# 一种具有 CO 催化氧化稳定性的金铜双金属/介孔氧化钛催化剂

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**摘要**: 将金、铜前驱体沉积沉淀到介孔氧化钛材料上, 再经氢气活化后制备了双金属催化剂 Au-Cu/$TiO_2$, 并采用 $N_2$ 吸附/脱附、X 射线粉末衍射、紫外-可见光谱和高分辨透射电镜等对样品进行了表征. 结果显示, 金和铜形成合金相, 且良好地分散在介孔氧化钛上. CO 氧化反应结果表明, Cu 可以提高 Au 催化剂的催化性能, Au-Cu/$TiO_2$ 催化剂比 Au/$TiO_2$ 和无孔氧化钛负载的 Au 催化剂具有更好的 CO 催化氧化稳定性. 这可能与 Au, Cu 合金化和氧化钛的介孔结构有关.

**关键词**: 金; 铜; 介孔氧化钛; 稳定性; 一氧化碳; 氧化

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# An Au-Cu Bimetal Catalyst Supported on Mesoporous TiO$_2$ with Stable Catalytic Performance in CO Oxidation

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**Abstract:** An Au-Cu bimetal catalyst was prepared by deposition-precipitation (urea) of gold and copper species on mesoporous $TiO_2$ and activation with $H_2$. The sample was characterized by $N_2$ adsorption/desorption, X-ray diffraction, ultraviolet-visible spectroscopy, and high-resolution transmission electron microscopy. The results showed that the Au and Cu species formed an Au-Cu alloy and were well dispersed on the mesoporous $TiO_2$. According to CO oxidation test results, it was found that the catalytic activity of gold was enhanced by copper. The Au-Cu bimetal catalyst supported on mesoporous $TiO_2$ showed better catalytic stability in CO oxidation than the Au catalyst supported on mesoporous $TiO_2$ and the nonporous $TiO_2$-supported catalysts. This may be related to the effects of both Au-Cu alloying and the mesostructure of $TiO_2$.

**Key words:** gold; copper; mesoporous titania; stability; carbon monoxide; oxidation

Gold catalysts have attracted much attention since Haruta and coworkers [1–4] discovered the excellent low-temperature catalytic activities of gold nanoparticles. However, the low catalytic stability of gold catalysts, caused by the ease of sintering and agglomeration of gold nanoparticles, has severely limited further applications [5,6]. The devel-

opment of gold-based catalysts with high catalytic stabilities is therefore a major topic of scientific research.

To date, a number of studies have focused on this subject and can be divided into two main categories: the synthesis of support materials with specific nanostructures and the introduction of new species. Goodman et al. [7] reported that gold nanoparticles can be stabilized by surface defects via the substitution of Ti atoms for Si in a silica thin-film network. Accordingly, Kunitake et al. [8] incorporated gold into porous titania and zirconia and found that these materials can effectively suppress the fusion of gold nanoparticles. Furthermore, Bore et al. [9] deposited gold nanoparticles in the pores of mesoporous silica and found that sintering of gold nanoparticles was reduced. The confinement of gold nanoparticles in the pores of support materials can therefore effectively improve the catalytic stability of gold catalysts.

Alternatively, there are methods for introducing new species into gold-based catalysts to improve their stability. Dai et al. [10] prepared an ultrastable gold catalyst by covering the $Au/TiO_2$ surface with an $Al_2O_3$ thin film to anchor the gold nanoparticles. Subsequently, they used various oxides to modify the gold catalysts and achieved some good results [11,12]. Instead of the introduction of inert materials, alloying gold with a metal of relatively high melting point is an alternative effective way of improving the stability of gold catalysts. In particular, there may be a synergistic effect between the two metals, which can further enhance the activity of the catalysts [13]. Introduction of another metal can also reduce the cost of the catalyst. Among various metals, copper is an ideal candidate because of its cheapness, stability, and catalytic activity [14]. Zhang et al. [13] found that an Au-Cu alloy exhibited a much better performance than Au nanoparticles in catalyzing CO oxidation, but the authors did not investigate its catalytic stability. Furthermore, Chen et al. [15] reported that a gold-based catalyst supported on nonporous titania (P25) showed no deactivation through 49 h of tests in the presence of copper species.

