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Highly active Au₁/Co₃O₄ single-atom catalyst for CO oxidation at room temperature

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ABSTRACT

CO oxidation is of great importance in both fundamental studies and practical applications. Oxide-supported noble metal catalysts are well known to be excellent CO oxidation catalysts. However, the high cost and limited supply of these noble metals pose significant challenges for sustainable applications. Maximizing the atom efficiency of supported noble metal catalysts is therefore highly desirable. In this work, a Co₃O₄ supported Au single-atom catalyst with very low Au (0.05 wt%) loading has been developed. This catalyst showed extremely high activity for CO oxidation and exhibited total conversion of CO at room temperature. The high activity originates from the isolated Au atoms distributed on the Co₃O₄ nanocrystallites, although the exact catalytic mechanism is still under investigation. The catalyst deactivation observed during the CO oxidation was attributed to the accumulation of CO₂ rather than sintering of the single Au atoms. This extremely low loading of Au coupled to high activity is critical to reducing the cost of noble metal catalysts and making them more practical and attractive.

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Low-temperature CO oxidation is valuable as a prototypical reaction for heterogeneous catalysis in fundamental studies [1]. It is also of great importance in practical applications, including automotive emissions control [2] and proton exchange membrane fuel cells [3]. Metal oxides such as copper–manganese (Hopcalite) [4], copper–chromite [5] and cobalt oxides [2,6] are highly active in CO oxidation, even at ambient temperatures. However, the low thermal stability, undesirable behaviors in cycled transient conditions, and a high susceptibility to be poisoned by sulfur and water [7,8] severely limit their practical applications. In contrast, noble metals are excellent CO oxidation catalysts with high activity and thermal stability and are widely used in industrial applications; the high cost and limited

supply of these noble metals, however, pose significant challenges for sustainable applications [5,7]. While these noble metals are usually finely divided into nanometer-scale active units and dispersed on high-surface-area materials, their atom efficiency is still very low because only the surface atoms of a nanoparticle are involved in the catalysis. Therefore, it would be highly desirable to maximize the atom efficiency of these supported noble metal catalysts.

Recently, we demonstrated that ferric oxide-supported Pt single-atom catalysts were highly active for CO oxidation [3]. It was subsequently shown by others that Pt [9,10] and Rh [11] single atoms dispersed on various supports were also highly active, suggesting that the development of single-atom catalysts

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is a general approach that can maximize the atom efficiency of noble metals [12–14].

It is generally accepted that oxide-supported Au nanoparticles are the most active catalysts for CO oxidation. However, the activity of single Au atoms in CO oxidation remains elusive. While some theoretical calculations suggested that single Au atoms could be catalytically active for CO oxidation [15], others have suggested CO adsorption could poison Au atoms on FeO_x and thus deactivate the catalyst [16]. It has been reported that cationic Au species dispersed on oxide supports showed activity for CO oxidation at room temperature; however, the reported activity was much less than that of the more common small Au nanoparticles [17–19]. Studies on model catalysts also suggested that when compared with their sub-nanometer-sized cluster counterparts, Au single atoms were much less active [20]. Recently, we found that an FeO_x -supported Au single-atom catalyst is not only highly active, but extremely stable for CO oxidation, suggesting a potential application of oxide-supported Au single-atom catalysts [21]. For certain applications, the total oxidation of CO at ambient temperatures is of great practical value. In this work, we report the recent development of single Au atoms supported on Co_3O_4 as an extremely active catalyst for CO oxidation showing total conversion of CO at room temperature with an extremely low Au loading of only 0.05 wt%.

Co_3O_4 nanocrystallites were synthesized by co-precipitation of $\text{Co}(\text{NO}_3)_2$ and Na_2CO_3 at room temperature and then calcined

at 400 °C for 5 h. The isolated Au atoms at 0.05 wt% Au loading were dispersed onto the Co_3O_4 by adsorption and calcined at 400 °C for 5 h (denoted as $\text{Au}_1/\text{Co}_3\text{O}_4$). Details of the Co_3O_4 support and $\text{Au}_1/\text{Co}_3\text{O}_4$ catalysts preparation procedures are presented in the supporting information (SI).

