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Pretreatment effect of gold/iron/zeolite-Y on carbon monoxide oxidation

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Abstract

A gold/iron/zeolite-Y catalyst was prepared by cation-exchange of iron-impregnated zeolite-Y with a chloroauric acid solution and subjected to various pretreatments prior to being used in carbon monoxide oxidation. The physical properties of the pretreated catalyst were characterized by X-ray powder diffraction, UV-Vis diffuse reflectance spectroscopy, temperature-programmed reduction and temperature-programmed desorption of carbon monoxide. By comparing to gold/zeolite-Y, the presence of iron oxide was found to hinder the sintering of gold metal during high-temperature treatment. The most active and water-durable catalyst was obtained by heating gold/iron/Y in a stream of humidified inert gas flow. The active sites on the catalyst were proposed to be gold hydroxide species surrounded by iron oxide.

Keywords: Gold; Iron oxide; Zeolite; Pretreatment; Water; Carbon monoxide oxidation

1. Introduction

The use of catalysts for carbon monoxide oxidation around room temperature is an important subject in a large number of industrial processes, in environmental protection and in special apparatus [1–4]. For instance, because the separation of carbon dioxide from a mixture of gases (e.g. also containing nitrogen, oxygen or methane) is usually much easier than that of carbon monoxide, the removal of carbon monoxide through oxidation to carbon dioxide is required in many industrial processes. On the other hand, it was reported that the amount of CO emitted into the atmosphere was the greatest among all of the air pollutants, or even to exceed the sum of all the other air pollutants [5]. Hence, carbon monoxide oxidation is one of the most important reactions in environmental protection. In the case of a CO_2 laser, the re-combination of CO and O_2 formed by dissociation of CO_2 during discharge is essential to sustain the efficiency of laser performance, because the presence of O_2 can cause a breakdown of the electrical field in the laser cavity.

Up to now, Hopcalite catalyst (mainly composed of Mn and Cu mixed oxides) has been the most important commercialized catalyst for CO oxidation. However, its water-durability is poor and it is not active around ambient temperature [6]. Recently, Haruta et al. [7,8] reported that gold catalysts prepared by coprecipitation method were active for carbon monoxide oxidation even at a temperature as low as −70°C. However, by such a coprecipitation method, the surface areas of catalysts were low and the gold loadings were usually larger than 10 wt.-%. As a result, a signif-

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icant amount of gold probably buried inside the host metal oxide particles and could not be used for CO oxidation. Since gold is a noble metal, it is important to reduce the gold loading and to increase gold dispersion in the catalysts before they can be commercialized.

In our previous work, supported gold catalysts were prepared by cation-exchange of gold ions into varied exchangeable supports, e.g. zeolite Y, iron-impregnated zeolite Y, etc. [9–11]. The preparation procedures were generally as follows: a support was added into a stirring solution of chloroauric acid, then the solution was heated and maintained at 80°C for 16 h. After filtration, washing and drying, the exchanged gold catalysts were obtained. The as-prepared gold/zeolite-Y was found to be highly active without any pretreatment, but it irreversibly deactivated during the reaction tests or after thermal treatment. The deactivation was mainly attributed to the transformation of gold ions into gold metal of poor activity. In contrast to gold/zeolite-Y, gold/iron/zeolite-Y possessed high activity even after reduction at high temperatures. This was ascribed to the fact that the reduced gold/iron/zeolite-Y catalyst can catch and release oxygen at low temperature. Hsiao [12] used silica alumina as the support for cation-exchange gold ions and concluded that the pH of the filtrate determined the activities as well as the gold loadings of the as-prepared gold catalysts. Under the same gaseous flow rates as those in the work of Haruta et al. [8], some of the as-prepared gold catalysts in Hsiao's work could possess 100% CO conversion at 0°C, although the amount of gold used was only about one twentieth of that used in ref. [8].

In the present study, the pretreatment effect of gold/iron/zeolite-Y on carbon monoxide oxidation, either in the presence or absence of water vapour, were investigated. Characterization techniques used were X-ray powder diffraction (XRD), UV-Vis diffuse reflectance spectroscopy, temperature-programmed reduction (TPR) and temperature-programmed desorption of carbon monoxide (TPD of CO). The aim of this study is to rationalize the catalytic activity of gold/iron/zeolite-Y in CO oxidation after pretreatment under various conditions.

