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Highly Active and Stable Au@Cu<sub>x</sub>O Core-Shell Nanoparticles Supported on Alumina for Carbon Monoxide Oxidation at Low Temperature

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Au@Cu<sub>x</sub>O (x=1 or 2) core-shell heterostructure nanoparticles (NPs) are synthesized by a facile aqueous solution approach.  $\gamma$ -alumina support Au@Cu<sub>x</sub>O (Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) catalysts used for CO oxidation at low temperature are prepared by dispersing the core-shell NPs on the surface of  $\gamma$ -alumina. It proves that the formation of the core-shell structure has led to the interaction between Au and Cu<sub>x</sub>O and the co-existence of Au<sup>6+</sup> and Au<sup>0</sup>, which accounts for the catalytic activity improvement. It can even catalyze CO oxidation at room temperature and the conversion of CO can reach to 38%. In the same case , Au / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has not any catalytic activity. In particular, the embedding Au NPs into Cu<sub>x</sub>O shell has also improved the catalytic stability of Au based catalysts remarkably, which remains unchanged after 108 hours reaction. To our knowledge, Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is really one of the most stable catalyst with adequate activity at room temperature.

### Introduction

More and more studies and applications focus on Au NPs as catalysts have been reported since the earliest report on the outstanding catalytic activity for oxidizing CO at low temperature by Haruta in 1987<sup>1</sup>. CO oxidation on Au based catalyst at room temperature is generally following the size-dependent reaction pathways<sup>2, 3</sup> and Au NPs tend to sinter to larger particles<sup>4-6</sup> or change to bicarbonate-like species under the reaction conditions<sup>6-13</sup> and thus leads to a substantial loss of activity<sup>14</sup>, which is a major drawback of Au based catalysts and this undesirable characteristic has reduced their potential for industrial applications<sup>8, 15</sup>.

Up to now, many strategies have been proposed to solve the deactivation problem of Au based catalysts, which includes: (1) the replacement of Au particles with alloy or bimetallic particles <sup>16-18</sup>, (2) the modification of the catalysts with other additives <sup>19, 20</sup> and (3) the fabrication of core-shell type structure particles using Au as core <sup>21-24</sup>. Actually, the first two methods can really improve the catalytic stability to some extent, but cannot completely avoid the deactivation caused by sintering or poisoning. Compared with the first 2 methods, the encapsulation of Au NPs as a core inside of an oxide as a shell is more practicable to maintain the size and shape of Au NPs as well as to protect them from poisoning, which leads to the stability and compatibility enhancement of Au based catalysts <sup>25</sup>.

Among the various types of core-shell NPs, metal@semiconductor particles represent a significant class of core-shell structure. The semiconductor shell plays both the role of masker to protect metal particles from sintering and poisoning and

the role of additives to improve the physical and chemical activities of the metal particles by interacting with them within nanoscale <sup>26</sup>. It has been extensively demonstrated that the strong metal-support interaction (SMSI) plays a significant role in affecting catalytic performance<sup>27-34</sup>. However, the SMSI between Au and support can't normally exist because Au has a lower work function and surface energy <sup>35, 36</sup>. The encapsulation of Au Nps by metal oxide can strengthen the SMSI thus lead to the electron transfer between Au and support <sup>37</sup>.

Cu<sub>2</sub>O is an important p-type semiconductor with the direct band gap of 2.17 eV, which could find practical applications in many aspects, such as solar energy conversion <sup>38</sup>, hydrogen production by photocatalytic decomposition of water <sup>39, 40</sup>, and lithium-ion batteries as electrode material <sup>41</sup>. It is also a promising alternative to expensive noble metals as the catalyst for CO oxidation at moderate temperatures, owing to its higher natural abundance and lower price. It has been reported that Cu<sub>2</sub>O layers can grow epitaxially on the surface of Au-Cu particles with small lattice mismatch and the CO oxidation reactions can occur on the Cu<sub>2</sub>O-Au interfaces <sup>42</sup>. CuO is also a good catalyst for CO oxidation <sup>43</sup>. Consequently, Cu<sub>x</sub>O (x=1 or 2) is a reasonable choice as the shell material to improve the catalytic performance of Au NPs.