The X-ray diffraction (XRD) pattern of the synthesized Co_3O_4 support is presented in Fig. S1 in the SI. It shows typical Co_3O_4 diffraction peaks. The Brunauer–Emmett–Teller (BET) surface area of the synthesized Co_3O_4 was 35 $\text{m}^2 \text{g}^{-1}$. Representative high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst are presented in Figs. 1 and S2. Isolated single Au atoms (in the circles) dispersed on the Co_3O_4 surfaces are clearly visible. The low-magnification images show that no Au particles or clusters can be observed on the catalyst. By analyzing many low and high magnification images of different regions of the catalyst, we have concluded that only single Au atoms are present in the catalyst without the presence of any Au clusters/particles.

CO oxidation was performed at a gas composition of 1 vol% CO + 1 vol% O_2 balanced with He. The sample (50 mg) was diluted with 100 mg Al_2O_3 , loaded into a quartz tube reactor, and the reactant gas was allowed to pass through the reactor at a total flow rate of 33.3 ml min^{-1} , giving a space velocity (SV) of 40,000 $\text{ml g}_{\text{cat}}^{-1} \text{h}^{-1}$. Fig. 2 plots the CO conversion by the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst as a function of the reaction temperature. For the first cycle, CO oxidation started at room temperature (20 °C) and achieved total CO conversion at 120 °C. However,

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Tao Zhang (Dalian Institute of Chemical Physics, Chinese Academy of Science) **received the Catalysis Award for Young Scientists in 2008**, which was presented by The Catalysis Society of China. Professor Tao Zhang received his Ph.D. degree from Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, in 1989, and he joined the same institute and was promoted to full professor in 1995. He did postdoctoral research with Prof. Frank Berry at Birmingham University in 1990. Prof. Zhang was an invited professor at University of Poitiers (France) in 2006–2007, and he has been a guest professor at University of Namur (Belgium) since 2011. He is currently the director of DICP (since 2007). Prof. Zhang has also received several research awards, including the Distinguished Award of Chinese Academy of Sciences (2010), Zhou Guangzhao Foundation Award for Applied Science (2009), National Award of Technology Invention (2008, 2006, 2005). He was selected as an academican of the Chinese Academy of Sciences. In the past decades, Prof. Zhang has successfully designed a great number of nano and subnano metallic catalysts for applications in energy conversion and environmental control. His research interests include (1) Design and synthesis of nano- and subnano catalytic materials; (2) utilization of biomass for production of chemicals.

Fig. 1. STEM-HAADF images of the 0.05 wt% $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst with different magnifications. The high resolution image (a) clearly shows the isolated single Au atoms (white circles) and the low magnification image (b) suggests that there are no Au clusters or particles in the catalyst.

on the second cycle, the CO total conversion occurred at room temperature, suggesting that the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst was activated during the first cycle of the reaction process. Co_3O_4 is a highly active catalyst for the oxidation of CO [2,6,22]. To show that the observed high activity originated from the isolated, supported Au single atoms rather than the Co_3O_4 support, we used the pure Co_3O_4 support under exactly the same reaction conditions. As shown in Fig. S3 in the SI, for the first cycle, the CO oxidation started at 50 °C and achieved total CO conversion at 160 °C, suggesting a much lower activity of the support. In the second cycle, the activity increased as well: 30% CO conversion at 20 °C and total conversion of CO at 160 °C. Clearly, the conditioning of the Co_3O_4 during the first cycle improved its activity significantly, but the Co_3O_4 support was still much less active than the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst. This comparative study unambiguously demonstrates that the high activity of the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst originates from the Au single atoms supported on the Co_3O_4 nanocrystallites. Schuth [23] proposed a definition of high activity for CO oxidation on supported Au catalysts. To be considered a high-activity catalyst, a supported Au catalyst with about 1 wt% Au loading should yield at least 75% CO conversion at a space velocity of $60,000 \text{ ml g}_{\text{cat}}^{-1} \text{ h}^{-1}$ with 1% CO in the feed gas at 20 °C. Such a definition corresponds to a rate of about $20 \text{ mmol}_{\text{CO}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$, or $\sim 2 \text{ mol}_{\text{CO}} \text{ g}_{\text{Au}}^{-1}$

Fig. 2. CO conversion as a function of reaction temperature for CO oxidation on $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst. Reaction condition: 1 vol% CO + 1 vol% O_2 balance with He; total flow rate = 33.3 ml/min , 50 mg catalyst diluted with 100 mg Al_2O_3 , space velocity = $40,000 \text{ ml g}_{\text{cat}}^{-1} \text{ h}^{-1}$.

h^{-1} for a Au loading of 1 wt%. We estimated the specific rate of our $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst by subtracting the contribution of the Co_3O_4 support at 20 °C and obtained a value of $\sim 25 \text{ mol}_{\text{CO}} \text{ g}_{\text{Au}}^{-1} \text{ h}^{-1}$, which is about ten times greater than the value in Schuth's definition.

