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Research on unsupported nanoporous gold catalyst for CO oxidation

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Abstract

Nanoporous gold (NPG), a novel unsupported gold catalyst prepared by dealloying, exhibits exceptional catalytic activity for CO oxidation. Systematic studies were carried out on this new catalytic system, including the active sites of catalysts, the reaction kinetics, and activity dependence as functions of space velocity and temperature. Our results show strong evidence that metallic gold atoms on NPG are the intrinsic active sites at which the reaction of CO with O_2 occurs. The kinetic study found that the reaction rate of CO oxidation on unsupported NPG depends significantly on CO concentration but only slightly on O_2 concentration. We suggest that CO adsorption plays a decisive role in CO oxidation on NPG as the rate-limiting step. By completely ruling out the support influence, our findings provide considerable insight into the role of gold catalysts.

Keywords: CO oxidation; Gold catalysts; Nanoporous gold; Dealloying; Support effect

1. Introduction

Supported gold catalysts have attracted increasing interest in recent years because they exhibit exceptional catalytic activity toward many important reactions, including low-temperature CO oxidation [1,2]. Despite the extensive research in this field, however, the catalytic nature of gold catalysts remains incompletely identified. Various explanations have been proposed to account for their apparently high catalytic activity: high concentrations of low-coordinated gold atoms [3,4], a quantum size effect [5], a strain effect [6], or a charge transfer effect from the support [7,8]. Concerning the active species, metallic gold clusters [9–11], cationic gold [12,13], and anionic gold species [14–16] have all been reported to be possible active sites.

In supported gold catalysts, many factors have been correlated with the catalytic activity, including preparation methods [17], nature of the support [18], pretreatment conditions [19–21], and many others. Among these factors, catalyst support is usually considered crucial to determining the catalytic activity [22,23]. "Active" and "inert" supports have been classified in accordance with the reducibility [18] or semiconducting properties of transition metal oxides [22]. With regard to preparation methods, various routes generate markedly different catalyst structures. Besides the factors mentioned above, nanoparticle size and distribution [24], Au loading [25], and Au–support interface structure [26] also contribute to the catalytic diversity.

Because a comprehensive understanding of the catalytic nature of gold catalysts is of great significance to industrial and environmental applications, there is a need to develop and investigate a new catalyst system that can overcome or bypass the complexity of the supported catalyst systems as mentioned above. In a recent study, Sanchez-Castillo et al. reported that unsupported gold-nanotube membranes could exhibit high catalytic activity for CO oxidation, especially at the gas-water interface [27]. More recently, Zielasek et al. [28] and our group [29] independently reported that NPG, prepared by a simple dealloying method, could display exceptional catalytic performance for CO oxidation at low temperatures in the absence of any catalyst support. NPG is created by anodic etching of Ag from Ag/Au alloys and exhibits a three-dimensional spongy morphology with tunable pore and ligament sizes at nanometer scale [30–32]. Compared with supported gold catalysts, NPG has several unique characteristics: (i) it is truly support-free;

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(ii) the preparation methodology is very simple and thus reproducible; (iii) the structural unit is tunable in a wide range from a few nanometers to many microns, which allows the study of the size dependence very easily; and (iv) it has extremely clean nanostructured surfaces, because it is processed in concentrated nitric acid. This latter feature is markedly different from the current wet-chemistry method, in which auric solution is usually used as the gold source, even though chloride ion has a well-known poisoning effect on gold catalysts. In the present work, we extend our study with a systematic investigation of the catalytic properties of NPG toward CO oxidation, including the reaction active sites, reaction kinetics, and activity dependence as functions of space velocity and temperature. By excluding the support effect, our research on NPG continues to pave the way to a better understanding of this exciting new era of gold catalysis.

2. Experimental

2.1. Preparation of NPG catalyst

The 25-um-thick Au/Ag alloy (42:58, wt%) foils were purchased from Changshu Noble Metal Company, which were created by melting high-purity (>99.99%) Ag and Au at 1100 °C in air, followed by cold rolling. They were annealed at 850 °C for 20 h, followed by ultrasonic rinsing in acetone and ultra-pure water for several times before electrochemical dealloying. The dealloying was carried out in concentrated nitric acid (∼67%) for 10–15 min under an applied voltage in the range of 0.6–0.9 V, using platinum electrode as a cathode. The prepared samples were washed to neutral with ultra-pure water and dried in a vacuum desiccator at room temperature. FTIR analysis found no detectable water in NPG before the activity measurements.