Herein we report an entirely new design of Au based catalyst for CO oxidation at low temperature. Instead of pure Au particles, Au@Cu<sub>x</sub>O core-shell NPs are fabricated and dispersed on the surface of  $\gamma$ -alumina and a new kind of CO oxidation catalyst (Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) is synthesized. By coating Au NPs with Cu<sub>x</sub>O, both the catalytic activity and stability of Au particles have been improved. It not only can catalyze CO oxidation at room temperature with 38% CO conversion, but also can maintain the activity. The stability is tested in 108 hours and after the 108 hours

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### ARTICLE

application, the catalytic activity has not any loss. As the comparison, the general Au based catalyst without  $Cu_xO$  has not any catalytic activity at room temperature.

### **Experimental section**

### Materials preparation

**Preparation of Au** NPs: Au NPs are synthesized following the previously reported traditional Frens's citrate reduction synthesis method. Briefly, 150 mL of aqueous HAuCl<sub>4</sub> (0.25 mM) is prepared in a 250-mL beaker and brought to boil in a 100 °C water bath under magnetic stir. Then, 7.5 mL of 0.1 M sodium citrate solution is added rapidly. When the reaction mixture begins to change color and finally reaches a wine red color, it meants the end of the reaction. The solution is kept stirring for 30 min, cooled to room temperature, and then Au colloids are collected by centrifugation, washed with anhydrous ethanol and water for 3 times , and finally redispersed in 7 mL of water.

**Preparation of Au@Cu<sub>x</sub>O Core-Shell** NPs: Au@Cu<sub>x</sub>O is prepared using the method reported by Zhang et al <sup>26</sup>. 1.0 g of polyvinylpyrrolidone (PVP, average M.W. 40000, TCI Shanghai) is dissolved in 50 mL of 0.01 M Cu(NO<sub>3</sub>)<sub>2</sub> (Sinopharm Chemical Reagent Co., Ltd.) aqueous solution under constant magnetic stir and the solution is kept stirring for another 10 min to ensure the PVP solution uniformly. Subsequently, 17 µL of N<sub>2</sub>H<sub>4</sub>•H<sub>2</sub>O solution (85 wt %, Sinopharm Chemical Reagent Co., Ltd.) is immediately introduced into the reaction mixtures after 6 mL of fresh prepared Au colloid solution is added. The colloid solution turns dark green within 10 s, which is the characteristic color of Au@Cu<sub>x</sub>O core-shell NPs typically. The reaction liquid is kept stirring for 2 min, and then the Au@Cu<sub>x</sub>O core-shell NPs are washed with anhydrous ethanol and water for 3 times and finally redispersed in anhydrous ethanol and kept in freezer at 6 °C.

**Preparation of γ-Al<sub>2</sub>O<sub>3</sub>:** The amorphous Al<sub>2</sub>O<sub>3</sub> (Sinopharm Chemical Reagent Co., Ltd.) are calcined from room temperature to 550 °C with the heating rate of 5 °C·min<sup>-1</sup> in the air and then maintains 6 hours and cools to room temperature naturally.

**Preparation of Au@Cu<sub>x</sub>O/γ-Al<sub>2</sub>O<sub>3</sub>:** Au@Cu<sub>x</sub>O ethanol solution is taken to the beaker with a certain amount of γ-Al<sub>2</sub>O<sub>3</sub> and stirred at room temperature until the ethanol is entirely volatilized. Then Au@Cu<sub>x</sub>O/γ-Al<sub>2</sub>O<sub>3</sub> is got. Au contents are measured by the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

**Preparation of Au/\gamma-Al<sub>2</sub>O<sub>3</sub>:** Au colloid is added to the beaker with a certain amount of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and stirred at room temperature until the solution is completely volatilized.

**Preparation of Cu<sub>x</sub>O/γ-Al<sub>2</sub>O<sub>3</sub>:** Cu<sub>x</sub>O solution is prepared by the method of Au@Cu<sub>x</sub>O preparation where the adding of Au is omitted and then the solution is added to the beaker with a certain amount of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and stirred at room temperature until the solution is completely volatilized.

### **Catalytic activity Test**

For CO activity measurement, about 0.1 g catalyst specimen (40 ~ 60 mesh) is placed into a stainless flow reactor ( $\Phi$  8 × 150 mm) with a fixed bed. Then, the gas mixture consisted of 2 vol% CO and 98 vol% air are introduced into the reactor at a flow rate of 50 ml·min<sup>-1</sup>, and the GHSV (Gaseous Hourly Space Velocity) is 30,600 mL·g<sup>-1</sup>·h<sup>-1</sup>. The activity tests of the samples are carried out in the continuous flow reactor from room temperature to the temperature that the CO had been completely converted into CO<sub>2</sub> with the heat-up period of 1 °C·min<sup>-1</sup> rising and analyzed by the gas chromatograph (GC).