2. Experimental

2.1. Catalysts

In the present study, a gold/iron/zeolite-Y catalyst was prepared first by incipient-wetness impregnation of zeolite-Y (Si/Al = 2.28, Conteka) with iron(III) nitrate solution. After calcination, the resultant sample termed Fe/Y was added into a chloroauric acid ($HAuCl_4 \cdot 3H_2O$, Merck) solution under stirring, and then the solution was heated and maintained at 80°C for 16 h. The solid was filtered, washed and dried at 60°C for 6 h in air. The resultant catalyst was termed Au/Fe/Y. The gold and iron contents were 3.6 and 4.9 wt.-%, respectively. A reference sample was prepared by incipient-wetness impregnation of zeolite-Y with an aqueous solution of chloroauric acid, and then dried under the same conditions as above. This reference sample, termed as $HAuCl_4$/Y, contained 0.94 wt.-% of Au.

2.2. Characterization

The X-ray diffraction studies were performed by using a MAC Science diffractometer (model MXP-3) with Cu Kα 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 Au/Fe/Y were identified by comparing with the JCPDS powder diffraction file. The experimental procedures and the apparatus for TPR were described in detail in ref. [13]. TPD of CO was carried out in the same apparatus as TPR except that the trap used for condensing water vapor in TPR was removed. After being pretreated under the desired conditions, the sample was exposed in a stream of CO/He gas mixture (6 ml/min of CO and 30 ml/min of He) at 40°C for 1 h, and then cooled to room temperature. The TPD profile was

Table 1
Various pretreatment procedures and their designations

Designation	Pretreatment procedures
NP	Not pretreated
O	Calcined in a stream of air (32.67 ml/min) at 400°C for 2 h
R	Reduced in a stream of H_2/N_2 (30 ml/min, v/v = 1/9) at 570°C for 2 h
T	Thermal treated in a stream of He (30 ml/min) at 570°C for 2 h
W	Treated in a stream of He (30 ml/min) containing 3 vol.-% of water vapour at 570°C for 2 h, and then thermally treated in a stream of He (30 ml/min) at 400°C for 1/2 h

obtained by heating the sample at a rate of 10°C/min from 30°C to 800°C under a 30 ml/min helium flow. For each TPR or TPD experiment, 0.056 g of Au/Fe/Y was used. The UV-Vis reflectance spectrum was measured with a Hitachi U3410 spectrophotometer with zeolite-Y served as reference.

2.3. Activity measurements

The catalytic activity of Au/Fe/Y for carbon monoxide oxidation, either in the presence or absence of water vapour, was measured in a continuous flow fixed-bed, quartz-tubular reactor (9 mm O.D.) at 40°C under atmospheric pressure. Before the reaction, 0.1 g or 0.05 g of Au/Fe/Y was either pretreated under various conditions, or directly used without any pretreatment. Table 1 lists the various pretreatment procedures and their designations. For the sake of simplicity, these designations will be used hereafter to describe the pretreatment procedures. For instance, if Au/Fe/Y was calcined at 400°C for 2 h and then reduced at 570°C for 2 h before the reaction test or characterization, it will be named as OR catalyst.

During the reaction test, 32.67 ml/min of air and 0.33 ml/min of carbon monoxide controlled by Brooks mass flow controllers were fed into the reactor. Water vapor was incorporated into the reactant mixture by bubbling the reactant gases through an evaporator. The concentration of water vapour was maintained at ca. 3% by controlling the temperature of the evaporator at 25°C. The products were analyzed by a gas chromatograph (China Chromatograph, 8700T) with hydrogen as carrier gas. A 15 ft. Carboxen™ 1000 (1/8 in. O.D., stainless steel, Supelco) was used for the separation of O_2, N_2, CO and CO_2.

3. Results

3.1. X-ray powder diffraction

Fig. 1 shows the XRD patterns of as-prepared and pretreated Au/Fe/Y. The as-prepared sample has a diffraction pattern similar to that of zeolite-Y, and no crystalline structures of iron(III) oxide or gold(III) species were detected. After Au/Fe/Y was pretreated under various conditions, some differences in diffractograms could be observed around 38.2° and 44.4° in 2Θ. They were the characteristic diffraction lines of Au(111) and Au(200), respectively. The mean crystalline diameter of gold metal was determined by Scher-

