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Effect of supports on the gold catalyst activity for catalytic combustion of CO and HCHO

Meilin Jia,[1],* Yuenian Shen,[2] Changyan Li,[2] Zhaorigetu Bao[1] and Shishan Sheng[3]

[1] *College of Chemistry and Environmental Science, Inner Mongolia Normal University, Huhhot, 010022, P.R.China*
[2] *College of Chemistry and Chemical Engineering, Inner Mongolia University, Huhhot, 010021, P.R. China*
[3] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, P.R. China*

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The deposition–precipitation method was used to prepare gold catalysts based on different supports. Their catalytic activities for combustion of carbon monoxide (CO) and formaldehyde (HCHO) were investigated. All these catalysts showed good activity for the two reactions and the Au/CeO_2-a catalyst exhibited the highest activity for the two reactions. Furthermore, catalysts derived from the as-precipitate hydroxides exhibited higher activity than that from corresponding oxide supports. The BET, XRD, TEM and XPS were carried out. The results indicated that the gold dispersed more homogeneous on the as-precipitate hydroxide supports than that on the corresponding oxide supports.

KEY WORDS: gold catalyst; catalytic combustion; carbon monoxide; formaldehyde; TiO_2; CeO_2.

1. Introduction

Gold has been considered as one of the least catalytically useful metal because of its chemical inertness and the difficulty to obtain a high dispersion on common support materials in the past years. However, since Haruta *et al.* discovered that gold nanoparticles dispersed on metal oxides are exceptionally active for low temperature CO oxidation, the interest in studying supported Au catalysts has increased substantially [1–3].

It was reported that supported Au catalysts are not only active for CO oxidation at very low temperatures but also active for a wide variety of reactions, including hydrogenation of carbon oxides and hydrocarbons, alkene epoxidation, NO reduction, hydrochlorination of ethylene, water–gas shift and the oxidation of volatile organic compounds (VOCs) [4–12]. VOCs are major contributor to air pollution because of their toxic and malodorous nature and its contribution to ozone and smog formation. Due to the high catalytic activity for these reactions, Au catalysts are attractive for purification of contaminated air. However the study for catalytic combustion of formaldehyde (HCHO), a general hazardous indoor air pollutant, which may reasonably be anticipated to be a carcinogen, was very few.

The catalytic properties of Au catalysts were found to be depended on the method of preparation. Furthermore, the interaction between gold and the support could also markedly influence the catalyst activity [13,14]. In this paper, all the catalysts were prepared by a relatively simple method among many existing methods, the deposition–precipition method. However, different compounds were chose as supports to study the effect of supports on the catalyst's activity. Firstly, catalysts supported on the high surface area TiO_2, CeO_2 or mixture of TiO_2 and CeO_2 were made to compare the effect of support‘ property on the catalyst activity. Secondly, the difference between loading the Au on the oxide supports and on the respective precursor of the supports (the as-precipitates of hydrated samples) was compared. We hope such a preliminary introduction of gold may be beneficial for the texture of the catalyst. The corresponding preparation techniques were described in detail in the experimental section. Then the catalytic activity for both the CO oxidation and HCHO oxidation was investigated to illustrate the influence of support materials on the catalytic activity.

2. Experimental

2.1. Catalyst preparation

As-precipitated samples of "TiO_2-a" and "CeO_2-a" were prepared by aqueous precipitation method. Ammonia (5 M) was added into $TiCl_4$ or $Ce(NO_3)_4$ solution (1 M) quickly, with precipitate formed. After the precipitates were centrifuged and dried, the as-precipitated hydrated samples were obtained and designated as TiO_2-a or CeO_2-a accordingly.

The corresponding oxide supports TiO_2 and CeO_2 were obtained after the as-precipitated samples further calcined at 550 °C in air for 2 h. The TiO_2-CeO_2 support was the mechanical mixture of TiO_2 and CeO_2 with the weight ratio of 1:1.

