



# Influence of pretreatment conditions on low-temperature CO oxidation over Au/MO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts

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## Abstract

Composite oxide MO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> supported gold catalysts for low-temperature CO oxidation were prepared and investigated. The presence of transition metal oxide was proved to be beneficial to the improvement of catalytic performance of Au/Al<sub>2</sub>O<sub>3</sub> catalysts for low-temperature CO oxidation. Furthermore, the influence of various pretreatment conditions on Au/MO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts was studied carefully. The image of TEM showed that gold catalyst with small gold particles only in the form of a fine dispersion exhibited highly catalytic activity. The XPS, Fourier transform infrared (FTIR) spectroscopy characterization results of Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst showed that gold catalysts having partially oxidized gold species have the best catalytic performance. One possible pathway for CO oxidation on Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is that the CO adsorbed on gold particles reacts with adsorbed oxygen, which is possible to occur on oxygen vacancies on the support or at the metal–support interface. © 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Gold catalyst; CO oxidation; Composite oxide support; Pretreatment conditions; Gold nanoparticle

## 1. Introduction

The low reactivity of gold is attributed to the completely filled 5d atomic orbital and the relatively high value of its first ionization potential [1]. Since Haruta et al. [2] reported that CO oxidation could be achieved at room temperature over gold catalysts when very small gold nanoparticles were dispersed on suitable oxide supports. The last decade has witnessed a rapid growth of interest in the catalysis by gold. Recently, Bond and Thompson [3] have reviewed the advancement of gold catalysts in tension and depth.

The choice of the prepared method is very critical for gold catalyst performances. Among the reported

methods, co-precipitation (CP) or deposition precipitation (DP) was employed frequently. CP is easy to control with a powder sample obtained. DP has the advantage over CP in that all of the active components remain on the surface of the support and none active gold component is buried within it. This method is also applicable to any form of support, such as beads, honeycombs and thin film [4]. But it is very difficult to control the properties of a supported gold catalyst prepared by DP, because they are highly sensitive to preparation condition [5].

Although the use of gold catalysts for low-temperature CO oxidation has been studied intensively, many aspects concerning gold catalytic behaviors are yet unclear. The presence of gold as small particles appear to be crucial for the high-activity [6,7]. Previous comparative studies showed that the activity of supported

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gold catalysts depends sensitively on the support materials [8–10]. Gold catalysts on a single oxide support were extensively studied. Also, some composite oxide supports, such as  $\text{ZnFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$  [11] were investigated. Recently, the composite oxides supports of  $\text{MO}_x/\text{Al}_2\text{O}_3$  were employed by Grisel and Nieuwenhuys to prepare the  $\text{Au}/\text{MO}_x/\text{Al}_2\text{O}_3$  catalysts, and used for oxidation of CO and  $\text{CH}_4$  [12] and CO selective oxidation in  $\text{H}_2$ -rich gas [13].

$\text{Al}_2\text{O}_3$  is a most common kind of oxide used as support in industrial catalytic process. However,  $\text{Al}_2\text{O}_3$  is not regarded as a good support for gold catalysts. Schubert et al.'s studies [8] showed that  $\text{Al}_2\text{O}_3$  was very different from reducible oxides such as  $\text{FeO}_x$ ,  $\text{NiO}_x$ ,  $\text{CoO}_x$  and so on. When gold supported on the former oxide, which is believed to behave as neutral in the reaction process, only moderately active catalysts obtained. However, Au catalysts supported on reducible transition metal oxides exhibited very high activities. Perhaps, this resulted from synergistic effects between the gold nanoparticles and support material [2,8,10,14,15]. Therefore, gold catalysts supported on composite  $\text{MO}_x/\text{Al}_2\text{O}_3$  supports seem to have the possibility to realize the commercialization of high-activity catalysts. It is desirable to develop this kind of  $\text{Au}/\text{MO}_x/\text{Al}_2\text{O}_3$  catalysts for practicable applications.

In this paper, various composite  $\text{MO}_x/\text{Al}_2\text{O}_3$  supported gold catalysts were prepared, and the influence of pretreatment conditions on the catalytic activity was investigated. Characterization techniques, such as XPS, X-ray diffraction (XRD), TEM and Fourier transform infrared spectroscopy (FTIR) were employed to study the CO oxidation on  $\text{Au}/\text{FeO}_x/\text{Al}_2\text{O}_3$  catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

$\gamma\text{-Al}_2\text{O}_3$  (surface area =  $169\text{ m}^2\text{ g}^{-1}$ , total pore volume =  $0.41\text{ ml g}^{-1}$ , particle size = 1  $\mu\text{m}$ ) was used as support.  $\text{M}(\text{NO}_3)_n \cdot m\text{H}_2\text{O}$  was the precursor of the corresponding metal oxide ( $\text{MO}_x$ ). Composite  $\text{MO}_x/\text{Al}_2\text{O}_3$  supports were prepared via iso-volume impregnation. The samples were dried at 373 K over night, heated to 673 K with a heating rate of

$10\text{ K min}^{-1}$  and kept for 2 h. An aqueous solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was used as Au precursor. Au was dispersed on support materials, such as  $\text{Al}_2\text{O}_3$  and  $\text{MO}_x/\text{Al}_2\text{O}_3$ , by homogeneous deposition precipitation (HDP) using urea as a precipitation reagent. The suspensions were kept at 350 K under vigorous stirring to ensure a slow and gradual increase of pH value. When the pH reached 8.0, the suspensions were filtered and washed thoroughly to remove chloride ions. The samples were dried overnight at 373 K and subsequently calcined at different temperatures under a heating rate of  $10\text{ K min}^{-1}$ .