2.2. Activity measurements

In all experiments, crushed NPG catalyst was intermixed with 1 g of 1-μm quartz sand to ensure adequate contact between gas reactants and the catalysts. It must be emphasized that in our previous work [29], we did not use quartz sand, but still observed significant activity of NPG toward CO oxidation. All catalysts were tested directly with on activation pretreatment. The mixed NPG catalysts were placed into a 4-mm-i.d. glass tube and tested in a continuous-flow fixed-bed microreactor at atmospheric pressure. The reactant gas was a dry mixture of high-purity CO, O_2, and N_2. Before measurement, the system was first purged with high-purity N_2 for 30 min at room temperature. Unless stated otherwise, for each measurement, CO/N_2 mixed gas was preferentially introduced into the system to reduce possible gold oxides on NPG, after which O_2 was added to the flow to form the actual gas mixture. The gas flow rates were adjusted and controlled by mass flow meters according to the experimental requirements. For all experiments, data were obtained until a steady conversion (no less than 30 min) was achieved, and repeated measurements were made under the same conditions. To gain more actual insight into the reaction kinetics, the CO conversion in many experiments was *intentionally* kept at lower value by, for example, operating at lower temperatures, raising the CO concentration in the feed gas mixture, or increasing the gas flow rate. For apparent activation energy calculation, only the temperature points with CO conversion <70% were adopted, to avoid possible systematic error at high conversion.

The gas mixture was detected with three online infrared gas analyzers (GXH-3011, Gasboard-3121, Gasboard-3131, China Wuhan Cubic Co.) to simultaneously detect CO and CO_2 with different resolutions at 100, 10, and 1 ppm, to fit different measurement ranges. These online gas analyzers were chosen to dynamically monitor the actual performance of NPG catalysts in real time; their reliability was confirmed with a Shimadzu Gas chromatograph (GC-14C). The GC has combined columns of 1 m TDX-01 carbon molecular sieve and 2 m 5 Å Molecular Sieve 13X, coupled with a 10-port gas sampling valve, which allows simultaneous analysis of O_2, N_2, CO, and CO_2 by a thermal conductivity detector (TCD).

The surface area of NPG used in this experiment is $\sim 30\ \mathrm{m^2\,g^{-1}}$, which was measured with Quadrasorb SI-MP (Quantachrome Instruments) using the BET method. The unit for the reaction rate (R_{CO}) is expressed as moles of CO molecules converted per gram of Au catalyst per second ($\mathrm{mol\,g^{-1}\,s^{-1}}$).

2.3. Characterization

The microstructure of NPG was characterized with a JEOL JSM-6700F field emission scanning electron microscope, equipped with an Oxford INCA x-sight energy-dispersive X-ray spectrometer (EDS) for compositional analysis. All electrochemical measurements were performed in a standard three-electrode cell on a CHI 1130 potentiostat at room temperature. The curves were recorded in 1.0 M H_2SO_4 solution with reference to a saturated calomel electrode (RHE) at a scan rate of 50 mV/s. The working electrode was created by attaching an NPG sample onto a 3-mm-diameter glassy carbon (GC) electrode using dilute Nafion solution (0.5%) as glue. The surface state of NPG was probed with electrochemical linear scan voltammetry (LSV) by scanning from an open-circuit potential of 1.34 to 0 V.

3. Results and discussion

3.1. Catalytic activity of NPG

NPG has a bi-continuous foam structure with porosity >70%, which is particularly advantageous to such applications as catalysis and sensing. A typical SEM image, shown in Fig. 1 (inset), illustrates a uniform porous morphology with narrow ligament size distribution around 6 nm. Compared with supported gold catalysts, the highly reproducible dealloying method generates very uniform porous nanostructures, consequently avoiding the possible effect stemming from the wide size distribution [33]. The catalytic activity of NPG is also shown; with a space velocity of 201,000 $\mathrm{mL\,h^{-1}\,g_{cat}^{-1}}$, NPG can