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*To whom correspondence should be addressed.
E-mail: jml@imnu.edu.cn

For preparing the 2% loading gold catalyst, the procedures were as follows: a suitable amount of chloroauric acid ($HAuCl_4 \cdot 3H_2O$) was dissolved in deionized water (with the concentration of 4.2 mM); 0.1 M sodium hydroxide solution was added into the chloroauric acid solution for adjusting the solution pH to 8; then the support was added, followed by heating the solution to 70 °C with vigorous stirring for 2 h; after that the precipitates were centrifuged and washed until free from Cl^- ion; finally, the samples were dried at 80 °C for 2 h and calcined at 200 °C for 2 h in air. These catalysts were denoted as: Au/TiO_2-a, Au/CeO_2-a, Au/TiO_2, Au/CeO_2 and Au/TiO_2 – CeO_2 respectively. Au/TiO_2-a and Au/CeO_2-a represented that the catalysts derived from the as-precipitate hydroxide supports.

2.2. *Activity evaluation*

The activity of the catalysts for CO oxidation was evaluated in a continuous flow U-shaped glass reactor (8 mm i.d.). The gas mixture of 1.0% CO balanced with purified air was passed through 200 mg catalyst at a flow rate of 170 ml/min. The produced CO_2 was detected by FQ-W CO2 IR analysis instrument on-line.

For the HCHO oxidation, the catalytic test was also measured in a U-shaped glass reactor as above mentioned. However the feed gas was formed by the purified air passing through a HCHO liquid bottle which was set in the water ice to keep the constant pressure of HCHO under the constant temperature of 0 °C. The composition of the inlet and outlet gases was analyzed by a gas chromatograph (GC-8A), equipped with a TCD detector and connected with a GDX column.

Catalytic activity was indicated by the lowest complete conversion temperature (denoted by $T_{100\%}$). The lower the $T_{100\%}$, the higher the activity of the catalyst was.

2.3. *Catalyst characterization*

X-ray diffraction measurements were carried out on a Philips PW1700 X-ray automated powder diffraction with CuK radiation. Specific areas of catalysts were determined by BET method. Physisorbed nitrogen quantity at 77 K was measured by a volumetric apparatus on Micromeritics-ASAP-2010 instrument. The transmission electron microscopy (TEM) measurements were performed on a JEM-2010 electron microscope. The surface composition was examined by X-ray photoelectron spectroscopy (XPS), a VG ESCALAB MK2 instrument.

3. Results and discussions

3.1. *The influence of supports on the catalyst activity*

The deposition–precipitation method was used to prepare Au/TiO_2-a, Au/CeO_2-a, Au/TiO_2, Au/CeO_2 and Au/CeO_2-TiO_2 catalysts. The surface areas and catalytic activity for CO and HCHO oxidation were listed in table 1. The results in table 1 showed: (1) the sequence of $T_{100\%}$ for CO oxidation over different catalyst was as follows: Au/CeO_2-a ≈ Au/TiO_2-a < Au/CeO_2–TiO_2 < Au/CeO_2 < Au/TiO_2. (2) In the case for HCHO oxidation, the order of $T_{100\%}$ was Au/CeO_2-a < Au/CeO_2 < Au/CeO_2-TiO_2 < Au/TiO_2-a < Au/TiO_2. At same time, the catalytic activity of these catalysts for the CO oxidation as function of temperature was shown in figure 1. The conversion of CO increased with the temperature increasing.

Table 1
Surface areas and catalytic activity for HCHO and CO oxidation of Au-based catalysts

Catalysts	The surface areas of catalysts	Catalytic activity for HCHO oxidation	Catalytic activity of CO oxidation
	S (m^2/g)	$T^a_{100\%}$ (K)	$T^a_{100\%}$ (K)
Au/CeO_2	47.19	373	311
Au/TiO_2	113.85	523	363
Au/CeO_2–TiO_2	61.95	438	303
Au/CeO_2-a	122.35	353	258
Au/TiO_2-a	192.13	503	258

