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Minireview (Special Issue on Gold Catalysis)

Single atom gold catalysts for low-temperature CO oxidation

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ABSTRACT

Low-temperature CO oxidation is important for both fundamental studies and practical applications. Supported gold catalysts are generally regarded as the most active catalysts for low-temperature CO oxidation. The active sites are traditionally believed to be Au nanoclusters or nanoparticles in the size range of 0.5–5 nm. Only in the last few years have single-atom Au catalysts been proved to be active for CO oxidation. Recent advances in both experimental and theoretical studies on single-atom Au catalysts unambiguously demonstrated that when dispersed on suitable oxide supports the Au single atoms can be extremely active for CO oxidation. In this mini-review, recent advances in the development of Au single-atom catalysts are discussed, with the aim of illustrating their unique catalytic features during CO oxidation.

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1. Introduction

Low-temperature CO oxidation is of significant importance, not only with regard to fundamental studies as a prototypical reaction but also in terms of practical applications, such as automobile emission control and the purification of gas streams derived from petrochemical industry [1]. Among various types of catalysts developed for this reaction, supported gold catalysts, with gold nanoparticles (NPs) finely dispersed on oxides, have attracted extensive attention over the past decades since Haruta discovered their extremely high activity, even at temperatures as low as $-70\text{ }^{\circ}\text{C}$ [2–4]. It is now generally accepted that oxide-supported Au NPs are the most active catalysts for CO oxidation, although a few reports have suggested that Rh/TiO₂ [5] and Co₃O₄ [6–8] showed similar activities at temperatures below $-80\text{ }^{\circ}\text{C}$.

The CO oxidation on supported Au catalysts has been a paradigm in the last two decades. This seemingly simple reaction is difficult to understand on supported Au catalysts. Many factors, including the size of the gold NPs, the valence state of the gold, and the nature of the support oxide as well as the interactions between gold and the support, can dramatically affect the activity of CO oxidation. These effects are not only fundamentally intriguing but also practically important because an in-depth understanding of why and how these factors influence the catalytic performance would be helpful for refining the synthesis of such catalysts, thus promoting their performance. Of more importance, the learning gained from the studies of supported Au catalysts may provide guidance for the design and development of other supported noble metal catalysts [9]. In fact, the reference role of study on gold catalysts has been realized and there are an increasing number of examples that

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demonstrate the development of new Pt-group metal catalysts based on the knowledge and understanding gained from the studies on supported Au catalysts [5,9–11].

Among various factors that affect the activity of CO oxidation, the size of Au NPs might be the most important one [12–16]. In his recent “Spiers Memorial Lecture” [16], Haruta summarized the active species for CO oxidation and suggested that the optimum size of Au NPs for CO oxidation may range from 0.5 to 5 nm (Figure 1). In contrast, Au^{3+} and Au^+ cations are believed to be less active, by approximately one to two orders of magnitude. Studies on model catalysts have also suggested that supported Au atoms are less active compared with Au clusters containing more than eight atoms [17]. Therefore, it has generally been thought that supported single Au atoms, if they are active at all, are much less active for CO oxidation than the Au NPs and the subnano Au clusters. Despite this, recent experimental data have demonstrated that Au single-atom catalysts (SACs) can be active for several reactions [18], such as the water-gas-shift (WGS) [19–22], methanol steam reforming (MSR) [23] and ethanol dehydrogenation reactions [24]. Especially, the progresses in both theoretical and experimental studies over the last few years have suggested that single Au atoms supported on suitable oxides can be as active for low-temperature CO oxidation as Au NPs and subnano clusters [25–31]. These studies suggested that oxide-supported single Au atoms could provide a new type of catalyst for CO oxidation and other reactions.

The recent development of aberration-corrected scanning transmission electron microscopy (AC-STEM) techniques, especially the high-angle annular dark-field (HAADF) imaging technique, has made it possible to routinely image noble metal single atoms dispersed over many types of catalyst supports [32]. The AC-HAADF imaging technique is the only characterization technique that can provide fundamental and exclusive information regarding the presence, dispersion, and location of individual metal atoms on the support surfaces, and has proved indispensable to optimizing the synthetic protocols of SACs. The AC-HAADF technique is most valuable for examining heavy-element metal atoms dispersed onto light-element supports due to its special image formation mechanism [32]. Further developments are needed to unambiguously identify the

nature of light-element metal atoms on supports.