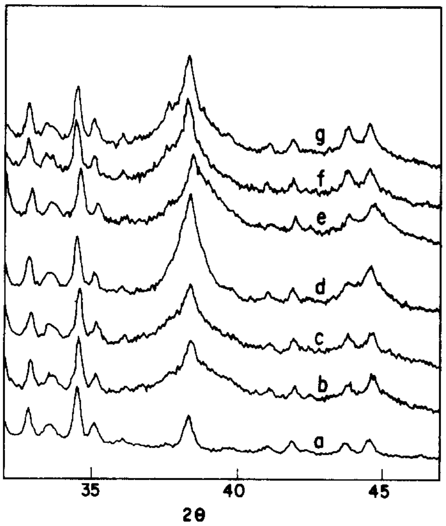

Fig. 1. The XRD patterns of as-prepared and pretreated Au/Fe/Y. (a) NP, (b) R, (c) RO, (d) O, (e) OR, (f) T, (g) W.

Table 2
Average diameters of gold metal on pretreated Au/Fe/Y or Au/Y

Catalyst	Pretreatment procedures	Au diameter (Å)
Au/Fe/Y	W	79
	T	79
	OR	68
	O	110
	RO	72
	R	47
	NP	–
Au/Y	OR	200
	O	200
	NP	–

rer equation according to the procedures described previously [10]. Table 2 lists the resultant particle diameters of gold metal on Au/Fe/Y after various pretreatment procedures. The O catalyst (calcination at 400°C) has the largest average particle size of gold metal. However, the large gold metal particles seem to break into smaller particles, from 110 to 68 Å in diameter, when the O catalyst was high-temperature reduced. Because gold metal particles on Au/Y, which was prepared by the same procedures as Au/Fe/Y except that the impregnation of iron oxide was omitted, could not redisperse after reduction as also shown in Table 2, the redispersion of gold metal might have something to do with the presence of iron oxide. Furthermore, the average particle sizes of gold metal on pretreated Au/Fe/Y were significantly smaller than those on Au/Y. These results suggest that there is probably a strong interaction between gold and iron oxide on Au/Fe/Y, and iron oxide has the effect of hindering the sintering of gold metal as well as the redispersion of the sintered gold metal particles. On the other hand, the R catalyst possesses the best gold dispersion, while the average particle diameters of gold metal on the RO, OR, T and W catalysts were relatively larger and all in a close range.

3.2. Temperature-programmed reduction

The TPR results of Fe/Y and as-prepared Au/Fe/Y were shown in profiles (a) and (b) in Fig. 2. As reported in our previous work [10], the peaks at 120 and 440°C of profile (b) correspond to the reduction of gold(III) species to gold metal and iron(III) oxide to iron(II) oxide, respectively. By calculating the area under profile (b), the peak at 150°C was suggested to be the reduction of iron oxide catalyzed by gold species [10]. The TPR results of Au/Fe/Y after varied pretreatment are shown in profiles (c)–(e) in Fig. 2 and profiles (a)–(c) in Fig. 3. Before the TPR tests, the R, OR and T catalysts were exposed in air at 40°C for 24 h. Among the six pretreated samples, the R catalyst possessed the lowest TPR peak which appears at 79°C. That suggests that the reduced gold surface could chemisorb oxygen at 40°C and re-reduce at 79°C. However, if the R catalyst was exposed to a humidified air stream, the amount of chemisorbed oxygen decreased and the reduction temperature increased to 122°C (Fig. 3(d)). This suggests that water vapour is probably strongly adsorbed and suppresses the ability of R catalyst to chemisorb oxygen. On the other hand, the peak intensity of the first reduction peak of profile (d) in Fig. 2 was larger than that of profile (e). In other words, the sites available for the chemisorption of oxygen on the R catalyst

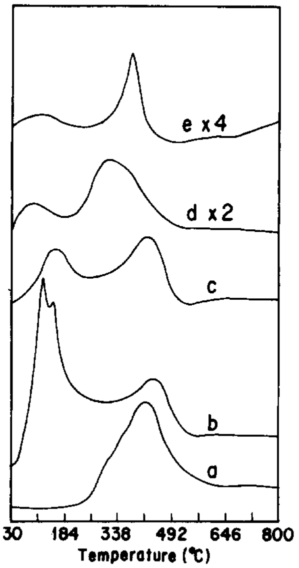

Fig. 2. TPR profiles of: (a) Fe/Y; (b) as-prepared Au/Fe/Y, and pretreated Au/Fe/Y; (c) O; (d) R and then exposed in a stream of air at 40°C for 24 h; (e) OR and then exposed in a stream of air at 40°C for 24 h.