### 2.2. Activity evaluation

The activity of the catalysts for CO oxidation was evaluated in a fixed bed reactor. The  $\text{CO} + \text{O}_2 + \text{N}_2$  ( $\text{CO}$ : 0.5%,  $\text{O}_2$ : 21.1%,  $\text{N}_2$ : 78.4%) mixture passed through the catalyst bed with a space velocity (SV) of about  $8000\text{ h}^{-1}$ . The reactants and the products were analyzed using a gas chromatograph (SQ-206), equipped with a hydrogen flame ionization detector connected with a carbon sieve 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.

### 2.3. Catalyst characterization

A NOVA 1200 high-speed gas sorption analyzer was used to determine the BET surface area and the pore volume distribution of the samples. The Au content of the catalysts was analyzed with inductively coupled plasma-atom emission spectroscopy (ICP-AES) using a IRIS Advantage spectrometer. X-ray diffraction measurements were carried out on a Rigaku D/Max-Rc X-ray diffractometer with  $\text{Cu K}\alpha$  radiation. A XSAM 800 system was used for XPS measurements, with  $\text{Al K}\alpha$  radiation as a target. The TEM measurements were performed on a Hitachi H-700 electron microscope equipped with an EDAX 9100 spectroscopy. Maximum resolution was 0.34 nm at 250,000 magnifications.

The Fourier transform infrared spectroscopy measurements were performed on a Hitachi 270-30 infrared spectrophotometer with a  $2\text{ cm}^{-1}$  resolution at room temperature. The catalysts were pressed in flake, and then placed into a special vacuum cell, which

allowed catalyst evaluation and sequential CO adsorption. The samples were evaluated at 473 K for 2 h and then cooled down room temperature. IR spectra were in situ scanned at room temperature for 1 h after sequential CO adsorption. The spectra were obtained by subtracting the background of the sample prior to the CO adsorption and IR adsorption of CO in gas phase.

### 3. Results and discussion

#### 3.1. Influence of composite $\text{FeO}_x/\text{Al}_2\text{O}_3$ supports

The activity of  $\text{FeO}_x/\text{Al}_2\text{O}_3$  and various gold catalysts on different supports are listed in Table 1.  $\text{FeO}_x/\text{Al}_2\text{O}_3$  was found not to be particularly active in CO oxidation. In fact, no obvious CO conversion was detected until 420 K. Table 1 gives an example of the activity of different catalysts. Au/ $\text{Fe}_2\text{O}_3$  catalyst made by CP [9] is more active than Au/ $\text{Al}_2\text{O}_3$  catalyst prepared by HDP, and Au/ $\text{FeO}_x/\text{Al}_2\text{O}_3$  catalyst clearly exhibits a better performance than Au/ $\text{Al}_2\text{O}_3$  catalyst. Support  $\text{Al}_2\text{O}_3$  has a specific surface area of approximately  $169 \text{ m}^2 \text{ g}^{-1}$ . The surface area of Au/ $\text{Al}_2\text{O}_3$  and Au/ $\text{FeO}_x/\text{Al}_2\text{O}_3$  catalyst is about 166.7 and  $154.8 \text{ m}^2 \text{ g}^{-1}$ , respectively, which are very close to  $\text{Al}_2\text{O}_3$ . Fig. 1 shows that the pore volume distribution of  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}_x/\text{Al}_2\text{O}_3$  and Au/ $\text{FeO}_x/\text{Al}_2\text{O}_3$ . Just a slight loss of pore volume is observed when prepared gold catalyst on composite  $\text{FeO}_x/\text{Al}_2\text{O}_3$  support.

Fig. 2 shows a TEM image of Au/ $\text{Al}_2\text{O}_3$  and Au/ $\text{FeO}_x/\text{Al}_2\text{O}_3$  catalysts. Gold particles are clearly visible as spherical dark particles embedded in lighter patches of metal oxide. In Fig. 2b, no isolated areas of  $\text{FeO}_x$  are formed.  $\text{FeO}_x$  is rather homogeneously distributed on the surface. TEM investigations reveal that Au/ $\text{FeO}_x/\text{Al}_2\text{O}_3$  and Au/ $\text{Al}_2\text{O}_3$  catalysts, which have comparable gold particle size distributions (most of the particles in the range of 3–6 nm), result to be

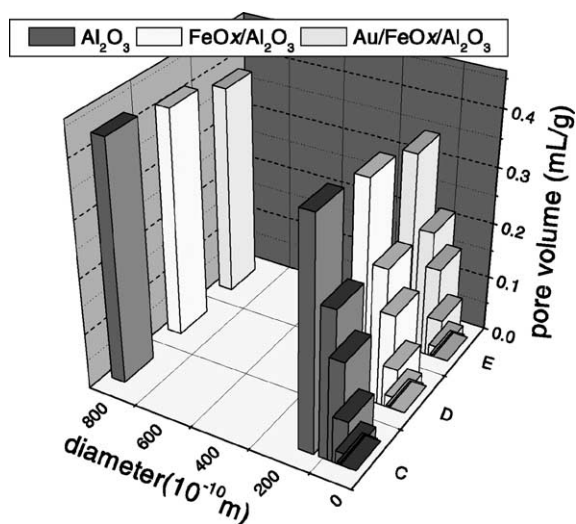


Fig. 1. Pore volume distributions of  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}_x/\text{Al}_2\text{O}_3$  and Au/ $\text{FeO}_x/\text{Al}_2\text{O}_3$ .

significantly different in the catalytic activities in CO oxidation. The  $T_{100\%}$  of Au/ $\text{FeO}_x/\text{Al}_2\text{O}_3$  catalyst is much lower than Au/ $\text{Al}_2\text{O}_3$  catalyst. This shows that the catalytic activity depends on both the gold particle size and the nature of the support.