In this mini-review, we discuss the recent advances in Au SACs, with the aim of illustrating their unique catalytic features for CO oxidation.

2. Recent advances in Au SACs for CO oxidation

2.1. Experimental progress

Gates' group has performed an intensive study on the catalytic performance of cationic Au species for CO oxidation [33–40], including isolated Au^+ atoms [33,36]. In their studies, the catalytic activity for CO oxidation decreased with a decreasing fraction of the cationic Au existed either on NPs [34] or in the form of an isolated mononuclear complex species [33], suggesting a role of cationic Au as the catalytic sites for CO oxidation. Mononuclear complexes were stable during the CO oxidation reaction [33,36]; their activities were, however, relatively low and the TOF (turn-over-frequency) was generally at the level of 0.01 s^{-1} or less. Such a TOF value is at least one order of magnitude lower than that of the most active supported Au catalysts with a TOF values in the range of $0.1\text{--}1 \text{ s}^{-1}$. Their much lower activity seems to suggest that isolated Au atoms are less active compared with Au nanoclusters and Au NPs [16]. However, it should be noted that many factors may account for the observed low activity of the isolated atomic Au species. First, in their studies they employed non- or less reducible support materials such as zeolite, MgO and La_2O_3 . The nature of the support surface can significantly affect the CO oxidation activity of supported Au catalysts [4,41]. With a reducible oxide as support, better CO oxidation performance has been observed due to the support's role in either activating O_2 species [41] or directly participating in the reaction through a redox process [9,42]. Therefore, the support materials used in their studies may have not made a synergistic contribution to the activity of the mononuclear cationic Au species. Second, in their studies the mononuclear species are complexes containing ligands. Although extend X-ray adsorption fine structure (EXAFS) characterizations have suggested that Au can directly bond to the support via one or two Au–O bonds [37], the ligands may still have been present in the final catalyst, because there was no direct evidence showing that the ligands were removed during the catalytic reactions. Whether the presence of the ligands had a negative effect on the observed activity is still unclear. In their later studies, they found that the samples became more active after being treated at elevated temperatures [39,43–45]. This could be ascribed to the formation of more active gold clusters, but a possible effect resulting from the removal of the ligands cannot be ruled out completely. Therefore, from the limited data available, it is difficult to unambiguously determine whether or not Au SACs have catalytic activity similar to, or even better than, that of Au NPs or clusters.

In contrast to the above studies, we recently developed a series of oxide-supported single-atom Au catalysts prepared by simply depositing Au atoms on various oxide supports with atomic dispersion [25–27]. These catalysts were proven highly

Fig. 1. Turn-over-frequency (TOF) of CO oxidation at room temperature for various types of supported Au catalysts. Reprinted with permission from Ref. [16]. Copyright 2011, Royal Society of Chemistry.

active for CO oxidation, with much higher specific rates and TOF values, similar to those of small Au NPs on the same supports. The observation that supported Au single atoms and Au NPs possess similar TOF values, calculated on the assumption that the active sites are all Au atoms in the SACs as opposed to only the surface atoms of Au NPs, suggests that isolated Au atoms dispersed on suitable oxide supports can be as active as those Au atoms on the corners, steps and/or surfaces of Au NPs on the same oxide supports. The much higher specific rates, calculated on the basis of total metal mass, also demonstrate the higher atom efficiency of the SACs. More importantly, these SACs showed better stability compared with their NP/cluster counterparts.

