Preparation of gold in Y-type zeolite for carbon monoxide oxidation

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Abstract

Gold Y-type zeolite catalysts were prepared by adding Y-type zeolite to a stirred aqueous solution of chloroauric acid. It was demonstrated that the ion-exchange process between gold ions and the zeolite dominated the preparation of gold into Y-type zeolite. The exchanged gold/Y catalysts possessed high catalytic activities for low-temperature carbon monoxide oxidation without any pre-treatment. The activity could be promoted by addition of sodium hydroxide to the preparation solution. Promotion was attributed to the substitution of OH^- for the chloride around the gold ions. During the activity test, these gold catalysts were deactivated as a result of the transformation of active gold(III) species into gold metal of poor activity.

Keywords: Carbon monoxide oxidation; Gold; Ion exchange; Zeolite

1. Introduction

The removal of carbon monoxide is an important subject in environmental protection. Several catalysts, such as gold mixed with cobalt oxide, iron oxide, etc., have been found to be effective for the oxidation of carbon monoxide at temperatures as low as 203 K and are moisture tolerant [1,2]. However, the coprecipitation method used for the preparation produced catalysts of low surface area, and a significant amount of gold was buried within the catalyst particles and was not available for reaction. Haruta et al. [3] reported an improved preparation technique that supported gold and iron oxide on high surface area alumina and honeycomb carrier.

Because the high activities of coprecipitated gold catalysts were attributed to the formation of ultrafine gold particles smaller than 10 nm and stabilized by host metal

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oxide [3,4], several researchers investigated the preparation of gold clusters. The preparation of hydrosols of gold clusters down to 2 nm are reportedly formed by photoreduction of AuCl_4^- -cationic surfactant complexes [5] and by reduction of gold(III) ions with tetrakis(hydroxymethyl)phosphonium chloride [6]. A AuCl_3/NaY sample prepared by spontaneous monolayer-dispersion of AuCl_3 with NaY zeolite powder has also been reported [7]. The AuCl_3 was said to be in the zeolite pores as a monolayer or highly dispersed. In addition, Au fine particles were dispersed on ferrite films of Fe_3O_4 or $\alpha\text{-Fe}_2\text{O}_3$ by ferrite plating in an aqueous solution below 100°C [8].

The most commonly practiced techniques for preparing supported catalysts are incipient wetness impregnation and ion exchange. In the latter, the interaction between the deposited salt and the support is stronger than that in the former. Consequently, the exchanged sample can achieve much higher metal dispersion and more homogeneous metal distribution than the impregnated sample [9]. Thus, in the present study, ion exchange was used to prepare gold into exchangeable Y-type zeolite.

2. Experimental

Y-type zeolite with $\text{Si}/\text{Al} = 2.28$, sodium loading = 3.42 wt.-% (designated Y1) and with $\text{Si}/\text{Al} = 28.7$, sodium loading = 0.72 wt.-% (designated Y2) from Conteka were used as supports in this research. According to the characterization report provided by Conteka, the unit cell sizes and the BET surface areas were 24.50 Å and 730 m^2/g of Y1, and 24.25 Å and 720 m^2/g of Y2. Therefore, the change in the number of exchange sites is the only significant difference between the two zeolites. Ion exchange was used for the preparation of gold in Y-type zeolite, and the procedures were as follows: 0.25 g of chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Merck) was dissolved in 500 cm^3 of deionized water. Sodium hydroxide (0.06–0.16 g) was used to adjust the pH of the solution. After stirring for 1 h, 5 g of Y-type zeolite was added, then the solution was heated to 353 K and maintained at this temperature for 16 h. The exchanged gold/Y samples (Au-13/Y1, Au-16/Y1, Au-10/Y1 and Au-16/Y2) were obtained after filtration, and were washed until free from Cl^- ions, as detected by a AgNO_3 solution. They were then dried at 333 K for 6 h under air. A reference sample, $\text{HAuCl}_4/\text{Y1}$, for X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR) analysis was prepared by incipient wetness impregnation of Y1 with an aqueous solution of chloroauric acid, and then dried under the same conditions as above. The pH of the gold solution used for the incipient wetness impregnation was lower than 2.7, and consequently AuCl_4^- anion has its initial form in the solution. Thus, it is considered that gold would not be exchanged onto the cation exchange sites of Y-type zeolite when the incipient wetness technique was used. $\text{HAuCl}_4/\text{Y1}$ contained 0.94 wt.-% of Au.

