

Effects of Gold Species and Support Properties on Nano-gold Loading Process onto Y-type Zeolites in the Solution

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Abstract

Au/Y catalysts with nano-gold on Y-type zeolite were prepared in this research. Gold species is from the precursor of HAuCl_4 and zeolite supports are NaY, HY and H(Na)Y (while H(Na)Y is from HY after surface modification by using sodium hydroxide in NaNO_3 solution). The resulting catalysts have been characterized by using AA, ICP, HRTEM, solid state NMR, XPS and Zeta-potential. Several conclusions have been drawn from this research: First, gold loading on Y-type zeolite decreases with the increase of solution pH. When pH is close to 7, all the chloride on gold atom has been replaced by hydroxide. Some large gold species appear in the solution and can only be deposited on exterior surface of zeolite. Second, there are always gold monomers in the solution below pH 7, which can be prepared in the cages of Y. Third, surface charges on NaY, HY and H(Na)Y are different, which influence gold loading process significantly. Through the electrical attraction, these gold species can easily diffuse into the interior of zeolite. Fourth, the presence of salt, such as NaNO_3 , in zeolite influence the surface charge of H(Na)Y significantly. Fifth, most gold species loaded physically on Y at room temperature, which are easily flushed away during washing; in contrast, they are chemically adsorbed on the surface of Y at 80 °C. Sixth, more defect sites are produced when NaY is treated to become HY, and HY becomes H(Na)Y. Seventh, amount of Al close to exterior surface of zeolite is increased with the increase of defect sites. They have strong interaction with gold species located close to exterior surface of zeolite.

Keywords: nano-gold, Y-type zeolite, salt effects, defects sites

Introduction

Since the catalytic activity of nano-gold for catalyzing CO oxidation at low temperature was discovered by Haruta et al. [1], many scientists have devoted themselves to this field. Until now, preparation of nano-gold with sizes below 2 nm and the mechanism of the preparation are important subjects in recent research area of nano-catalysts [2-7]. Y-type zeolite possesses window sizes of 0.74 nm and inner supercages with size of 1.2 nm. By preparation of nano-gold on or in zeolite Y, one can understand the sizes of gold species in the solution at different conditions, only those smaller than 0.74 nm can possibly be into the cages, and those larger than 1.2 nm on zeolite should be on the exterior surface of zeolite. Therefore, the mechanism of gold species in the solution loaded on or into Y-type zeolite, and the effects of gold solution properties and zeolite status on loading nano-gold are studied in this research.

Experimental

Preparation of Au/Y catalysts

JRC-Z-Y5.3 and JRC-Z-HY5.3 (from The Catalysis Society of Japan) with Si/Al₂ ratio = 5.3 was used as supports. The former is sodium type with 14.0 wt% Na_2O and the latter is proton type with 1.1 wt% Na_2O . They were both calcined at 550°C for 12 hours. These two calcined zeolite are abbreviated as NaY and HY. HY surface modified with NaOH was also prepared in this research. The procedure is described as follows: HY was put in 1N NaNO_3 solution and pH value was adjusted by 1 N sodium hydroxide solution to pH 6 or 7 for 24 h. After that, it was filtered with or without washing and dried at room temperature. The unwashed sample was named H(Na)Y and the washed one was named H(Na)Y-w. Part of dried

H(Na)Y-w sample were immersed into 1N NaNO₃ solution again, and then filtered without washing and dried at room temperature. This sample is named H(Na)Y-w-NaNO₃.

For loading gold into zeolite supports, 230 ml of 1.6×10^{-3} M chloroauric acid (HAuCl₄·3H₂O) solution was prepared. 0.1 N sodium hydroxide solution was added for adjusting the solution pH to 6. 4 g of zeolite supports was added, followed by heating the solution to 80°C and maintained at this temperature for 1 h. They were filtered with washing and dried at room temperature. Au/Y catalysts with gold loading onto NaY, HY, H(Na)Y, H(Na)Y-w and H(Na)Y-w-NaNO₃ supports are designated Au/NaY, Au/HY, Au/H(Na)Y, Au/H(Na)Y-w and Au/H(Na)Y-w-NaNO₃, respectively.

Au/Y catalysts prepared from 80 °C or 30 °C gold solution, and filtered with or without flushing process were prepared in this research. H(Na)Y were used as supports. Accordingly, they are named Au/[H(Na)Y]-80-f (prepared in 80 °C solution and flushed with water after filtration), Au/[H(Na)Y]-30-f, Au/[H(Na)Y]-80 (without flushed with water), Au/[H(Na)Y]-30, respectively. On the other hand, Au/Y catalysts with different pH value in the gold solution were also made. H(Na)Y were still used as supports. The preparation parameters, except of pH value, are the same as those illustrated in the second paragraph. These samples are named as Au/[H(Na)Y]-pH5, Au/[H(Na)Y]-pH6, Au/[H(Na)Y]-pH7 to represent they were prepared in the gold solution of pH 5, pH 6 and pH 7.3, respectively.

Characterization

Au loading of each sample was determined by GBC 906 atomic absorption unit. Si and Al contents were characterized by 7500CE ICP-MS. HRTEM pictures were taken with a Philips Tecnai G2 electron microscope operated at 200 kV with a modified specimen stage. Bruker DSX300 solid-state NMR was used for characterization. For the measurement of binding energy (BE) and atomic ratio on the exterior surface of Au/Y catalysts, VG Scientific ESCALAB 250, using Al K α monochromatic X-rays, was applied. Zeta-potential of zeolite support was measured by Malvern Nano ZS.

