nørskov's observations [41,43].

We investigated Au–O interactions in various surroundings by DFT calculations, and found that the adsorption of oxygen on gold (Au–O bond) could be strongly weakened by the neighboring gold atoms locating in the plane perpendicular to the Au–O bond, while the neighboring gold at the downside would strengthen Au–O bond [28]. It might be used to explain the inconsistency between the observations of Nørskov et al. [41,43] and Liu et al. [37]. It indicates that the O adsorption as well as CO adsorption depends not only on the Au CN but also on the location of the neighboring gold atoms.

2.4. The formation of gold oxide films

Since the formation of gold oxide films was believed to be related to the unique oxidation catalysis of gold [63,64], the nature of gold oxide films has been theoretically explored in the last decades. Shi et al. [58] investigated the adsorption of oxygen on Au(111) surface by DFT calculations, and found that a thin surface-oxide-like configuration was the most favorable structure compared to atomic oxygen adsorption. In this structure, the oxygen atoms are quasi 3-fold coordinated to gold atoms and the gold atoms in the surface layer are 2-fold coordinated to oxygen atoms. The surface-oxide-like structure is illustrated in Fig. 3(a). It was expected to be stable up to about 420 K at atmospheric pressure. They also calculated the adsorption of oxygen on Au(100) and Au(110) surface, and found that a low coverage (0.1ML) on added-row reconstructed surface and 1 ML oxygen covered (2×1) missing row structure were the most stable structures on Au(100) and Au(100) surfaces, respectively [65].

Fajín et al. [61] studied the consecutive deposition of oxygen atoms on the Au(321) surface by DFT calculations, and observed that the increase of the oxygen coverage resulted in the formation of highly oxidized structures. The simulation results from Baker et al. [66] showed that oxygen chemisorbed on the surface was the primary species at lower coverage and lower temperature. At higher coverage and temperature, the gold

Fig. 3. The stable surface-oxide-like structure on Au(111) surface predicted by Shi et al. [58] (a), dual chain structure (b), graphene-like 12MR structure (c), and connected dual chain structure (d). The golden and red balls are gold atoms and oxygen atoms, respectively.

oxide-like species became dominant. The energy barrier for the formation of the surface oxide was less than 0.1 eV. Boronate et al. [67,68] investigated O₂ dissociative adsorption on Au₃₈, and found that O–O bond break on Au(100) facet was favored. The activation barrier was only 7.6 kcal/mol and the process was highly exothermic. They proposed that the oxygen adsorption could reach coverage of one monolayer oxide, where all oxygen atoms were forming the most stable O–Au–O linear structure.

We calculated the structures and stabilities of gold oxide films on gold surfaces in O₂ atmosphere by a combination of thermodynamics and DFT calculations [69], and found that the dual chain structure (Fig. 3(b)) was more stable on most gold surfaces at lower oxygen chemical potential except for on an Au(111) surfaces, on which the graphene-like 12MR structure (Fig. 3(c)) was more stable. While at the higher oxygen chemical potential, the connected dual chain structure (Fig. 3(d)) became more stable. The phase transformation point from the dual chain structure or graphene-like 12MR structure to connected dual chain structure depended on the lattice mismatch between the connected dual chain structure and the gold surface.

3. Reaction mechanisms

3.1. CO oxidation mechanisms on gold surfaces

In general, there are at least three reaction mechanisms for CO oxidation reaction on gold surfaces, namely Eley-Rideal (ER) mechanism, Langmuir-Hinshelwood (LH) mechanism, and O₂ dissociation mechanism, as shown in Fig. 4. For the ER mechanism [27], the adsorbed CO reacts directly with gaseous O₂. While for the LH mechanism [17], the adsorbed CO reacts with coadsorbed O₂. Normally, an OCOO (also known as CO–O₂) intermediate complex is formed and then it decomposes to CO₂ and adsorbed O [70]. The remaining adsorbed O reacts with another CO molecule to generate a CO₂ molecule. For the O₂ dissociation mechanism, O₂ dissociates to two adsorbed oxygen atoms before reacting with adsorbed CO to form CO₂.

Fig. 4. Possible reaction mechanisms involving Eley-Rideal (ER), Langmuir-Hinshelwood (LH), trimolecular Langmuir-Hinshelwood mechanisms (3LH), and O_2 dissociation mechanism for CO oxidation on gold surfaces.