Table 1
Solution pH during preparation and gold loadings of the catalysts

Catalyst	Preparation solution			Au loadings (wt.-%)	d^d (nm)
	NaOH ^a (g)	pH1 ^b	pH2 ^c		
Au-13/Y1	0.059	3.60	6.6	1.78	22
Au-16/Y1	0.119	6.56	6.7	1.59	31
Au-10/Y1	0.159	10.80	6.8	1.24	39
Au-16/Y2	0.119	6.6	6.4	0.26	10

^a The amount of NaOH was added into the chloroauric acid solution.

^b pH of solution right before Y-type zeolite was added into the solution.

^c pH of filtrate.

^d The average diameter of gold species measured by TEM.

The elemental content in each sample was determined by a GBC 906 atomic absorption unit. The average diameter of the particles on the outer surface of the samples was measured using a Hitachi H7100 electron microscope operated at 75 kV. The average particle diameter was determined by measuring over 100 individual particles on at least 25 sections of a TEM photograph. The experimental procedures and the apparatus for temperature-programmed reduction (TPR) were described in detail before [10]. 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 analyses of ESCA spectra were carried out at room temperature. All measured binding energies (BE) were referred to the C 1s line at 284.6 eV.

Carbon monoxide oxidation was carried out in a quartz tube reactor at 303 K under atmospheric pressure. The catalysts which contained 0.00162 g of gold were directly used without any pretreatment. During the reaction, 32.67 cm³/min of air and 0.33 cm³/min of carbon monoxide were mixed before the inlet of the reactor.

3. Results and discussion

3.1. Loading process of gold into Y-type zeolite

Table 1 shows that the amount of gold prepared in Y1 decreased with the increase of the amount of sodium hydroxide added to the preparation solution, although the pH of each solution was in close range at the final stage of the preparation. It appears that the amount of gold prepared in this zeolite was a function of solution pH at the time when Y-type zeolite was added to the solution.

When 0.25 g of chloroauric acid dissolves alone in 500 cm³ of deionized water, the pH of this gold solution is 2.7. If AuCl₄⁻ anion has its original form in this aqueous solution, gold cannot be exchanged onto the cation exchange sites of the zeolite and will be removed by washing. However, it was reported [11–13] that

various complexes, i.e. $\text{AuCl}_3(\text{H}_2\text{O})$, $\text{AuCl}_2(\text{H}_2\text{O})\text{OH}$, $\text{AuCl}_3(\text{OH})^-$, $\text{AuCl}_2(\text{OH})_2^-$, $\text{AuCl}(\text{OH})_3^-$ and $\text{Au}(\text{OH})_4^-$ were formed as the pH was increased. Moreover, a zero-charged complex — $\text{Au}(\text{en})_2\text{Cl}_3$ (en = ethylene diamine), similar to the first two above, had been prepared into silica gel [14] and Y-type zeolite [15]. Presumably, the gold cations from $\text{Au}(\text{en})_2\text{Cl}_3$ played the major role in the exchange process during preparations. In the present study, because the pH of the gold solution was higher than that of a pure chloroauric acid solution, it is possible that gold cations from gold hydroxide complexes were loaded into Y-type zeolite by a cation exchange process. In order to confirm this, the effect of the number of ion-exchange sites on the preparation of gold in Y-type zeolite was investigated. Another Y-type zeolite with a higher Si/Al ratio of 28.7 and a lower sodium loading of 0.72 wt.-% (designated Y2) than Y1 was used to prepare Au-16/Y2. The preparation procedures were the same as those of Au-16/Y1. It can be observed in Table 1 that the gold loading on Au-16/Y1 was more than 6 times that on Au-16/Y2, while the number of exchange sites of Y1 was more than 11 times that of Y2 (based on Si/Al ratios). This indicates that the cation exchange sites have a strong influence on the preparation of gold compounds into Y-type zeolite, and that cation exchange may be the major process during preparation. Moreover, two amorphous materials — silica alumina with Si/Al = 5.0 (Davison) and silica gel (Merck) — were used as supports in our recent work [16], to prepare gold catalysts. The preparation procedures were similar to those used in the present work. It was found that the amount of gold loaded onto silica alumina was more than 5 times that onto silica gel. The gold loading on Au/silica gel was less than 0.2 wt.-%. This indicates again that the presence of cation exchange sites on the supports would certainly make cation exchange dominate the gold loading process.