#### 3.2. Influence of different support materials

The experimental results (Table 2) indicated clearly that the performances of Au catalysts were greatly improved by using composite oxide supports. Compared with literature data [12], the catalysts in this study showed excellent catalytic behavior. The  $T_{100\%}$  of Au/ $\text{Al}_2\text{O}_3$  catalyst is lower 136 K than Grisel's reaction data [12]. It was  $\text{FeO}_x/\text{Al}_2\text{O}_3$  as composite oxide support that enhanced the catalyst performance enormously. Au/ $\text{FeO}_x/\text{Al}_2\text{O}_3$  catalyst can oxidize CO to  $\text{CO}_2$  even at 223 K. The activity order for low-temperature CO oxidation is Au/ $\text{FeO}_x/\text{Al}_2\text{O}_3 >$

Table 1  
CO conversion over different catalysts

Catalyst	Preparation method	Surface area ( $\text{m}^2 \text{ g}^{-1}$ )	Conversion (273 K) (%)	Conversion (573 K) (%)	$T_{100\%}$ (K)
$\text{FeO}_x/\text{Al}_2\text{O}_3$	Impregnation	160	0	43	>673
Au/ $\text{Al}_2\text{O}_3$	HDP	166	85	100	288
Au/ $\text{Fe}_2\text{O}_3$	CP	136	100	100	251 [11]
Au/ $\text{FeO}_x/\text{Al}_2\text{O}_3$	HDP	154	100	100	223

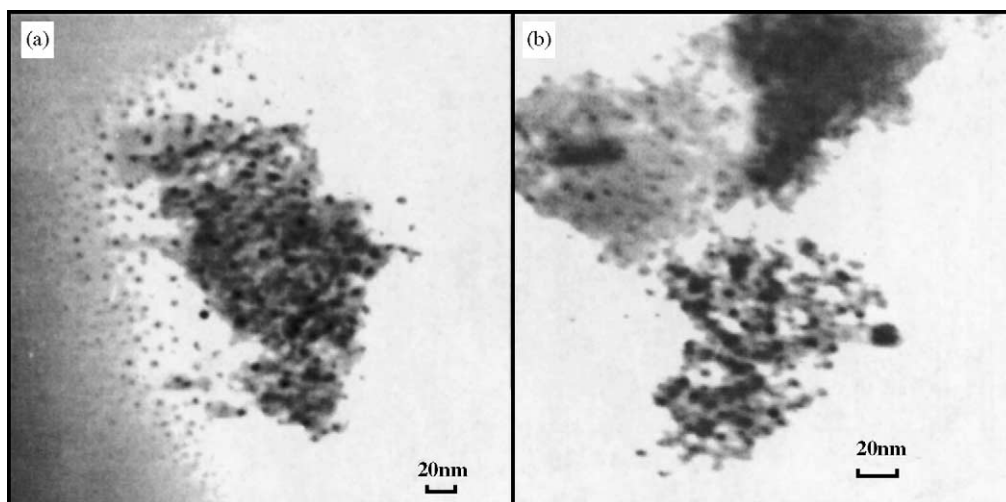


Fig. 2. TEM images of (a) Au/Al<sub>2</sub>O<sub>3</sub> catalyst, and (b) Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts.

Au/MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, Au/CoO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> > Au/CuO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> > Au/NiO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. This shows that the nature of the composite oxide supports plays an important role on the activity improvement of gold catalysts.

Fig. 3 shows an acceptable homogeneous size distribution of Au/MO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. All the observed

gold particles are very small, most of them in the range of 3–6 nm. It shows that nano-sized, well-dispersed gold particle is necessary to obtain high-activity Au catalysts, which also confirms that nano-sized gold particles are prerequisite for high-activity gold catalysts. However, the interaction between gold and transition metal oxide appears to be also of substantial importance in the case of CO oxidation.

Table 2

CO oxidation activity of MO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and Au/MO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts

	$T_{100\%}^a$ (K)	$T_{99\%}^b$ (K)
Catalyst MO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>		
Al <sub>2</sub> O <sub>3</sub>	>673	
MnO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	>673	
FeO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	608	
CoO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	563	
NiO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	>673	
CuO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	623	
Catalyst Au/MO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>		
Au/Al <sub>2</sub> O <sub>3</sub>	288	424
Au/MnO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	243	<298
Au/FeO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	223	373
Au/CoO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	243	387
Au/NiO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	311	350
Au/CuO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	250	417

<sup>a</sup> The Au loading is 0.5 wt.%, M 5 wt.%, determined by ICP-AES; 0.5% CO + 21.1% O<sub>2</sub> + 78.4% N<sub>2</sub> was passed the catalysts bed at the flow of 30 ml min<sup>-1</sup>, the space velocity of 8000 h<sup>-1</sup>.

