# Catalysis of oxidation of carbon monoxide on supported gold nanoparticle

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## ARTICLE INFO

## ABSTRACT

Gold used to be considered to have no catalytic activity. In the 1980s, however, Masatake Haruta found that nano-sized gold particles supported by metal oxides can catalyze the oxidation of carbon monoxide. This work examines the oxidation of carbon monoxide (CO) and the adsorption/desorption behaviors on nano-sized gold catalyst at room temperature by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Carbonate, bicarbonate and carboxylate were observed. The effects of various factors (relative humidity, CO gas concentration, and total surface area) on the CO conversion efficiency were studied using the response surface designs in the Experiment Design Method. The results indicate that the conversion efficiency of CO was high when the ratio of CO and $O_2$ was close to 1:1. The gas concentration is the most important factor, followed by the weight of gold catalyst, followed by relative humidity. An appropriate humidity enhances the catalytic reaction in the long-term.

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## 1. Introduction

Gold (Au), element number 79 in the periodic table has an electronic structure of -4f$^{14}$5d$^{10}$6d$^1$. It is the metal with highest electronegative and high oxidation potential. Gold used to be considered to have no catalytic activity because its electrons are not easily transferred [1]. In 1987, however, Masatake Haruta identified the catalytic oxidation of carbon monoxide by the nano-sized gold particles on metal oxide at $-73\,^\circ$C [2]. His work initiated more investigations on gold catalyst [3].

Carbon monoxide (CO) is an odorless, colorless, hazardous gas, and generally is formed by the incomplete combustion of any carbon substance. Materials that oxidize CO to $CO_2$ must be developed to eliminate the hazard. The use of gold catalyst in carbon monoxide oxidation is challenging but promising. This study investigates the factors that affect the conversion efficiency of CO on nano-sized gold catalyst.

## 2. Literature review

Gold effectively catalyzes various reactions, especially with appropriate supporting materials. W.A. Bone et al. (1906) discovered the oxidation reaction of hydrogen on a golden net. W.A. Bone and G.W. Andrew (1925) reported the catalytic oxidation of CO by gold [4]. B.J. Wood and H. Wise (1970) demonstrated the catalytic activity of gold film in the hydrogenation of cyclohexene and 1-butene [5,6]. In the early 1970s, G.C. Bone et al. dispersed gold particles (0.01–0.05%) on various carriers (MgO, Al$_2$O$_3$, SiO$_2$), and found that they catalyzed the hydrogenation of linear alkenes at low temperature (373 K). However, its catalytic ability is weaker than that of other noble metals (such as platinum and palladium) [4,7]. In 1977, D. McIntosh and G.A. Ozin found that $CO_2$ was formed when oxygen/carbon monoxide and gold steam were mixed at 30–40 K. In 1985, G.J. Hutchings proved that gold can catalyze the hydrochlorination of acetylene to vinyl chloride [5,8]. In 1980s, M. Haruta et al. determined that gold dispersed on the surface of metal oxide by co-precipitation and deposition–precipitation can catalyze CO oxidation at room temperature [9]. His research motivated more research on gold catalyst.

Many debates proceed on the location of the carbon monoxide oxidation catalyzed by gold, and the adsorption of gases (especially the adsorption of oxygen). Several possible reaction mechanisms have been proposed [10–12]. M.M. Schubert, however, proposed two carbon monoxide oxidation mechanisms based on supporting materials—active supporting materials (TiO$_2$) and nonactive supporting materials (MgO) [13]. Fig. 1 presents possible mechanisms.

The mechanism by which gold catalyst on a nonactive support is elucidated using the first model: the Langmuir–Hinsheloow mechanism (Fig. 1 mechanism #1). Oxygen is assumed to be directly adsorbed on gold particles, oxygen atoms are formed by the breaking of O–O bonds. On gold sites or metal surface defect sites, oxygen atoms react with adsorbed carbon monoxide to yield $CO_2$. This model explains the mechanism of gold catalysts on inert support.
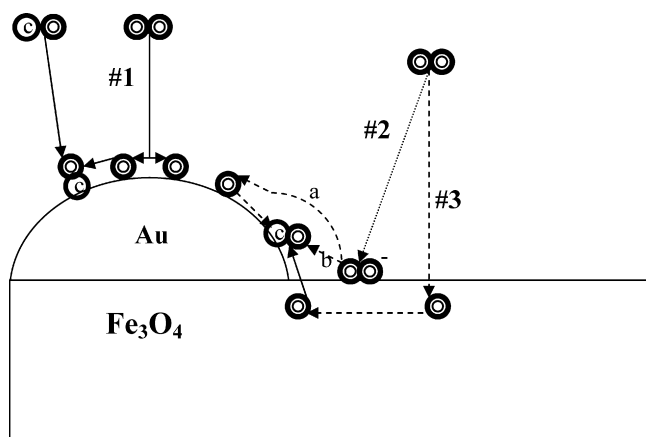
**Fig. 1.** The mechanisms of carbon monoxide oxidation on gold catalyst [13].

Catalytic (capacity OR ability) depends on particle size, and the adsorption of oxygen is the rate-control step.

Another model indicates that oxygen is adsorbed on the support (or the interface between metal and support) [11,14,15]. This model works for semiconductor materials, such as $TiO_2$, $Fe_2O_3$, ZnO and others. Using ESR, Iwasawa et al. proved that the adsorbed oxygen is in the form of superoxide oxygen ($O_2^-$) (Fig. 1 mechanism #2). However, whether the carbonate-like intermediate is formed from the $O_{ad}$, resulting in the separation of $O_2^-$ on the interface (Fig. 1 #2a), or from a direct reaction with the adsorbed carbon monoxide (Fig. 1 #2b) [12], is unclear.

The last possible mechanism (Fig. 1 mechanism #3) assumes that oxygen is separated and adsorbed on the support and a lattice of oxygen is formed, followed the reaction occurs on the interface, or the oxygen spills over to gold particles [15]. Despite the fact that both $Au/TiO_2$ and $Au/Fe_3O_4$ supports are activate materials, they are associated with different catalytic mechanisms in the oxidation of carbon monoxide. In $Au/Fe_3O_4$, $Fe_3O_4$ provides the oxygen, and the gold particles promote the motion and supplement of lattice oxygen, while also helping to adsorb oxygen [15] (path #3). The free oxygen separated from $O_{ad}$ reacts with adsorbed carbon monoxide (path #2a). In $Au/TiO_2$, however, carbon monoxide and oxygen are simultaneously adsorbed and reacted on the surface of gold particles [11]. Boccuzzi et al. [16], however, proposed two independent paths: one reaction rapidly and directly occurs on the surface of metallic gold particles, another reaction slowly converts gaseous oxygen to the lattice oxygen on the surface of the support or at the interface of gold particles. Recently, Chen et al. [17] summarized some properties of the Au/oxide system which contribute to the enhanced bonding energy of CO and $O_2$: the low-coordination sites and interfaces of the Au atoms; the charge transfer effect of their electronic structure; the tensile strain enhances the adsorption of atomic and molecular oxygen; the effect of metal–insulator transitions; and the effect of dynamic structural fluxionality.

