Gold and iron supported on Y-type zeolite for carbon monoxide oxidation

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Abstract

Gold and iron supported on Y-type zeolite for carbon monoxide oxidation have been studied. They were prepared by ion exchange of gold(III) compounds with Y-type zeolite, iron-impregnated Y-type zeolite, or iron-exchanged Y-type zeolite in a chloroauric acid solution. The as-prepared gold/Y sample possessed high activity for carbon monoxide oxidation, but it gradually and irreversibly deactivated during the reaction. The deactivation was attributed to the transformation of some gold ions to gold metal. The activities of as-prepared gold/iron/Y samples were poor when compared with that of gold/Y, but their activities were markedly promoted by a high-temperature reduction treatment at 570°C. This is ascribed to the fact that the reduced gold/iron/Y catalyst could catch and release oxygen at low temperature.

Keywords: Carbon monoxide oxidation; Deactivation; Gold/zeolite-Y; Iron/zeolite-Y

1. Introduction

The use of catalysts for the oxidation of carbon monoxide, particularly at low temperatures, is of importance in industrial processes, in environmental protection [1–3], and in orbiting, closed-cycle CO_2 lasers [4,5]. In the past, gold has been less frequently considered as a catalyst due to its chemical inertness. An upsurge of interest in gold as a catalytic material was aroused by the work of Haruta et al. [6–10]. They reported that Au/Fe_2O_3, Au/Co_3O_4, Au/NiO and $Au/Be(OH)_2$, which were prepared by coprecipitation method, were effective

in promoting the oxidation of carbon monoxide even at a temperature as low as $-70°C$. This low-temperature activity was attributed to the high dispersion of gold and the combined effect of gold and the host oxides. However, to obtain these highly active catalysts, preparation and treatment with care are necessary [11,12]. Besides, by coprecipitation method, the surface area of the catalysts were usually low, and consequently significant amount of gold buried within the catalysts particles could not be used for the reaction. On the other hand, these gold-host oxide catalysts prepared by precipitation method should be supported on appropriate carriers before being practically used. Therefore, the improvement has been reported by supporting gold and iron oxide on various carriers by

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Haruta et al. [13] and by a number of patents [14–16].

In addition to the coprecipitation method, other groups have used the ferrite plating method [17] and photoreduction of $AuCl_4^-$-cationic surfactant complexes [18] to prepare fine Au particles. It has been reported that intrazeolite gold(I) which exhibits remarkable catalytic activities in the decomposition of NO at low temperatures was formed by the reductive carbonylation of monolayer-dispersed $AuCl_3$ in NaY and ZSM-5 zeolites [19,20].

In the earlier studies, the Volcano Principle [2] has been developed and supported by a number of researchers [21–24]. According to the Volcano Principle, the metal–oxygen bond strength of active oxidation catalysts should not be too strong or too weak. In the volcano curve, gold is located on the left arm, indicating the Au–oxygen bond strength is too weak; conversely, over iron oxides located on the right arm, the Fe–oxygen bond strength is too strong. Therefore, it is predictable that the catalytic activity of gold or iron oxide for the oxidation of carbon monoxide is very poor. However, as expected in Ref. [21], the combination of gold and iron oxide, prepared by coprecipitation method, exhibits a surprising activity increase [6–10]. Although numerous studies [25–29] have also been devoted to study the performances of gold catalysts and to characterize gold catalysts, no previous study has examined whether the oxidation–reduction character of gold and the host oxide affect each other in combined form.

In the present study, catalysts were prepared by ion exchange of gold(III) compounds with Y-type zeolite, iron-impregnated Y-type zeolite, or iron-exchanged Y-type zeolite. The oxidation–reduction character of gold and iron in combined and separated form will be investigated mainly by temperature-programmed reduction (TPR), and will be correlated to their catalytic activity for carbon monoxide oxidation. The effects of iron, prepared by impregna-

tion or ion exchange method, on the behaviours and activities of gold catalysts will be explored.

2. Experimental

2.1. Catalysts

Y-type zeolite with $Si/Al = 2.28$ from Conteka was used as a support in this research. The procedures for the preparation of Au/Y were as follows: 0.2 g of chloroauric acid ($HAuCl_4 \cdot 3H_2O$, Merck) was dissolved in 710 mL deionized water. 3 g of Y-type zeolite was added into the solution under stirring, and then heated to 80°C and maintained at this temperature for 16h. After filtration, the Au/Y sample was washed until it was free of Cl^- ions as detected by $AgNO_3$ solution and then dried at 60°C for 6h in air. The pH of gold solution before filtration was 5.2. The Au/Fe-13/Y sample was prepared firstly by the incipient-wetness impregnation of Y-type zeolite with aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Riedel–deHaen). The impregnated sample was dried and calcined at 550°C for 4h in air. Then, the iron-containing sample, i.e., Fe-13/Y, was used as a support for the preparation of Au/Fe-13/Y and the procedures were the same as Au/Y. The pH of gold solution before filtration was 4.6. The Au/Fe-1/Y sample was prepared firstly by ion exchanging of $Fe(NO_3)_3 \cdot 9H_2O$ solution with Y-type zeolite at 25°C. The zeolite was then filtered off, washed with deionized water, dried and calcined at 550°C for 4h in air. After calcination, the iron-containing sample, i.e., Fe-1/Y, was used as a support for the preparation of Au/Fe-1/Y and the procedures were also the same as Au/Y. Another two samples, Au/Fe-2/Y and Au/Fe-3/Y, were prepared by the same method as Au/Fe-1/Y, but with iron solution of different concentrations. The pH of gold solution before filtration was 3.8–3.9 for these three samples. The above four iron-containing gold catalysts will be called ''gold/iron/Y'' hereafter. A reference sample,

HAuCl$_4$/Y, for XPS and TPR analysis was prepared by incipient-wetness impregnation of Y-type zeolite with an aqueous solution of chloroauric acid, and then dried under the same conditions as above. HAuCl$_4$/Y contained 0.94 wt% of Au.