<sup>b</sup> The reaction data from reference [12]. The Au loading is 5 wt.%, Au:M atomic ratio of 1; 2% CO + 2% O<sub>2</sub> + 96% He was passed the catalysts bed at the flow of 30 ml min<sup>-1</sup>.

### 3.3. Influence of Au loading

The relationship between the activity and the Au loading of Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is listed in Table 3. The high-activity depended on the content of gold in the catalyst, the higher the gold content, and the lower the  $T_{100\%}$ . The optimum Au content

Table 3

Influence of pretreatment conditions on catalytic performance of Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts

Catalyst	Au loading (wt.%)	Precipitation reagent	$T_{100\%}$ (K)
1	0.05	NH <sub>2</sub> (CO)NH <sub>2</sub>	>373
2	0.1	NH <sub>2</sub> (CO)NH <sub>2</sub>	251
3	0.5	NH <sub>2</sub> (CO)NH <sub>2</sub>	223
4	0.1	Na <sub>2</sub> CO <sub>3</sub>	281
5	0.1	NaOH	283
6	0.1	KOH	280
7	0.1	NH <sub>4</sub> OH	285

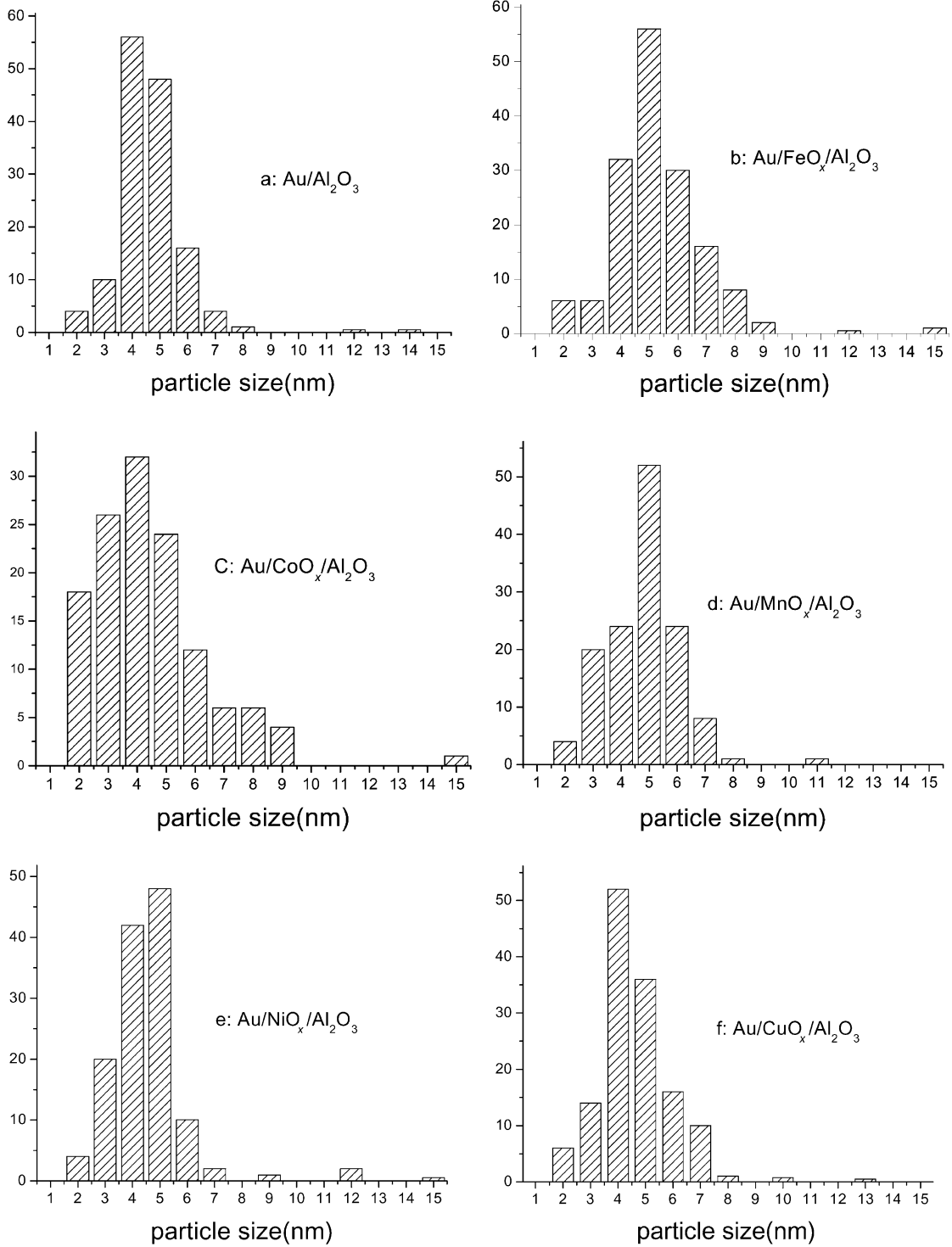


Fig. 3. Gold particle size distributions of Au/MO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts determined by TEM.

is 0.5 wt.%, which has an appreciably high catalytic activity ( $T_{100\%}$  is 223 K). On the other hand, the long-term stability of the catalyst was also related to the gold content. 0.1 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was found to have a sustained activity without deactivation during 57 h at room temperature in the condition of SV 8000 h<sup>-1</sup>. However, the activity for 0.5 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is more than 150 h in SV of 11,000 h<sup>-1</sup>. Changing SV from 11,000 to 25,000 h<sup>-1</sup>, the catalyst still converted CO to CO<sub>2</sub> completely for more than 20 h without any deactivation. This indicates 0.5 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst possesses high-activity and good catalytic durability.