It should be noted that Liu et al. [71] proposed a trimolecular LH mechanism (3LH) for CO oxidation on gold surface. They found that the coadsorbed CO molecule at a unique triangular Au_3 site could act as a promoter for the bond break of an O–O bond, and spontaneously forming two CO_2 as product. The coadsorbed CO on the triangular Au_3 site significantly promotes the O–O bond scission in OCO intermediate, therefore, it is a CO self-promoting oxidation reaction.

Liu et al. [17,37] performed a DFT calculation on CO oxidation reaction on gold surfaces and found that the calculated reaction barrier involving O_2 dissociation was much higher than that of CO reaction with molecular O_2 . Therefore, they believed that the possibility of O_2 direct dissociation mechanism on gold surfaces was ruled out at low temperature, and they suggested that the reaction mechanism followed the reaction between O_2 and CO through $CO-O_2$ intermediate complex. Molina et al. [27,72] found that CO oxidation for all gold systems proceeded via CO adsorption, trapping of O_2 , formation of $CO-O_2$ intermediate, generation of CO_2 and reaction of remaining atomic oxygen with gaseous CO to form CO_2 . They found that the direct separation or dissociation of O_2 was not favorable.

Fajín et al. [38] investigated CO oxidation on $Au(321)$ surface, and found that the predissociation of molecular oxygen on the $Au(321)$ surface for CO oxidation was energetically less favorable than the CO direct reaction with molecular oxygen. Chang et al. [73] calculated CO oxidation on unsupported Au_{55} clusters and found that the reaction path consisted of an intermediate involving $CO-O_2$ complex. Chen et al. [74] investigated the CO oxidation on a gold nanoparticle by DFT calculations, and found that Au_{29} nanoparticle exhibited high catalytic activity for CO oxidation. The catalytic process preferred via the LH mechanism at lower temperature, whereas the ER mechanism became more competitive at higher temperature. These DFT results clearly showed that CO direct reaction with molecular oxygen was more favorable than the predissociation of molecular oxygen before reacting with adsorbed CO on gold surfaces.

3.2. CO reaction with O_2 on Au/TiO_2

Liu et al. [17] studied CO oxidation on TiO_2 supported Au by DFT calculations, and found that CO oxidation reaction occurred at the interface between gold and the oxide and the reaction barrier was very low. The key step of CO oxidation on Au/TiO_2 was the adsorption of molecular O_2 at the interface. The TiO_2 support enhanced electron transfer from the gold to the antibonding states of O_2 , which significantly promoted O_2 adsorption and activates O_2 towards CO oxidation.

Molina et al. [50] investigated O_2 adsorption and CO oxidation on gold nanoparticles supported on $TiO_2(110)$ surface, and found that O_2 adsorption occurred either at the trough Ti (Ti^{5c}) or leaning against the gold particles. The presence of gold strongly stabilized the adsorbed O_2 through the electronic charge transfer from the Au to O_2 . The adsorbed O_2 could react with adsorbed CO at the edge sites of gold particles and form CO_2 easily. Molina et al. [50] found that $CO-O_2$ intermediate complex was no longer formed as a metastable reaction intermediate on Au/TiO_2 , which is different from the conclusion from other researchers that the adsorbed CO reaction with an oxygen molecule normally gave formation of a $CO-O_2$ intermediate complex [18,37,75,76].

Li et al. [77] systematically studied the size and shape dependence of Au_n/TiO_2 on CO oxidation reaction, and found that the perimeter sites of Au-cluster/ TiO_2 could significantly promote the CO oxidation. The reaction occurred between the adsorbed CO at a perimeter Au site and a dangling O_2 on the neighboring Ti^{5c} site. They simulated the generation of oxygen vacancies at the interface between gold cluster and $TiO_2(111)$, and found that both of LH mechanism and Mars-van Krevelen (M-vK) mechanism were possible towards CO oxidation reaction on Au/TiO_2 and the selection depended on the structural fluxionality of the gold cage clusters on TiO_2 .