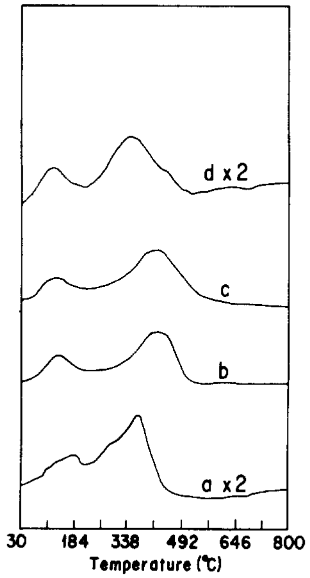

Fig. 3. TPR profiles of pretreated Au/Fe/Y: (a) RO, (b) T and then exposed in a stream of air at 40°C for 24 h, (c) W, (d) R and then exposed in a stream of water/air (3/97, v/v) at 40°C for 24 h.

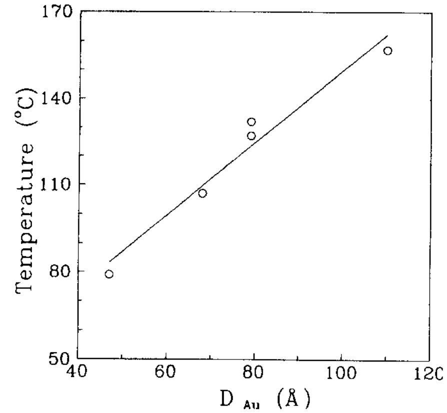

Fig. 4. A correlation between the temperatures of the first reduction peaks of pretreated Au/Fe/Y in TPR experiments and the average particle diameters of gold metals.

were more than those on the OR catalyst. It implies that the gold dispersion on the former is higher than that on the latter, which was consistent with the results of XRD.

It was found that the second reduction peaks of profiles (d) and (e) in Fig. 2 and profiles (a) and (d) in Fig. 3 were shift toward lower temperatures. This may be due to the redispersion of iron oxide which caused a decrease in the particle diameter of iron oxide. In addition, the fact that the reduced iron oxide may not be fully reoxidized and only the outer surface of it was oxidized may be also responsible for the shift in reduction temperature.

A linear relationship was found between the temperatures of the first reduction peaks of pretreated Au/Fe/Y and the mean particle diameters of gold metals on them, as shown in Fig. 4. The only exception was RO catalyst, which had the first reduction peak at 180°C and 72Å mean particle diameter of gold metal and possessed a point far away from the correlation line, probability due to the inhomogeneous particle distribution on zeolite-Y.

3.3. *TPD of carbon monoxide*

During the TPD measurement, the decomposition of gold or iron species and the degradation of zeolite-Y may occur and hence produce an extra profile which will append to the 'true' TPD profile of CO, as shown in Fig. 5. It is noticed that the profile (c) became a horizontally straight line if a trap of −85°C was positioned immediately after the TPD reactor. This indicates that during the

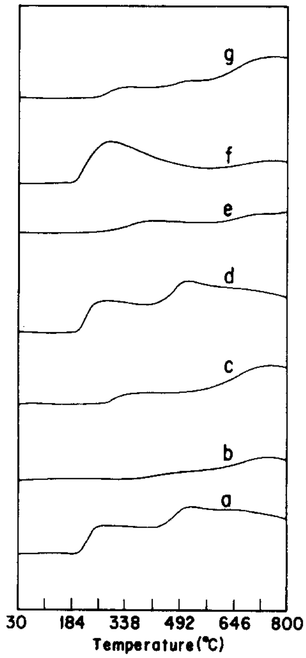

Fig. 5. TPD profiles of Au/Fe/Y after varied pretreatment: (a) O, (b) R, (c) W, (d) O, (e) OR, (f) R, (g) W, where (d)–(g) samples were exposed in a stream of CO/He (1/5, v/v) at 40°C for 1 h before TPD measurement.

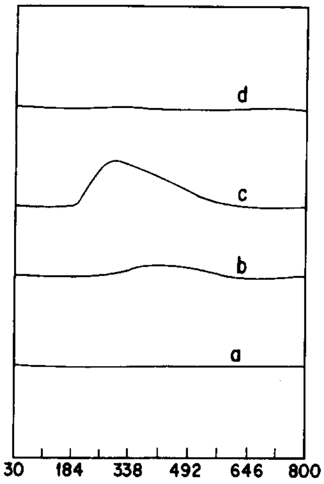

Fig. 6. The profiles of TPD of carbon monoxide of Au/Fe/Y after varied pretreatment: (a) O, (b) OR, (c) R, (d) W.