### 3.4. Influence of precipitation reagents

It can be seen from Table 3 that the variation of the precipitation reagents did not affect the catalytic activity of gold catalysts more except for urea. Using NaOH, KOH or NH<sub>4</sub>OH instead of Na<sub>2</sub>CO<sub>3</sub> elucidated that Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, CO<sub>3</sub><sup>-</sup> and so on have little effect on the catalytic activity of the synthesized materials. Compared with the other precipitation reagents, the high-activity of Au catalyst prepared by urea precipitation is due to its slow and uniform decomposition to produce hydroxide ions in preparation process.

### 3.5. Influence of pH value of precipitation solution

The catalytic activity of supported gold catalysts was found to depend strongly on the pH value of

the precipitation solution, since dissolution of HAuCl<sub>4</sub> (gold precursor) in water may yield three kinds of possible gold species. At pH 5.5–7.0, most of the Au precursor is present as AuCl<sub>n</sub>(OH)<sub>4-n</sub><sup>-</sup>, which can dissolve in water. At pH value around 7–8, most of the Cl<sup>-</sup> will be displaced by OH<sup>-</sup> then leading to a neutrally charged Au(OH)<sub>3</sub> species, which precipitates from the solution. Under basic condition, the Au(OH)<sub>3</sub> can dissolve again as Au(OH)<sub>4</sub><sup>-</sup>.

The pH of the precipitation solution is very important not only to determine the speciation of AuCl<sub>n</sub>(OH)<sub>4-n</sub><sup>-</sup>, but also influences the amount of chloride adsorbed on the support. The amount of adsorbed chloride on a support depends on the isoelectric point of the support and its adsorption capacity [16]. The varied metal oxide has different optimum pH value for the synthesis of active gold catalysts. The optimum pH of Au/Al<sub>2</sub>O<sub>3</sub> (the isoelectric points of Al<sub>2</sub>O<sub>3</sub> is ~9) is 5.5–8.5 [17]; that of Au/TiO<sub>2</sub> (the isoelectric points of TiO<sub>2</sub> is ~6–7) 7.0; and that of Au/MgO (the isoelectric points of MgO is ~12) 9.6 [18].

Fig. 4 shows the effect of pH value of precipitation solution on the  $T_{100\%}$  of 0.1 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. The pH value dramatically affected the activity of the gold catalysts. Below pH 7, the  $T_{100\%}$  was as high as 312 K. With an increasing of the pH value, the  $T_{100\%}$  became lower and lower. When the pH value reached 8.0, the best catalytic activity was obtained which can catalytically oxidize CO to CO<sub>2</sub> even at 251 K. The activity decreases slowly with the

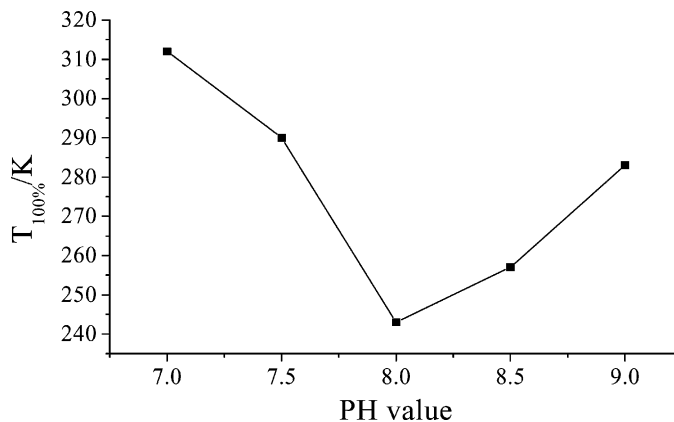


Fig. 4. Influence of pH on catalytic performance of 0.1 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.



continuous increasing of the pH. As a result, the optimum pH to prepare Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst from precipitating solution was around 8.0–8.5.

### 3.6. Influence of calcinations temperature

Among the gold species on supported Au catalysts prepared by the DP method, Au(OH)<sub>3</sub> of deposited gold species is thermally unstable at 373 K, and tends to decompose into metallic gold during the drying treatment.



The dominant gold species remaining on the dried sample could be the chloride-contaminated gold species (mainly AuCl<sub>n</sub>(OH)<sub>4-n</sub><sup>-</sup>), which are not active gold species. It is therefore of interest to determine the minimum temperature required for decomposition of this chloride-contaminated gold to active gold species.