Water molecules are important in the oxidation of carbon monoxide by gold catalyst. Bond et al. [18] noted that the oxidation of carbon monoxide must involve —OH. Daté and Haruta [19] demonstrated that $Au/TiO_2$ with the proper amount of water (200 ppm $H_2O$) yields a high reaction rate. Since water-derived species can either activate oxygen or change the status of electrons on the surface of gold, if the $H_2O$ concentration exceeds 200 ppm, then the water can block the activation sites, reducing the reaction rate.

Kung et al. [20] investigated the role of water in carbon monoxide oxidation: the regeneration of the deactivated catalyst is related to the —OH functional group. The reaction can continue in a steady state for 30 min in a humid environment, while convection declines with time in a dry environment. In the oxidation of carbon monox-

ide, bicarbonate, the intermediate, is converted to the inactive carbonate, and occupies the active sites. However, the following inverse reactions occur if the catalyst is in an environment with water.

$$Au-(CO_3H) + Al-OH \rightarrow Au-(CO_3)-Al + H_2O_{ad}$$

$$Au-(CO_3H) + Au-OH \rightarrow Au-(CO_3)-Au + H_2O_{ad}$$
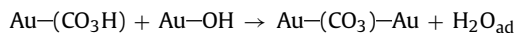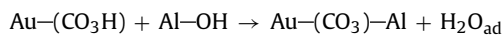
Therefore, the presence of water can prevent deactivation of the catalyst. Okumura and coworkers [21] tested $Au/TiO_2$, $Au/SiO_2$ and $Au/Al_2O_3$ and found that the conversion of carbon monoxide was greater in a more humid environment. He proposed two possible roles of water in the catalytic reaction—the activation of oxygen and the decomposing of carbonate. Liu et al. [22] explained the oxygen activation in the presence of water in $Au/TiO_2$ systems in detail. $O_2$ is supplied by $O_2$ adsorption on $TiO_2$ in the presence of OH and can diffuse to the interface of $Au/TiO_2$ to participate in CO oxidation. Furthermore, in the presence of OH, a charge is transferred from $TiO_2$ to $O_2$, and the $O_2$ adsorption energy depends linearly on the $O_2$ charge.

The catalytic oxidation of carbon monoxide by nano-sized gold can be applied in [23] controlling auto exhaust gas, fuel cells [24,25], air cleaners and gas sensors/detectors [26].

## 3. Methodology

### 3.1. Properties of gold catalyst

In this work, the composition of the catalyst was analyzed by an X-ray diffraction (XRD, Rikaku RINT 2000) (voltage 30 kV, current 20 mA, X ray source: Cu Kα, scan rate 3°/s, scan angle 20–80° $2\theta$). The semi-quantitative analysis was conducted using an X-ray fluorescence spectrometer (XRF, SII SEA1000A), to study the distribution of gold particles to understand the dispersion of nano-sized gold particles on a support (operating voltage of X-ray tube = 50 kV, current = 50 μA, measurement period 300 s). A BET surface area analyzer (CHEMBET 3000) was utilized to calculate the total specific surface area of the catalyst.

The active site on the surface of nano-sized gold catalyst was measured by electron spectroscopy for chemical analysis (ESCA, VG Scientific ESCALAB 250). Transmission electron microscopy (TEM, Philips Tecnai G2 F20) was used to observe the size of the catalyst particles.

### 3.2. Diffuse reflectance infrared Fourier transform spectroscopy, DRIFTS

DRIFTS (Fig. 2) was adopted to observe directly the interaction between nano-sized gold catalyst and adsorbents (carbon monoxide and carbon dioxide), to study the chemical reactions and kinetics of adsorbed molecules on the surface of catalyst. $Au/Fe_2O_3$ catalyst was placed in an airtight cell (Fig. 3). Water and other impurities were purged by helium at 120 °C for 1 h. The background spectra of the $Au/Fe_2O_3$ catalyst were analyzed after cooling, and the adsorption/desorption of $Au/Fe_2O_3$ catalyst was then tested.

### 3.3. Experiment design

The model of response surface design was used to set the experimental conditions with $2^3$ factors plus one surface center. The duplicate tests of the surface center were conducted to estimate the experimental errors. Primary factors were catalyst surface area, gas concentration and relative humidity. The effects of these factors on carbon monoxide oxidation in various conditions were studied.
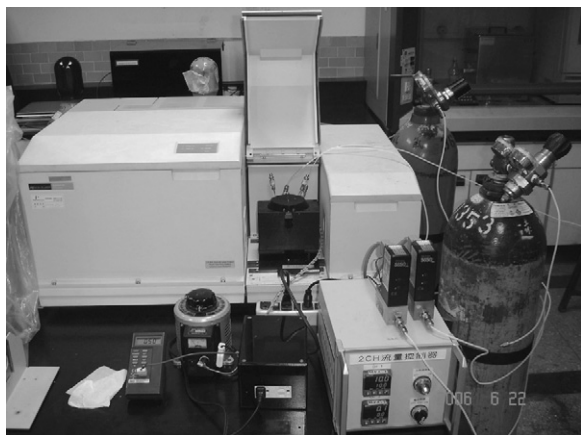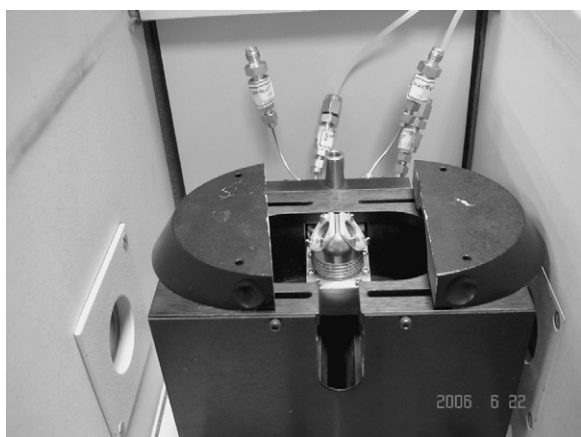
**Fig. 2.** DRIFTS system.



**Fig. 3.** DRIFTS unit.

(1) *Surface area of gold catalyst*: The weight of catalyst multiplied by the total specific surface area in the BET isotherm adsorption test ($168\,m^2/g$). The minimum mass is 0.02 g (total surface area $3.36\,m^2$); the maximum mass is 0.2 g (total surface area $33.6\,m^2$).