2.2. Characterization

The element content in each sample was determined by a GBC 906 atomic absorption unit. The BET surface area was measured with a Micromeritics unit (model 2100D). Nitrogen was used as an adsorbate. The UV–Vis reflectance was measured on a Hitachi U3410 spectrophotometer by using Y-type zeolite as a reference. The average diameter of particles on the outer surface of samples was measured using a Hitachi H7100 electron microscope operated at 75 kV and was determined by measuring over 120 individual particles on at least 21 pieces of TEM photograph. The experimental procedures and the apparatus for temperature-programmed reduction were described in detail in reference [30]. Before TPR measurements, several samples were in situ pretreated by reducing at 570°C for 2h under a 30 mL/min H$_2$/N$_2$ (1/9) flow, and then exposed in a 30 mL/min air flow at 40°C for 24 h or 0.5h.

A Perkin Elmer (Model 548) ESCA spectrometer, using Mg K_α monochromatic X-rays and equipped with a charge-compensating electron gun, was used for the investigation. The vacuum inside the analysis chamber was better than 5×10^{-8} N/m^2. Before the measurement, the sample had been pressed (5×10^7 N/m^2) to a pellet and then heated at 200°C under vacuum for 0.67 h (for Au/Fe-2/Y and Au/Y) or brought under vacuum at room temperature for 2 days (for HAuCl$_4$/Y) in order to remove water adsorbed on the support. The collection of ESCA spectra was carried out at room temperature. All measured binding energies (BE) were referred to the C$_{1s}$ line at 284.6 eV.

The XRD investigations were performed by using a MAC Science diffractometer (model MXP-3) with Cu K_α radiation at 40 kV and 30 mA. The patterns were obtained by the fixed-time method, namely, the scanning was held for 5 second over 0.02° of 2Θ intervals. The forms of gold or iron species over as-prepared or pretreated gold catalysts were identified by comparing with the JCPDS powder diffraction file. The mean crystalline size of gold metal was determined from XRD line broadening measurements. The Scherrer equation [31], we applied, was

$$D = \frac{\lambda}{(B - b)\cos \Theta},$$

where λ ($= 1.5405$Å) is the wavelength of X-ray; B is the angular breadth of the 38.2° diffraction line (the characteristic XRD line of Au(111)) of the investigated sample at half-maximum intensity; b is the instrumental line breadth; and Θ is equal to 19.1.

2.3. Activity measurements

The catalyst activity for carbon monoxide oxidation was measured in a continuous flow fixed-bed, quartz-tubular reactor (7 mm I.D.) at atmospheric pressure and 40°C. Before the reaction, 0.1 g of catalyst was either subjected to various pretreatment procedures or directly used without any pretreatment. During the reaction studies, 32.67 mL/min of air (99.99%, San Fu) and 0.33 mL/min of carbon monoxide (99.3%, CP grade, Linde Division, Union Carbide) were purified by 4 A molecular sieves, then mixed before the inlet of the reactor. The products were analyzed by a gas chromatrograph. The details of the separation column and the operation conditions of gas chromatrograph have been described previously [32].

3. Results

3.1. Element content, surface area and loaded particle size

The BET surface area and element content of each sample are listed in Table 1. It can be

Table 1
Metal loading, BET surface area and loaded particle size of iron or gold iron Y-type zeolite, and the pH of filtrate for the preparation of gold/Y or gold/iron/Y

Catlyst	Metal loading (wt%)				S.A. [δ]	d^{α}	pH [ε]
	Au	Fe	Al	Na	(m^2/g)	(nm)	
Y	0	0	14.4	3.4	553	–	–
Fe-1/Y [β]	0	2.3	11.9	1.0	529	–	–
Fe-2/Y [β]	0	4.0	10.5	0.8	546	–	–
Fe-3/Y [β]	0	5.7	8.9	0.6	593	–	–
Fe-13/Y [γ]	0	5.3	11.5	3.3	–	–	–
Au/Y	2.7	0	11.4	1.4	497	34 ± 9	5.2
Au/Fe-1/Y	2.5	2.1	10.2	0.3	506	52 ± 13	3.9
Au/Fe-2/Y	2.5	3.6	9.3	0.3	529	50 ± 14	3.8
Au/Fe-3/Y	2.5	5.6	8.2	0.3	563	48 ± 17	3.8
Au/Fe-13/Y	3.6	4.9	11.4	0.5	–	–	4.6

[α] Average diameter of particles was determined by TEM.

[β] The catalyst was prepared by ion-exchange method with ferric nitrate solution.

[γ] The catalyst was prepared by incipient-wetness impregnation with ferric nitrate solution.

[δ] BET surface area.

[ε] The pH of filtrate for the preparation of gold/Y or gold/iron/Y.

observed that although the Al loadings of these gold-containing samples are lower than that of Y-type zeolite, the surface areas of these gold-containing samples are approximately equal to that of Y-type zeolite. Besides, from XRD measurements, it was observed that all the samples had similar diffraction patterns as Y-type zeolite. Therefore, although the pH of ferric nitrate $(Fe(NO_3)_3 \cdot 9H_2O)$ solution was lower than 2.0, the crystallite structure of Y-type zeolite was not destroyed after the preparation of samples. From TEM, there was no particle observed on iron/Y samples, but particles were clearly observed on gold-containing samples as shown in Fig. 1. It can be observed in Table 1 that the average diameter of particles on as-prepared Au/Y was the smallest among those as-prepared gold-containing samples.