We investigated the influence of the calcinations temperature on the catalytic activity by treating the as-made materials at different temperatures. The results show in Fig. 5. The catalysts pretreated in air at 373 K over night had already had certain activity, which can oxidize CO to CO<sub>2</sub> at 295 K. With the increase of calcinations temperature, the catalytic activity increased higher. The catalyst calcined at 573 K showed the best catalytic activity ( $T_{100\%}$  is 251 K). Above 573 K, the catalytic activity began to decrease. Perhaps for the reason of sintering, the catalyst cal-

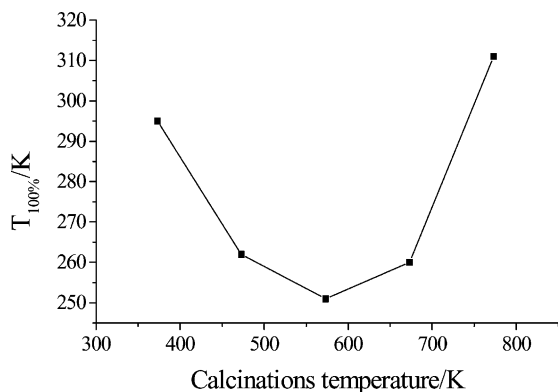


Fig. 5. Influence of calcinations temperature on catalytic performance of 0.1 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.

culated at 773 K showed a very low activity for CO oxidation.

### 3.7. Catalyst structure characterizations

XPS spectra of the Au 4f and Fe 2p binding energies of 0.5 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, which was calcined at 573 K with  $T_{100\%}$  223 K, are showed in Fig. 6. The peaks of Au 4f<sub>5/2</sub> and 4f<sub>7/2</sub> are centered at 87.7 and 84.3 ( $\Delta = 3.4$  eV), respectively, which are very close to the binding energy of metallic Au, and far from the binding energy of Au<sup>δ+</sup>. While Au 4f<sub>7/2</sub> peaks of Au<sup>0</sup> (e.g. Au), Au<sup>+</sup> (e.g. AuCl) and Au<sup>3+</sup> (e.g. NaAuCl<sub>4</sub>) are centered at 83.8, 86.1 and 87.3 eV, respectively. The results of XPS indicated that the most portion of gold species on the catalyst surface were metallic gold, with minor portion gold species might be in an oxidized state. Our previous studies [11] showed that the catalyst precipitation precursor was Au(OH)<sub>3</sub>, when it was treated in an oxygen

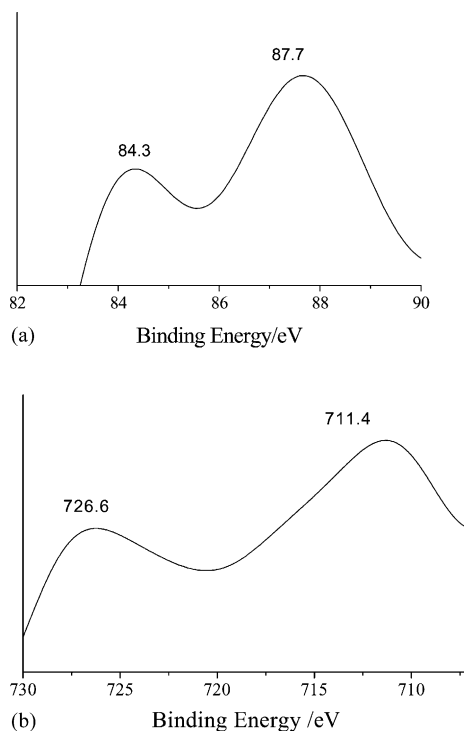


Fig. 6. (a) XPS spectra of Au 4f peak of 0.5 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. (b) XPS spectra of Fe 2p peak of 0.5 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.

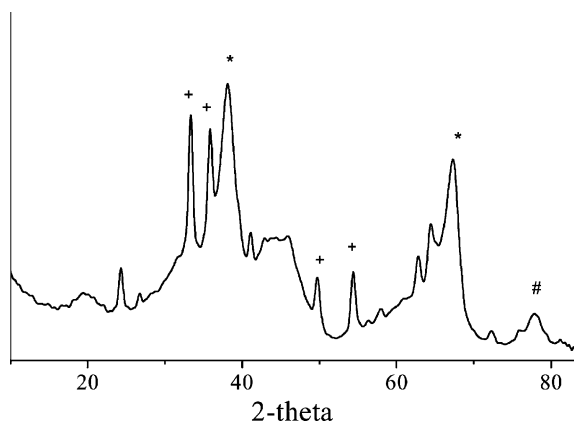


Fig. 7. XRD spectra of 0.5 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts; (#) metallic gold; (\*)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; (+) Fe<sub>2</sub>O<sub>3</sub>.

atmosphere at a relatively low-temperature, gold retained certain oxidized state. The oxidized Au phase was reduced almost completely to metallic Au with the increasing calcinations temperature. However, the gold catalysts with partially oxidized gold species had the best catalytic performance for CO oxidation. Park and Lee [19] also proved that the oxidation of gold species was important for CO oxidation, and they concluded that oxidized gold species were more active than metallic gold. This is different from our results. Our results supported the hypothesis suggested by Bond and Thompson [20], and Kung and co-workers [21] that an active catalyst contained both gold atoms and ions, and the initial activity depended on the ratio of both phases.

Only the peaks of metallic gold are detected in XRD spectra (Fig. 7), no oxidized gold is observed. The average particle size calculated from the Scherrer's equation was about 14 nm. The TEM image of the same sample shows that numerous small particles are present in gold catalysts. These small particles gave such a large diffraction peak broadening that they were easily disappearing from the background of XRD spectra. A few large Au crystallites observed by XRD suggested that the small amount of Au particles were contained in gold catalysts. Therefore, it is reasonable that no oxidized gold is observed in XRD spectra.