Although most of the gold species on Y-type zeolite is loaded by ion exchange, it should be noticed that not all of the gold species loaded were the result of ion exchange, because from TEM (also listed in Table 1), the observed gold particle sizes (more than 10 nm) should not have occurred if only gold ions were in Y-type zeolite (which consists of an array of cavities having internal diameters of only about 1.2 nm) [17]. It can be observed that the average diameter of the gold particles increased with increasing sodium hydroxide addition.

Fig. 1 presents the results of TPR experiments. It can be observed that Au-13/Y1, Au-16/Y1 and Au-10/Y1 showed two reduction peaks (at 125°C and 525°C) and one shoulder (at 190°C). The peak around 525°C can be ascribed to the reduction of gold ions which were located in sodalite cages [18], because there was no such a high-temperature reduction peak for Au/ β -zeolite and Au/mordenite [19], although they were prepared by the same procedure as Au-16/Y1. The oxidation state of gold in these three samples (Au-10/Y1, Au-16/Y1 and Au-13/Y1) was determined by comparing the TPR areas under spectra b–d with that under spectrum a from $\text{HAuCl}_4/\text{Y1}$. The peak areas (under the TPR spectra) per gram of gold (obtained from atomic absorption) were 4.0, 3.5 and 3.5 for Au-13/Y1, Au-16/Y1 and Au-10/Y1, respectively. All of them were closely equal to that of

Fig. 1. TPR profiles of as-prepared catalysts which contained 0.00135 g of Au. (a) $\text{HAuCl}_4/\text{Y1}$, (b) Au-13/Y1 , (c) Au-16/Y1 , (d) Au-10/Y1 , (e) Au-16-2/Y1 .

$\text{HAuCl}_4/\text{Y1}$, which was 3.6. Therefore, the three samples all have the same oxidation state, Au^{III} , as that in $\text{HAuCl}_4/\text{Y1}$. Furthermore, the binding energy of $\text{Au } 4f_{7/2}$ of Au-10/Y1 (85.10 eV) obtained by XPS measurement, which was much higher than that of gold metal powder (83.05 eV) [20] but close to that of impregnated $\text{HAuCl}_4/\text{Y1}$ (84.93 eV), was another evidence for Au^{III} in gold exchanged Y1 samples.

From Fig. 1, it can be found that the first peaks (at 125°C) of spectra b–d were sharp and symmetric. All of these first peaks had broad shoulders at higher temperature (190°C). These shoulders could be assigned to the reduction of large gold particles which were too large to exist inside the cavities of the zeolite, and could deposit only on the outer surface of the zeolite (because large particles generally show broader reduction peaks and higher reduction temperatures than ions and small clusters). To confirm this assignment, another reference sample, Au-16-2/Y1 , was prepared following procedures similar to those for Au-16/Y1 ; except no zeolite was added into the chloroauric acid solution, and the solution was filtered on 5 g of Y1 after being stirred at 80°C for 16 h. The resulting Au-16-2/Y1 contained only 0.18 wt.-% of gold (much less than 1.59 wt.-% on Au-16/Y1), and by TEM the average particle size was about one third of that on Au-16/Y1 . Because Y1 was contacted with the gold solution only at short time periods of the filtration process

for the preparation of Au-16-2/Y1, it is considered that almost all gold species on Au-16-2/Y1 were present as large particles (about 10 nm in diameter from TEM) and located right on the outer surface of Y1. Fig. 1e shows the TPR spectrum of Au-16-2/Y1. A reduction peak appears around 190°C, which is in close range with the shoulders of spectra b–d in Fig. 1. Therefore, the results clearly demonstrate that the broad shoulders at 190°C of spectra b–d were the reduction of large gold particles deposited on the outer surface of the zeolite.

Based on the total peak areas under spectra b–d in Fig. 1, it could be calculated that the shoulders from the reduction of the large gold particles deposited on the outer surface of the zeolite contained only 14, 19 and 21% of the loaded gold in Au-13/Y1, Au-16/Y1 and Au-10/Y1, respectively. This further confirmed that most of the loaded gold species existed inside the cavities of Y-type zeolite, and the dispersion of gold in these exchanged catalysts was high.