3.2. Temperature-programmed reduction

The results of TPR are shown in Fig. 2, Fig. 3 and Fig. 4. When only iron species prepared in Y-type zeolite, Fig. 2 presents that the reduc-

tion temperature of impregnated sample (Fe-13/Y) was higher than that of ion-exchanged samples (Fe-1/Y etc.). The reduction extent of iron in these four iron/Y samples was determined by comparing the areas under spectra (a)–(d) in Fig. 2 with that under spectrum (a) in Fig. 3. The peak areas per mole of gold or iron were 7.1, 2.2, 2.1, 2.3 and 2.3 for HAuCl$_4$/Y, Fe-1/Y, Fe-2/Y, Fe-3/Y and Fe-13/Y, respectively. The value of HAuCl$_4$/Y was closely equal to three times that of iron/Y. Because it was considered all of the Au(III) species in as-prepared HAuCl$_4$/Y could be reduced to zero-charged gold metal during the TPR measurement, the reduction peaks in Fig. 2 were ascribed to the reduction of Fe^{3+} to Fe^{2+}. This
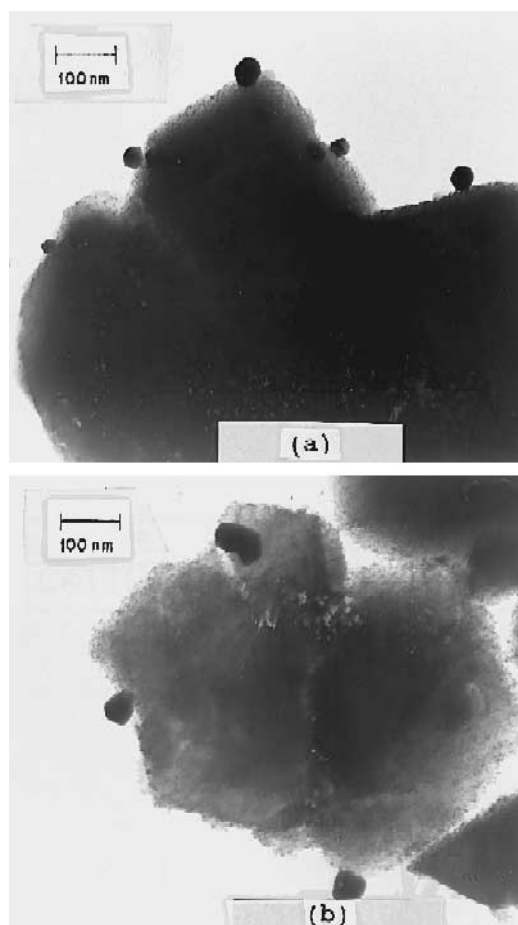

Fig. 1. TEM photographs of: (a) as-prepared Au/Y, and (b) as-prepared Au/Fe-1/Y.
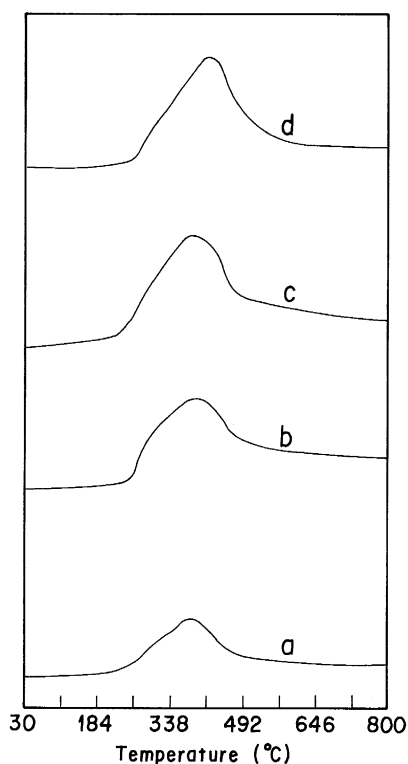
Fig. 2. The TPR profiles of 0.077 g of various catalysts which had been calcined at 550°C for 4h: (a) Fe-1/Y, (b) Fe-2/Y, (c) Fe-3/Y, and (d) Fe-13/Y.

160°C). This indicates that the reduction of Fe^{3+} is catalyzed by gold species. The catalysis may be due to a decrease of the Fe–O bond strength of iron species localized near gold [36]. On the other hand, when compared with (b) in Fig. 3, the peaks of (c) and (d) around 125°C shifted to 160°C of higher temperature, indicating stabilization of gold species by interaction with iron species, possibly the formation of mixed gold iron oxide species. However, it can be observed in Fig. 3 that the reduction peak of pure gold species (at 125°C) and that of pure iron species (around 400°C) gradually appeared again when iron loading was increased in gold/iron/Y as shown in Fig. 3 (e) and (f). By calculating each total area under spectra (c)–(f) in Fig. 3, it is found that the total TPR peak areas were probably from the reduction of
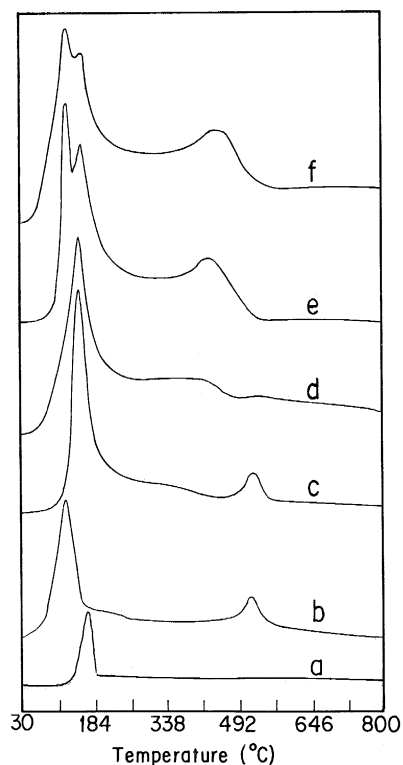
was in agreement with the results of Ref. [33]. When only gold species prepared in Y-type zeolite, Fig. 3 presents that Au/Y possessed two reduction peaks (at 125°C and 525°C) and one shoulder (at 190°C). As illustrated in our previous work [34], the peak around 525°C could be ascribed to the reduction of gold species which were located in sodalite cages [35], because there was no such a high-temperature reduction peak obtained on Au/β-zeolite and Au/mordenite. The oxidation state of gold in Au/Y was determined as Au(III) by comparing the area under spectrum (b) with that under spectrum (a) in Fig. 3. Moreover, when both gold and iron species were prepared in Y-type zeolite, the reduction peaks of Fe^{3+} to Fe^{2+} (around 380°C) in Fig. 3 were either absent or smaller than those in Fig. 2, and were mixed with the reduction peak of gold species (around