Iwasawa and co-workers [10] found that the phase of iron oxide support played an important role in the synthesis of gold catalysts using gold phosphine complexes and as-precipitated wet iron hydroxide. Hor-

vath et al. [22] concluded that the most active sample was the oxidized gold in which the FeO<sub>x</sub> support contains Fe<sub>2</sub>O<sub>3</sub> in hematite phase and also contains FeO and FeO(OH).

It can be observed from Fig. 7 that FeO<sub>x</sub> shows in four main diffraction peaks, which can be ascribed to hematite phase of Fe<sub>2</sub>O<sub>3</sub>. The XPS spectra (Fig. 6b) obtained from the 0.5 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst depicted a predominant peak at around 711.4 eV, a band assigned to Fe(III) 2p<sub>3/2</sub> in amorphous Fe<sub>2</sub>O<sub>3</sub>. This was similar to the related literature [23].

### 3.8. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of CO adsorbed on 0.5 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst were obtained (Figs. 8 and 9). Four main bands are shown in Fig. 8. The band at 2116 cm<sup>-1</sup>, in principle, is assigned to CO chemisorptions on Au<sup>0</sup>. Because the peak is apparently asymmetric and a shoulder appears from the high-frequency side at 2131 cm<sup>-1</sup>. Judging from the result for Au/TiO<sub>2</sub> [6], we can assign the peak to CO adsorbed on oxidized gold sites. The band at 2170–2190 cm<sup>-1</sup> is usually attributed to CO adsorbed in the typical support oxide [24]. So we attributed the band at 2172 cm<sup>-1</sup> to CO adsorbed on FeO<sub>x</sub>. Another two bands at 2361 and 2341 cm<sup>-1</sup> were assigned to CO<sub>2</sub> adsorbed on the catalyst [25].

The bands observed in the 1700–1000 cm<sup>-1</sup> ranges can be assigned to carbonate-like species adsorbed on the support. Boccuzzi et al.'s study [26] showed that the carbonate-like species might be produced without the participation of molecular oxygen. In fact, no molecular oxygen was fed into the IR analysis system. So the oxygen involved in these carbonate-like species came from the active oxygen species occurred on catalyst surface. A slight reduction of these bands was observed in Fig. 9 because of the slow decomposition of these carbonate-like species.

As time passed, the band intensity of CO<sub>2</sub> adsorption (in Fig. 8) decreased, which indicated that the desorption of CO<sub>2</sub> was relatively easy and that this process was not a rate-determining step. CO<sub>2</sub> was produced by the interaction of CO with adsorbed oxygen, which is possible to occur on oxygen vacancies on the support or at the metal–support interface. As a consequence of the Schottky junction [27], the oxygen



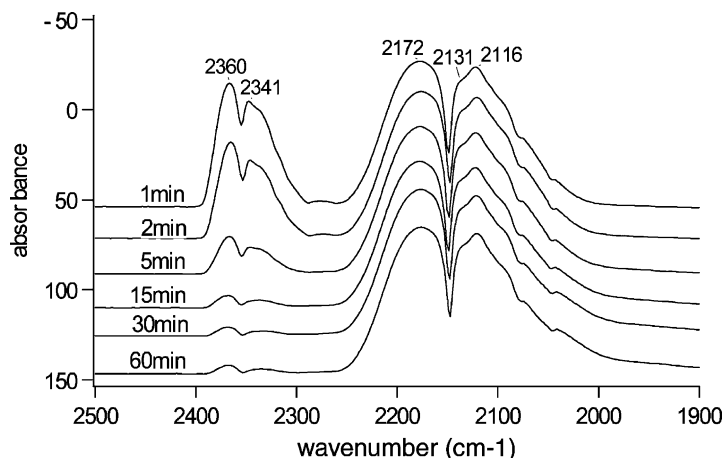


Fig. 8. IR absorption spectra obtained at different absorption times on 0.5 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst in the range of 2500–1900 cm<sup>-1</sup>.

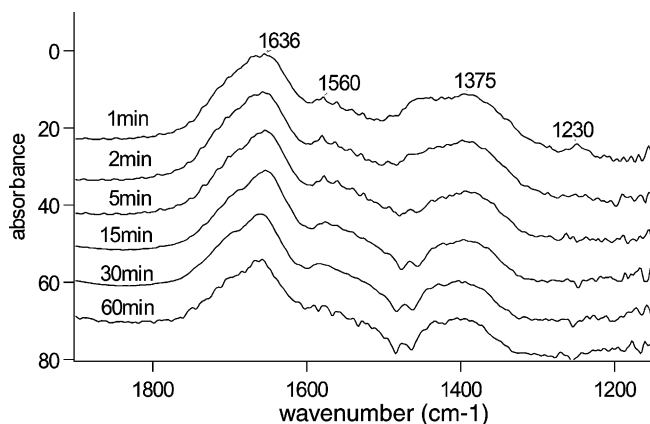


Fig. 9. IR absorption spectra obtained at different absorption times on 0.5 wt.% Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst in the range of 1800–1100 cm<sup>-1</sup>.

vacancies could be present in the proximity of the Au particles at the metal–semiconductor interface. This is in agreement with the conclusion of Hao et al.'s studies [28,29]. In order to explore the reaction of CO with surface oxygen species in absence of gas phase oxygen, CO pulse reaction was conducted on gold catalysts, which showed that the surface adsorbed oxygen species could react with CO adsorbed on gold particles. However, the surface oxygen species were limited and used up gradually with the increase in CO pulse. Gupta and co-workers [30] also suggested that oxygen adsorbing on the support dissociated immediately, producing lattice oxygen which can subsequently re-

act with CO at the interface or after a spillover of oxygen to small Au particles.