However, there has been little work on the effects of a combination of alloying and confinement in pores on improving the catalytic stability of gold-based catalysts. Based on analyses of the work mentioned above, we consider that an Au-Cu alloy catalyst supported on a mesoporous material definitely has a better catalytic stability than other catalysts using only one of these effects. In our previous work, mesoporous $TiO_2$ was prepared from potassium titanate via hydration and ion-exchange [16]. The corresponding gold catalyst exhibited excellent low-temperature CO oxidation performance [17]. Moreover, the gold nanoparticles deposited on mesoporous $TiO_2$ were not liable to increase in size, unlike those on titania with a nonporous structure [18]. In this work, the catalytic stability in CO oxidation of an Au-Cu bimetal catalyst supported on mesoporous $TiO_2$ was studied.

# 1 Experimental

## 1.1 Catalyst preparation

Mesoporous $TiO_2$ was prepared as in our previous work [16,17]. Briefly, $K_2Ti_2O_5$ was ion-exchanged with HCl aqueous solution (0.1 mol/L) to give hydrated titanate ($H_2Ti_2O_5$). Then, calcination of $H_2Ti_2O_5$ was performed in a muffle oven at 600 °C to obtain mesoporous $TiO_2$.

The loading of gold and copper on $TiO_2$ was carried out by a one-step deposition-precipitation (urea) method using aurochlorohydric acid ($AuCl_3 \cdot HCl \cdot 4H_2O$, Sinopharm Chemical Reagent Co., Ltd) and copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, Sinopharm Chemical Reagent Co., Ltd) as the precursors. Excess urea (1.286 g) was dissolved in 50 ml of an aqueous solution of $HAuCl_4$ and $Cu(NO_3)_2$ at room temperature. The Au/Cu molar ratio was 1. Then, 1 g of mesoporous $TiO_2$ powder was added to the solution and the resulting mixture was kept at 80 °C for 3 h under vigorous stirring and in the absence of light. The resulting suspension was filtered and washed several times with 500 ml of distilled water. The solid product was dried overnight at 60 °C under vacuum and then activated in $H_2$ at 300 °C for 2 h. The obtained sample was denoted $Au-Cu/TiO_2$. Inductively coupled plasma-atomic emission spectroscopy results showed that the loadings of gold and copper were both 1 wt% for $Au-Cu/TiO_2$. For comparison, a gold catalyst and a copper catalyst were also prepared by the one-step deposition-precipitation (urea) method; these were denoted $Au/TiO_2$ and $Cu/TiO_2$. The metal loadings of $Au/TiO_2$ and $Cu/TiO_2$ were 2 wt%. Degussa P25 was used as the nonporous titania, and its corresponding catalysts were denoted Au-Cu/P25 and Au/P25. The metal loadings of these catalysts were identical to those of their corresponding mesoporous $TiO_2$-supported catalysts.

## 1.2 Catalyst characterization

X-ray diffraction (XRD) analysis of the samples was carried out on a D8 Advance X-ray diffractometer using Cu $K_\alpha$ radiation with settings of 40 kV and 30 mA. The scan range was from 5° to 60° at a rate of 0.2 s/step. The textural properties of the samples were studied by $N_2$ adsorption/desorption measurements (Tristar II 3020M) at −196 °C. Before analysis, the samples were degassed for 2 h at 150 °C under vacuum. An ultraviolet-visible (UV-vis) spectrometer (Perkin-Elmer Lambda 900) was used to identify the spectral properties of the samples. The morphology of the gold nanoparticles was characterized by high-resolution transmission electron microscopy (HRTEM) conducted on a

JEM-2010 UHR (JEOL Co., Japan) at 200 kV.

### 1.3 Catalyst activity measurements

Measurements of catalyst activity in CO oxidation were performed in a fixed-bed reactor using 40 mg of catalysts, accurately weighed for each sample. The reactant gas (1 vol% CO and 1.98 vol% $O_2$ balanced with helium) was admitted at a flow rate of 20 ml/min, corresponding to a space velocity of 30 L/(h·$g_{cat}$). The flow rate of the reactant gas was monitored using mass flow controllers. The temperature was controlled by a thermocouple placed inside the catalyst bed. The off-gas was analyzed with an HP-6890 gas chromatograph equipped with a thermal conductivity detector and a molecular 139 column using helium as carrier gas.