Fig. 3. The TPR profiles of 0.077 g of as-prepared catalysts: (a) HAuCl$_4$/Y, (b) Au/Y, (c) Au/Fe-1/Y, (d) Au/Fe-2/Y, (e) Au/Fe-3/Y, and (f) Au/Fe-13/Y.
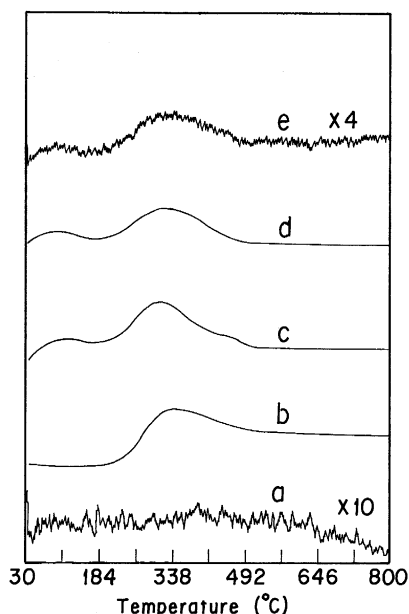
Fig. 4. The TPR profiles of pretreated catalysts: (a) Au/Y, (b) Fe-2/Y, (c) Au/Fe-2/Y, (d) Au/Fe-13/Y, and (e) Au/Fe-2/Y. The pretreatment procedures are as follows: For (a)–(d): reduced at 570°C for 2h, then exposed in air at 40°C for 24h. For (e): reduced at 570°C for 2h, then exposed in air at 40°C for 1/2h.

3.3. UV–Vis diffuse reflectance

Fig. 5 and Fig. 6 show the UV–Vis reflectance of the investigated samples, before and after pretreatment. It can be observed in Fig. 5 that in contrast to the sharp absorption bands from as-prepared impregnated $HAuCl_4/Y$, the as-prepared Au/Y had a broad absorption band around 220 nm and a shoulder around 320 nm. They were close to the ligand-to-metal charge transfer band and the ligand field band of $AuCl_4^-$ reported in the literature [37]. An absorption band appeared around 523 nm after Au/Y had been either calcined in air at 200°C for 1 h, used as a catalyst for CO oxidation reaction at 40°C for 44 h, or reduced up to 800°C. The absorption band around 523 nm is ascribed to the appearance of gold metal
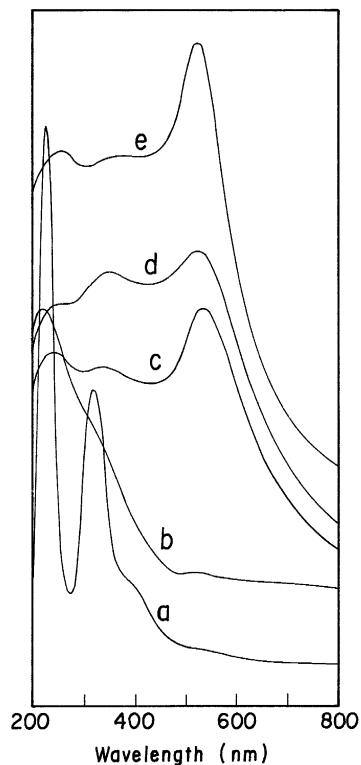
Au(III) to gold metal and the reduction of iron(III) oxide or ions to iron(II) species.

Fig. 4 shows the TPR results of pretreated gold catalysts (which contain 0.00202 g of Au) and of pretreated Fe-2/Y sample (weighed 0.077 g). It can be observed that the reduced Au/Y could not be reoxidized at 40°C under an air flow, because no reduction peak was obtained from TPR spectrum; but the reduced Fe-2/Y could be reoxidized, because a reduction peak at 340°C was obtained from TPR spectrum. When gold and iron species coexisted in Y-type zeolite, besides the reduction peak at 310°C, a broad peak which started at temperatures as low as 30°C appeared at 110°C. The peaks at 310°C could be assigned to the reduction of iron oxide catalyzed by gold. The peaks starting from 30°C may be due to the reduction of gold oxide or gold–iron mixed oxides. In other words, both of gold metal and iron(II) oxide in reduced gold/iron/Y samples could be reoxidized at 40°C under an air flow.

Fig. 5. UV–Vis reflectance of gold catalysts: (a) as-prepared impregnated $HAuCl_4/Y$, (b) as-prepared Au/Y, (c) Au/Y after being calcined in air at 200°C for 1h, (d) Au/Y after being used for CO oxidation reaction test at 40°C for 44h, and (e) Au/Y after being reduced upto 800°C.
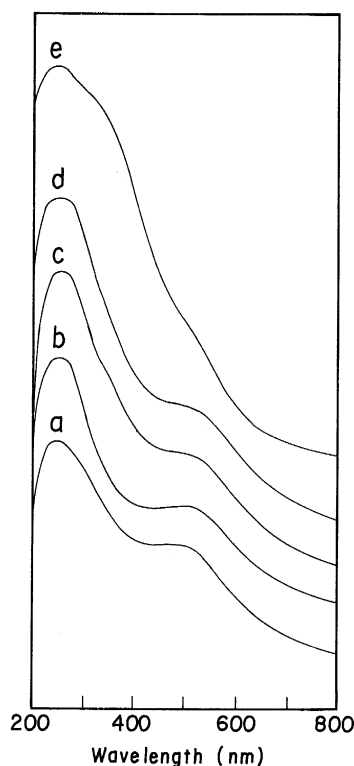
Fig. 6. UV–Vis reflectance of Au/Fe-3/Y catalysts. (a)–(d): reduced at 570°C for 2h, then exposed in air at room temperature for: (a) 1/6h, (b) 1h, (c) 17h, (d) 64h, and (e) as-prepared sample.