#### 4. Conclusions

The following conclusions were drawn on CO oxidation over the MO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> supported gold catalysts:

1. The Au/MO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (M = Fe, Co, Mn, Cu) catalysts are more active than Au/Al<sub>2</sub>O<sub>3</sub> catalysts. HDP is more suitable to prepare gold catalysts for commercial applications.

2. It is necessary for a good catalytic performance to prepare gold catalysts with small gold particles only in the form of a high dispersion.
3. From the characterizations of an Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, it seems reasonable that for developing high catalytic activity, the gold catalyst should have minor portion oxidized gold species and the transition metal oxide supports should be amorphous which can result in synergistic effects between gold and supports.
4. One possible pathway for CO oxidation on Au/FeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is that the CO adsorbed on gold reacts with adsorbed oxygen, which is possible to occur on oxygen vacancies on the support or at the metal–support interface.

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### References

- [1] G.C. Bond, P.A. Semon, *Gold Bull.* 6 (1973) 102–105.
- [2] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, *J. Catal.* 115 (1989) 301–309.
- [3] G.C. Bond, D.T. Thompson, *Catal. Rev. Sci. Eng.* 41 (1999) 319–388.
- [4] M. Haruta, *Catal. Surv. Jpn.* 1 (1997) 61–73.
- [5] A. Wolf, F. Schuth, *Appl. Catal. A: Gen.* 226 (2002) 1–13.
- [6] F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta, *J. Phys. Chem.* 100 (1996) 3625–3631.
- [7] B. Nkosi, N.J. Coville, G.J. Hutchings, M.D. Adams, J. Friedl, F.E. Wagner, *J. Catal.* 128 (1991) 366–377.
- [8] M.M. Schubert, S. Hackenberg, A.C. van Veen, M. Muhler, V. Plzak, R.J. Behm, *J. Catal.* 197 (2001) 113–122.
- [9] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, *J. Catal.* 144 (1993) 175–192.
- [10] A.I. Kozlov, A.P. Kozlova, H. Liu, Y. Iwasawa, *Appl. Catal. A: Gen.* 182 (1999) 9–28.
- [11] Z.P. Hao, L. An, H. Wang, *Sci. Chin. (Ser. B)* 44 (2001) 596–605.
- [12] R.J.H. Grisel, B.E. Nieuwenhuys, *Catal. Today* 64 (2001) 69–81.
- [13] R.J.H. Grisel, B.E. Nieuwenhuys, *J. Catal.* 199 (2001) 48–59.
- [14] M.A.P. Dekker, M.J. Lippits, B.E. Nieuwenhuys, *Catal. Today* 54 (1999) 381–390.
- [15] J.D. Grunwaldt, A. Baiker, *J. Phys. Chem.* 103 (1999) 1002–1008.
- [16] H.-S. Oh, J.H. Yang, C.K. Costello, Y.M. Wang, S.R. Bare, H.H. Kung, M.C. Kung, *J. Catal.* 210 (2002) 375–386.
- [17] R.J.H. Grisel, P.J. Kooyman, B.E. Nieuwenhuys, *J. Catal.* 191 (2000) 430–437.
- [18] S. Tsubota, M. Haruta, T. Kobayashi, in: G. Poncelet, P.A. Jacobs, P. Grange, B. Delmon (Eds.), *Preparation of Catalysts V*, 1991, Amsterdam, pp. 695–704.
- [19] E.D. Park, J.S. Lee, *J. Catal.* 186 (1999) 1–11.
- [20] G.C. Bond, D.T. Thompson, *Gold Bull.* 33 (2000) 41–51.
- [21] C.K. Costello, M.C. Kung, H.-S. Oh, Y. Wang, H.H. Kung, *Appl. Catal. A: Gen.* 232 (2001) 159–168.
- [22] D. Horvath, L. Toch, L. Guzzi, *Catal. Lett.* 67 (2000) 117–128.
- [23] W.S. Epling, G.B. Hoflund, J.F. Weaver, *J. Phys. Chem.* 100 (1996) 9929–9934.
- [24] F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, *J. Catal.* 188 (1999) 176–185.
- [25] F. Boccuzzi, S. Tsubota, M. Haruta, *J. Electron Spectrosc. Relat. Phenom.* 64–65 (1993) 241–250.
- [26] F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta, *Sens. Actuators B* 24–25 (1995) 540–543.
- [27] J.C. Frost, *Nature* 18 (1988) 577–581.
- [28] Z.P. Hao, L. Fen, G.Q. Lu, J. Liu, *Appl. Catal. A: Gen.* 213 (2001) 171–177.
- [29] Z.P. Hao, S.C. Zhang, Z.M. Liu, H.P. Zhang, *J. Environ. Sci.* 14 (2002) 489–494.
- [30] A.K. Tripathi, V.S. Kamble, N.M. Gupta, *J. Catal.* 187 (1999) 332–342.