To directly synthesize metal oxide-supported Au single atoms by the traditional wet chemistry approach one generally needs to use low levels of the Au precursor species. Thus, gold atoms on FeO_x with very low loading amount of Au (< 0.03 wt%) were used to synthesize the Au SACs [25]. The FeO_x was pre-synthesized by a co-precipitation method and then the Au atoms were directly deposited to allow the Au atoms dispersed all on the surfaces of the FeO_x support. These catalysts are active for CO oxidation at room temperature and show a TOF of $\sim 0.5 \text{ s}^{-1}$, a value similar to that of the most active Au/ FeO_x catalysts (in the range of $0.5\text{--}1 \text{ s}^{-1}$) prepared by depositing 2–3 nm colloidal Au NPs onto the pre-synthesized FeO_x so as to ensure the sole, or at least primary, existence of Au NPs [46]. By comparing the activity of these two sets of catalysts, it is evident that the single Au atoms dispersed on FeO_x can be as active as the Au NPs in the size range of 2–3 nm. Furthermore, the TOF values obtained from the SACs were similar to those of the Au clusters and NPs in the optimum size range of 0.5–5 nm (approximately 1 s^{-1}). This work represented the first-ever proof that Au SACs can be as active as the most active Au NPs, although not as active as the reported bilayer structure Au species [15,47]. It should be noted that the amount of residual Cl^- in the above work is unknown. It is believed that the residual Cl^- generally has a negative effect on supported Au catalysts, especially for the CO oxidation reaction. However, recent studies show that, in the case of iron oxide-supported Au catalysts, the Cl^- anion has negligible or even positive effects, depending on the preparation method and the residual amounts of the anion [48,49]. Therefore, the possible effects of residual Cl^- needs to be clarified by further investigations. More interestingly, the authors have also found that the Au SACs are not only active but also extremely stable for CO oxidation at temperatures above 200°C (Figure 2) [25]. This observation is intriguing because it is generally believed that highly dispersed atoms are much less thermostable and thus easy to sinter to form small clusters and/or NPs [50]. There are two possibilities that may account for the experimentally observed excellent stability. The first is that the Au atoms interact more strongly with the support than Au NPs do. Another possibility is that, given the low density of Au atoms on the support surface, even if the Au atoms move during a catalytic reaction, they have a small probability to encounter one another to form clusters or NPs. However, the latter possibility can be primarily excluded by comparing the behaviors of different supported Au catalysts. First,

Fig. 2. Stability tests of the $0.03\text{Au}_1/\text{FeO}_x$ and $0.3\text{Au}/\text{FeO}_x$ catalysts for CO oxidation at 200°C . The test for the FeO_x support is also shown as a reference. Test conditions: 1 vol% CO + 1 vol% O_2 + 98 vol% He. Reprinted with permission from Ref. [25]. Copyright 2015, Springer.

the number density of Au NPs in the 0.3 wt% Au/ FeO_x reference sample should be lower than the density of Au atoms in the 0.03 wt% Au/ FeO_x sample because each Au NP (2–5 nm in size) contains much more than 10 atoms. However, after the stability test, the Au NPs exhibited significant sintering, suggesting that even with sparse distribution the Au NPs still sinter. Second, after the stability test, the number density of the isolated Au atoms in the 0.3 wt% Au/ FeO_x (which was higher than that in the 0.03 wt% Au_1/FeO_x) was not changed appreciably, suggesting that the isolated Au atoms may be anchored more strongly on FeO_x than are Au NPs. To better understand and explain the excellent stability of the Au SACs, density functional theory (DFT) calculations were performed, and the results demonstrated that the experimentally observed excellent stability originated from the strong covalent metal-support interaction (CMSI) between Au atoms and the FeO_x support, as detailed in Section 2.2.

In the study described above [25], although Au SACs showed high activity for CO oxidation even at ambient temperature, the total CO conversion was only realized at 160°C due to the very low Au loading, making the catalyst less attractive for practical applications at low temperatures. Subsequent work by the same group focused on dispersing Au atoms on Co_3O_4 which is itself a highly active CO oxidation catalyst [6–8]. Despite the activity of pure Co_3O_4 for CO oxidation, the Au/ Co_3O_4 catalysts are usually slightly less active and less studied compared with other oxides such as FeO_x and TiO_2 -supported Au catalysts [4,51]. However, when isolated Au single atoms were used, the $\text{Au}_1/\text{Co}_3\text{O}_4$ was found to be extremely active for CO oxidation even at ambient temperatures that even with only 0.05 wt% Au loading it could realize total CO conversion, as shown in Figure 3 [26]. To the best of our knowledge, for the first time, CO total conversion has been realized with such a low loading amount of Au at ambient temperature. The specific reaction rate was estimated, after subtracting the contribution of the Co_3O_4 support, to be approximately $25 \text{ mol}_{\text{CO}} \text{ g}_{\text{Au}}^{-1} \text{ h}^{-1}$, about 10 times higher than the definition of “highly active catalyst” proposed