## 2 Results and discussion

The structures of $TiO_2$ and Au-Cu/$TiO_2$ were characterized by nitrogen adsorption/desorption. As shown in Fig. 1, $TiO_2$ and the Au-Cu/$TiO_2$ catalyst have a similar type IV isotherm, corresponding to a mesostructure. The pore size distribution curve (the inset) shows that $TiO_2$ and the catalyst have a uniform pore distribution of about 15 nm. There are no obvious differences between the $N_2$ adsorption/desorption isotherms and pore size distribution of $TiO_2$ and Au-Cu/$TiO_2$. This indicates that the Au and Cu species are well dispersed on $TiO_2$.
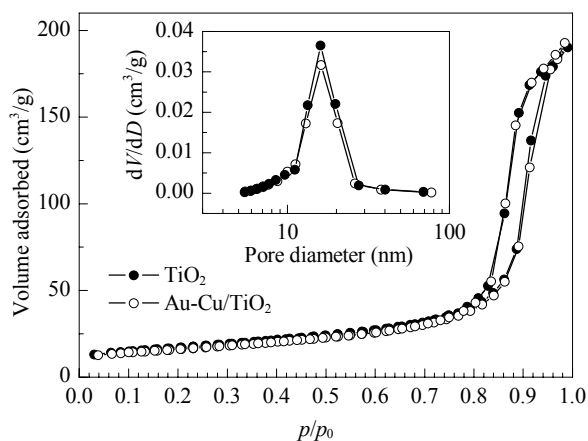


**Fig. 1.** $N_2$ adsorption/desorption isotherms and pore size distribution of $TiO_2$ and Au-Cu/$TiO_2$.

The XRD pattern of Au-Cu/$TiO_2$ is shown in Fig. 2. The strong peaks at 25.3°, 37.8°, 48.0°, 53.9°, and 55.1° are ascribed to the diffraction patterns of the (101), (004), (200), (105), and (211) planes of anatase $TiO_2$ [19]. Moreover, an ultraweak characteristic peak is observed at $2\theta = 40.5°$, which is assigned to an Au-Cu alloy (PDF 65-0937). However, no characteristic peaks corresponding to gold or copper species are observed in the XRD pattern. This suggests the formation of an Au-Cu alloy in the Au-Cu/$TiO_2$ catalyst.
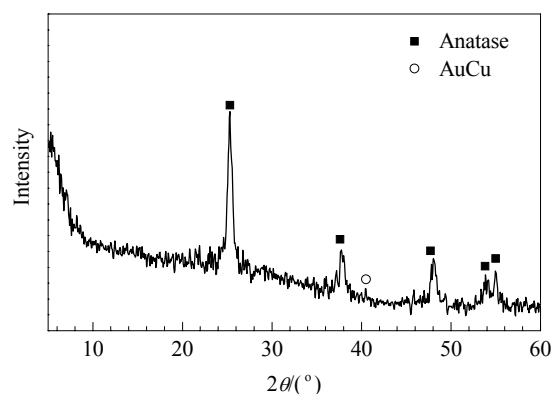


**Fig. 2.** XRD pattern of Au-Cu/$TiO_2$.

UV-vis absorption spectroscopy was performed to measure the spectral properties of $TiO_2$ after loading with metal particles. Figure 3 shows that Au-Cu/$TiO_2$ and Au/$TiO_2$ both have an absorption peak in the UV region (about 340 nm), assigned to the optical response of $TiO_2$. Au/$TiO_2$ exhibits an extra absorption peak in the visible region (about 558 nm). This peak can be attributed to surface plasma resonance of the gold nanoparticles. For Au-Cu/$TiO_2$, a broadened absorption peak can be seen in the visible region, and the peak is at about 553 nm, similar to that of Au/$TiO_2$. However, the entire absorption peak in the visible region of Au-Cu/$TiO_2$ displays a red shift compared with that of Au/$TiO_2$. Apparently, this red shift is caused by the existence of copper species and is attributed to the formation of an Au-Cu alloy [20].
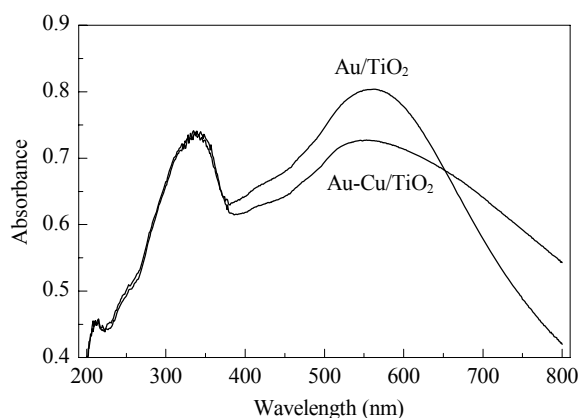