[18]. This demonstrates that besides reduction treatment, gold species in Au/Y can gradually transform into gold metal during CO oxidation reaction or during calcination in air. Moreover, it can be observed in Fig. 5 that Au/Y sample had a sharper band around 523 nm in spectrum (c) than that in spectrum (d). This suggests that more gold species in Au/Y were reduced to gold metal during calcination in air at 200°C than during CO oxidation reaction at 40°C.

The spectrum (e) in Fig. 6 shows that the as-prepared Au/Fe-3/Y sample had a broad absorption band around 240 and a shoulder around 330 nm. They were close to the ligand-to-metal charge transfer band of $FeCl_6^{3-}$ reported in the literature [38]. It is noticed that the scale of the ordinate in Fig. 6 was two times as large as that in Fig. 5. Besides, because the pattern and intensity of the UV–Vis reflectance of as-prepared Au/Fe-3/Y was almost the same

as those of calcined Fe-3/Y, these bands were mainly attributed to the existence of iron(III) oxide. The spectra (a)–(d) are the UV–Vis reflectance of Au/Fe-3/Y which had been reduced at 570°C for 2h and then exposed in air at room temperature for different period of time. It can be observed that the band intensities at 240 nm gradually increased with time, which corresponded to the oxidation of reduced iron species, Fe(II), to Fe(III) under air. This confirms the results of TPR measurement in Fig. 4 that iron in reduced gold/iron/Y could be reoxidized in air around room temperature. On the other hand, bands around 520 nm were also observed in spectra (a)–(d) of Fig. 6, which attributed to the appearance of gold metal after reduction.

3.4. X-ray photoelectron spectroscopy

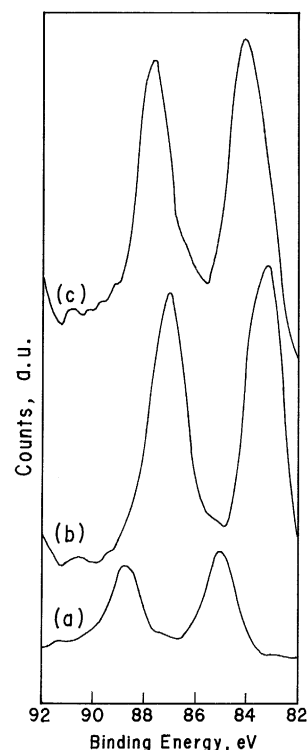The Au 4f XPS spectra for HAuCl4/Y, Au/Y and Au/Fe-2/Y appear in Fig. 7. The

Fig. 7. Au 4f XPS spectra of: (a) as-prepared $HAuCl_4$/Y, (b) Au/Y which had been used for CO oxidation reaction test at 40°C for 44h, and (c) Au/Fe-2/Y which had been reduced at 570°C for 2h.

Table 2
Binding energies of Au $4f_{7/2}$ and Fe $2p_{3/2}$ on various catalysts

Catalyst	Au $4f_{7/2}$	Fe $2p_{3/2}$
Au/Fe-2/Y [α]	84.33	711.3
Au/Y [β]	83.33	–
HAuCl$_4$/Y [γ]	84.93	–
Pure Au powder [δ]	83.05	–
Fe$_2$O$_3$ [ε]	–	710.7
Fe [ε]	–	706.8

[α] Au/Fe-2/Y had been reduced at 570°C for 2h before measurement.

[β] Au/Y had been used for CO oxidation reaction test at 40°C for 44 h before measurement.

[γ] Fresh sample, prepared by incipient-wetness impregnation.

[δ] From the work of Haruta et al., Ref. [10].

[ε] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder and G. E. Muilenberg, Handbook of X-ray Photoelectron spectroscopy, Perkin-Elmer Co., Eden Prairie, 1979.

peaks in the three spectra were symmetric and the differences of binding energy between them were significant. Table 2 collects the XPS results of investigated samples. The first three samples had already been exposed in air at room temperature while being pressed to pellets and in transit. It can be observed in Table 2 that the BE of Au $4f_{7/2}$ of Au/Fe-2/Y was significantly higher than that of Au/Y, and the BE of Au $4f_{7/2}$ of Au/Y was a little higher than that of pure gold powder. This suggests that gold metal in the reduced gold/iron/Y sample can
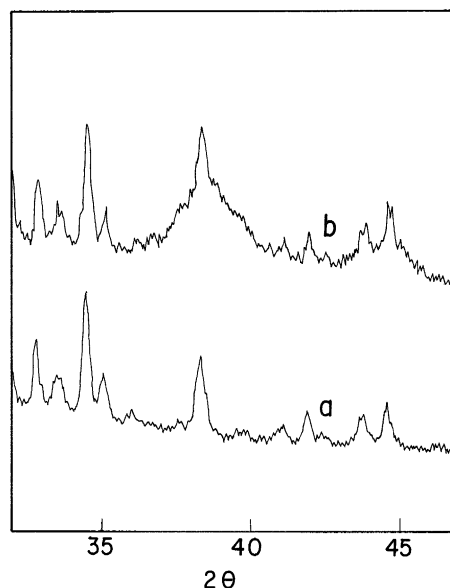

Fig. 8. The XRD patterns of as-prepared and pretreated Au/Fe-13/Y catalysts: (a) as-prepared, and (b) reduced at 570°C for 2h.

be reoxidized. Moreover, the BE of Fe $2p_{3/2}$ of Au/Fe-2/Y was close to that of Fe$_2$O$_3$, indicating iron species on the prereduced Au/Fe-2/Y sample were reoxidized to Fe(III) during being exposed in air. These XPS results support the results of TPR measurement that the peaks in Fig. 4b–4d are due to the reduction of metal oxides or mixed metal oxides.