TPD measurement almost all of the desorbed species from the W catalyst were water. The TPD profiles of CO, which were obtained by subtracting the decomposition or degradation profiles from the 'apparent' TPD profiles of CO, of Au/Fe/Y after varied pretreatment are shown in Fig. 6. For instance, profile (c) in Fig. 6 was obtained by subtracting profile (b) in Fig. 5 from profile (f) in the same figure. It can be observed that the amount of chemisorbed CO on the R catalyst was much more than those on the O, OR and W catalysts, and CO desorbed from R catalyst at a temperature higher than 190°C. This suggests that carbon monoxide is more strongly adsorbed on the active sites of the R catalyst than on those of the O, OR and W catalysts.

3.4. *UV-Vis diffuse reflectance spectra*

Fig. 7 shows the UV-Vis reflectance spectra of the investigated samples before pretreatment. The as-prepared impregnated $HAuCl_4$/Y has two sharp absorption bands appeared around 226 and 318 nm (Fig. 7(a)), corresponding to the ligand-to-metal charge transfer band and the d–d transition band, respectively, of $AuCl_4^-$ [14]. The UV-Vis reflectance spectrum of Fe/Y shows a broad band with the maximum at ca. 250 nm. The spectrum has little changes after Fe/Y being thermally treated under water vapour.

Fig. 8 shows the spectra of Au/Fe/Y after varied pretreatment. It was found that a new adsorption band appears around 550 nm after Au/Fe/Y being treated at high temperature. This absorption band is considered to have something to do with gold metal [15], and the appearance of gold metal on these pretreated samples was confirmed by the XRD results. In addition, it was found that the intensities of the shoulder around 340 nm on the O, T and W catalysts were more pronounced than that on the as-prepared one. Because the major desorbed species from the W catalyst were water during the TPD measurement, the shoulder around 340 nm on the W catalyst was assigned to the existence of gold hydroxide. However, the 340 nm shoulder was also observed on the O and T catalysts which were obtained by treating the as-prepared Au/Fe/Y in a dry gas (air or helium) stream. Therefore, the shoulder around 340 nm on the O and T catalysts were ascribed to the existence of gold oxides. When subjected to high temperature treatment in an inert gas, the gold oxide

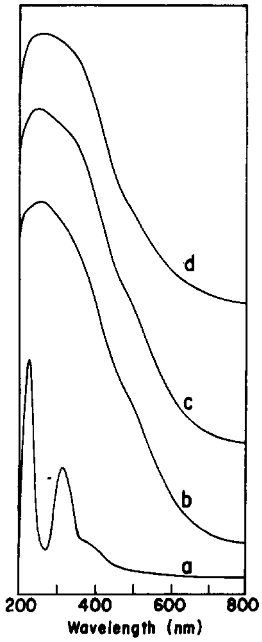

Fig. 7. UV-Vis reflectance spectra of (a) as-prepared $HAuCl_4$/Y, (b) Fe/Y, (c) Fe/Y heated in a stream of water/helium (3/97, v/v) at 570°C for 2 h, (d) as-prepared Au/Fe/Y.

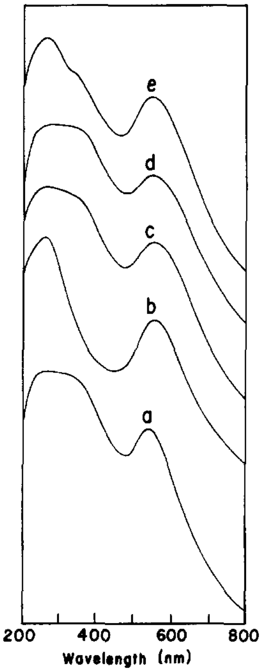

Fig. 8. UV-Vis reflectance spectra of Au/Fe/Y after varied pretreatment: (a) O, (b) R, (c) T, (d) W, (e) W and then heated in a stream of helium up to 800°C.

or gold hydroxide may be dissociated to gold metal and oxygen or water. Therefore, it can be observed in Fig. 8(e) that the shoulder around 340 nm on the W catalyst decreased after the catalyst was treated to 800°C in a helium stream. Moreover, the shoulder around 340 nm of the R catalyst disappeared completely, due to the complete reduction to gold metal as shown in Fig. 8(b).