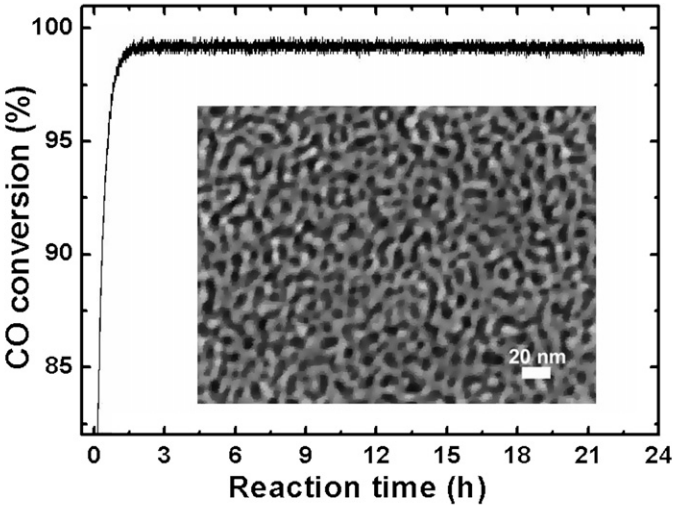


Fig. 1. Catalytic performance at 298 K using 20 mg catalyst with 1% CO, 10% O_2, and 89% N_2 gas mixture at a total flow rate of 66.7 mL min^{-1}. Inset is a typical SEM image of NPG.

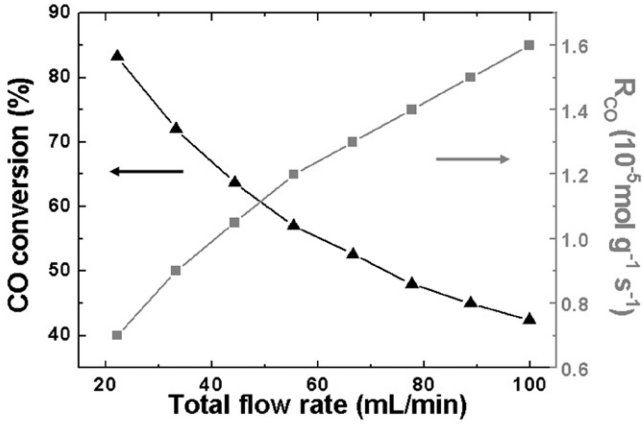


Fig. 2. The catalytic activity of NPG under different space velocity at 253 K. The measurement was performed using 20 mg catalyst with 1% CO/10% O_2/89% N_2 mixed gas at a flow rate from 22.2 to 99.9 mL min^{-1}.

maintain a CO conversion $>99.0\%$ for 24 h without deactivation at room temperature. The high and stable catalytic activity of NPG provides a substantial basis for a series of further investigations on NPG.

Fig. 2 shows the catalytic performance of an NPG sample at 253 K as a function of space velocity. As the total gas flow rate increases from 22.2 to 99.9 mL min^{-1}, CO conversion gradually declines from the initial 83.2 to 42.4%. Because gas transport is kinetically controlled, as the space velocity increases, some gas may have insufficient contact time with the active surface sites, leading to a lower apparent conversion rate. At the same time, the total amount of gas reactants passing through the reaction cross-section per unit of time actually becomes larger, so eventually we see an increase of R_{CO}. In this study, under different measurement conditions, R_{CO} was calculated to be in a range of 0.7–14.3 ($\times 10^{-5}$ mol g_{Au}^{-1} s^{-1}). These values compare favorably to those for supported gold catalysts tested at similar conditions; for example, Bamwenda et al. [24] reported rates ranging from 6.5 to 64.5 ($\times 10^{-5}$ mol g_{Au}^{-1} s^{-1}) in Au/TiO_2 catalysts made by a deposition–precipitation (DP) method, and Overbury et al. [33] reported a reaction rate for CO oxidation on Au/TiO_2 in the range of 0.06–37.1($\times 10^{-5}$ mol g_{Au}^{-1} s^{-1}) under different measurement conditions.