Table 3
Catalytic activities for CO oxidation [α]

Catalyst	Pretreatment procedures	CO conversion (%)	
		initial	latter (h on stream)
Au/Y	No pretreatment	100.0	56.8 (44 h)
	then Air, 200°C, 1h	25.0	–
Au/Y	H$_2$/N$_2$, 120°C, 1/2h	62.3	53.2 (15 h)
Au/Fe-1/Y	No pretreatment	0.7	2.0 (27 h)
Au/Fe-1/Y	H$_2$/N$_2$, 570°C, 0	53.9	21.1 (16 h)
Au/Fe-2/Y	No pretreatment	1.8	3.5 (7 h)
Au/Fe-2/Y	H$_2$/N$_2$, 570°C, 0h	48.8	14.7 (22 h)
Au/Fe-2/Y	H$_2$/N$_2$, 570°C, 2h	72.1	36.0 (27 h)
	then H$_2$/N$_2$, 570°C, 2h	95.1	43.9 (36 h)
	then Ar, 570°C, 2h	93.3	29.7 (48 h)
Au/Fe-3/Y	No pretreatment	1.3	2.4 (5 h)
Au/Fe-13/Y	No pretreatment	10.3	11.1 (4 h)
Au/Fe-13/Y	H$_2$/N$_2$, 570°C, 2h	86.8	47.9 (16 h)
	then N$_2$, 570°C, 2h	83.4	–

[α] Reaction conditions: 0.1 g of catalyst, 40°C, 1 atm. 32.67 ml/min of air, and 0.33 ml/min of CO.

3.5. X-ray powder diffraction

Fig. 8 shows the XRD patterns of as-prepared and reduced Au/Fe-13/Y. The as-prepared one had a diffraction pattern similar to Y-type zeolite. This indicates that iron oxide (Fe_2O_3 or Fe_3O_4) and gold(III) species over the as-prepared one did not have enough long-range three dimensional order to produce the characteristic X-ray diffraction lines. Some differences in diffractograms could be observed around 38.2° and 44.4° in 2Θ after Au/Fe-13/Y was reduced. The two peaks, at 38.2° and 44.4° in 2Θ, were the characteristic XRD lines of Au(111) and Au(200), respectively. Before we employed the Scherrer equation (31) to estimate the average particle size of gold metal, the diffractogram of as-prepared Au/Fe-13/Y had been subtracted from those of pretreated samples because Y-type zeolite also had a diffraction line at 38°. The average particle diameter of gold metal on the reduced Au/Fe-13/Y was 47Å. This seems to indicate that almost all the gold species in as-prepared Au/Fe-13/Y transformed into gold metal and then sintered on the outer-surface of Y-type zeolite during reduction. On the other hand, the as-prepared Au/Y also had a diffraction pattern similar to Y-type zeolite. Although gold(III) species in as-prepared Au/Y were gradually reduced to gold metal during the CO oxidation reaction test as suggested in Fig. 5, the produced gold metal was not large enough to be detected by XRD.

3.6. Catalytic activities

The catalytic activities of all the gold catalysts for CO oxidation reaction are presented in Table 3. It can be observed that Au/Y possessed a much higher catalytic activity than gold/iron/Y when these catalysts were directly used for CO oxidation reaction without any pretreatment. The Au/Y catalyst, however, became deactivated during experiment. The deactivated Au/Y catalyst could not be regenerated by thermal treatment at 200°C in an air or a N_2 flow, and even worse, it lost its activity further after these thermal treatment. For gold/iron/Y catalysts, it can be observed that these catalysts became active after being reduced upto 570°C in a H_2/N_2 (1/9) flow. Although these reduced gold/iron/Y catalysts also deactivated during CO oxidation as Au/Y, the initial activity could be recovered by heating the deactivated catalysts in a flow of N_2 or Ar at 570°C for 2h. Furthermore, if the regeneration process was carried out in a H_2/N_2 flow at 570°C for 2h, the initial activity could not only be recovered but also be promoted to a higher level. In contrast to the above gold catalysts, all of the iron/Y samples, as-prepared or treated, were inactive under the reaction conditions of this work.

4. Discussion

4.1. Locations of gold or iron over as-prepared gold/Y and gold/iron/Y

Most studies of iron-containing zeolite catalysts have concentrated on Fe(II)-exchanged Y-type zeolites which were prepared by an anaerobic ion-exchange technique with the Fe(II) cation [39,40]. The location and coordination of Fe(II) and Fe(III) (which was formed from the oxidation of Fe(II)) in Y-type zeolite was reported in sodalite cage (site I′) and hexagonal prism (site I), not in supercage. However, this is not the case for the present study. In this work, the Fe-exchanged Y-type zeolites (Fe-1/Y, Fe-2/Y and Fe-3/Y) were prepared with ferric nitrate solution in the atmosphere of air. According to the work of Hidaka et al. [41,42] and Inamura et al. [43], three types of the Fe-species are present in the Fe-treated Y-type zeolites which were prepared by treating Y-type zeolite with ferric nitrate solution: ion exchanged species, small Fe oxide clusters bonded to zeolite framework, and superfine ferric oxide with particle size of about 10 Å. The latter two Fe-species were situated inside the supercages

of Y-type zeolite, and consequently the distribution of iron over the Fe-treated Y-type zeolite were homogeneous. In addition, iron(III) species in the Fe-treated Y-type zeolite can also be reduced only to iron(II) below 700°C. The preparation procedures of the Fe-treated Y-type zeolites in Ref. [41–43] were similar to those of Fe-1/Y, Fe-2/Y and Fe-3/Y in this work. Therefore, although not all of the iron species in Fe-1/Y, Fe-2/Y and Fe-3/Y samples were in ionic form, it was considered that iron species over the three iron/Y samples were also homogeneously distributed in Y-type zeolite. On the other hand, Yun et al. [44] studied impregnated iron/mordenite catalyst by Mossbauer and ferromagnetic resonance spectroscopy, and reported the average particle size of iron oxide was about 100 Å which was much larger than that of the Fe-treated Y-type zeolite in Ref. [41–43]. Accordingly, in contrast to Fe-1/Y, Fe-2/Y and Fe-3/Y, the dispersion of iron oxide over Fe-13/Y was low due to the impregnation method was used for the preparation.