(2) *CO gas concentration*: The minimum carbon monoxide concentration is set to 10% by mixing 2 sccm (ml/min) pure carbon monoxide and helium with 20% oxygen. The total flow rate

**Table 1**
Experiment design of three variables.

| Test # | Pattern | Surface area ($m^2$) | CO gas concentration (%) | Relative humidity (%) |
|---|---|---|---|---|
| 1 | 0 0 A | 18.48 | 30 | 100 |
| 2 | a 0 0 | 3.36 | 30 | 50 |
| 3 | 0 0 0 | 18.48 | 30 | 50 |
| 4 | 0 0 0 | 18.48 | 30 | 50 |
| 5 | − − + | 3.36 | 10 | 100 |
| 6 | A 0 0 | 33.6 | 30 | 50 |
| 7 | 0 0 a | 18.48 | 30 | 9.0 |
| 8 | 0 a 0 | 18.48 | 10 | 50 |
| 9 | 0 A 0 | 18.48 | 50 | 50 |
| 10 | − − − | 3.36 | 10 | 9.0 |
| 11 | + + + | 33.6 | 50 | 100 |
| 12 | + − + | 33.6 | 10 | 100 |
| 13 | − + − | 3.36 | 50 | 9.0 |
| 14 | − + + | 3.36 | 50 | 100 |
| 15 | + + − | 33.6 | 50 | 9.0 |
| 16 | + − − | 33.6 | 10 | 9.0 |

is 20 sccm. The highest concentration of carbon monoxide is 50%.

(3) *Relative humidity*: The lowest achievable relative humidity is approximately 7.5%, so the minimum relative humidity is set to 9%. The maximum relative humidity is 100%.

Table 1 shows the 16 experimental conditions designed by Experiment Design Method. Fig. 4 displays the experimental setup.

(1) *Gas flow and flow rate*: The carrier gas was helium with 20% oxygen to simulate the oxygen ratio in the atmosphere. The flow rates of the carrier gas and carbon monoxide gas were controlled using mass flow controllers. The inlet gas concentration was calculated from the flow ratio. The outlet concentration was measured using a quadruple mass spectrometer, QMS.

(2) *Humidification*: The gas mixture was passed through the pipe and merged with liquefied nitrogen, before being humidified in an aeration bottle. It then flowed into the reactor. Constant-temperature aeration controlled using a water bath generated saturated water vapor. The relative humidity was measured using a humidity sensor at the outlet of the aeration bottle.

(3) *Reactor and temperature control*: The gas mixture flowed into the glass reactor of the BET surface area analyzer. The gold catalyst was carried by quartz wool. The glass reactor was covered with heat insulation material to make the temperature distribution uniform. The temperature was measured using thermocouples.
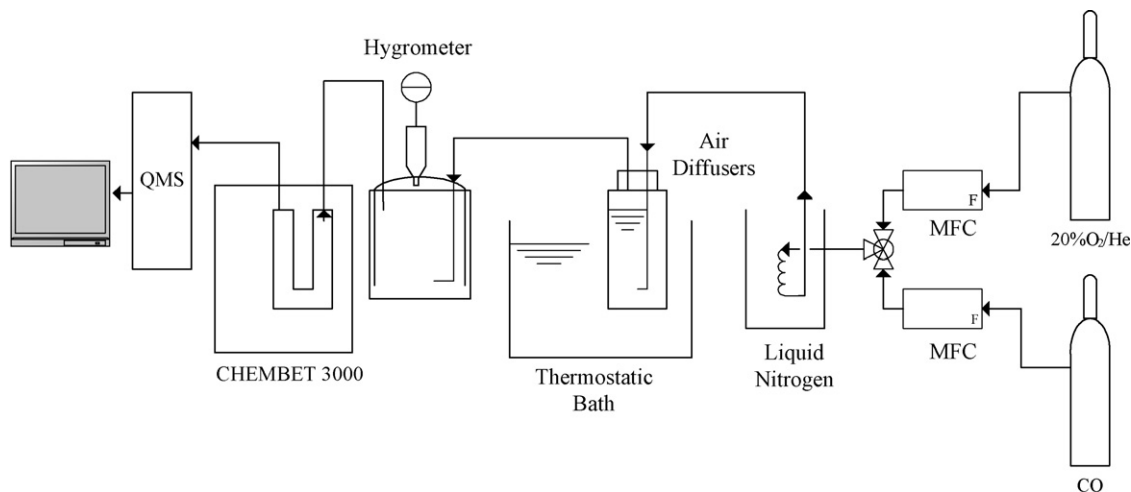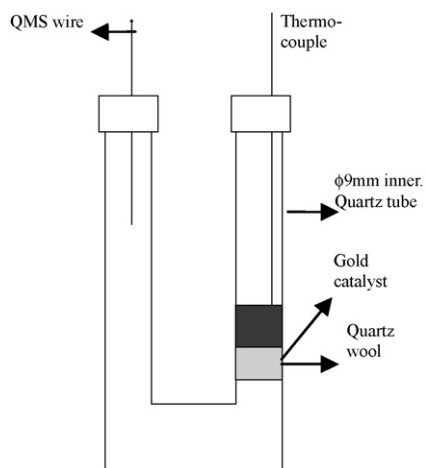


**Fig. 4.** Experiment setup.

**Fig. 5.** Glass reaction tube.

QMS sampling tube was placed at the outlet of the glass reactor to measure the gas concentration (Fig. 5).

At first, helium (20 sccm) flowed continuously and the reactor temperature was maintained at 120 °C for 1 h as the initial condition. The carbon monoxide oxidation tests were performed. The carbon monoxide concentrations were recorded. The convection of carbon monoxide was given by

$$X \ (\%) = \frac{C_i - C_o}{C_i} \times 100 \qquad (1)$$

where $C_i$: inlet carbon monoxide concentration (ppm) and $C_o$: outlet carbon monoxide concentration (ppm).

## 4. Results and discussion

### 4.1. Catalyst specification

The existence of gold particles on the catalyst is demonstrated using X-ray spectroscopy (Fig. 6) with gold (1 1 1) at $2\theta \sim 38°$, $2\theta \sim 44°$, 64° and 77°. A comparison with the JCPDS database reveals two species of iron oxide. One is $2\theta \sim 31°$, 36°, 43°, 58°, 63° maghemite or magnetite. The other is $2\theta \sim 24°$, 34°, 41°, 50°, 54° haematite.
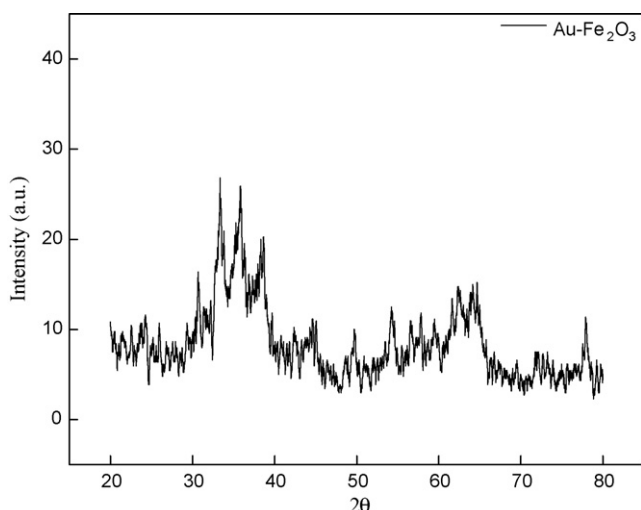