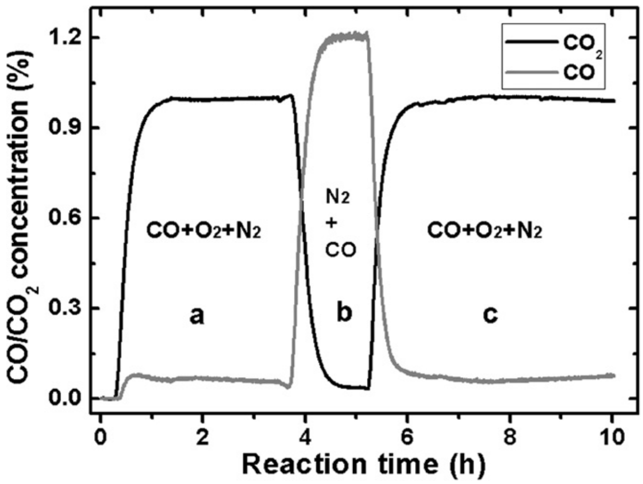


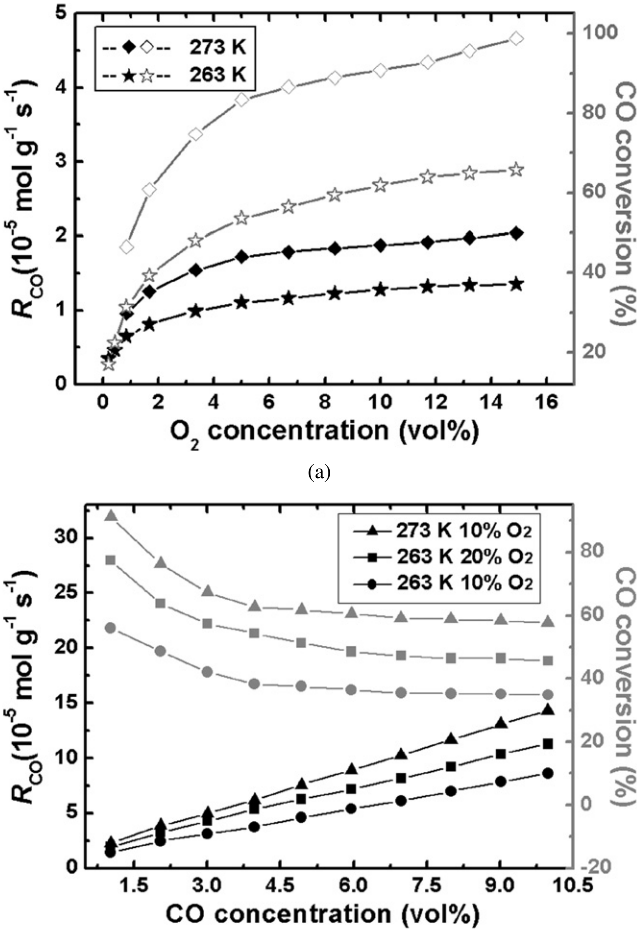
Fig. 3. Catalytic performance of NPG under different testing conditions at 273 K. (a) 1% CO/10% O_2/89% N_2 mixed gas, flow rate 66.7 mL min^{-1}, 200 min; (b) 1.11% CO/N_2 balanced gas, flow rate 60 mL min^{-1}, 120 min; (c) 1% CO/10% O_2/89% N_2 mixed gas, flow rate 66.7 mL min^{-1}, 240 min.

3.2. *Active sites on NPG*

The active species on supported gold catalysts remains a subject of debate, because the particle–support interaction complicates the understanding of the catalyst behavior. Free from the influence of support on NPG, we were motivated to first identify the active species in this reaction. During the catalyst preparation process, we used a rather severe dealloying recipe by anodic etching in concentrated nitric acid to obtain smaller ligament size. This approach is based on the idea that the dealloying process is a competition between Ag dissolution–induced surface roughening and Au diffusion–induced surface smoothing [34,35], which also means that increasing the Ag dissolution rate is beneficial to the formation of narrow gold ligament. Under such harsh conditions, some gold atoms on NPG surfaces may be oxidized; indeed, XPS analysis and electrochemical linear scanning have revealed the surface gold oxides on NPG [29]. Although gold oxides are quite unstable under normal conditions, this observation actually provides a good opening to discuss whether oxidized gold itself may work as catalytic species for CO oxidation.