It has been reported that pretreatment by various atmospheres could enhance the activity of Co_3O_4 [22,24–26]. We therefore investigated the effects of pretreatment by various types of gas atmospheres on the performance of the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst in an attempt to enhance the catalytic performance. The results are presented in Fig. S4. It clearly shows that after treatment at 200 °C with different gases (pure He, 5% O_2/He and 5% CO/He), the CO conversion increased only slightly with respect to the untreated catalyst, suggesting a slight improvement in performance. However, compared with the observed enhancement of the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst after the first cycle, the improvement due to gas treatment is almost negligible. Therefore, this significant improvement in the activity after the first cycle of the reaction should originate from other factors such as the subtle changes of the catalyst (surface) structure during the reaction process.

In our previous work, we found that for iron oxide-supported Au [27–31] and other metal [32–34] catalysts, the as-synthesized, non-calcined catalysts possessed higher activities. To investigate the effects of the calcination on the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalysts, we further tested the as-synthesized catalyst without any heat treatment (denoted as $\text{Au}_1/\text{Co}_3\text{O}_4\text{-UC}$). As shown in Fig. S5, $\text{Au}_1/\text{Co}_3\text{O}_4\text{-UC}$ shows a slightly higher activity at 50 °C compared with that of the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst for the first cycle. However, at elevated temperatures, the activity is lower and achieved total CO conversion at the higher temperature of 140 °C. For the second cycle, it demonstrated a slightly lower activity at 20 °C compared with the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst, but still realized total CO conversion at 40 °C. It is worth noting that during the third cycle, the activity did not change significantly, suggesting a good cycle stability of the conditioned $\text{Au}_1/\text{Co}_3\text{O}_4$ catalysts. This result shows that calcination at elevated temperatures (e.g., 400 °C in this work) did not cause a decrease in activity, suggesting that the $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst is probably resistant to calcination.

The long-term stability of the catalyst is important in practical applications. We therefore tested the stability of the $\text{Au}_1/\text{Co}_3\text{O}_4\text{-UC}$ sample for CO oxidation at room temperature after a third cycle, to avoid activity saturation. As shown in Fig. 3, the catalyst deactivated rapidly in the initial 400-min experiment, with the CO conversion decreasing from 70% to about 40%, while during the next 400 min, the deactivation slowed, with only a 10% decrease in the CO conversion over this time. Supported gold catalysts have been shown to deactivate during catalytic reactions because of sintering of the Au nanoparticles. However, for CO oxidation at low temperatures, the formation and accumulation of carbonates due to CO_2 adsorption is usually the main reason for the deactivation [35]. This is generally reversible [3,36]. To confirm the deactivation of the $\text{Au}_1/\text{Co}_3\text{O}_4\text{-UC}$ was reversible, we performed various in situ treatments to regenerate the catalyst. Fig. 3 shows that after treatment in He at 200 °C for 30 min, the activity had al-

Fig. 3. CO conversion as a function of reaction time for CO oxidation at 20 °C on $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst, and with different types of treatment (indicated by the arrows).

most completely recovered (CO conversion of ~65%), suggesting that the deactivation can be reversed. During heat treatment under He, carbonates have been shown to decompose [3,36]. Fig. 3 also indicates that treatment under 5% H_2/He not only did not regenerate the sample but made it worse, which might be due to the formation of H_2O during the H_2 reduction treatment. Co_3O_4 catalysts are very sensitive to the presence of H_2O [2]. The subsequent 5% O_2/He treatment then recovered the CO conversion to 100%, suggesting that the carbonates could be more efficiently removed in an O_2 atmosphere. To confirm the effect of H_2O , we further added 2% H_2O into the reaction gas. As expected, the CO conversion dropped rapidly, demonstrating the severely negative effects of H_2O .