3.5. Catalytic activities of pretreated Au/Fe/Y

The catalytic activities of 0.1 g of as-prepared or pretreated Au/Fe/Y in carbon monoxide oxidation in the absence of water vapour were examined at 40°C, and the results are illustrated in Table 3. It was observed that the O catalyst was inactive while the OR, T and W catalysts were highly active. The conversion of carbon monoxide over the OR catalyst was retained at 100% for 5 h, and then gradually decreased to 68% after 43 h on stream. The deactivation also occurred on other pretreated catalysts, but the activities were fully regenerated by a thermal treatment in an inert gas flow.

Although the R, OR and T catalysts were active for carbon monoxide oxidation in the absence of water vapour, they became nearly or essentially

Table 3
Catalytic activities of as-prepared or pretreated Au/Fe/Y for carbon monoxide oxidation[a]

Pretreatment procedures	CO conversion (%)	
	Initial	Latter (h on stream)
NP	10.3	11.1 (4 h)
O	0.0	-(-)
R	86.8	47.9 (16 h)
then T	83.4	-(-)
OR	100.0	67.7 (43 h)
RO	33.3	24.5 (63 h)
T	100.0	-(-)
W	100.0	-(-)

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

Table 4
Effect of water vapour on the catalytic activities of pretreated Au/Fe/Y[a]

Pretreatment procedures	Reactants	CO conversion (%)	
		Initial	Latter (h)
W	CO/air	87	–
then	CO/air/H_2O	85	81 (13 h)
then	CO/air	74	65 (5 h)
then	CO/air/H_2O	66	78 (2 h)
then	CO/He/H_2O	0	–
OR	CO/air	62	–
then	CO/air/H_2O	0	0 (2 h)
OR[b]	CO/air	18	–
then	CO/air/H_2O	0	–
R	CO/air	49	–
then	CO/air/H_2O	0	–
R[b]	CO/air	21	–
then	CO/air/H_2O	0	–
RO	CO/air	11	–
then	CO/air/H_2O	0	0 (2 h)
T	CO/air	67	–
then	CO/air/H_2O	9	–
then T	CO/air	71	48 (3 h)

[a] Reaction conditions: 0.05 g of catalyst, 40°C, 1 atm, 32.67 ml/min of air or helium, 0.33 ml/min of carbon monoxide; if used, water vapour concentration = 3 vol.-%.
[b] The OR and R catalysts had been exposed in a stream of air at 40°C for 24 h prior to the reaction test.

inactive when water vapour was incorporated into the reactant mixture, as shown in Table 4, where only 0.05 g of catalyst was used for each test run. Because the activities could be regained by a thermal treatment, the drastic decrease in activities was ascribed to the strong adsorption of water molecules on the active sites. In addition, it was found that if the OR and R catalysts were exposed in a stream of air at 40°C for 24 h prior to the reaction test, the produced catalysts possessed much lower activities than the OR and R catalysts, and they were also not water-durable as the above three catalysts. In contrast to the activity drops on the R, OR, RO and T catalysts, the water durability of the W catalyst was very good. Furthermore, the reaction activity of the latter catalyst was better in the presence of water vapour than in a dry atmosphere run. Also shown in Table 4 was that water-gas shift reaction over the W catalyst was absent since no CO conversion was detected when He instead of air was used in the reactant mixture.

4. Discussion

According to the Volcano Principle [16–18], metals or metal oxides will possess high catalytic activities in the oxidation of volatile organic compounds (VOCs) and carbon monoxide if they can catch and release oxygen at relatively low temperatures. In our previous work [10], the TPR tests were carried out on a series of catalysts Au/Y, Fe/Y and Au/Fe/Y which had been subjected to the R pretreatment procedures and then exposed in a stream of air at 40°C for 24 h. The results showed that Au/Y was easy to be reduced at low temperature, but the reduced Au/Y could not be reoxidized in air at 40°C. On the other hand, iron oxide on Fe/Y was difficult to be reduced at temperatures lower than 300°C, but the reduced iron oxide could be reoxidized at room temperature. These indicate that the bonding between gold–oxygen was so weak that oxygen was easily dissociated from gold oxides. On the contrary, the bonding between iron–oxygen was too strong. In other words, either iron oxide or gold metal alone is not good catalyst to fulfill the oxidation–reduction cycle, and consequently the activities of Fe/Y and reduced Au/Y were very poor in carbon monoxide oxidation. In contrast to Au/Y and Fe/Y, the reduced Au/Fe/Y could catch and release oxygen at low temperatures. Therefore, the reduced Au/Fe/Y could exhibit much higher activity than either Fe/Y or reduced Au/Y.