**Fig. 3.** UV-vis spectra of Au-Cu/$TiO_2$ and Au/$TiO_2$.

HRTEM was used to study the morphology of the metal nanoparticles in Au-Cu/$TiO_2$. Figure 4(a) shows that all the nanoparticles (black spots) are uniformly distributed on the mesoporous $TiO_2$. According to the particle size distribution
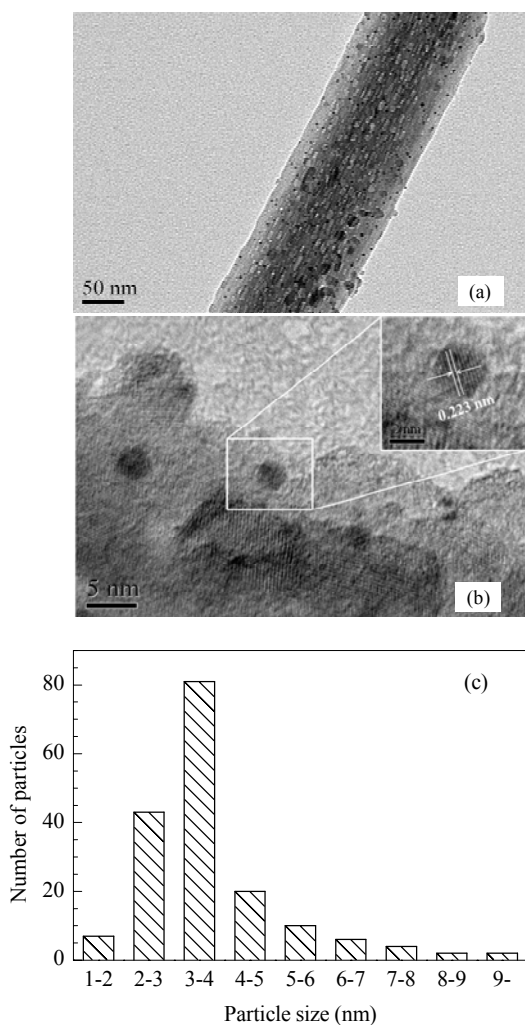
**Fig. 4.** HRTEM images of Au-Cu/TiO$_2$ ((a) low-resolution image; (b) high-resolution image) and particle size distribution (c).

(Fig. 4(c)), most of the nanoparticles are of diameter 3–4 nm. Furthermore, HRTEM examination of the Au-Cu/TiO$_2$ shows that the *d*-spacing value in a single particle is about 0.223 nm. This confirms that the particles are not a mixture of separate gold and copper particles but composed of Au-Cu alloy [13]; this is in agreement with the analyses discussed above.

Catalytic properties of various samples are shown in Ta-

ble 1. The performance of the catalysts can be qualitatively evaluated from $T_{50}$, i.e., the reaction temperature at which CO conversion by the catalyst is 50%. The $T_{50}$ value of Au-Cu/TiO$_2$ is 57 °C, higher than that of Au/TiO$_2$ (33 °C). This indicates that the catalytic performance of Au-Cu/TiO$_2$ is a little worse than that of Au/TiO$_2$, as is also quantitatively confirmed by the reaction rate (*r*). In contrast, Au-Cu/TiO$_2$ has a higher specific reaction rate ($r_{Au}$) than that of Au/TiO$_2$; $r_{Au}$ for Au-Cu/TiO$_2$ is 78.2 $\mu mol_{CO}/(g_{Au} \cdot s)$. This suggests that the activity of the gold in Au-Cu/TiO$_2$ is enhanced by the copper, and this may be related to a synergistic effect between gold and copper. For comparison, we prepared a catalyst Au/TiO$_2$+Cu/TiO$_2$ by physically mixing Au/TiO$_2$ and Cu/TiO$_2$ in a 1:1 mass ratio. Clearly, for the gold species and copper species located in separated substrates in Au/TiO$_2$+Cu/TiO$_2$ there is no synergistic effect between gold and copper. The *r* and $r_{Au}$ values of Au/TiO$_2$+Cu/TiO$_2$ are 0.63 $\mu mol_{CO}/(g_{cat} \cdot s)$ and 63.2 $\mu mol_{CO}/(g_{Au} \cdot s)$, respectively, which are almost half of the *r* value and similar to the $r_{Au}$ value, respectively, of Au/TiO$_2$. This indicates that copper has no effect on the activity of gold nanoparticles in the physically mixed catalyst Au/TiO$_2$+Cu/TiO$_2$. However, both *r* and $r_{Au}$ of Au-Cu/TiO$_2$ are obviously higher than those of Au/TiO$_2$+Cu/TiO$_2$. This confirms that the activity of gold in an Au-Cu bimetal catalyst supported on TiO$_2$ is enhanced by the copper, and this is related to the synergistic effect between gold and copper.