In summary, we have successfully developed a highly active Co_3O_4 -supported Au single-atom catalyst with an extremely low Au loading level of 0.05 wt%. This catalyst completely converted CO at room temperature and yielded a specific rate of $\sim 25 \text{ mol}_{\text{CO}} \text{ g}_{\text{Au}}^{-1} \text{ h}^{-1}$. The experimentally obtained high activity originated from the isolated Au single atoms supported on the Co_3O_4 nanocrystallites, although the exact catalytic mechanism is not clear at this stage and further study is warranted. The catalyst is susceptible to the accumulation of CO_2 , but resistant to sintering. To our knowledge, this is the first report to

unambiguously demonstrate that a supported Au catalyst with such a low loading of Au can realize the total conversion of CO at ambient temperatures. The extremely low loading of noble metal is critical to reducing the cost of supported noble metal catalysts and therefore makes them more practical and attractive.

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Graphical Abstract

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Highly active $\text{Au}_1/\text{Co}_3\text{O}_4$ single-atom catalyst for CO oxidation at room temperature

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Total CO conversion at ambient temperatures was realized with extremely low loading of Au, demonstrating the high atomic efficiency and suggesting the potential application of gold single-atom catalysts.

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高活性 Co_3O_4 负载单原子Au催化剂室温催化CO氧化

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摘要: CO低温氧化是多相催化领域研究最多的反应之一。作为简单、典型的探针反应, 其不仅具有重要的基础研究价值, 而且在环境污染消除等方面也有着非常重要的实际应用价值。金属氧化物如铜锰(Hopcalite)、铜铬复合氧化物以及氧化钴等都具有优异的低温CO氧化活性。然而氧化物催化剂热稳定性低、反复启动性能差、以及对硫化物、水等物质敏感, 严重制约了其实际应用。相对而言, 负载型贵金属催化剂因具有较高的CO氧化活性、反应稳定性以及热稳定性而受到关注。但是贵金属价格昂贵、资源稀少, 使其持续应用面临严峻挑战。为了提高贵金属利用效率、降低贵金属使用量, 在负载型贵金属催化剂中, 贵金属多以纳米尺度分散于高比表面载体上。由于多相催化一般在纳米粒子表面发生, 只有表面金属原子能够接触到反应物, 因而贵金属原子利用率仍然有待提高。

最近本课题组成功开发以原子级分散的单原子催化剂并提出“单原子催化”的概念。后续研究以及其他研究人员相继证明氧化物负载贵金属单原子具有高活性和/或不同于纳米粒子的反应性能, 表明开发单原子催化剂是最大化贵金属利用效率、降低贵金属用量的可行途径。对于CO氧化而言, 目前普遍认为负载Au催化剂具有最高活性。然而负载Au单原子催化剂是否具有活性仍存争议: 理论计算表明氧化物负载Au单原子催化剂具有很好的活性, 但是缺少实验证据; 目前已有一些氧化物负载Au正价离子催化剂的报道, 结果也都表明Au单原子活性远低于纳米粒子或纳米团簇。最近本课题组发现氧化铁负载Au单原子不仅具有与Au纳米粒子相当的单位活性位(TOF)活性而且具有更高的单位金属重量(反应速率)活性以及非常高的反应稳定性。本文将载体拓展到氧化钴, 开发了具有更高活性的氧化钴负载Au单原子催化剂, Au负载量仅为0.05 wt%即可在室温条件下实现CO完全转化。

Co_3O_4 载体用 $\text{Co}(\text{NO}_3)_3$ 与 Na_2CO_3 通过共沉淀法制备, 400 °C焙烧。然后通过简单的沉淀吸附法制备 Co_3O_4 负载Au单原子催化剂($\text{Au}_1/\text{Co}_3\text{O}_4$), 确保Au单原子能够分散于载体的表面。具有原子分辨率的球差校正高分辨电镜照片显示Au原子确实以单原子形式分散于载体上。催化剂在第一个循环中活性并不非常高, 但是在第二个循环中活性提高非常明显, 可以在室温条件下实现CO全转化。为了弄清楚活性提高的原因, 我们用惰性气体(He)、氧化性气体(5% O_2/He)以及还原性气体(5% CO/He)对催化剂进行了热处理, 但是活性提高并不明显。由此推断催化剂是在第一个循环反应过程中发生了某些变化, 导致活性显著提高。空白载体实验表明 Co_3O_4 载体本身虽然具有反应活性, 但是远不如负载少量Au原子活性高, 表明Au原子或Au原子与载体一起起到高活性的作用。稳定性研究表明该催化剂在室温条件下容易失活, 但经惰性气体或氧化气体处理后活性可恢复, 表明不是结构性失活而是可逆失活, 说明单原子非常稳定。