In the present study, although the R catalyst could chemisorb oxygen at 40°C and release it at 79°C (the lowest temperature among catalysts of varied pretreatment), its activity was lower than the OR, T and W catalysts. Therefore, the Volcano principle cannot be used alone to explain the present results on the activities of pretreated Au/Fe/Y. In addition, the average particle diameter of gold metal on pretreated Au/Fe/Y was also not the unique determinant for the activity, although Haruta et al. [19] reported that the turnover frequencies for CO oxidation per surface gold atom increased with a decrease in the diameter of gold metal. The R catalyst which possessed the smallest gold metal particle size and the highest gold dispersion was not the most active catalyst.

Almost all of the loaded gold ions on the as-prepared Au/Fe/Y were transformed into gold metal and migrated to the outer-surface of zeolite-Y during high-temperature pretreatment as suggested by the results of XRD and ref. [10]. However, portions of gold ions, especially around iron oxide, were transformed into gold hydroxide, gold oxide or gold–iron mixed oxide according to the results of TPR, TPD and UV-Vis reflectance.

The state of gold sat near iron oxide is catalytically important because it is considered that carbon monoxide oxidation occurs at the interfacial perimeter of gold metal and iron oxide [8,19,20]. In other words, the gold species, either as gold metal, gold oxide, gold–iron oxide or gold hydroxide, around iron oxide are thought to be the active sites for carbon monoxide oxidation. However, it is difficult to differentiate gold oxide from gold–iron mixed oxide on pretreated Au/Fe/Y because the first reduction peaks of pretreated Au/Fe/Y in Fig. 2 and Fig. 3 were broad and both of the gold compounds gave rise to an absorption band around 340 nm. For simplification, both of the gold compounds will be called 'gold oxides' hereafter. If we combined the results of TPR, TPD and UV-Vis reflectance, the state of gold around iron oxide on pretreated Au/Fe/Y can be known. When the R and OR catalysts were exposed in air, gold metal around iron oxide could be oxidized to gold oxides. On the O and RO catalysts, most of gold near the interface of gold metal and iron oxide were gold oxides. On the W catalyst, gold hydroxide as well as gold metal and gold oxides existed at the perimeter of gold metal particle. In addition, it was noticed that the first reduction peak of the T catalyst was 182°C (not shown in the figures) instead of 132°C shown in Fig. 3(b), in which the profile was obtained by exposing the T catalyst to a stream of air at 40°C for 24 h prior to the TPR measurement. It was considered that the internal portion of the active particles on the T catalyst right after high-temperature pretreatment was gold oxide which could be reduced at 182°C, and the exterior surface of that was rich in gold metal which could be oxidized at 40°C. The 132°C peak is attributed to the reduction of gold oxide on the exterior surface of the re-oxidized T catalyst. Therefore, in addition to gold oxides as suggested by the results of UV-Vis reflectance, some gold metal was probably also present around iron oxide on the surface of T catalyst.

Since the activities of the OR and R catalysts evidently decreased if they were exposed in air prior to the reaction test (Table 4), gold oxides were considered to be less active than gold metal. This also accounts for that the activities of the RO and O catalysts were lower than those of the R, OR and T catalysts. In fact, because the O catalyst possessed the poorest gold dispersion and the least active sites, it was inactive during the reaction tests. Nevertheless, it was also noticed that the presence of gold oxides around the active sites could make catalyst water-durable, because the T catalyst did not become inactive in a humidified run. This suggests that the adsorption strength of water on the active sites aside gold oxides is weaker than that on plain gold metal surface. This is supported by the result of TPD in Fig. 6 that carbon monoxide (which is less polar than water) was adsorbed on the O catalyst much weakly and in less amount than on the R and OR catalysts. In addition, because carbon monoxide oxidation was carried out under an oxidizing condition in this work, the active sites in gold metal form would be partially or gradually oxidized to gold oxides during the reaction test. Therefore, the decay in activity occurred over the R, OR, T and RO catalysts during a dry run could not be attributed only to the strong chemisorption of produced formate or carbonate as described in refs. [10,19,20]. The transformation of the active sites in gold metal form to gold oxides should be considered responsible for the deactivation.