From the above results, it could be observed that the support affected the catalyst activity. For both oxide and as-precipitated hydroxide support, the Au supported on the Ce compounds showed higher activity than it supported on the Ti compounds. Scire *et al.* pointed out that gold nanoparticles could weak the Ce–O bond, thus increase the reactivity of the surface lattice oxygen [15]. It could also be noticed that the Au supported on as-precipitated hydroxide supports showed higher activity than that supported on oxide supports for both Ti and Ce compounds. Combined the surface areas with the catalytic activity, it could be found that the catalysts derived from as-precipitated hydroxide supports exhibited larger surface areas than that from respective oxide supports. So the difference in

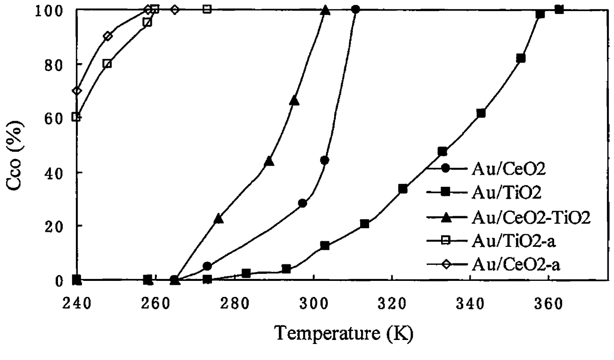

Figure 1. The influence of temperature on the catalyst activity for CO oxidation.

surface areas may be one reason for the difference in catalytic activity. Furthermore, the sample supported on the mixture of TiO_2 and CeO_2 showed higher activity than that supported on single TiO_2 or CeO_2 for CO oxidation reaction, which indicated that there was synergic effect between the two supports; In the case of HCHO oxidation reaction, the catalysts from supports containing Ce showed higher activity than that from supports no containing Ce. This result implied that ceria was a promising support for catalytic combustion of HCHO.

3.2. *Catalyst characterization*

In order to determine the structure and morphology of the gold catalyst supported on different catalysts, the samples were investigated with XRD (showed in figure 2). The peak detected at 38.2 was assigned to Au^0 (111). The XRD results revealed that the as-precipitated hydroxide support had become the oxide support for both Au/TiO_2-a and Au/CeO_2-a after calcination at 200 °C. In both Au/TiO_2 and Au/TiO_2-a catalysts, the support existed in anatase phase due to the peak at 25.3. However, from the XRD, it could also be observed that the catalysts derived from the hydroxide supports possessed broader peak of Au^0 than that of catalysts supported on oxide supports, implied that the catalysts from as-precipitated hydroxide possessed smaller Au particles than that from the respective oxide support. This may be another reason for the catalytic activity difference between catalysts from as-precipitated hydroxide and respective oxide supports. Meanwhile, it was found that the catalysts from supports containing Ce possessed broader Au(111) peak than that from supports containing Ti. Centeno *et al.* [12] pointed out that ceria participates in the fixation of gold and enhances its final dispersion, thus leading to the stabilization of gold particles with lower crystallites size. Under higher reaction temperature, this effect is extremely important. Our experimental results of catalytic combustion of HCHO supported this conclusion.

In order to studied the activity difference between Au/TiO_2-a and Au/TiO_2 deeply, TEM experiment was carried out. The TEM result (figure 3) uncovered that the spherical gold nanoparticles as dark spot was dispersed on the surface of support. And the mean diameter of gold in Au/TiO_2-a catalyst (about 5 nm) was smaller than that of Au/TiO_2 (about 6 nm). This result was consistent with the XRD.