Koga et al. [52,54] examined CO oxidation over $Au/TiO_2(110)$ by DFT calculations and found that O_2 was strongly adsorbed on the Ti^{5c} site next to the perimeter. CO was activated by the back donation from gold, which induced to the lower reaction barrier for CO with O_2 on the perimeter Ti^{5c} than that on a more remote Ti site. Therefore, the Ti^{5c} sites next to the perimeter of Au/TiO_2 played an important role for CO oxidation.

Vilhelmsen et al. [78] investigated the catalytic sites at the interface perimeter of Au/TiO_2 and found that the active sites were strongly dependent on the surface direction. The gold on the $[1\bar{1}0]$ direction of $TiO_2(110)$ surface showed much higher catalytic activity than that on the $[001]$ direction, and they assigned it to the too weak CO binding energy along the $[001]$ direction. Duan et al. [79] presented DFT calculations on CO oxidation mechanism on a gold rod on $TiO_2(110)$ surface along the $[1\bar{1}0]$ direction, and found that both LH mechanism with an adsorbed $Au/O/Ti^{5c}$ oxygen species and an Au-assisted M-vK mechanism with O_{bri} were acceptable reaction mechanisms for CO oxidation reaction.

3.3. CO reaction with O_2 on Au/CeO_2

Camellone et al. [80] investigated CO oxidation mechanism on Au/CeO_2 catalysts by DFT calculations with a Hubbard term

(DFT+U), and found that both of Au^+ and Au^{3+} were active centers for CO oxidation, but Au^+ would turn to $\text{Au}^{\delta-}$ and then be deactivated with the presence of oxygen vacancies. The catalytic cycle for Au^{3+} on CeO_2 was via formation of surface oxygen vacancies by CO reacting with surface oxygen, adsorption of molecular oxygen on oxygen vacancies, formation of oxygen adspecies and reaction with CO.

Henkelman et al. [81] investigated the CO oxidation mechanism on gold nanoparticles supported by CeO_2 and proposed three reaction pathways for CO oxidation: by coadsorbed O_2 at gold nanoparticles, by lattice oxygen of CeO_2 (M-vK mechanism), and by O_2 adsorbed at the Au– Ce^{3+} interface. They found that higher energy was required for the M-vK mechanism in the case of Au_{13} supported on CeO_2 , therefore, it was unfavorable and only active at high temperature.

Ghosh et al. [82] investigated small gold clusters on ceria surface during CO oxidation by DFT calculations and found that the morphology of gold clusters was influenced significantly by molecular adsorption. Their results indicated that M-vK mechanism displayed low activation energy on Au/ CeO_2 , and they assigned it to the gold cluster fluxionality and the lability of CO_2 intermediate at the interface.

Teng et al. [83] studied the structures of Au clusters on a $\text{CeO}_2(111)$ surface and found that the stability of surface oxygen vacancies depended on the size of the gold cluster and relative position of gold cluster and oxygen vacancy. Liu et al. [84] investigated the CO adsorption on Au/ CeO_2 and found that the CeO_2 support acted as an electron buffer which benefited the CO adsorption on Au/ CeO_2 .

Song et al. [85] performed a computational DFT study of CO oxidation on a gold nanorod supported on $\text{CeO}_2(110)$, and investigated three CO oxidation mechanism: M-vK mechanism, co-adsorption mechanism with adsorbed CO and O_2 , and stepwise mechanism with O_2 dissociation followed by CO oxidation, and found that all three mechanisms exhibited nearly similar overall reaction barriers, and M-vK mechanism and the stepwise mechanism strongly depended on the support termination of CeO_2 surface.

3.4. O_2 dissociation on gold catalysts

Liu et al. [37] calculated O_2 dissociation on Au(111) surface and found that the reaction barrier was very high. They found that the step sites were most active sites for O_2 dissociation after examining many gold structures. However, even on the most active step sites, the estimated initial sticking coefficient was too small that O_2 could not dissociate on them. Su et al. [86] confirmed that O_2 adsorption on Au(111) surface was very weak and direct dissociation barrier of O_2 was relatively high. Fajín et al. [46] calculated the dissociation of molecular oxygen on the Au(321) surface, and found that it was exothermic and the reaction barrier was 1.00 eV. Molina et al. [72] found that O_2 dissociation was not favorable on gold nanoparticles supported by MgO(100) surface.