Fig. 3. CO conversion as a function of reaction temperature for CO oxidation on Au₁/Co₃O₄ catalyst. Reaction conditions: 1 vol% CO + 1 vol% O₂ balance with He; total flow rate = 33.3 mL/min, 50 mg catalyst diluted with 100 mg Al₂O₃, space velocity = 40 000 mL g_{cat}⁻¹ h⁻¹. Reprinted with permission from Ref. [26]. Copyright 2015, Elsevier.

by Schuth [52]. The TOF of this catalyst, calculated from the specific rate based on 100% dispersion, was approximately 1.4 s⁻¹, which is similar to [9] or even higher than that of the most active Au catalysts [46], except the bilayer structure of Au [15,47]. It should be noted that, however, this catalyst has to undergo a high temperature reaction before it became highly active at ambient temperatures, suggesting some form of “conditioning” of the fresh SAC during the CO oxidation reaction occurred. In addition, while this catalyst is extremely active, it is less durable under long-term test at ambient temperature. Cycling tests and heat treatments with different gases have suggested that this deactivation is reversible and so may originate from the accumulation of carbonates and/or subtle changes in the oxidation states of the Au or Co species during the catalytic reaction. The fact that the catalyst remained active after calcination at 400 °C and that the Au was atomically dispersed confirm that the deactivation was not due to sintering of isolated Au single atoms.

Ceria (CeO₂) is another widely used support for highly active supported Au catalysts. As early as 2003, Flytzani-Stephanopoulos’ group, by using a sodium cyanide leaching method, for the first time, found that only isolated metal (Au/Pt) cations/clusters that strongly bonded to the La-doped CeO₂ support are the active sites for the WGS reaction [53]. Those metal NPs that could be easily leached from the support by sodium cyanide were therefore proposed to be only spectators. This synthetic approach to the fabrication of SACs has provoked various discussions [16] owing to the relatively lower activity of the resulting catalysts compared with that obtained from the Au/CeO₂ catalysts prepared by conventional wet chemistry methods [54], and to the fact that the possible formation of sodium gold cyanide compounds may affect the observed catalytic performance [55,56]. Subsequent reports from the same group [19–22,57], however, provided clear evidence that isolated Au(Pt) cations bonded with OH⁻ groups were active for WGS reaction. The ambiguity about the true nature of the active sites suggests that a precise identification

and comparison of the activity of the single-atom and NP active sites is quite complicated. Nevertheless, despite the debates on the nature of the active sites, it is speculated that Au SACs are either inactive or much less active than their NP/cluster counterparts for CO oxidation because the reported activity of leached catalysts was very low and was dramatically increased after heat-treatment in H₂ due to the formation of small clusters/NPs [58].

Our group, following a similar approach to that used to prepare Au₁/FeO_x and Au₁/Co₃O₄, developed a CeO₂-supported Au SAC (Au₁/CeO₂) with various Au loading levels [27]. Different from the FeO_x and Co₃O₄ materials, the prepared CeO₂ nanocrystallites possessed numerous Ce vacancies as suggested by the HAADF-STEM images [27]. Therefore, the Au loading amounts in these new materials should be higher provided that the Au atoms can be anchored to the Ce vacancy sites [28]. In fact, the characterization and reaction results demonstrated that a catalyst with a 0.3 wt% Au loading still primarily consisted of isolated Au atoms without the presence of any Au clusters and NPs. This loading level is much higher than those for Au₁/FeO_x and Au₁/Co₃O₄ catalysts, 0.03 and 0.05 wt%, respectively, suggesting that the creation of Ce vacancies on the support is crucial to the fabrication of SACs with high levels of metal loading. Similar to the Au₁/FeO_x systems, the Au₁/CeO₂ catalysts provided TOF values close to, and specific rates much higher than, those of their NP counterparts. Moreover, it was discovered that the Au₁/CeO₂ exhibited very low reactivity for the oxidation of H₂ molecules, even at relatively high temperatures, possibly due to their inability of dissociative adsorption of H₂, as shown in Figure 4. The TOF for pure H₂ oxidation on Au₁/CeO₂ was approximately two orders of magnitude lower than that on the Au NPs supported on ceria. As a consequence, the TOF for pure H₂ oxidation at 120 °C was at least two orders of magnitude lower than that for CO oxidation at 80 °C on the Au₁/CeO₂ SAC. In contrast, the TOF was only three to six times lower than that for CO oxidation on Au NPs supported on ceria. The inability of dissociative adsorption of H₂ on Au₁/CeO₂ was further verified by DFT calculations. This unique feature is ideal for the preferential oxidation of CO in H₂-rich gas stream