In a carefully designed experiment, a fresh NPG sample (with oxidized gold on the surface) was tested directly with the reactant gas (1% CO/10% O_2/89% N_2) at 273 K. Assuming that both oxidized and metallic gold atoms (ions or clusters) were playing the catalytic role simultaneously, we observed a CO conversion of ca. 92%. After reacting for 200 min, the NPG sample was exposed to CO/N_2 only for an additional 120 min, to reduce the residual gold oxides (if still present). Then the catalytic activity was continuously measured in the mixed CO/O_2/N_2 gas for another 240 min under the same conditions as in the first step. As shown in Fig. 3, there was no clear difference between the catalytic activity of NPG with and without oxidized gold. In a parallel experiment, electrochemical linear scanning (not shown) also demonstrated no detectable gold oxides on NPG after exposing the sample in CO/N_2 for 30 min. Furthermore, previous experiments have shown that free-corroded NPG containing no surface oxides also can exhibit high catalytic activity [29]. These results give very strong evidence that it is metallic gold that plays the catalytic role in this support-free system.

For supported gold catalysts, many studies [36–38] have proposed that cationic gold species at the metal–support interface or a combination of metallic and oxidized gold play the catalytic role. The periphery of gold–support is generally considered to be the active sites. However, van Bokhoven et al. [39], studying the CO reactivity of Au/Al_2O_3 catalyst by in situ X-ray adsorption near-edge structure (XANES) spectroscopy, found that the support is not required for gold to be active, and partially oxidized gold as a short-lived reaction intermediate can be rapidly reduced by CO to form CO_2 under catalytic conditions. In view of these findings, the oxidized gold on NPG may work solely as an *oxidizing* species at the very beginning of the reaction. Of course, the fresh metallic gold atoms/clusters produced from the redox reaction of gold oxides with CO may be highly low-coordinated and thus especially active for the catalytic reaction from then on. In our subsequent experiments, to prevent interference from the possible noncatalytic conversion of CO by gold oxides, all of the NPG catalysts were pretreated with CO/N_2 before activity measurements.



(a)

(b)

Fig. 4. The correlation between the reaction rates and reactant concentrations for CO oxidation over NPG catalyst under different conditions. The measurements were made under ambient pressure using 20 mg catalyst at a flow rate of 66.7 mL min^{-1}. (a) The dependence on O_2 concentration at 273 and 263 K; (b) the dependence on CO concentration at 273 and 263 K with 10 and 20% O_2 concentration, respectively.

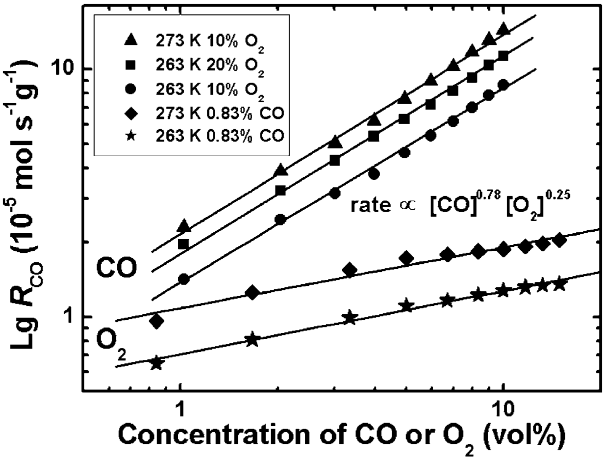


Fig. 5. The dependence of the reaction rate on CO and O_2 concentrations under different measurement conditions.

3.3. *Effect of gas concentrations*

O_2/CO ratio is known to have an important effect on the catalytic activity of gold catalysts for CO oxidation. Here we first studied the effect of oxygen concentration on the catalytic activity of NPG at a constant CO concentration (0.83%) under two different temperatures. Fig. 4a shows the correlation among CO conversion, reaction rate, and O_2 concentration. At 263 K, the CO conversion increased sharply, from 17.1 to 48.1%, as the O_2/CO ratio increased from 1:4 to 4:1. As O_2 concentration increased even further, the extent of increase slowed. Eventually the trend saturated at a conversion of around 66%. At 273 K, NPG showed similar performance, and, very interestingly, the CO conversion rates increased by 50% compared with those at 263 K.