Because the reduction peak of gold species at 125°C appeared from Au/Fe-3/Y but not from Au/Fe-1/Y and Au/Fe-2/Y (see Fig. 3), the probability for the contact between gold and iron species in Au/Fe-3/Y was lower than that in Au/Fe-1/Y and Au/Fe-2/Y. In other words, the dispersion of iron over Fe-3/Y seems to be the poorest among Fe-1/Y, Fe-2/Y and Fe-3/Y. This is supported by the TPR spectrum of Au/Fe-13/Y (similar to that of Au/Fe-3/Y), while impregnation method of poor iron dispersion was used for the preparation of Au/Fe-13/Y. Therefore, both of Au/Fe-3/Y and Au/Fe-13/Y have similar reduction peaks at 125°C and 160°C, indicating that some gold and iron species existed in separated form in these two samples.

It is noticed in Fig. 3 that the high-temperature reduction peaks of gold/iron/Y at 525°C (from gold ions in sodalite cages) were either absent or smaller than that of Au/Y. This may be the result that some of the iron ions may migrate into the sodalite cages and occupy the

ion exchange sites during calcination [35,39,40]. Another reason may be that some of the iron ions or oxides located in sodalite cages may reduce the window opening. Either of these two reasons would prevent gold species entering into sodalite cages and reduce the reduction peak at 525°C.

The pH of the gold solution during catalyst preparation was between 3.8 and 5.2. Although there may be no gold species found in the cationic form in this pH range, as suggested in Ref. [45], it was considered that zero-charged gold-containing complexes, e.g., $AuX_2(OH)$, may be exchanged on to the ion exchange sites of Y-type zeolite via the following equation:

$$AuX_2(OH)_{(aq)} + H^+Y \rightarrow [AuX_2]^+Y + H_2O,$$
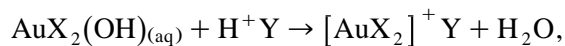
in which X was OH^- or Cl^-. The predominance of ion exchange process during the preparation of gold catalyst has been reported in our previous paper [46]. The preparation procedures of gold catalyst in this work is similar to that in Ref. [46]. Kang and Wan [46] had shown that gold ions of chloroauric acid can be exchanged into Y-type zeolite while the pH of solution is increased by the addition of sodium hydroxide. In the present study, the pH of the gold solution was increased due to the presence of sodium form of Y-type zeolite; thus, it is considered that the five gold catalysts of this work were also prepared mainly via ion exchange process. The fact that the TPR spectrum of Au/Y in Fig. 3 had the same pattern as that in Ref. [46] supports this inference. Besides, in Au/Fe-1/Y and Au/Fe-2/Y, the existence of gold ions which were located in sodalite cages also gave evidence for ion exchange process. Nevertheless, as in Ref. [46], some of the loaded gold species were not from the ion exchange process, because some large gold particles on the outer surface of zeolite were observed by TEM. The amount of gold of as-prepared gold/Y in large particles on the outside of the zeolite particles could be calculated from the shoulder area of the first reduction peak in the TPR spectrum [46]. Therefore, based on the shoulder area un-

der spectrum (b) in Fig. 3, it was calculated that 8% of the loaded gold in Au/Y was deposited on the outer-surface of Y-type zeolite. When gold and iron coexisted in Y-type zeolite, the broad reduction peak of large gold particles was covered by the reduction peak of iron oxide catalyzed by gold as shown in Fig. 3c–3f. From the spectra (c) and (d) in Fig. 3, it can be observed that most of gold species in Au/Fe-1/Y and Au/Fe-2/Y interacted with homogeneously distributed iron species. Therefore, most of gold species in Au/Fe-1/Y and Au/Fe-2/Y were located inside the cavities of Y-type zeolite. On the other hand, from the spectra (e) and (f) in Fig. 3, the reduction peak of pure gold species (at 125°C) can be observed. The peak was assigned to the reduction of gold ions existed in the cages of Y-type zeolite from previous work [46]. Based on the areas of the first peaks under spectra (e) and (f) in Fig. 3, it was calculated that 84 and 86% of the loaded gold in Au/Fe-3/Y and Au/Fe-13/Y existed in the cages of Y-type zeolite. To sum up, the five gold catalysts of this work were prepared mainly by cation exchange process, and more than 80% of the loaded gold was located in the cages of Y-type zeolite.

Because the gold(III) clusters formed in solution might attach on iron ions or oxide as well as on exchanged gold ions [46], and the distance between the attached sites might be shorter on iron/Y than on Y; consequently, the adsorbed gold(III) clusters were easier to coagulate each other on iron/Y than on Y. Therefore, it can be observed in Table 1 that the gold particles observed by TEM on gold/iron/Y were larger than those on Au/Y.

4.2. Locations of gold or iron over pretreated gold / Y and gold / iron / Y

The distribution of iron species over reduced gold/iron/Y were considered to be similar to that over as-prepared samples, because the characteristic XRD lines of iron species particles from the pretreated samples were not found.

Fe(II) ions from the reduction of Fe(III) ions of the exchange samples should interact strongly with the ion exchange sites in Y-type zeolite. In other words, iron species over pretreated Au/Fe-1/Y, Au/Fe-2/Y and Au/Fe-3/Y were uniformly distributed in Y-type zeolite; but, most of the impregnated iron species over pretreated Au/Fe-13/Y were located on the external surface of Y-type zeolite. In contrast, the distribution of gold species in Y-type zeolite was significantly affected by reduction treatment. Almost all the gold species in as-prepared gold catalysts transformed into gold metal and then migrated to and sintered on the outer-surface of Y-type zeolite during reduction as suggested by Fig. 8.