Fig. 4. H₂ conversion as a function of temperature for H₂ oxidation on Au/CeO₂ catalysts. Reaction condition: 1 vol% H₂ + 1 vol% O₂ balanced with He. Reprinted with permission from Ref. [27]. Copyright 2015, American Chemical Society.

(PROX) reaction [27]. The Au_1/CeO_2 SAC can realize total CO conversion in a H_2 -rich gas stream at either 50 to 100 or 70 to 120 °C, the typical temperature windows for practical proton exchange membrane fuel cell (PEMFC) operations, depending on the Au loading amounts (0.3 or 0.05 wt%, respectively), as show in Figure 5. Similar to the Au_1/FeO_x catalysts, the Au_1/CeO_2 catalysts are also highly stable during PROX reaction, indicating the potential for practical applications.

2.2. Theoretical studies

Single metal atoms often strongly bind to support surface atoms, and different supports can offer different anchoring sites to stabilize single metal atoms due to chemical bonding between the metal atoms and the support surfaces. Here we primarily focus on discussing the theoretical understanding of the oxidation states of single gold atoms, the mechanism of CO oxidation on different metal oxides, and single Au atoms on two dimensional supports. Qiao et al. [25] prepared the ultrastable single-atom gold catalyst Au_1/FeO_x that has excellent performance for CO oxidation. In order to investigate the oxidation states of Au_1 atoms and the change of their charge during the catalytic cycle of CO oxidation, we employed $\text{Au}(\text{OH})_x$ ($x = 1-3$) clusters as reference models for SACs containing Au^+ , Au^{2+} and Au^{3+} , respectively. These models allowed a comparison and evaluation of the Bader charges [25] of Au_1 atoms in the stable structures of Au_1/FeO_x with and without oxygen vacancies (Figure 6). The results showed that the oxidation state of the Au_1 atoms is close to Au(I) (with O vacancies) and Au(III) (without O vacancies), indicating electron transfer from the Au_1 atoms to the O atoms of the support. Similarly, the oxidation state of the Pt_1 atoms in the Pt_1/FeO_x catalyst [59] can be assigned as either Pt(II) (with O vacancies) or Pt(IV) (without O vacancies), which are isoelectronic with Au(I) and Au(III), respectively. These high-valent Au_1 atoms provide additional electrostatic interaction with the O atoms of the support due to the opposite charges of these ions. In addition, the sintering of these non-zero-valent Au_1 atoms into subnanometer-clusters

Fig. 5. CO conversion as a function of reaction temperature for PROX on Au/CeO_2 catalysts. Reaction condition: 1 vol% CO + 1 vol% O_2 + 40 vol% H_2 balanced with He. Weight hourly space velocity (WHSV) = 25 000 $\text{mL g}_{\text{cat}}^{-1} \text{h}^{-1}$. Reprinted with permission from Ref. [27]. Copyright 2015, American Chemical Society.

Fig. 6. The stable structures of Au_1/FeO_x and Pt_1/FeO_x with oxygen vacancy (i) and without oxygen vacancy (iv) in pathway I. The $\text{Pt}(\text{OH})_x$ ($x = 1-4$) and $\text{Au}(\text{OH})_x$ ($x = 1-3$) molecules are calculated in a cubic box of $20 \text{ \AA} \times 20 \text{ \AA} \times 20 \text{ \AA}$. Reprinted with permission from Ref. [25]. Copyright 2015, Springer.

or nanoparticles becomes energetically demanding because it requires back electron-transfer (i.e., reduction of the Au(I) and Au(III) ions) from the adsorbed species or the support and the breaking of the strong Au–O bonds to form weaker Au–Au bonds in metallic gold. The strong covalent Au–O bonding and the high oxidation states of Au atoms thus account for the exceptional stability and the observed high catalytic activity of Au_1/FeO_x during the CO oxidation reaction.