We also investigated the effect of CO concentration on the reaction rate at two constant O_2 concentrations (10 and 20%) and two temperatures (263 and 273 K). As shown in Fig. 4b, when CO concentration increased from 1 to 10%, the apparent CO conversion dropped gradually. Interestingly, by replotting the data using R_{CO}, we demonstrated a nearly linear increase of the CO reaction rate under all three testing conditions.

To obtain more detailed information regarding the reaction kinetics, the relationship between reaction rate and gas concentration was correlated in a logarithmic form, as shown in Fig. 5. It is interesting to see that the O_2 order were almost identical at ∼0.25 for two different temperatures. In the case of CO, the orders at 263 and 273 K were ∼0.78 under a constant 10% O_2 concentration. Moreover, raising the O_2 concentration from 10 to 20% at 263 K did not change the CO order. Taking these results into consideration demonstrates that the reaction order of CO oxidation on NPG is independent of the reaction temperature. Therefore, the rate of CO oxidation on NPG can be expressed by the following equation: $R_{CO} = K_{CO}[CO]^{0.78}[O_2]^{0.25}$.

Haruta et al. [40] studied the CO oxidation kinetics of three supported catalysts—Au/TiO_2, Au/Fe_2O_3, and Au/Co_3O_4—and found corresponding CO and O_2 orders of 0.05/0.24, 0/0.05, and 0.05/0.27. The evident discrepancy in the reaction orders among these was explained by the use of different oxide supports. Based on their results, these authors proposed that the adsorption of CO and O_2 on the catalyst surface was close to saturation and the reaction of CO with O_2 was the rate-limiting step. But Zielasek et al. [28] observed that increasing CO concentration could significantly increase the turnover of CO to CO_2 on NPG, which is consistent with our results demonstrating that the concentration of the reactants substantially influences the reaction rate. They suggested that gas transport to the NPG surface might be the rate-determining step; however, we believe that instead, gas adsorption onto the NPG surface may play a decisive role in the reaction. CO adsorption onto gold surfaces has been widely investigated by various techniques, including in situ FTIR.

Boccuzzi et al. [41,42] gave clear evidence that CO adsorption on Au/ZrO_2 catalyst does not immediately reach saturation, but rather intensifies gradually to achieve near full coverage with continuously increasing CO pressure and contact time between CO and gold at a fixed temperature. This observation indicates the CO adsorption on gold does not quickly reach saturation, which is instead kinetically controlled. Compared with CO, precisely determining the adsorption behavior of O_2 on gold surfaces is more difficult. However, using Au L_3-edge XANES spectroscopy, Weiher et al. [43] found that O_2 could be activated by metallic gold on Au/TiO_2 catalyst, suggesting that O_2 can adsorb on gold in a certain form. Theoretical calculations [44] also have revealed that O_2 can be chemisorbed onto gold clusters. The O_2 order of ∼0.25 obtained on NPG was very close to the previously reported value on TiO_2- and Co_3O_4- supported gold catalysts [40], indicating that the reaction rate of CO oxidation on gold catalyst does not depend as significantly on O_2 as on CO. Moreover, we believe that it is the CO adsorption onto the NPG surface that limits the reaction rate of CO oxidation.

We also tested the performance of NPG under low CO concentration conditions (100–5000 ppm, Fig. 6). At 273 K, when the initial CO concentration in the feed gas was <3000 ppm, NPG was able to convert >99% CO to CO_2, resulting in <10 ppm CO in the stream. When CO concentration was higher at 5000 ppm, CO content could still be brought down to <100 ppm. These results demonstrate NPG's high sensitivity and quick response for CO removal, which is of significant importance for its potential applications in gas sensors and fuel stream purification.

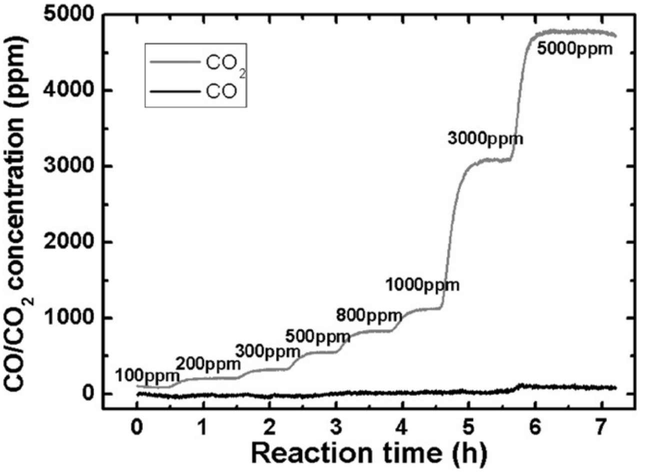


Fig. 6. The catalytic performance of NPG with low CO concentrations from 100 to 5000 ppm at a flow rate of 66.7 mL min^{-1} at 273 K. The O_2 concentration is fixed at 20%.