### Characterization

Nitrogen adsorption-desorption isotherms using the Barrett-Emmett-Teller (BET) technique on a Micromeritics ASAP2020 V4.00 surface areas and porosity analyzer is used to detect the specific surface areas of the samples. X-ray diffraction (XRD) patterns are collected on a Dandong Haoyuan Instrument Co., Ltd. DX-2200V/PC diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =0.154056 nm). Transmission electron microscope (TEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive spectroscopy (EDS) and high angle annular dark field scanning transmission electron (HAADF-STEM) are conducted on JEM-2010F microscopy transmission electron microscope with an acceleration voltage of 200 kV. The surface morphology of the samples is observed with a ULTRA55-36-69 Zeiss field-emission scanning electron microscopy (FESEM). Au content is measured by a Perkin-Elmer Optima 7300DV inductively coupled plasma-atomic emission spectrometry (ICP-AES). X-ray photoelectron spectroscopy (XPS) measurements are carried out on a Thermo ESCALAB 250 spectrometer using monochromatic Al Ka (ht =1486.6 eV). All binding energies (BE) are calibrated by the C 1 s signal (BE = 284.8 eV).

### **Results and Discussion**

## Characterization of Au@CuxO Core-shell ${\sf NPs}$ and Au@CuxO/ $\gamma-{\sf Al}_2O_3$ Catalysts

Au@Cu<sub>x</sub>O core-shell structure NPs are fabricated and dispersed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Herein,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is used as the catalyst support to anchor Au@Cu<sub>x</sub>O particles so as to increase the surface area and decrease the Au use to reduce costs. Au content in the catalysts is measured by the ICP-AES. As reference, Au / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are also prepared with the same method and same Au or Cu<sub>x</sub>O content.

Figure 1 shows the structural characterizations of Au@Cu<sub>x</sub>O coreshell NPs, Au / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. As shown in Figure 1a, Au@Cu<sub>x</sub>O core-shell Nps with multiple Au cores are formed. According the report of Zhang et al <sup>26</sup>, reducing HAuCl<sub>4</sub>•3H<sub>2</sub>O with sodium citrate leads to the formation of quasispherical Au NPs and the subsequent reduction of Cu(NO<sub>3</sub>)<sub>2</sub> with N<sub>2</sub>H<sub>4</sub>•H<sub>2</sub>O results in the formation of Cu<sub>x</sub>O shell in a self-assemble process, which deposits on the Au surface to form core-shell like particles with multiple cores. The Au particle size is mainly Published on 28 July 2016. Downloaded by Cornell University Library on 28/07/2016 14:12:51

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concentrated at 20 nm (Figure 1d) and the distribution interval is narrow. The diameter of Au@Cu<sub>x</sub>O nanospheres varies within the range of 60-120 nm and mainly concentrates at 100 nm (Figure 1e). The average shell thickness is about 40 nm and the core-shell structure is not uniform. The greater details of the Au@Cu<sub>x</sub>O coreshell structures can be observed by HAADF-STEM (Figure 1b) and HR-TEM (Figure 1c) image. The HR-TEM image recorded on the Au core region indicates that the interplanar spacing is about 0.235 nm corresponding to the (111) planes of face-centered cubic Au <sup>44</sup>. The (111) planes of Cu<sub>2</sub>O with a spacing of 0.248 nm are found to grow epitaxially on the facets of Au <sup>45</sup>. EDS line scan of an individual Au@Cu<sub>x</sub>O core-shell heterostructure reveals strong Cu and O signals across the entire particle. The signal for Au appears only in the central region of the particle, where the Au core is located (Figure 1b). It confirms further the formation of core-shell structure.



**Figure 1.** Structural characterization of Au@Cu<sub>x</sub>O and the catalysts. a) Bright-field TEM image of Au@Cu<sub>x</sub>O core-shell NPs, b) High-magnification HAADF-STEM image of an individual Au@Cu<sub>x</sub>O core-shell NPs with spatial elemental distribution analysis by EDS line-scan, c) HR-TEM image of the Au core and Cu<sub>x</sub>O shell, d) The particle size distribution of pure Au NPs, e) The particle size distribution of Au@Cu<sub>x</sub>O core-shell structure particles, f) HAADF-STEM image of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, g) TEM image of Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, h) The particle size distribution of Au in Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Figure 1f and 1g are the HAADF-STEM image of Au@Cu<sub>x</sub>O / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and TEM image of Au / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. It shows that the core shell structure of Au@Cu<sub>x</sub>O and the diameter of Au particles and Au@Cu<sub>x</sub>O nanospheres haven't changed after dispersing on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The particle size of Au is mainly concentrated at 20 nm (Figure 1h).