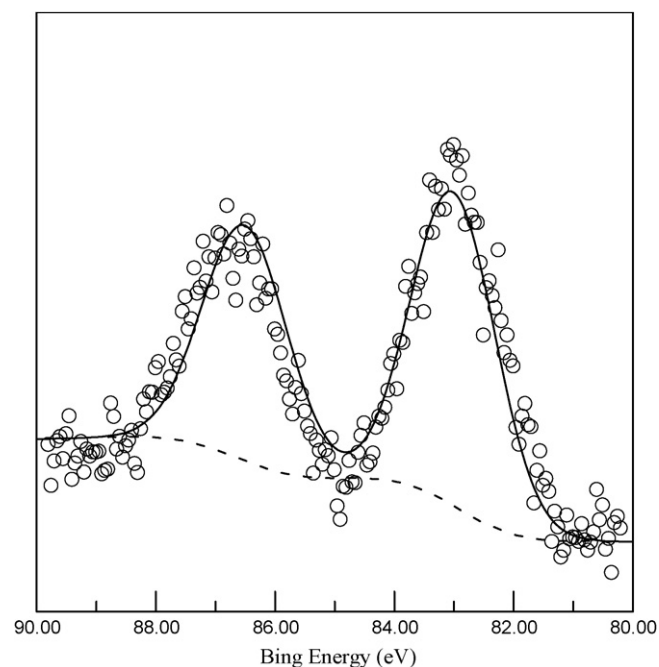**Fig. 6.** The X-ray spectroscopy of gold catalyst.



**Fig. 7.** the electron spectroscopy for chemical analysis (ESCA) spectroscopy of gold catalyst.

The semi-quantitative analysis based on XRF reveals an atom ratio of gold particles to iron oxides of 3.6%. From the BET isotherm adsorption, the total surface area of gold catalyst before the reaction is 168 m²/g, and the total surface area of the gold catalyst after the reaction is 142 m²/g. During the carbon monoxide oxidation, either gas molecules or intermediates are adsorbed on the surface of the catalyst and occupy the activation sites, reducing the total surface area. This assumption is proven by DRIFTS, which indicate
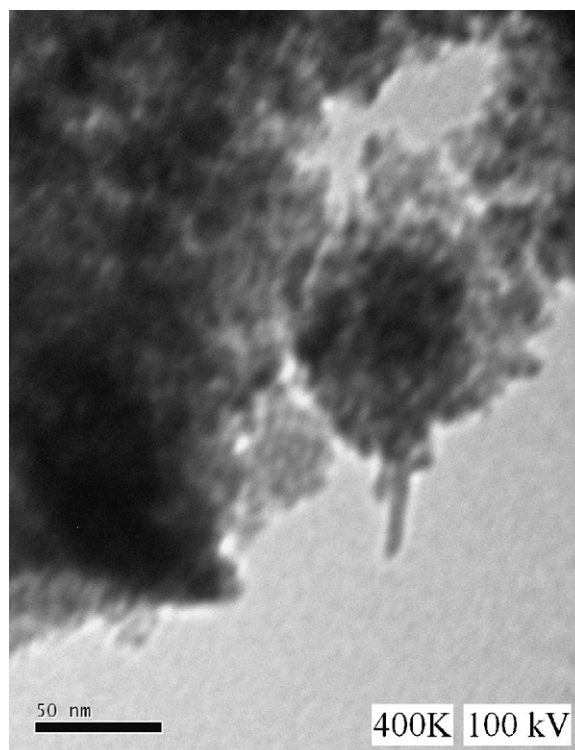


**Fig. 8.** Transmission electron microscopy (TEM) image of gold catalyst.

the functional groups of carbonate, bicarbonate and carboxylate on the catalyst after the carbon monoxide has been oxidized.

Electron spectroscopy for chemical analysis (ESCA) demonstrated that the gold catalyst used herein has two types of activation sites of gold particles (Fig. 7): $Au^{(0)}$ at 83.2 eV, and $Au^{(n+)}$ at 86.6 eV [23]. More gold particles are in the metal form. The transmission electron microscopic (TEM) image (Fig. 8) indicates that the gold particles on gold catalyst are 6–10 nm in size.

## 4.2. Diffuse reflectance infrared Fourier transform spectroscopy

DRIFTS (Fig. 2) was adopted to observe directly the interaction between nano-sized gold catalyst and adsorbate (carbon monoxide) to study the chemical reactions and kinetics of the adsorbed molecules on the surface of catalyst.

The DRIFTS spectra in Fig. 9 indicate the adsorption of 5 sccm carbon monoxide on catalyst at room temperature (without oxygen). At the beginning (Fig. 9a), carbon monoxide adsorption peaks were observed at 2116 cm$^{-1}$ and 2172 cm$^{-1}$. The 2116 cm$^{-1}$ peak indicates the adsorption of carbon monoxide by