关键词: 单原子催化; 贵金属; 金; 一氧化碳氧化; 四氧化三钴; 低温

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Supporting Information

1. Catalyst preparation

1.1. Preparation of Co_3O_4 support

Co_3O_4 was prepared by a co-precipitation method. Typically, 1 mol L^{-1} $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution was dropwise added into suitable amount of 1 mol L^{-1} Na_2CO_3 aqueous solution at room temperature until the pH value of the solution decreased to about 8.5. After 2-h stirring and aging at room temperature, respectively, the resultant precipitate was filtered and washed with de-ionized water for several times to remove the residual carbonates and nitrates. Then the recovered precipitate was dried at 60 °C for 5 h and further calcined at 400 °C for 5 h.

1.2. Deposition of Au atoms

The Au atoms were deposited on the Co_3O_4 catalyst by a simple adsorption method with 0.05 wt%. 1 g the pre-synthesized Co_3O_4 powders were dispersed in deionized water with rigorous stirring. Appropriate amount of HAuCl_4 (AuCl_3 dissolved in diluted hydrochloric acid, corresponding to

an Au loading of 0.05 wt%) solutions were added dropwise into the Co_3O_4 solution under stirring. After continuing stirring for 2 h and followed by aging for 2 h, the solution was filtered and washed with deionized water for several times, and then dried at 60 °C for 5 h and calcined at 400 °C for 5 h. The synthesized catalyst was denoted as $\text{Au}_1/\text{Co}_3\text{O}_4$. For comparison, a non-calcined catalyst was also prepared and denoted as $\text{Au}_1/\text{Co}_3\text{O}_4\text{-UC}$.

2. Catalyst characterization

The actual Au loading was determined by inductively coupled plasma spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

X-ray Diffraction (XRD) patterns were recorded on a PW3040/60 X' Pert PRO (PANalytical) diffractometer equipped with a $\text{Cu } K\alpha$ radiation source ($\lambda = 0.15432 \text{ nm}$), operating at 40 kV and 40 mA. A continuous mode was used for collecting data in the 2θ range from 20° to 80° at a scanning speed of 5° min^{-1} .

Sub-angstrom resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images were obtained on a JEM-ARM200F TEM/STEM with a

Fig. S1. XRD pattern of the synthesized Co_3O_4 .

Fig. S2. STEM-HAADF images of $\text{Au}_1/\text{Co}_3\text{O}_4$ catalyst with different magnifications.

Fig. S3. CO conversion as a function of reaction temperature for CO oxidation over Co_3O_4 support.

Fig. S4. Comparison of CO conversion of fresh $\text{Au}_1/\text{Co}_3\text{O}_4$ (without treatment) at 20 °C with that treated sequentially under different gas atmosphere at 200 °C.

Fig. S5. Different cycles of CO oxidation on Au₁/Co₃O₄-UC samples.

guaranteed resolution of 0.08 nm. Before microscopy examination, the catalyst powders were ultrasonically dispersed in

ethanol and then a drop of the solution was put onto a copper grid coated with a thin lacey carbon film.

3. Catalytic performance testing

The catalytic performances of the catalysts for CO oxidation were evaluated in a fixed-bed reactor. Typically, 50 mg of the catalyst diluted with 100 mg Al₂O₃ was loaded in a straight quartz reactor. After purged with He for 10 min, the feed gas containing 1 vol% CO, 1 vol% O₂ and balance He was allowed to pass through the reactor at a flow rate of 33.3 ml/min, corresponding to a space velocity (SV) of 40000 ml g⁻¹_{cat} h⁻¹. The effluent gas compositions were on line analyzed by a gas chromatograph (HP 7890A) equipped with an Agilent SC-ST 80/100 column and a thermal conductivity detector using He as carrier gas. The CO conversion rates were calculated based on the difference between inlet and outlet CO concentrations.