Although many theoretical results supported that the CO oxidation via CO reaction with O_2 was facile compared to O_2 dissociation before reacting with CO no matter on gold nano-

particles or on Au/oxide systems [17,18,27,37,75,76], some experimental results proved that Au/metal oxides catalysts could activate molecular oxygen directly [21,25,87–89]. For example, Weiher et al. [88] found that gold-oxygen complexes could be formed on active Au/ TiO_2 catalysts without the presence of CO by X-ray absorption near-edge structure (XANES). Widmann et al. [25] found that the active oxygen species was quite stable and should be adsorbed atomic oxygen, which was generated by dissociation of molecular oxygen. Takeda et al. [21] observed the morphology changes of gold nanoparticles on CeO_2 and formation of surficial gold oxide in O_2 atmosphere by transmission electron microscopy (TEM).

To understand the mechanism of O_2 direct activation on gold catalysts, a great deal of theoretical fundamental studies has been performed. Roldan et al. [90] found a common pathway for O_2 dissociation on gold nanoparticles by DFT calculations and concluded that it was very important for the presence of low-coordinated gold atoms and the critical size of gold nanoparticles. Boronat et al. [67,68] investigated the adsorption and dissociation of O_2 on gold surfaces, gold nanoparticles and Au/ TiO_2 surface, and found that the arrangement of the gold surface atoms was vital for O_2 dissociation and the Au(100) facet was favored for scission of O–O bond.

Hussain et al. [91] calculated CO oxidation on extended gold surfaces and found that a site consisting of four gold atoms in a square geometry had sufficient ability to dissociate O_2 , and a Au_{38} cluster exposing this site provided the most favorable energetics for CO oxidation, which were in good agreement with Boronat et al.'s results [67,68]. Duan et al. [79] identified Au/ Ti^{5c} site at the interface boundary to activate O_2 and found that O_2 dissociation with a reaction barrier of 0.5 eV was facile at room temperature. Koga et al. [92] found that O_2 dissociation between two Ti^{5c} sites was probable if the relative O_2 population was small enough. Furthermore, they proposed that both of undissociated and dissociated O_2 on Ti^{5c} sites were possible active oxygen species, depending on the ratio of O_2 population to the contact area.

To find out the most active sites for O_2 dissociation on gold catalysts, we analyzed O_2 activation in an Au–O–O–Au structure by Hückel theory, and found that an increase of Au–O orbital interaction could significantly promote O_2 adsorption and dissociation [93]. Since the O–Au–O structure could increase Au–O interaction remarkably [62,28], we built a realistic model with a unique double linear O–Au–O structure at the perimeter of the Au/metal oxide interfaces to activate adsorbed O_2 , as shown in Fig. 5.

It was found that the O_2 dissociation barriers with this structure were only 0.12 and 0.17 eV for Au/ TiO_2 and Au/ CeO_2 systems, respectively [93]. Therefore, the direct O_2 dissociation mechanism is also a possible reaction pathway in Au/oxide systems. In addition, the unique double linear O–Au–O structure at the perimeter of the Au/metal oxide interfaces implies that the active centers with at least two-layer gold atoms are necessary towards CO oxidation, which agrees well with the experimental observations by Goodman et al. [22,94] that two-layer gold particles supported on TiO_2 showed the highest catalytic activity for low-temperature CO oxidation reaction.

Fig. 5. The model of the unique double linear O–Au–O structure at the perimeter of the Au/oxide interfaces structure for O_2 adsorption and dissociation.

4. Influences of coordination number, charge transfer and relativity of gold

CO oxidation on gold has been investigated from a theoretical point of view, and some relevant conclusions about the influences of coordination number, charge transfer and relativity of gold have already been obtained. Since the experimental results showed that the gold nanoparticles exhibited higher reactivity towards CO oxidation than larger ones [22,23], and the fraction of low-coordinated gold atoms decreased with the increasing the size of gold nanoparticles [43,95], the low-coordinated gold atoms at the step, corner or edge were well investigated by DFT calculations.

Nørskov et al. [36] found that the adsorption energy of O and CO was not dependent on the number of gold layers if there were more than two layers. They found that the steps and the strained surface were crucial for CO oxidation on gold surface and they suggested that the gold atoms on the corners and edges of gold nanoparticles were the active sites [43]. Liu et al. [37] also found that gold steps were the most active sites for CO and atomic oxygen adsorption, therefore, they believed that these steps were reaction active sites.