Au$^0$ [27], and the 2172 cm$^{-1}$ peak shows the adsorption of carbon monoxide by either the support or Au$^{n+}$. The adsorption peak of carbon dioxide is found at 2340 cm$^{-1}$ [10], which indicates that even without oxygen, carbon monoxide is catalytically oxidized to carbon dioxide at room temperature. The adsorption peaks at 1667 cm$^{-1}$, 1616 cm$^{-1}$, 1541 cm$^{-1}$, 1507 cm$^{-1}$, 1417 cm$^{-1}$, 1405 cm$^{-1}$ and 1220 cm$^{-1}$ represent carbon monoxide adsorption on either gold particles or the support, forming bidentate carbonate (1667 cm$^{-1}$, 1616 cm$^{-1}$) [28]; monodentate carbonate (1507 cm$^{-1}$) [10]; bicarbonate (1417 cm$^{-1}$, 1220 cm$^{-1}$) [29], and carboxylate symmetric stretching (1405 cm$^{-1}$) [30]. The literature has demonstrated that these intermediates (bicarbonate, carboxylate) and inactive products (carbonate) can accumulate and block the sites required for oxygen chemisorption, finally deactivate the catalyst [31,32]. A comparison of Fig. 9b and c indicates that the amount of carbon monoxide adsorption did not increase with time, which suggests that the adsorption of carbon monoxide saturated in the first 5 min. At the 15th min (Fig. 9c), however, carbon monoxide and Au$^0$ bonding appeared at 2047 cm$^{-1}$. As adsorbed carbon monoxide increased, the carbon monoxide and Au$^0$ bonding at
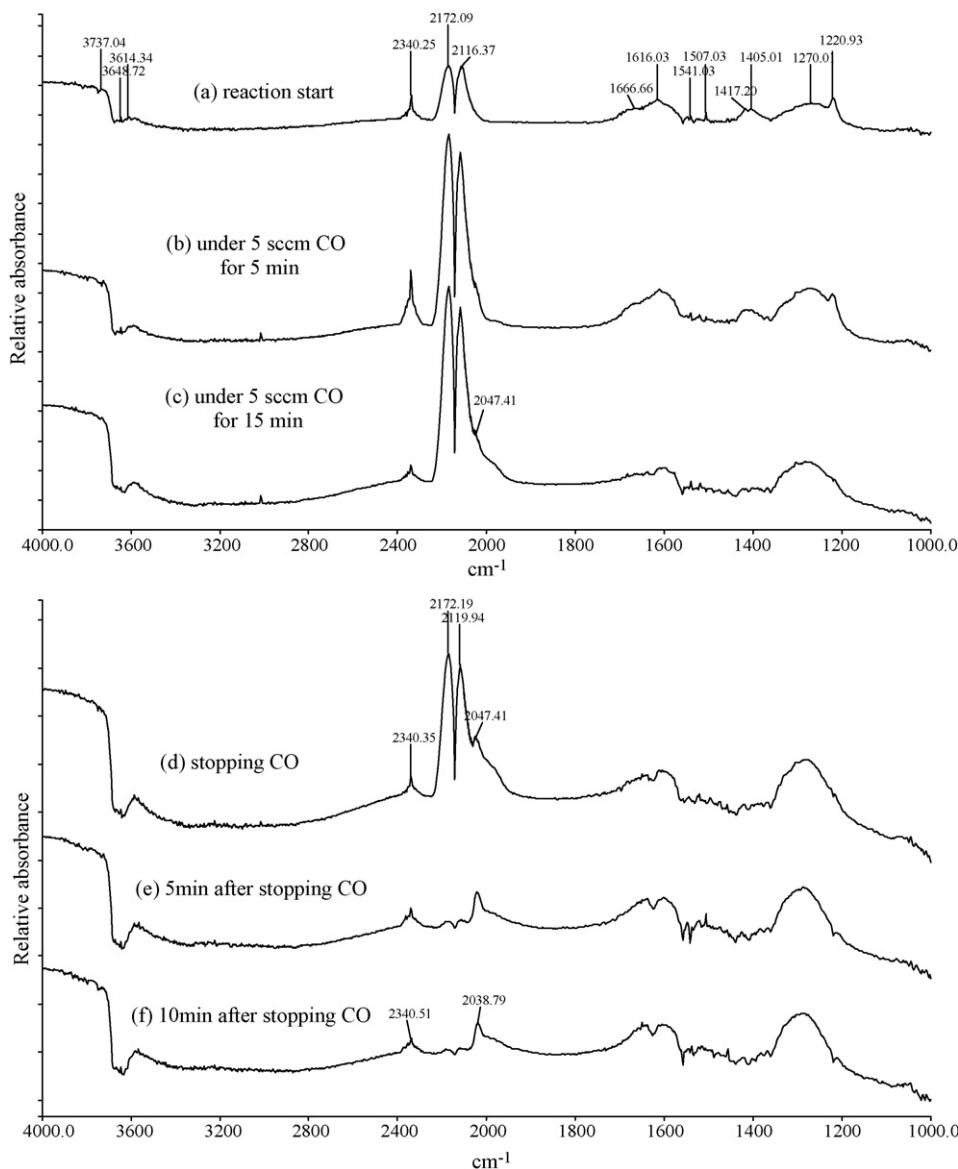


**Fig. 9.** The DRIFTS spectra of gold catalyst at oxygen-free, 5 sccm carbon monoxide. (a) Carbon monoxide 5 sccm was introduced at the beginning. (b) 5 min under carbon monoxide. (c) 15 min under carbon monoxide. (d) Stopped carbon monoxide, purged by helium. (e) 5 min after carbon monoxide stopping. (f) 10 min after carbon monoxide stopping.
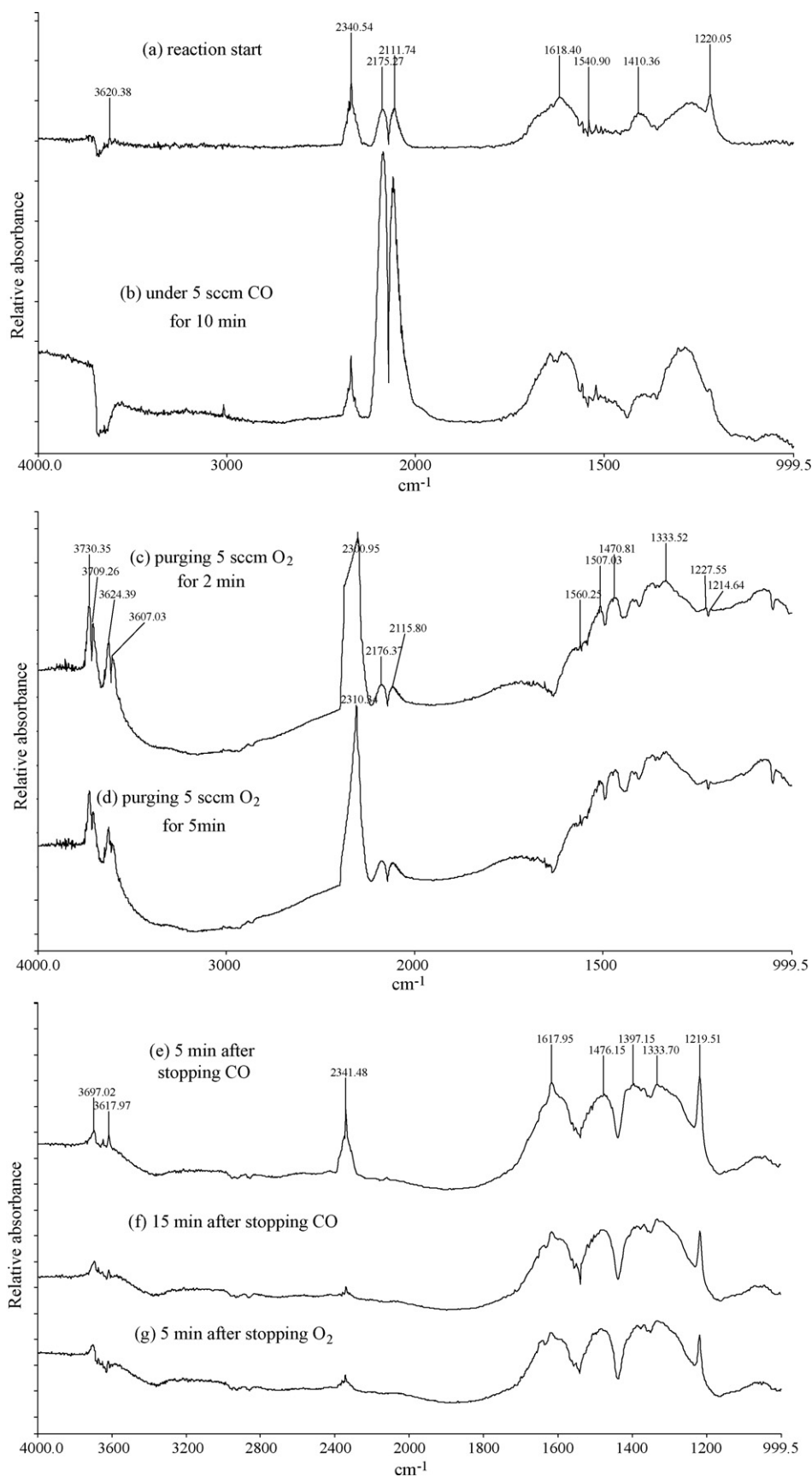
**Fig. 10.** The DRIFTS spectra of gold catalyst at 5 sccm oxygen and 5 sccm carbon monoxide. (a) Carbon monoxide 5 sccm was introduced at the beginning. (b) 10 min under carbon monoxide. (c) Oxygen 5 sccm was added for 2 min. (d) 5 min after adding oxygen. (e) Stopped carbon monoxide for 5 min. (f) Stopped carbon monoxide for 15 min. (g) Stopped oxygen and purged by helium for 5 min.