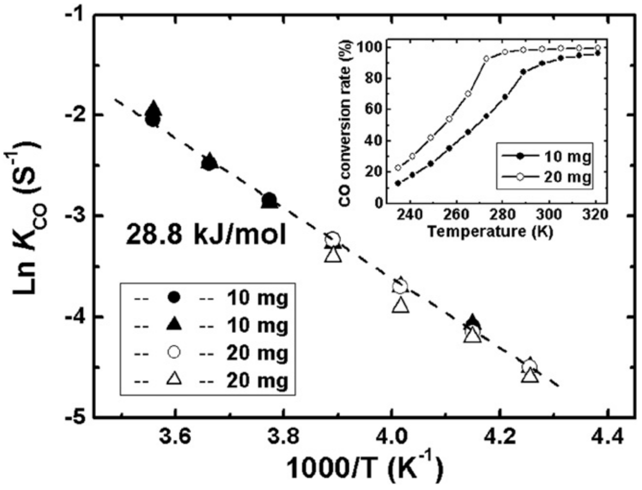


Fig. 7. The Arrhenius relationship between rate constant of reaction and temperature for four independent experiments with two different NPG loadings. The inset is the typical performance of two NPG samples as a function of temperature. The measurements were carried out with 1% CO/10% O_2/89% N_2 mixed gas at a flow rate of 66.7 mL min^{-1} under different temperatures.

3.4. *Effect of temperature*

Finally, we tested the influence of temperature on the catalytic activity of NPG at different catalyst loadings (10 and 20 mg). As shown in Fig. 7 (inset), CO conversion rapidly increased as the temperature rose from 235 to 273 K. At higher temperatures, the increase slowed, and CO reached near-complete conversion. It is noteworthy that at high temperatures, the structure of NPG can coarsen greatly [29], causing partial loss of the surface active sites. Fig. 7 shows the relationship between the rate constants and temperature in an Arrhenius form. To avoid possible systematic error at high conversions, here only those temperature points with CO conversion below ∼70% were considered. Very surprisingly, we found that for four independent measurements with different NPG loadings, the reaction rate constants (K) measured under the same temperature were very similar to one another at 233–289 K. The good Arrhenius behavior allows extrapolation of the apparent activation energy, which is ∼28.8 kJ/mol, a value very close to that from supported gold catalysts, such as Au/TiO_2 [33]. One catalytic reaction usually comprises several parallel steps that have different degrees of contributions to the reaction rate. The simple linear Arrhenius form indicates that only one rate-limiting step dominates in this temperature region, which we believe is the CO adsorption onto NPG.

4. Conclusion

In this work, based on a new catalyst system known as NPG, a sequence of systematical studies were carried out to clarify some confusion generated on supported gold catalysts. Our results indicate that NPG can exhibit excellent catalytic activity for CO oxidation at and below room temperature in the absence of metal oxide support. It is unambiguously the metallic gold on NPG that is the intrinsic active species, at which the oxidation of CO occurs. In addition, the reactant concentrations dramatically influence the reaction rate, displaying orders of 0.78 for CO and 0.25 for O_2. The reaction rate of CO oxidation on NPG increases linearly as temperature increases in the region of 233–289 K, with this trend gradually slowing at higher temperatures, possibly due to local coarsening of the NPG ligaments. Analysis of the Arrhenius behavior permitted the estimation of the apparent activation energy of $\sim$28.8 kJ/mol. Our findings also suggest that CO adsorption onto the NPG catalyst surface might be the rate-limiting step, especially in the temperature region discussed. The exact adsorption behavior of CO onto NPG surfaces remains unclear, and in situ FTIR studies are currently ongoing to give a clearer picture of the reaction mechanism, with the ultimate goal of uncovering the underlying physics of this exciting subfield of catalysis.

Acknowledgments

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