Xu et al. [96] investigated the O_2 dissociation on strained and stepped gold surface by DFT calculations, and found that the steps and tensile enhanced the adsorption of atomic oxygen, and substantially facilitated O_2 activation on a gold surface. Brodersen et al. [97] concluded that the reactivity of nano gold particles was dominated by low-coordinated corner-like atoms. Pascucci et al. [98] compared the reactivity of Cu, Ag and Au for CO oxidation by DFT calculation, and found that the reactivity of gold nanoparticles should be attributed to large number of low-coordinated sites.

The fact that low-coordinated gold atoms or tensile gold surface structures benefit the CO adsorption and O_2 activation can be easily understood by the relativistic effects [28]. For the Au–O (or Au–CO) bond at the step sites or in a tensile surface, the inhibiting effects from the neighboring gold locating in the plane perpendicular to the Au–O (or Au–C) bond is weakened due to smaller Au CN or longer Au–Au bond length, therefore, the Au–O (or Au–CO) bond will be stronger. Furthermore, the reaction barrier for O_2 activation decreases according to the Hückel theory [93]. As a result, the low-coordinated gold or gold in a tensile surface displays higher catalytic activity for CO

oxidation.

Li et al. [77] studied CO oxidation on subnanometer gold on $\text{TiO}_2(110)$ by a combination of DFT calculations and microkinetics analysis, and found that a hollow-cage $\text{Au}_{18}/\text{TiO}_2$ displayed the highest catalytic activity towards CO oxidation among of $\text{Au}_{1-4}/\text{TiO}_2$, Au_7/TiO_2 and $\text{Au}_{16-20}/\text{TiO}_2$. In addition, the pyramidal Au_{18} isomer exhibited lower activity comparable to hollow-cage Au_{18} isomer, but it displayed much higher activity than pyramidal Au_{19} and Au_{20} isomers. They assigned the higher catalytic activities to the weaker CO adsorption on TiO_2 than on gold clusters, which led to an increase of the ratio of O_2/CO adsorption energy, an increase of the probability for O_2 to occupy the Ti sites, and a decrease of the requirement for meet the critical line for CO oxidation.

The effects of charge transfer in CO oxidation reaction were deeply investigated by DFT calculations. Sanchez et al. [99] found that electron transfer from the surface to the gold cluster played an essential role in the activation of nano-size gold cluster for CO oxidation. Liu et al. [17] found that the oxide promoted the charge transfer from gold to anti-bonding orbitals of O_2 , which stabilized the adsorbed O_2 and activates O_2 for CO oxidation. Koga et al. [52,54,100] found that the charge transfer from Au to O_2 did not require direct bonding between Au and O_2 , and Ti^{5c} sites could activate O_2 towards CO oxidation even ~ 1 nm away from gold cluster. They also found that the charge transfer occurred even on the inversed $\text{TiO}_2(110)/\text{Au}(112)$ catalyst.

Molina et al. [72] investigated CO oxidation on gold nanoparticles supported by $\text{MgO}(100)$ and found that the local reactivity of gold atoms was determined by Au–Au coordination and the MgO supports provided excess electrons to gold to form ionic bonds with CO– O_2 intermediate. The DFT results of Guo et al. [101] showed that negative charge not only benefited the O and O_2 adsorption but also lowered the dissociation barrier for O_2 . However, Henkelman et al. [81] found that positively or negatively charged gold ions had no direct effect on the pathway and rate of CO oxidation. Based the analysis by Hückel theory, we found that the excess electrons from gold or some electron donors benefited the O adsorption and O_2 activation, but the excess electrons on surface oxygen ions in metal oxide blocked the O adsorption and O_2 activation and thus hindered the CO oxidation reaction [93].

Since gold displays the strongest relativistic effects among the first 100 elements, the relativistic effects play an important role on color of gold, Au–Au bond strength, Au–Au bond lengths etc. [35]. The relativistic effects on catalytic activity of gold were discussed in some recent theoretical work. Tang et al. [102] calculated CO oxidation reaction on gold nanoclusters by all-electron relativistic DFT calculations, and found that high spin energy profiles and spin crossing played an important role in CO oxidation reaction.