2116 cm$^{-1}$ saturated and the oxygen molecules were exhausted, so the carbon monoxide bonded at another Au$^0$ site 2047 cm$^{-1}$. The amount of carbon dioxide decreased with time, while amounts of bicarbonate and carbonate remained unchanged. The flow of carbon monoxide was later stopped and the reactor was purged by helium (Fig. 9d). Peaks at 2116 cm$^{-1}$ and 2172 cm$^{-1}$ decreased with time because of the lack of carbon monoxide. The 2038 cm$^{-1}$ peak clearly decreased more slowly than the others, probably because of the strong bonding between carbon monoxide and gold particles (Fig. 9d–f).

DRIFTS spectra in Fig. 10 present the reactions with oxygen. When 5 sccm carbon monoxide was initially introduced (Fig. 10a and b), the signal of the adsorption of carbon monoxide on gold particles, and the signals of bicarbonate, carboxylate and carbonate increased as time, while the amount of carbon dioxide generated decreased as time. 5 sccm oxygen was introduced after 10 min. The adsorption peaks after purging oxygen for 2 min and 5 min (Fig. 10c and d) indicate that the adsorption of carbon monoxide decreased, the signals of carbon dioxide increased, and its peak shifted from 2340 cm$^{-1}$ to 2310 cm$^{-1}$, red-shift phenomenon. Furthermore, the vibration of water molecules at 3400 cm$^{-1}$ decrease, and the higher adsorption peak at 3700–3600 cm$^{-1}$ (the vibration of OH) appeared, suggesting that the water molecules participated in the reactions. After purging oxygen for 5 min, carbon monoxide was stopped (Fig. 10e). The adsorption peak of carbon monoxide on gold particles disappeared; the vibration frequency of carbon dioxide returned to its original position (2310 cm$^{-1}$ → 2340 cm$^{-1}$), and its peak height adsorption decreased with time (Fig. 10e and f). After the 15th min, oxygen was cut off and helium was introduced (Fig. 10f and g) for 5 min. The carbon dioxide signal was weak. However, the bicarbonate, carboxylate and carbonate signals did not decrease.

The possible role of water in the reaction of carbon monoxide oxidation remains unknown. However, water (−OH) was indeed involved in the gold catalytic reaction, as shown in the above DRIFTS spectra. Furthermore, the adsorption/desorption of carbon monoxide and carbon dioxide are observed, along with the intermediate carboxylate, bicarbonate and inactivate carbonate by-products, as described by Okumura [33]. These materials accumulate and deactivate the catalyst. Gold catalysts often lose much of their activity in hours due to either the formation of stable carbonates or the sintering of metal [34].

This deactivation is reversible by heating the catalyst surface [31] or by treatment with water (or H$_2$ + O$_2$) [35]. Therefore, the DRIFTS spectra of Fig. 11 reveal whether the inactive carbonate can be removed by increasing the temperature. Intermediates (carboxylate 1541 cm$^{-1}$ and bicarbonate 1219 cm$^{-1}$) or by-products (carbonate 1479 cm$^{-1}$, 1370 cm$^{-1}$) are present on the gold catalyst following the carbon monoxide oxidation (Fig. 11a). Purging with 10 sccm helium increased the temperature of the reaction chamber. The bicarbonate peak at 1219 cm$^{-1}$ clearly disappeared when it was heated at 50 °C for 20 min (Fig. 11b), but the signals of carboxylate and carbonate did not change. After it had been heated to 100 °C for another 20 min, the signals slightly decreased, but remain unchanged after heating at 150 °C for another 20 min (Fig. 11c). After it had been heated to 200 °C and 250 °C for 20 min, the signals were similar to those after heating at 100 °C. Only the bonding of physical adsorption is assumed to be able to be broken below 250 °C. Heating (<250 °C) to remove the intermediates or by-products works only for bicarbonate, and not for carboxylate or carbonate. The result is similar to the observation that the poisoning by carbonates, in the case of Au/TiO$_2$, is reversible by oxidation at 573 K [32], by evacuation at 673 K, but large particle size is not easily reversed [34].

### 4.3. Experimental design method and analysis of variance

Analysis of variance was performed to study the effects of three experimental variables (total surface area of gold catalyst: 3.36, 18.48, 33.6 m$^3$; CO gas concentration: 10%, 30%, 50%; relative humidity: 9%, 50%, 100%) on the experimental CO conversion (Table 1). Table 2 presents the analysis of variance of the CO conversion at the 10th and 40th min after the start of the reaction. A smaller Prob. > |$t$| value corresponds to a greater effect. Table 2 indicates that the CO gas concentration has the most effect on the CO conversion, followed by the amount of gold catalyst (total surface area), and relative humidity. Increasing the amount of catalyst and reducing the gas concentration (or relative humidity can increase the CO conversion. Additionally, the interaction between the amount of gold catalyst (total surface area) and concentration of CO gas, and the amplification of gas concentration may significantly influence the results.