Camellone et al. [28] provided insights into the catalytic mechanisms by which single Au atoms promote the oxidation of CO on CeO_2 (111) surfaces. Their results indicated that the positively charged Au atoms, substituting for Ce lattice sites, are more active for CO oxidation. However, these Au^+ adatoms eventually diffuse into the oxygen vacancies and become negatively charged $\text{Au}^\delta-$ adspecies that prevent the adsorption of molecular CO or O_2 , thus deactivating the catalyst. Recently, Wang et al. [60,61] performed *ab initio* molecular dynamics (AIMD) simulations on the well-known low temperature CO oxidation process catalyzed by approximately 1 nm Au NPs on partially reduced CeO_2 and TiO_2 supports. They found an unprecedented phenomenon of the dynamic formation of single-atoms from Au NPs on both supports, which they termed as dynamic single-atom catalysis (DSAC). In this DSAC process, the Au atoms can be carried by adsorbed CO molecules to migrate on the Au NPs and even migrate to the metal oxide support during the catalytic reaction. A similar phenomenon was reported by a recent work, in which the migration of Au–CO complexes was found to occur on a Au (111) surface, even at low temperature and low CO pressure [62]. These findings provide another perspective of how the reactants, active sites and the support dynamically interact with one another during a catalytic reaction, especially when the reactants are adsorbed on different sites of a heterogeneous surface.

Yang et al. [31] investigated the CO oxidation behavior of single Au atoms embedded in two-dimensional *h*-BN monolayers using first-principle calculations, quantum Born-Oppenheimer molecular dynamic simulations (BOMD) and micro-kinetic analysis. They determined that CO oxidation on Au_1/h -BN preferentially proceeds via the tri-molecular Eley-Rideal (E-R) reaction mechanism, in which an O_2 molecule is activated by two pre-adsorbed CO molecules. The catalytic activity of CO oxidation on Au-embedded graphene was also investigated using the first-principle method by Lu et al. [63]. Their data suggest that the first step of CO oxidation catalyzed by this ma-

terial most likely proceeds via the Langmuir-Hinshelwood reaction mechanism ($\text{CO} + \text{O}_2 \rightarrow \text{OOCO} \rightarrow \text{CO}_2 + \text{O}$), and that the associated activation barrier is as low as 0.31 eV. The second step of the oxidation would be the Eley-Rideal reaction ($\text{CO} + \text{O} \rightarrow \text{CO}_2$) with a much lower activation barrier of 0.18 eV.

3. Summary

It has been several decades since Haruta discovered the extremely high activity of supported Au catalysts for low temperature CO oxidation, and more than ten years have passed since Flytzani-Stephanopoulos discovered that isolated non-metallic Au species are the active sites for the WGS reaction. However, for various reasons, evidence demonstrating the high activity of Au₁ SACs for low temperature CO oxidation has appeared only recently. This mini-review summarized the recent experimental results and that clearly show that, using suitable oxide supports, Au₁ single atoms can be as active as Au NPs and clusters when the activity is measured by the true TOF. In addition, when measured by the mass of the Au, which is a critical aspect of industrial applications, the Au SACs exhibit a much higher specific activity, showing the high atom efficiency of SACs. Of more interest and importance, the Au₁ SACs are more stable than their Au NPs and clusters counterparts during CO oxidation. These novel features of the Au₁ SACs make it possible to develop supported Au catalysts with low cost and high stability which are important for practical applications. On the other hand, studies on Au₁ SACs for catalytic reactions are still in the initial stage. Further studies aimed at understanding the nature of catalysis by Au₁ SACs and their potential applications for a plethora of catalytic transformations should be explored in the future.

Theoretical calculations, which can provide fundamental understanding and probably prediction of experimental results, have generated helpful information for evaluating the electronic and energetic properties of catalytic processes on an atomic level. It is expected that the further development of computational algorithms not only provide mechanistic details of single-atom catalytic processes but also provide guidance for

designing SACs and ultimately are able to predict the activity, selectivity and stability of SACs.

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Graphical Abstract

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Single atom gold catalysts for low-temperature CO oxidation

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Recent studies revealed that gold single-atom catalysts are not only highly active but also extremely durable for CO oxidation, which may provide a new way to develop practical Au catalysts with low cost and high stability.