Haruta et al. [19] reported that the superiority of their gold catalyst over Pt group catalysts was ascribed to the fact that CO adsorption on the former was reversible at room temperature and was much weaker than that on the latter. In the present study, because carbon monoxide is more strongly adsorbed on the R catalyst than on the O, OR and W catalysts, it may block the active sites of the R catalyst and intensely compete with oxygen for the active sites. That was thought to be the reason that the R catalyst was not the most active.

In contrast to the poor water-durability of the R, OR, RO, and T catalysts, the W catalyst was water-durable, and even the deactivated W catalyst, which was obtained when water vapour was not present in the reactant feed, could gradually recover its activity by incorporating water vapour into the reactant mixture. Based on the TPD results in Fig. 6, the amount and the strength of carbon monoxide adsorbed on the R or OR catalyst were more and stronger than those on the W catalyst. Because both of carbon monoxide and water are polar molecules, it is proposed that water may be also more strongly adsorbed on the active sites of the R and OR catalysts than on the W catalyst. Hence, the W catalyst did not become inactive as water was present in the reactant mixture. In addition, because the catalytic behavior of the W catalyst was apparently different from those of the others, the active sites on the W catalyst was also considered to be not the same as those of the others. From the results of TPD and UV-Vis reflectance, hydroxyl groups coordinated to gold(III) ions were observed. Therefore, it is considered that gold hydroxide may play an important role in the activities of the W catalyst.

Knell et al. [20] proposed a reaction sequence for CO oxidation over Au/ZrO_2. They reported that CO_2 is desorbed from surface carbonate which is produced by oxidizing formate with surface oxygen, and formate is formed by insertion of CO into a surface hydroxyl group. In addition, they ascribed the deactivation of Au/ZrO_2 to the high concentration of surface formate which is very stable in the presence of excess oxygen and consequently blocks the active sites. A similar mechanism is proposed for the oxidation of carbon monoxide over the W catalyst in the present study. When CO is admitted to an empty site of the W catalyst, formate is formed by inserting CO into the hydroxyl group of gold hydroxide, and then the formate is oxidized by the surface oxygen to yield carbonate. The surface oxygen is provided by the neighboring active sites of gold metal or gold oxides form. Finally, CO_2 is desorbed from surface carbonate.

Because carbon monoxide did not strongly adsorb on the W catalyst as suggested by the results of TPD, the deactivation of the W catalyst occurred in the absence of water vapour was not considered to be the result from the same reason as that of Knell et al. [20]. In our previous work [9–11], the deactivation of as-prepared gold/Y was mainly attributed to the fact that gold(III) ions transformed into gold metal of poor activity during the reaction test. Recently, we found that the deactivated gold/Y could be partly regenerated by exposing it in a humidified gas flow. Therefore, the deactivation of the W catalyst in the absence of water vapour is also attributed to the transformation of active sites, namely, proceeds via the following proposed reaction:

The gold hydroxide in the left-hand side was more active than the gold oxide species in the right-hand side. This was supported by that the activity of the W catalyst was much higher than that of the RO catalyst. Although it is assumed that the rate of the above undesirable reaction is slow because formic acid was not observed in the outlet stream from the reactor in the present study, the amount of the gold oxide species would increase with the time-on-stream and consequently the W catalyst was gradually deactivated. As water was incorporated into the reactant mixture, the gold oxide species would react with water to regenerate gold hydroxide and consequently the activity of W catalyst was regained. This also explains that the W catalyst could sustain its highly initial activity for a long time while water was present in the reaction feed.

5. Conclusions

Because of the presence of iron oxide, the average particle diameter of gold metal on pretreated Au/Fe/Y was smaller than that on the pretreated Au/Y, and even the sintered gold metal particles on the O catalyst could be broken into smaller particles after high-temperature reduction. Although the R catalyst possessed the highest gold dispersion and the lowest oxygen-releasing temperature, its activity was not the best. This is ascribed to that the adsorption competition between carbon monoxide and oxygen on the active sites of the R catalyst was more sever than that on the others. In addition, the R, OR and T catalysts, possessing high activity in dry atmosphere, became nearly or essentially inactive as water vapour was present in the reactant mixture. This was due to the strong adsorption of water on the active sites of the catalyst. In contrast to the activity drop of the R, OR, RO and T catalysts, the W catalyst was water-durable, and even the deactivation occurred in dry reactant mixture could be gradually regenerated by incorporation of water vapour into the reactant feed. The active sites of the W catalyst was considered to be mainly composed of gold hydroxide surrounded by iron oxide.

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