The XRD patterns of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are shown in Figure 2. The peaks at 37.6, 45.8 and 67.0° of all the samples are due to the (311), (400), (440) reflections of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. As the content of Au and Cu<sub>x</sub>O in the samples is very

low (0.11 and 0.088 wt%), their diffraction peaks could not clearly made out, which suggests a well dispersed metal phase  $^{\rm 46}$ .



Figure 2. XRD patterms of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.11 wt% Au and 0.088 wt% Cu<sub>x</sub>O, Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.11 wt% Au , Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.088 wt% Cu<sub>x</sub>O and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The intensity scale for all the samples are the same.

Figure 3 shows the SEM images of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Au / $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The crystals surface of all the samples is rough and their shapes show a perceptible similarity to each other, which are stacked loosely by irregular alumina particles and we could not clearly find out the Au, Cu<sub>x</sub>O or Au@Cu<sub>x</sub>O coreshell NPs. Otherwise, the addition of a little amount of Au, Cu<sub>x</sub>O or Au@Cu<sub>x</sub>O has no effect on the morphology of alumina support.



Figure 3. The SEM image of a) Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.11 wt% Au and 0.088 wt% Cu<sub>x</sub>O, b) Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.11 wt% Au, c) Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.088 wt% Cu<sub>x</sub>O and d)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. All SEM images share the same scale-bar in panel a).

To further study the physical properties of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, Brunauer-Emmett-Teller (BET) surface area and pore structure of the catalyst is measured by nitrogen adsorption at 77 K and is compared with that of pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Figure 4 displays a type of IV isotherms with a hysteresis loop at relative pressure (P/P<sub>0</sub>) between 0.5 and 1, indicating the presence of mesopores. BET surface area is calculated to be 118 m<sup>2</sup> • g<sup>-1</sup> for Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which is almost same to that of pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. In the Barret-Joyner-Halenda (BJH) pore size distribution analysis, the sharp peak at about 4.6 nm and 4.9 nm for pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> inset in Figure 4 suggests a relatively narrow pore size distribution

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iterval. It shows that Au@Cu<sub>x</sub>O has little effect on the pore structure of alumina support, while the relatively high surface area of alumina will provide abundant active sites for catalytic reaction  $_{\rm 47}$ 



Figure 4. Nitrogen adsorption isotherms and pore size distribution of a) pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and b) Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.11 wt% Au and 0.088 wt% Cu<sub>x</sub>O.

### CO Oxidation on Au@Cu<sub>x</sub>O/γ-Al<sub>2</sub>O<sub>3</sub> Catalysts

Figure 5a shows the catalytic activity of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Au/ $\gamma$ - $Al_2O_3$ ,  $Cu_xO/\gamma$ - $Al_2O_3$  and pure  $\gamma$ - $Al_2O_3$ . Here, the 90% CO conversion temperature  $(T_{90\%})$  is used to estimate the catalytic activity of the catalysts. The low  $T_{90\%}$  indicates the high activity of the catalyst.  $T_{90\%}$ of pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is about 216 °C, and the introduction of a little amount Au (0.11 wt%) makes the  $T_{90\%}\,decrease$  to 203  $^{\circ}\text{C},$  which indicates a little improvement of the catalytic activity. Generally, the Au content in the Au based catalysts is equal to or greater than 1 wt %, and it even reaches to 5 wt% in some catalysts 48-50, the low catalytic activity of  $Au/\gamma$ -Al<sub>2</sub>O<sub>3</sub> here can be ascribed to the low Au content. On the other hand, the large Au particle size (~20 nm) is also a cause leads to the low catalytic activity of Au/y-Al<sub>2</sub>O<sub>3</sub> because that CO oxidation on the simple supported Au catalyst at low temperature is generally following the size-dependent reaction pathways  $^{\rm 2,\ 3}.$  For this kind of catalysts, 3~5 nm Au particles are more active. The introduction of only a little amount Cu<sub>x</sub>O (0.088 wt%) has not obvious effect on the catalytic activity of pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.  $T_{90\%}$  of  $Cu_x O/\gamma$ -Al<sub>2</sub>O<sub>3</sub> is about 220 °C, which is even a little higher than that of pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. In brief, the effect of a little (0.11 wt%) pure Au or pure Cu<sub>x</sub>O (0.088 wt%) alone on the catalytic activity of y-Al<sub>2</sub>O<sub>3</sub> is weak. However, the combination of these two kinds of material and the fabrication of Au@CuxO core-shell structure generate a material more suitable to be used as CO oxidation catalyst. Although the content and particles size of Au in Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is same to Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the catalytic activity has been improved a lot.  $T_{90\%}$  of Au@Cu<sub>2</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is only 158 °C, which is 58  $^{\circ}$ C lower than that of pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It indicates that Au@Cu<sub>x</sub>O hybrid NPs exhibit good catalytic activity due to the combination of the properties from the individual components and nanoscale interactions between the disparate metal and semiconductor components.