Table 3 presents the estimated conditions for maximizing the CO conversion at the 10th and 40th min. The results suggest that a greater surface area results in greater CO conversion.
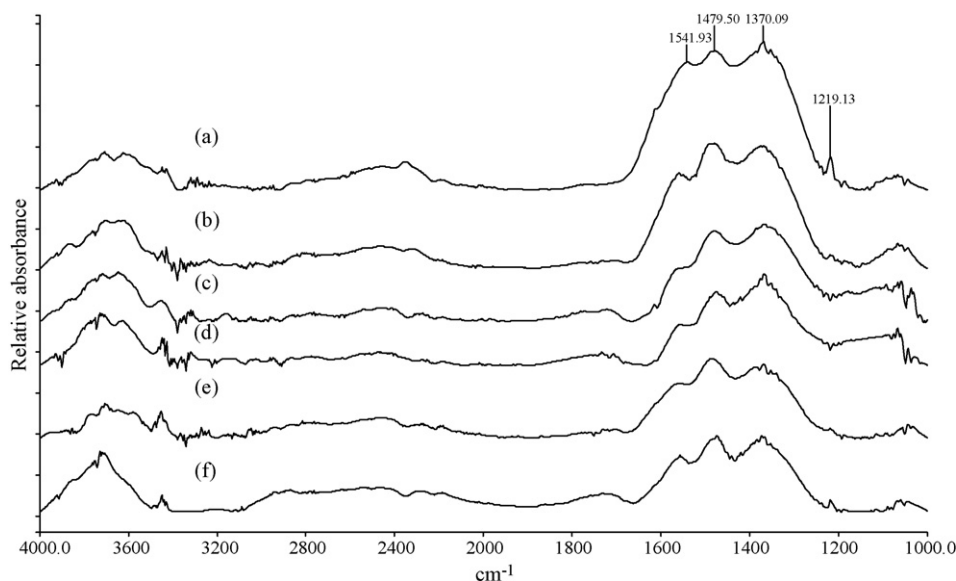


**Fig. 11.** The DRIFTS Spectra of the Gold Catalyst after Carbon Monoxide Oxidation, at 10 sccm Helium. (a) Room temp. (right after carbon monoxide oxidation) (b) 50 °C 20 min. (c) 100 °C, 20 min. (d) 150 °C, 20 min. (e) 200 °C, 20 min. (f) 250 °C, 30 min.

**Table 2**
The analysis of variance at the 10th and 40th min.

| Analysis of variance | At the 10th min | | At the 40th min | |
|---|---|---|---|---|
| | Estimate | Prob. > \|t\| | Estimate | Prob. > \|t\| |
| Intercept | 88.323685 | <0.0001 | 84.061603 | <0.0001 |
| Total surface area & RS | 2.373686 | 0.0137 | 2.3637872 | 0.0892 |
| Gas concentration & RS | −28.43978 | <0.0001 | −28.16031 | <0.0001 |
| Relative humidity & RS | −1.574 | 0.0624 | −0.190 | 0.8760 |
| Total surface area × gas concentration | −0.955 | 0.02614 | −2.8875 | 0.0688 |
| Total surface area × relative humidity | −0.521409 | 0.5234 | −1.830759 | 0.2097 |
| Gas concentration × relative humidity | 0.2131106 | 0.7912 | −0.521233 | 0.7030 |
| Total surface area × total surface area | −0.846207 | 0.5516 | −2.1051724 | 0.3900 |
| Gas concentration × gas concentration | −25.94621 | <0.0001 | −24.14483 | <0.0001 |
| Relative humidity × relative humidity | −1.555754 | 0.2953 | −3.459879 | 0.1828 |

**Table 3**
The conditions for the best CO conversion at the 10th and 40th min.

| | Surface area of gold catalyst ($m^2$) | CO concentration (%) | Relative humidity (%) |
|---|---|---|---|
| 10 min | 33.69 | 18.63 | 22.31 |
| 40 min | 33.69 | 17.22 | 43.28 |

The best CO gas concentrations were approximately 18.63% and 17.22% at the 10th and 40th min, respectively. In this work, the carrier gas of carbon monoxide was 20% oxygen balanced with helium. Therefore, the optimal CO concentration 17.22–18.63% was obtained at a $CO:O_2$ ratio of 1.04–1.14, which is approximately 1:1. This ratio differs from the regular ratio of carbon monoxide oxidation $(2CO + O_2 \rightarrow 2CO_2)$ $CO:O_2 = 2:1$. Water molecules (and water-derived species) were assumed to be involved in the gold catalytic process. This assumption must be verified in the future because uncertainty exists regarding the mechanism of the gold-catalyzed reaction. The optimal relative humidity was 22.31% and 43.28% at the 10th and 40th min, respectively. The effect of water varies with time. According to the literature [19], excess water molecules block the activation sites, reducing the reaction rate at the beginning of the reaction. However, more intermediates are generated later, and the appropriate amount of water can promote the conversion of intermediates to carbon dioxide.

Finally, experiments with the two optimal conditions listed in Table 3 were conducted to confirm the predicted results based on the Experiment Design Method. The actual CO conversion rates in these experiments were very close to the predicted CO conversion rates, with errors of 6.7% and 1.5% at the 10th and 40th min, respectively. Therefore, catalyst surface area, CO gas concentration and relative humidity are very important in determining the catalytic reaction of carbon monoxide on gold catalyst.

## 5. Conclusions

1. Gold particles on the catalyst are identified by X-ray spectroscopy. The support is a mixture of maghemite and magnetite. Semi-quantitative analysis based on XRF indicates that the atomic ratio of gold particles to iron oxides is 3.6%. The BET specific surface area tests indicates that that after the oxidation of carbon monoxide, some gas molecules or intermediates can be adsorbed on the surface of catalyst and occupy the activate sites, reducing the total surface area.
2. DRIFTS spectra indicate the following.
   (1) Carbon monoxide can be adsorbed on gold particles or the support and form carbonate, bicarbonate and carboxylate.
   (2) In the presence of oxygen, the molecular vibration of carbon dioxide is red-shifted. The frequency of the vibration of the water molecule is reduced, and the −OH adsorption peak appeared at 3700–3600 $cm^{-1}$, suggesting that the water molecule was involved in reactions.
   (3) Purging with helium cannot repel the carboxylate and carbonate after the reaction. Other methods should be considered.
3. The effects of catalyst surface area, gas concentration and relative humidity on carbon monoxide oxidation under various conditions were studied.
   (1) The variance analysis indicates that the gas concentration is the most important factor, followed by the mass of the gold catalyst and the relative humidity. The CO convection rate increases as the mass of catalyst increases, the gas concentration decreases or the humidity decreases. Furthermore, the interaction between the amount of gold catalyst, the CO gas concentration and the amplification of gas concentration may significantly affect the results.
   (2) The results show that the conversion efficiency of CO was high when the ratio of CO and $O_2$ was close to 1:1. Water was assumed to participate in the gold-catalyzed process.
   (3) In the initial stage of the reaction, excess water molecules block the activated sites and reduce the oxidation rate of carbon monoxide. However, appropriate humidity enhances the catalytic reaction over the long term by converting intermediates into carbon dioxide.
4. The oxidation of carbon monoxide catalyzed by gold catalyst is an exothermic reaction. Future detailed studies should be performed to understand the reaction mechanisms.