Liu et al. [103] calculated the adsorption of many small molecules on helical gold nanorods by a relativistic DFT method, and found that the Au–C, Au–N, Au–S and Au–O bonds were surprisingly strong, but the Au–H bond was relatively weak. Kanoun et al. [104] calculated the activation of molecular oxygen on noble metal nanoparticles, and found that the reaction

Fig. 6. The schematic diagram of extension of 5d orbitals of gold due to the relativistic effects. The circles by solid and dot lines represent the orbitals with and without the relativistic effects, respectively.

barrier for O₂ dissociation on Au₃₈ was reduced from 30.1 to 11.4 kcal/mol after involving of the relativistic effects.

We have investigated the Au–O interactions in different surroundings by DFT calculations in the scalar relativistic level [28] and found that Au–O bond could be significantly enhanced by the linear O–Au–O structure, because π -bonding play a key role in Au–O interaction. The strengthened Au–O bond in linear O–Au–O structure could be used to activate molecular O₂ in CO oxidation, as shown in Fig. 5. The Au–O interactions can be strongly suppressed by the presence of neighboring gold atoms in the plane perpendicular to the Au–O bond [28]. All the interesting phenomena that some Au–O bonds especially for linear O–Au–O bonds are strengthened and some Au–O bonds are weakened can be assigned to the spatial extension of d orbitals of gold wider than other transition metals, which is induced by the strong relativistic effects of gold, as shown in Fig. 6.

The widely spatial extension of d orbitals of gold could strongly strengthen significantly the Au–X (X = C, S, O, etc.) π -bonding interactions, but could not remarkable enhance the σ -bonding interactions (for example Au–H interaction) [28]. In addition, the neighboring gold atoms, especially for the neighboring gold atoms in the plane perpendicular to the Au–X bond, would dramatically weaken the Au–X bond. As a result, gold atoms in the bulk region with higher coordination number are strongly suppressed by neighboring gold atoms and thus are chemically inert towards CO oxidation reaction or some other reactions. However, low-coordinated gold atoms abounding at the steps, corners or edges in gold nanoparticles are capable to adsorb CO and atomic oxygen, and benefit the CO oxidation reaction. The oxygen atoms locating at the perimeter of Au/oxide enlarge the differences between gold nanoparticles and bulk gold by the linear unique O–Au–O structures.

5. Conclusions

Some theoretical works about CO, O₂ and O adsorption and CO oxidation on gold catalysts and the influences of coordination number, charge transfer and relativity of gold on CO oxidation were briefly reviewed in this work. It was found that CO preferentially adsorbed above the gold atoms with smaller

coordination number. There is a near-linear relationship between CO adsorption energies and CN of gold in most cases except for the Au(100)–hex(1×5) surface, since CO adsorption depends on Au CN as well as the relative location of the neighboring gold atoms.

O₂ adsorption on gold surfaces is normally very weak unless adsorption on wire-structured gold or some special gold clusters. The O₂ adsorption is relatively strong at the interface of Au/TiO₂ or on the surface of CeO₂ in Au/CeO₂ system. The most stable structure for the atomic oxygen adsorption relies on gold surfaces, and a linear O–Au–O structure is preferable in most cases at low coverage of oxygen. At high coverage, a surface gold oxide film can be formed on the gold surfaces and the structure of gold oxide film depends on the gold surfaces and oxygen chemical potential.

Some theoretical results supported that CO oxidation mechanism followed CO reaction with O₂ via CO–O₂ intermediate on gold surface, Au/TiO₂ and Au/MgO system. The reaction mechanism for CO oxidation on Au/CeO₂ is still under debate. Although the mechanism of O₂ predissociation before reacting with CO on gold catalysts was not supported by many theoretical works, some theoretical researchers still found some ways for O₂ direct dissociation with low reaction barrier, for example, a unique double linear O–Au–O structure at the perimeter of the Au/metal oxide interfaces to activate adsorbed O₂.