Why the catalyst derived from as-precipitated hydroxide possessed smaller gold particle than that of the catalyst derived from oxide support? The most

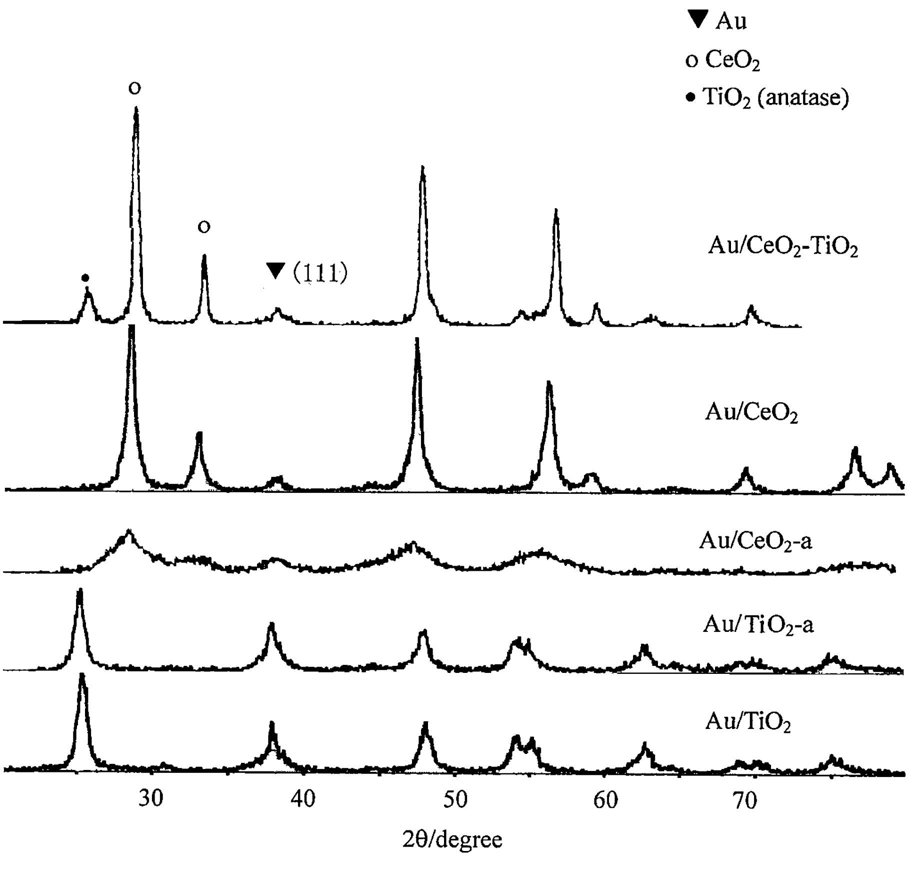

Figure 2. XRD spectra of Au catalysts.