The stability of the catalytic performance of various catalysts was examined using long-term time tests. As shown in Fig. 5, there is only about 4% deactivation of Au-Cu/TiO$_2$ after reaction for 600 min. However, Au/TiO$_2$ exhibits about 25% deactivation after reaction for 600 min. This indicates that the introduction of copper can indeed improve the catalytic stability of gold catalysts, as was also confirmed by a comparison of the stabilities of Au-Cu/P25 (27%) and Au/P25 (62%). Furthermore, it can be seen that the deactivation degree of TiO$_2$-supported catalysts is lower than that of P25-supported catalysts. As is well known, P25 consists of nonporous titania nanoparticles. The nitrogen adsorption/desorption results in Fig. 1 show that the TiO$_2$ used in the present work has a typical mesostructure. This

**Table 1** Physicochemical properties and catalytic activities ($T_{50}$, *r*, and $r_{Au}$) for various catalysts

| Sample | Metal | Surface area (m$^2$/g) | $T_{50}$[a]/°C | $r$[b]/($\mu mol_{CO}/(g_{cat} \cdot s)$) | $r_{Au}$[b]/($\mu mol_{CO}/(g_{Au} \cdot s)$) |
|---|---|---|---|---|---|
| TiO$_2$ | – | 56.2 | – | – | – |
| Au-Cu/TiO$_2$ | 1wt%Au, 1wt%Cu | 54.8 | 57 | 0.78 | 78.2 |
| Au/TiO$_2$ | 2wt%Au | 52.4 | 33 | 1.30 | 65.1 |
| Cu/TiO$_2$ | 2wt%Cu | – | 115 | 0 | – |
| Au/TiO$_2$+Cu/TiO$_2$ | 2wt%Au+2wt%Cu | – | 74 | 0.63 | 63.2 |

[a]$T_{50}$ is the reaction temperature when the CO conversion of catalyst is 50%.

[b]The reaction rate (*r*) and the specific reaction rate ($r_{Au}$) of CO oxidation at low conversions under a kinetically controlled regime at 25 °C.

[c]The catalyst is obtained by physical mixture of Au/TiO$_2$ and Cu/TiO$_2$ in the mass ratio of 1 to 1.
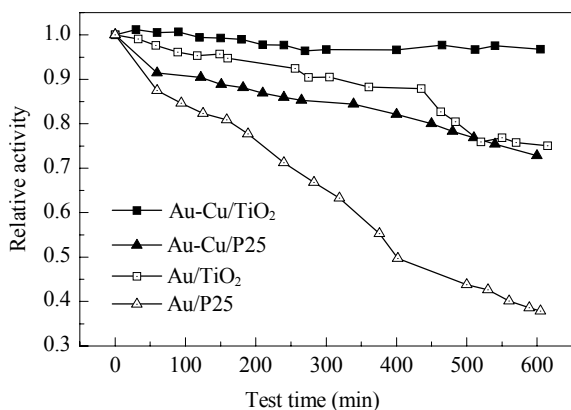
**Fig. 5.** Long-term time tests for CO oxidation over various samples.

suggests that the mesostructure of titania is beneficial to the stability of the gold catalyst; this was also demonstrated in our previous work [18]. Compared with the other catalysts, Au-Cu/TiO$_2$ displays the lowest deactivation, suggesting the best catalytic stability. Thus, as expected, excellent catalytic stability of gold-based catalysts can be obtained by alloying and using mesoporous materials as supports.

## 3　Conclusions

We prepared a gold-based catalyst with high catalytic stability in CO oxidation by codeposition of Au and Cu precursors on mesoporous TiO$_2$. The characterization results showed that Au and Cu species formed an Au-Cu alloy, which was well dispersed on mesoporous TiO$_2$. CO oxidation tests showed that the Au-Cu/TiO$_2$ catalyst had better catalytic stability than the gold catalyst and the nonporous catalyst. This may be related to the effects of Au-Cu alloying and confinement by the TiO$_2$ mesostructure. Further studies on the as-prepared catalysts are underway in our group. We hope that the present work may help to improve the catalytic stability of gold-based catalysts.

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