## References

[1] Y. Ho, G. Cho, High activities gold catalyst, Chemical Engineering Technology 11 (2003) 178–183 (in Chinese).
[2] M. Haruta, N. Yamada, T. Kobayashi, H. Sano, Catalysis Letters 405 (1987).
[3] M. Tung, Y. Chen, Nano-sized gold catalyst, Science Development 390 (2005) 46–49 (in Chinese).
[4] G.C. Bond, Gold: a relatively new catalyst, Catalysis Today 72 (2002) 5–9.
[5] G.C. Bond, The catalytic properties of gold, Gold Bulletin 5 (1972) 11–13.
[6] R.S. Yolles, B.J. Wood, H. Wise, Hydrogenation of alkenes on gold, Journal of Catalysis 21 (1971) 66–69.
[7] M. Haruta, Catalysis of gold nanoparticles deposited on metal oxides, CATTECH 6 (2002) 102–115.
[8] M. Shibata, Y. Ohbayashi, N. Kawata, T. Masumoto, K. Aoki, Methanol synthesis reaction over copper-group IV metal amorphous alloys as catalyst precursor, Journal of Catalysis 96 (1985) 292–298.
[9] M. Haruta, N. Yamada, T. Kobayashi, Gold catalysts prepared by coprecipitation for low-temperature oxidation of hydrogen and of carbon monoxide, Journal of Catalysis 115 (1989) 301–309.
[10] M.A. Bollinger, M.A. Vannice, A kinetic and DRIFTS study of low-temperature carbon monoxide oxidation over Au–TiO₂ catalysts, Applied Catalysis B: Environmental 8 (1996) 417–443.
[11] G. Srinivas, J. Wright, C.-S. Bai, R. Cook, Studies in Surface Science and Catalysis 101 (1996) 427.
[12] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, Low-temperature oxidation of co over gold supported on TiO₂, α-Fe₂O₃, and Co₃O₄, Journal of Catalysis 144 (1993) 175–192.
[13] M.M. Schubert, S. Hackenberg, A.C. van Veen, M. Muhler, V. Jtech Plzak, R.J. Behm, CO oxidation over supported gold catalysts—inert and active support materials and their role for the oxygen supply during reaction, Journal of Catalysis 197 (2001) 113–122.
[14] J.-D. Grunwaldt, A.J. Baiker, Gold/titania interfaces and their role in carbon monoxide oxidation, Journal of Physical Chemistry B 103 (1999) 1002–1012.

[15] A.K. Tripathi, V.S. Kamble, A.P. Kozlova, T. Shido, K. Asakura, Y. Iwasawa, Active oxygen species and mechanism for low-temperature CO oxidation reaction on a $TiO_2$-supported Au catalyst prepared from $Au(PPh_3)(NO_3)$ and As-precipitated titanium hydroxide, Journal of Catalysis 185 (1999) 252–264.

[16] F. Boccuzzi, A. Chiorino, S. Tusbota, M. Haruta, FTIR study of carbon monoxide oxidation and scrambling at room temperature over gold supported on ZnO and $TiO_2$, Journal of Physical Chemistry 100 (1996) 3625–3631.

[17] Y. Chen, P. Crawford, P. Hu, recent advances in understanding CO oxidation on gold nanoparticles using density functional theory, Catalysis Letters 119 (2007) 21–28.

[18] G.C. Bond, D.T. Thompson, Gold-catalyzed oxidation of carbon monoxide, Gold Bulletin 33 (2000) 41–51.

[19] M. Daté, M. Haruta, Moisture effect on CO oxidation over $Au/TiO_2$ catalyst, Journal of Catalysis 201 (2001) 221–224.

[20] H.H. Kung, M.C. Kung, C.K. Costello, Supported Au catalysts for low temperature CO oxidation, Journal of Catalysis 216 (2003) 425–432.

[21] M. Daté, M. Okumura, S. Tsubota, M. Haruta, Vital role of moisture in the catalytic activity of supported gold nanoparticles, Angewandte Chemie International Edition 43 (2004) 2129–2132.

[22] L.M. Liu, B. McAllister, H.Q. Ye, P. Hu, Identifying an $O_2$ supply pathway in CO oxidation on $Au/TiO_2$ (1 1 0): a density functional theory study on the intrinsic role of water, Journal of the American Chemical Society 128 (2006) 4017–4022.

[23] J.M.C. Soares, P. Morrall, A. Crossley, H. Peter, B. Michael, Catalytic and non-catalytic CO oxidation on $Au/TiO_2$ catalysts, Journal of Catalysis 219 (2003) 17–24.

[24] D.T. Thompson, G.C. Bond, Catalysis by gold, Catalysis Reviews: Science and Engineering 41 (1999) 319–388.

[25] S. Galvagno, G. Parravano, J. Schwank, Isotopic oxygen exchange on supported Ru and Au catalysts, Journal of Catalysis 63 (1980) 415–425.

[26] N. Funazaki, A. Hemmi, S. Ito, Y. Asano, S. Yamashita, T. Kobayashi, M. Haruta, Development of carbon monoxide detector using Au fine particles-doped $\alpha$-$Fe_2O_3$, Sensors and Actuators B: Chemical 14 (1993) 536–538.

[27] M.A. Debeila, N.J. Coville, M.S. Scurrel, G.R. Hearne, DRIFTS studies of the interaction of nitric oxide and carbon monoxide on $Au–TiO_2$, Catalysis Today 72 (2002) 79–87.

[28] K. Tanaka, J.M. White, Characterization of species adsorbed on oxidized and reduced anatase, Journal of Physical Chemistry 86 (1982) 4708–4714.

[29] G. Smit, N. Strukan, M.W.J. Craj, L. Karoly, A comparative study of CO adsorption and oxidation on $Au/Fe_2O_3$ catalysts by FT-IR and in situ DRIFTS spectroscopies, Journal of Molecular Catalysis A: Chemical 252 (2006) 163–170.

[30] A.A. Davydov, C.H. Rochester (Eds.), Infrared Spectroscopy on the Surface of Transition Metal Oxide, Wiley, Chichester, 1984, p. 316.

[31] P. Konova, A. Naydenov, C. Venkov, D. Mehandjiev, D. Andreeva, T. Tabakova, J. Molec, Activity and deactivation of $Au/TiO_2$ catalyst in CO oxidation, Journal of Molecular Catalysis A: Chemical 213 (2004) 235–240.

[32] F. Moreau, G.C. Bond, Gold on titania catalysts: influence of some physico-chemical parameters on the activity and stability for the oxidation of carbon monoxide, Applied Catalysis A: General 302 (2006) 110.

[33] M. Okumura, Report of The Research Achievements of Interdisciplinary Basic Research Section: The abilities and Potential of Gold as a Catalyst, Osaka National Research Institute, Report no. 393, 1999.

[34] F. Moreau, G.C. Bond, B. van der Linden, B.A.A. Silberova, M. Makkee, Gold supported on mixed oxides for the oxidation of carbon monoxide, Applied Catalysis A: General 347 (2008) 208–215.

[35] M. Azar, V. Caps, F. Morfin, J.-L. Rousset, A. Piednoir, J.-C. Bertolini, L. Piccolo, Insights into activation, deactivation and hydrogen-induced promotion of a $Au/TiO_2$ reference catalyst in CO oxidation, Journal of Catalysis 239 (2006) 307–312.