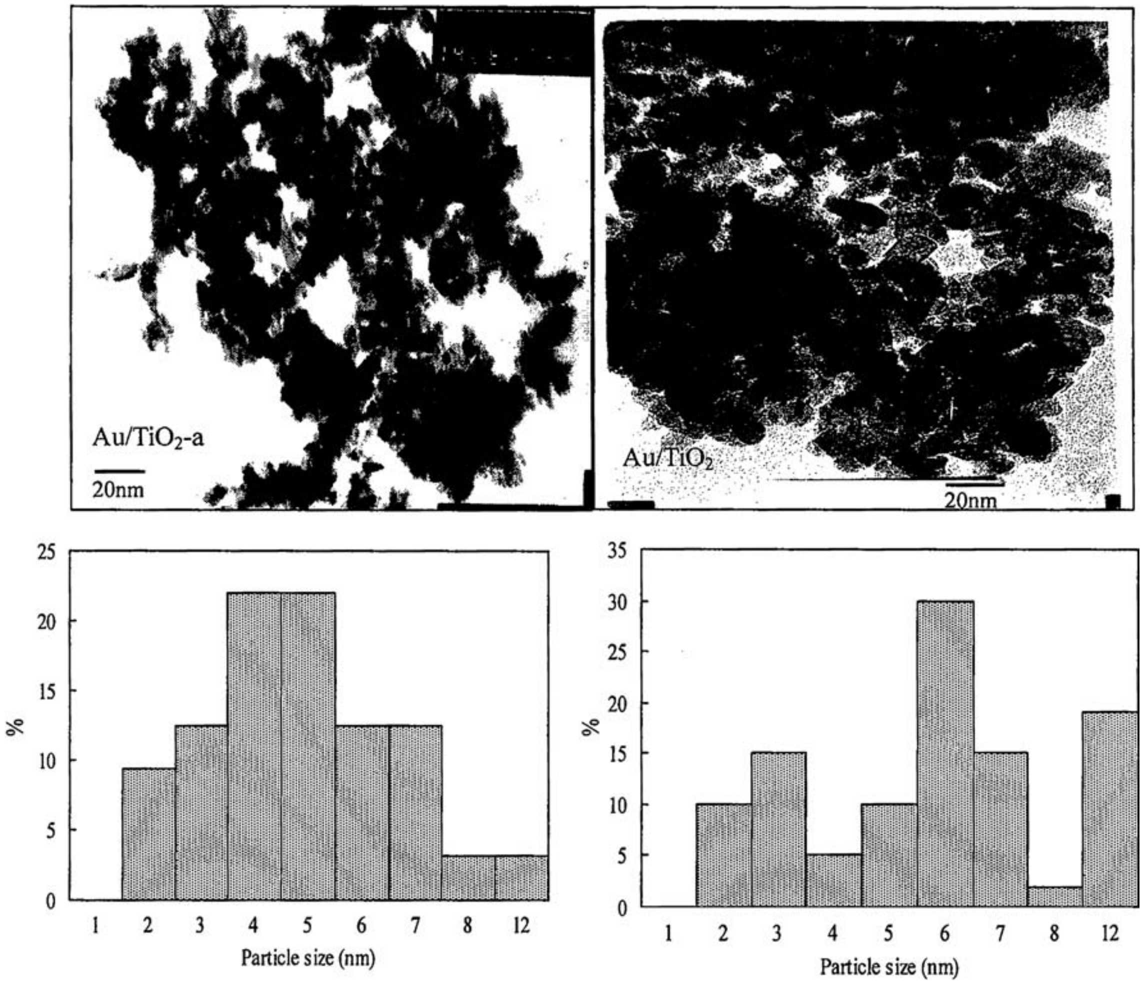

Figure 3. TEM photographs and the size distribution of Au particles for Au/TiO_2-a and Au/TiO_2 catalysts.

probability was that the interaction between the as-precipitated hydroxide support and gold, especially the interaction between OH and Au, may be useful for inhibiting the Au sintering and growing during the calcinations process, As a result, gold dispersion was therefore improved.

XPS results suggested that the gold existed in the metallic species for both Au/TiO_2-a and Au/TiO_2. The surface atomic ratios of Au/Ti (listed in table 2), was derived from the corresponding peak area. For Au/TiO_2-a and Au/TiO_2 catalysts with same gold loading, the XPS result demonstrated that the Au/TiO_2-a showed higher Au/Ti ratio on the surface than that of the Au/TiO_2. This result supported the conclusion of XRD, which indicated the Au could be dispersed more homogeneously on the surface for Au/TiO_2-a. Therefore, it was not difficult to understand that the more active sites on Au/TiO_2-a catalyst than that of the Au/TiO_2 catalyst accounted for the higher activity of Au/TiO_2-a.

Table 2
Surface atomic ratios of Au/Ti catalysts determined by XPS spectra

Catalyst	Au/Ti Ratio
Au/TiO_2	0.00582
Au/$Ti(OH)_4$	0.022

4. Conclusions

1. The support played an important role in the catalyst activity for both the CO oxidation and HCHO oxidation. The Au/CeO_2-a showed the highest activity for both reactions, with the $T_{100\%}$ 258 K for CO oxidation and $T_{100\%}$ 353 K for HCHO oxidation.
2. The catalyst derived from the as-precipitate hydroxide showed higher activity than that from the corresponding oxide support. The BET, XRD and XPS results demonstrated that catalysts from as-precipitate hydroxide could make the gold disperse homogenous on the catalyst surface and thus increase the number of active sites.

Acknowledgments

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