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金单原子催化剂上一氧化碳低温氧化

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摘要: CO 低温氧化对于基础研究和实际应用均具有重要意义. 自上世纪八十年代日本的 Haruta 教授发现氧化物负载金催化剂对 CO 氧化的超高活性以来, 负载金催化剂受到了广泛关注与深入研究, 被认为是目前活性最高的 CO 氧化催化剂. 在诸多影响 CO 氧化活性的因素中, 纳米金的粒子尺寸是最重要因素之一. 目前主流观点认为对于 CO 氧化, 纳米金有一个最优尺寸范围, 在 0.5–5 nm, 而 Au 原子/离子 (Au³⁺, Au⁺) 的活性则低一到两个数量级. 因此, 一般认为负载金单原子催

化剂对于 CO 氧化反应的活性要比金纳米粒子和团簇低很多。然而, 最近几年的理论与实验研究均表明, 金单原子负载于合适的载体上可以显示出与金纳米粒子和团簇相当的活性。本文对这些新进展进行综述, 阐述金单原子催化剂对 CO 氧化的独特反应性能。

Gates 教授研究组进行了大量关于正价金对 CO 氧化影响的研究, 其中包括孤立的金原子 (Au^+)。他们的研究发现, CO 氧化活性随价态降低而降低, 表明正价金对 CO 氧化至关重要。此外, 他们的研究也表明, 孤立金原子对 CO 氧化的活性 (TOF) 比金纳米粒子低一到两个数量级。然而, 在他们的研究中, 有几个因素可能导致催化剂的低活性。首先, 他们一般采用非或弱还原性的载体。而载体的还原性对金催化剂上 CO 氧化活性影响非常巨大。另外, 他们所用的金原子前驱体为配合物, 在催化剂制备与反应过程中配体并没有去除, 可能也是导致催化剂活性低的原因之一。

与此相反, 张涛课题组近期采用氯金酸为前驱体, 通过简单的吸附浸渍法制备了一系列负载金单原子催化剂。同时用相同的载体制备了负载金纳米粒子催化剂进行对比, 可以排除载体等其它影响因素。对比结果显示, 单原子催化剂均显示出与纳米粒子相当的 TOF(单位表面 Au 原子) 和更高的反应速率(单位重量金)。

首先制备了氧化铁负载金单原子催化剂, 该催化剂在室温即展现出可观活性, TOF 值与 2–3 nm 金粒子 TOF 值相当 ($\sim 0.5 \text{ s}^{-1}$)。更有趣也更重要的是, 该催化剂在高温 (200 °C 以上) 展现出非常高的反应稳定性, 在 200 °C 反应 100 h 无失活。在 300 和 400 °C 反应 50 h 也无失活发生, 为开发高温稳定的金催化剂提供了新途径。其次制备了氧化钴负载金单原子催化剂, 该催化剂以 0.05% 金负载量即可实现室温全转化, 其 TOF 值高达 1.4 s^{-1} 。然而该催化剂在达到高活性之前必须首先在反应气氛中进行高温处理, 这限制了其实用性。此外, 催化剂需经反应气氛活化的原因尚待进一步研究。随之又制备了氧化铈负载金单原子催化剂, 对富氢条件下 CO 选择氧化不仅具有高活性, 而且具有极高的 CO 选择性。进一步研究结合理论计算表明, 高选择性来自氧化铈负载的金单原子不能解离活化氢, 对于氢气氧化活性极低, 从而导致 CO 氧化的高选择性。

理论研究方面也有进展。Camellone 等计算发现金原子可以取代 $\text{CeO}_2(111)$ 面上的 Ce 原子形成 Au^+ 并促进 CO 氧化。然而该金原子会扩散至氧空位形成带负电荷的 Au^δ , 阻止 CO 和 O_2 吸附, 因而使催化剂失活。李隽课题组利用从头算分子动力学模拟首次发现氧化铈和氧化钛负载的 Au 纳米粒子在 CO 氧化过程中可以形成单原子的现象, 并将之称为动态单原子催化剂。Yang 等则计算了二维材料 BN 负载 Au 单原子催化 CO 氧化并发现反应优先通过三原子 E-R 机理进行。

关键词: 金; 单原子催化剂; 一氧化碳氧化; 稳定性; 低温

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