From the above results, the formation of large gold particles deposited on the outer surface of gold-exchanged Y-type zeolite was demonstrated. It seems that when the pH of the aqueous solution of chloroauric acid is increased by sodium hydroxide, gold(III) clusters are formed in the solution. If there is no suitable solid surface for deposition, these clusters will gradually combine to form precipitates. However, if they deposit on the zeolite surface, the clusters may coalesce (depending on the distance between them) to form large particles, as observed on exchanged Au-16/Y1 by TEM. By comparing the average diameter of gold particles of Au-16/Y1 with that of Au-16/Y2, it is found that the gold particle size on Y-type zeolites is positively influenced by the number of ion exchange sites on zeolites. This suggests that the gold ions which were ion exchanged onto the outer surface of Y-type zeolite may play the role of nuclei for further deposition of gold(III) clusters from solution onto the zeolite. Subsequently, because the average distance between the neighboring ion exchange sites on Y1 is much shorter than on Y2, the clusters which were attached on the exchanged gold ions were easier to coagulate on Y1 than on Y2. As a result, the gold particle size on Au-16/Y1 was larger than that on Au-16/Y2.

From Table 1, it is found that the gold loading on Y1 decreased but gold particle size increased with increasing amount of sodium hydroxide added to the chloroauric acid solution. This could be because there were larger and more gold(III) clusters formed in the solution, and therefore less gold ions were available for the cation exchange, which caused the decrease of gold loading in zeolite and the deposition of larger gold clusters on the outer surface of the zeolite.

3.2. Catalytic activities of gold/Y catalysts

The catalytic activities of Au-13/Y1, Au-16/Y1 and Au-10/Y1 for carbon monoxide oxidation are shown in Fig. 2. It is noticed that because the carbon balance between the inlet and outlet gases was maintained and did not change with the time-on-stream, the initial high conversion of carbon monoxide in Fig. 2 was

Fig. 2. Carbon monoxide conversion vs. time on stream at 30°C over as-prepared gold catalysts which contained 0.00162 g of Au. (a) Au-13/Y1, (b) Au-16/Y1, (c) Au-10/Y1.

not considered to come from the adsorption of carbon monoxide and carbon dioxide on the catalyst. It can be observed that although these gold catalysts possessed high activity without any pretreatment, they became deactivated during the experiment. The deactivated catalysts could not be regenerated by thermal treatment at 200°C in an air or a nitrogen flow, and even worse, they lost their activity further after thermal treatment. It has been reported in our previous work [21] that the deactivation of gold/Y during the activity test was attributed to the transformation of active gold(III) species into gold metal of poor activity. The further loss in activity after thermal treatment was also ascribed to the same reason as above. Besides, Knell et al. [22] reported that the deactivation of Au/ZrO₂ in the presence of excess oxygen was due to the progressive covering of the active sites by oxygenated carbon species. Because the reaction conditions applied in the present work were also highly oxidative, the type of deactivation reported by Knell et al. cannot be excluded.

Although Au-13/Y1 also had a good activity without any pretreatment, its activity was the poorest among the three catalysts in Fig. 2. It is reported [2,23] that chlorine can poison carbon monoxide oxidation catalysts. Using extended Hückel calculations, it is found [24] that the existence of chlorine results in a significant energy shift of the oxygen dissociation curves toward higher energies, thus inhibiting the chemisorption of oxygen and its dissociation. Consequently, a loss in oxidation activity occurs. In the present study, because the amount of sodium hydroxide added in the preparation of Au-13/Y1 was the lowest of the three catalysts in Fig. 2, less OH⁻ could substitute the chloride of chloroauric acid in the solution. By SEM-EDX, trace chloride was detected on Au-13/Y1, but no chloride on Au-16/Y1 or Au-10/Y1 was found. Therefore, the lower catalytic activity of Au-13/Y1 was ascribed to the presence of chloride.

4. Conclusions

Gold Y-type zeolite catalysts were prepared mainly by ion exchange. Although the amount of gold used for carbon monoxide oxidation in this study was one

seventh of that in the work of Haruta et al. [1,2], high conversions could also be achieved without any pretreatment. The addition of sodium hydroxide into the preparation solution promoted the activity of the exchanged gold/Y catalyst. This was attributed to the substitution of hydroxide for the chloride around the gold ions. On the other hand, due to the transformation of active gold(III) species into gold metal of poor activity, the gold catalysts gradually lost their activities.

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