The gold atoms with lower coordination number were regarded as active sites in some theoretical work, which could be clearly explained by the strong relativistic effects of gold. The relativistic effects could also be used to understand the unique behaviors of CO adsorption, O adsorption, O₂ activation on gold surfaces and the wide gap between the chemical inertness of bulk gold and high catalytic activity of gold nanoparticles especially supported by some oxides. Due to the complexity of gold catalysts, a combination of theoretical calculations and experiments is strongly desired to understand the mechanism of low temperature CO oxidation reaction catalyzed by gold nanoparticles.

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Graphical Abstract

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Theoretical investigations on CO oxidation reaction catalyzed by gold nanoparticles

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Some theoretical works about CO, O₂ and O adsorption and CO oxidation on gold catalysts and the influences of coordination number, charge transfer and relativity of gold on CO oxidation were briefly reviewed.

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纳米金催化一氧化碳氧化反应的理论研究

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摘要: 近年来, 纳米金催化剂独特的催化性质, 特别是其优异的低温催化氧化活性, 引起了人们极大的研究热情。除低温选择氧化外, 在精细化学品合成、大气污染物消除、氢能的转换和利用等领域也开发出了一系列有广泛应用前景的金催化反应。此外, 体相金的化学惰性和纳米金的超高活性之间差异的“鸿沟”也引起了理论工作者浓厚兴趣, 试图从原理上理解体相金和纳米金活性差异的根源。CO 催化氧化是最具有代表性的研究金催化活性的化学反应, 本文主要综述了近十多年来金催化 CO 氧化反应理论计算方面的研究工作。

一般认为, CO 在纳米金表面的吸附是 CO 氧化反应的初始步骤。密度泛函理论研究表明, CO 在金表面的吸附强度主要与被吸附金原子的配位数有关: 金配位数越低, CO 的吸附能越强, 部分研究结果表明两者之间存在近似的线性关系。我们研究发现, CO 吸附强度也与被吸附金周围配位金原子的相对位置有关, 其中位于正下方的配位金原子加强 CO 吸附, 而位于侧位的配位金原子则弱化 CO 吸附, 这显然削弱了 CO 吸附与金配位数线性关系的可靠性。理论研究表明, 在纯金表

面上 O_2 吸附强度一般很弱, 只有在一些特殊结构的金团簇上才有较强的吸附, 但在 Au/TiO_2 界面及 CeO_2 表面上 O_2 吸附较强. 金表面原子氧的吸附和金的表面结构有关. 我们发现, 原子氧倾向于在金的表面形成一种线性的 $O-Au-O$ 结构以增加其稳定性. 当金表面的氧覆盖度增大时, 会形成一种金氧化物薄膜结构, 其结构依赖于氧的化学势和金的表面结构.

纳米金催化 CO 氧化反应机理可能因体系、载体等的差异而不同. 大部分理论计算结果表明, 在纯金表面上 O_2 很难直接解离形成原子氧, 因此反应机理可能是吸附的 CO 先与 O_2 反应形成了一种 $CO-O_2$ 中间体, 然后解离形成 CO_2 . 在 Au/TiO_2 和 Au/CeO_2 催化剂上 CO 催化氧化机理争议很大, 均有计算结果支持 LH 机理和 M-vK 机理. 另外, 根据实验上观察到了负载型纳米金能直接活化分子氧的结果, 理论上提出了分子氧先解离为原子氧再与 CO 反应的氧解离机理. 针对如何解离分子氧问题, 人们分别提出了低配位金模型、正方形金结构模型、 Ti^{5c} 模型及 Au/Ti^{5c} 模型等. 我们也提出了一种独特的双直线 $O-Au-O$ 模型来理解 Au/TiO_2 或 Au/CeO_2 界面解离活化分子氧.

理论计算结果表明, 低配位的金, 金和载体之间的电荷转移, 以及金所表现出的强相对论效应对于纳米金的活性影响很大. 需要特别指出的是, 金的强相对论效应有助于理解金表面的 CO 吸附与金配位的关系、金表面原子氧的吸附特性、金氧化物薄膜的结构和分子氧的活化等过程. 我们认为, 金的强相对论作用导致了体相金的化学惰性以及纳米金的活性, 因此相对论效应的深入研究将有助于理解金催化 CO 氧化反应机理, 从而有助于深层次理解纳米金催化活性来源.

关键词: 一氧化碳氧化反应; 金纳米粒子; 反应机理; 理论计算; 相对论效应

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