To improve the catalytic activity further,  $Au@Cu_xO/\gamma-Al_2O_3$  catalysts with different Au content are prepared and the influence of Au content on the catalytic activity for CO oxidation is studied. Figure 5b shows that  $T_{90\%}$  decreases with Au content, which means that the catalytic activity can be improved by increasing Au content.

 $T_{90\%}$  of Au@Cu<sub>2</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 1.24 wt% Au is only 144 °C. The most important thing is that CO conversion on this kind of catalyst can reach to 18% at room temperature (Figure 5c).



**Figure 5.** Catalytic activity of the catalysts. a) The 90% CO conversion temperature of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.11 wt% Au and 0.088 wt% Cu<sub>x</sub>O, Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.11 wt% Au , Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.088 wt% Cu<sub>x</sub>O and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, b) The influence of Au content on the 90% CO conversion temperature of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, c) the CO conversion at different temperature on Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 1.24 wt% Au.

For CO oxidation at low temperature, the catalytic activity of Au based catalyst is high enough but the stability is still lower. Wang et al <sup>18</sup> have improved the catalytic stability of Au/Al<sub>2</sub>O<sub>3</sub> by adding Rh into the catalyst and Lin et al have improved the catalytic stability of Au/Al<sub>2</sub>O<sub>3</sub> by adding LaFeO<sub>3</sub> into alumina <sup>50</sup>. However, the stability of the catalyst is still limited. To study the catalytic performance of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> deeply, Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 1.24 wt% Au is chosen as example to study the catalytic stability at both 144 °C and room temperature. It can be seen from Figure 6a that, after 72 h reaction at 144 °C, the catalytic activity has not any loss, which means that the high temperature stability of the catalyst is quite high.

The catalytic stability test of the catalyst at room temperature in Figure 6b shows the catalytic activity increase rather than decrease before 30 hours. CO conversion on this catalyst can reach to 38 % at room temperature after 30 hours' application and then hold the line to 108 h. To our knowledge, this is one of the most stable Au based catalysts with high catalytic activity. The catalytic performance improvement of the catalyst may be ascribed to the reason that the interaction between Au and Cu<sub>x</sub>O has led to the high catalytic activity and the protection of Au by Cu<sub>x</sub>O has led to the high stability.



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Figure 6. Catalytic stability of Au@Cu\_xO/ $\gamma$ -Al\_2O\_3 with 1.24 wt% Au. a) At 144  $^\circ$ C and b) At room temperature.

### CO Oxidation Mechanism on Au@Cu<sub>x</sub>O/γ-Al<sub>2</sub>O<sub>3</sub>

In spite of a great number of contributions to reveal the origin of the high CO oxidation activity of Au catalysts, the reaction mechanism is still debated. The main debatable topics include the active Au species, the mechanism of activation of oxygen molecules, the role of the support and the Au-support interface, the interaction between supports and Au particles and the possible CO oxidation pathway. The difference of the catalysts system and the reaction conditions may be the mandatory reason leads to the controversies.