4.3. Catalytic activities of gold / Y

It has been demonstrated in the present study that Au/Y possesses a high activity for the oxidation of CO without any pretreatment. It, however, becomes deactivated during the test of CO oxidation reaction. Fukushima et al. [47] reported that the ability of gold metal for dissociating O_2 is very poor. Aida et al. [48] reported that CO adsorption does not occur on gold metal. These results coincide with the work of Haruta et al. [9], namely gold metal alone possesses a very poor catalytic activity for CO oxidation. From the results of UV–Vis reflectance in the present work, it is shown that Au/Y has a new absorption band around 523 nm after being used for CO oxidation reaction. The appearance of this band around 523 nm suggests that some gold(III) species in Au/Y gradually transforms into gold metal during CO oxidation. It, therefore, appears not unreasonable to attribute the deactivation of Au/Y to the fact that some gold(III) species is transformed into gold metal of poor activity. This is also the reason why Au/Y loses its high initial activity after being reduced, as shown in Table 3. Moreover, because calcination treatment at 200°C can lead to the reduction of some more gold(III) species in Au/Y (comparing spectrum (c) and (d) in Fig. 5), a dramatic and further decrease in

the activity of deactivated Au/Y sample after thermal treatment at 200°C can be observed as shown in Table 3.

4.4. Catalytic activities of gold / iron / Y

All the iron species, prepared by impregnation or ion exchange method, had similar effect on the activities of gold catalysts. The activities of all the as-prepared gold/iron/Y samples in the present study are much lower than that of as-prepared Au/Y. It is noticed that the pH of gold solution of all the catalysts before filtration is varied from 5.2 to 3.8. Such a difference may lead to variations in the composition of the loaded gold species, especially in the content of residual Cl. There is an obvious correlation between the pH of gold solution before filtration and the activity of as-prepared gold catalyst. The larger the pH of gold solution before filtration is, the higher the activity of as-prepared gold catalyst is. This may be the result that more Cl^- ions, which poison the catalysts [9,29], were substituted by OH^- ions during the preparation of catalyst if the pH of gold solution before filtration is high [45,49]. This inference can be somewhat supported by the fact that the impregnated $HAuCl_4/Y$ was essentially inactive.

Although the activities of as-prepared gold/iron/Y samples are poor, they achieve marked activities after being reduced at high temperature. From the results of TPR in Fig. 4a–4e, it can be observed that gold metal in reduced Au/Y sample cannot be reoxidized at 40°C in an air flow; but gold and iron(II) oxide in reduced gold/iron/Y samples can be reoxidized at 40°C in an air flow, and the resulted gold oxide or gold and iron mixed oxide can be reduced at temperatures as low as 30°C. This suggests that oxygen can be caught and then released by the reduced gold/iron/Y samples around room temperature, and these oxygen-catching and oxygen-releasing form a cyclic process. In other words, the high temperature reduction process makes gold/iron/Y simulta-

neously possess the oxidation–reduction properties of iron(II) oxide (easy to be oxidized) and gold oxide (easy to be reduced). According to the Volcano Principle [2,21–24], metals or metal oxides can exhibit highly catalytic activity for the combustion of VOCs and the oxidation of CO if they possess an optimum oxidation–reduction property, that is, the metal–oxygen bond strength should not be too strong or too weak. Therefore, the promotion in the catalytic activities of gold/iron/Y samples after being reduced at high temperature can be attributed to the fact that the reduced gold/iron/Y samples can catch and release oxygen cyclically at low temperature. Moreover, it is noticed that the catalytical activity of gold/iron/Y could be enhanced to a higher level if the high temperature reduction process was prolonged as listed in Table 3. Using Extended Huckel calculations, it has been found [50] that the existence of chlorine results in a significant energy shift of the O_2 dissociation curves toward higher energies, thus inhibiting the chemisorption of O_2 and its dissociation on catalyst. Thus, it was considered that the high temperature reduction process not only reduced the Cl^- content in catalyst but consequently promoted the ability of gold/iron/Y to catch and release oxygen at low temperature which enhanced the catalytical activity of gold/iron/Y.

It is noticed that although the reduced gold/iron/Y catalysts possess high activities, they also deactivate during CO oxidation reaction tests as Au/Y. However, the deactivation can be recovered by heating the deactivated catalysts in a stream of inert gas (e.g., Ar or N_2) at 570°C. Therefore, the temporary deactivation of the reduced gold/iron/Y catalysts may be due to a high concentration of surface intermediates, e.g., carbonate.

5. Conclusion

Highly dispersed gold catalysts could be prepared by ion exchange of gold(III) compounds

with Y-type zeolite, iron-impregnated Y-type zeolite or iron-exchanged Y-type zeolite in a chloroauric acid solution. The as-prepared gold/Y sample possessed high activity for carbon monoxide oxidation without any pretreatment, but it gradually deactivated during the experiment. The deactivation of Au/Y was irreversible and could be attributed to the fact that some gold compound gradually transformed into gold metal of poor catalytic activity during CO oxidation reaction. All the iron species, prepared by impregnation or ion-exchange method, had similar effect on the catalytic activity of gold catalysts. Although the activities of all the as-prepared gold/iron/Y samples were poor (compared with that of gold/Y), they achieved marked activities after being reduced at high temperature. The promotion in the activities of gold/iron/Y catalysts is attributed to the fact that the high-temperature reduced gold/iron/Y catalysts can catch and release oxygen at low temperature. The reduced gold/iron/Y catalysts also deactivated as gold/Y, but the deactivation was reversible and could be completely recovered by thermal treatment.

Acknowledgements

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