Generally speaking, the size of the Au particles, the valence state of Au and the interaction between Au and support are main factors influence dramatically the activity of the catalysts, which are difficult to isolate because they are normally intertwined together <sup>51</sup>. To study the possible reaction mechanism, XPS is employed to detect the surface elements and their valence states. The XPS profile of Au 4f region is shown in Figure 7a. The main peaks near 83.8 eV and 87.5 eV are corresponded to Au 4f7/2 and Au 4f5/2 of metal Au and the peaks at 84.3 eV and 88.0 eV are corresponded to Au 4f7/2 and Au 4f5/2 of Au<sup> $\delta^+$ </sup>. The Au signal of Au@Cu<sub>v</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is weaker than that of  $Au/\gamma$ -Al<sub>2</sub>O<sub>3</sub> due to the encapsulation of Au into Cu<sub>x</sub>O. However, the catalytic activity of the former is higher. It may be ascribed to the reason that the Au species on the 2 samples are quite different. All the surface Au of  $Au/\gamma$ -Al<sub>2</sub>O<sub>3</sub> are Au<sup>0</sup>, and there are 2 kinds of Au species (Au  $^{\rm 0}$  and Au  $^{\rm \delta+}$  ) on the surface of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It indicates that the interaction between Au and  $Cu_xO$  has led to the co-existence of  $Au^{\delta+}$  and  $Au^0$ . The ratio of  $Au^{\delta+}/$ Au<sup>0</sup> is 1.1 and the co-existence of the 2 kinds of Au species makes the catalyst more active. Au cations <sup>52</sup>, and pair of Au atoms and Au cations <sup>53</sup> have also been proposed as active sites by other researchers.

Figure 7b shows the XPS profile of Cu 3d region of Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The peaks at 932.3, 933.4 and 935.5 eV are ascribed to Cu<sup>+</sup> of Cu<sub>2</sub>O, Cu<sup>2+</sup> of CuO and Cu<sup>2+</sup> of CuCO<sub>3</sub> and Cu(OH)<sub>2</sub> respectively As the catalytic activity of the sample without Cu<sub>x</sub>O is lower, the function of Cu species may be ascribed to the interaction between Au and Cu<sub>x</sub>O, which plays a crucial role in the electronic properties of Au particles and strongly affects the catalytic activity. The reducing nature of Cu<sub>x</sub>O can donate <sup>54-58</sup> and withdraw <sup>59-65</sup> charge from Au and build up the possible charge at the metal/oxide interface.

As shown in Figure 7c, the O 1s XPS spectra are fitted with two peaks contributions. One peak at BE = 531.8–531.7 eV can be ascribed to adsorbed oxygen. The other peak at BE = 530.7–530.8 eV may belong to lattice oxygen  $O^{2-}$  of Cu<sub>x</sub>O. Li et al <sup>66</sup> have shown unambiguously that with the promotion of Au NPs, the surface lattice oxygen of the FeO<sub>x</sub> participates directly in the CO oxidation via an Fe<sup>3+</sup>÷Fe<sup>2+</sup> redox mechanism even well below the room temperature, and this redox mechanism predominates in low temperature CO oxidation on Au/FeO<sub>x</sub>. As Cu<sub>x</sub>O is similar to FeO<sub>x</sub>,

the same reaction mechanism may also occur via a  $\text{Cu}^{2^+} \widetilde{=} \text{Cu}^+$  redox mechanism.



Figure 7. The XPS spectra of different catalysts. a) Au 4f, b) Cu 3d and c) O 1s.

Figure 8 is the diagrammatic sketch for CO oxidation mechanism on Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. To sum up, the pairs of Au atoms and Au cations are active sites. Au clusters act as a reservoir of charge through the catalytic cycle facilitating both reduction processes involving the O<sub>2</sub> molecule and oxidation process such as the transformation of CO to CO<sub>2</sub>. The detail process is that Cu<sub>x</sub>O donate and withdraw charge from Au and build up the possible charge at the metal/oxide interface. CO molecules quickly attach to the oxygen species bond at the interface. It has been proved that CO can react with the bonded oxygen and release CO<sub>2</sub> within 4 Ps<sup>67</sup>.



Figure 8. The diagrammatic sketch for CO oxidation mechanism on Au@Cu\_xO/ $\gamma$ -Al\_2O\_3.

### Conclusion

In summary, Au  $/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> haven't any catalytic activity at room temperature and their 90% CO conversion temperature (T<sub>90%</sub>) are almost same to pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> not only can decrease the T<sub>90%</sub> but also can catalyze CO oxidation at room temperature and the stability is very high. The high catalytic activity of Au@Cu<sub>x</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can be ascribed to the reason that the formation of Au@Cu<sub>x</sub>O core-shell structure has led to the interaction between Au and Cu<sub>x</sub>O, which generates the Au<sup>δ+</sup> and Au<sup>0</sup> pairs and the co-existence of the 2 kinds of Au species makes the catalyst more active. The protective function of Cu<sub>x</sub>O

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### ARTICLE

shell may be one reason accounts for the catalytic stability improvement.

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