Results and Discussions

Gold complexes in the solutions adjusted to different pH values by using NaOH solution

Table 1. Properties of gold species and gold loading for Au/[H(Na)Y]-pH5, Au/[H(Na)Y]-pH6, Au/[H(Na)Y]-pH7 samples

sample	properties of gold species			Gold loading (wt%) *
	pH value of gold solution	No. of -Cl replaced by -OH (theoretical calculation)	dominant gold complex forms	
Au/[H(Na)Y]-pH5	5	2.2	AuCl ₂ (OH) ₂ ⁻	2.52
Au/[H(Na)Y]-pH6	6	3.2	AuCl(OH) ₃ ⁻ , Au(OH) ₃	0.87
Au/[H(Na)Y]-pH7	7.3	3.9	Au(OH) ₄ ⁻ , Au(OH) ₃	0.64

* wt% of gold on Au/Y

In this research, HAuCl₄ was used as gold precursors. The pH value of gold solution was about 2.8. By adding 0.1N sodium hydroxide into the solution, gold complexes were gradually changed. That is, chloride which was originally on gold atom was replaced by hydroxide [8, 9]. Solution pH can only be increased fast after all the chlorides on gold atoms are replaced. Through theoretical calculation, it can be found that the number of replaced chloride were 2.2, 3.2 and 3.9 in the gold solution of pH 5, 6 and 7.3, respectively. The dominant gold species is listed in the fourth column of Table 1. From the experimental results, it is evident that as the pH value of gold solution is increased, gold loading of Au/Y sample is decreased. Moreover, from HRTEM photographs in Figure 1, larger gold nanoparticles are deposited onto zeolite Y as pH value of gold solution is increased.

The results can be explained from the viewpoint of different sizes of gold complex formed in the solution with different pH values. In the acid solutions with pH lower than 6, most gold monomers possess negative charges. They suspend well in the solution because of electrical repulsive forces between each other. Accordingly, owing to the tiny size, they diffuse into the cages of zeolite easily. As the pH value approaches neutral (*i.e.*, pH 7), more Au(OH)₃ species are formed. Without the negative charge, they easily aggregate and precipitate in the solution [10]. As a result, large gold species exist in the solution. It is impossible for them to diffuse into the cages and can only

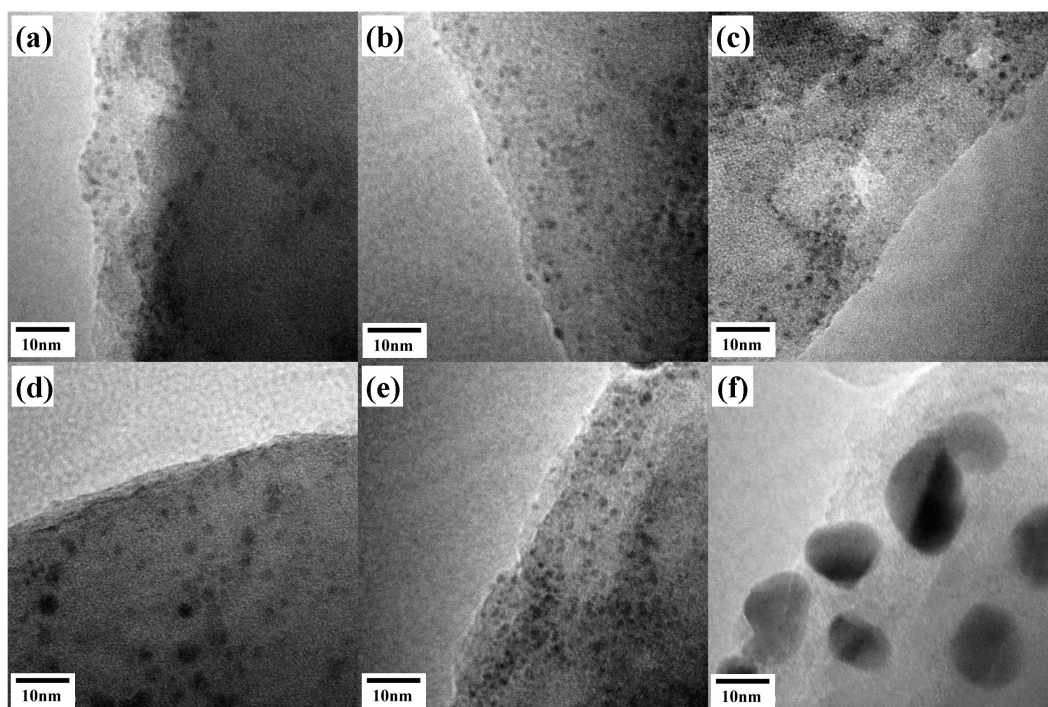


Figure 1. HRTEM characterization of (a)(b) Au/[H(Na)Y]-pH5, (c)(d) Au/[H(Na)Y]-pH6 and (e)(f) Au/[H(Na)Y]-pH7

be deposited on the exterior surface of Y-type zeolite.

Surface compositions of zeolite supports

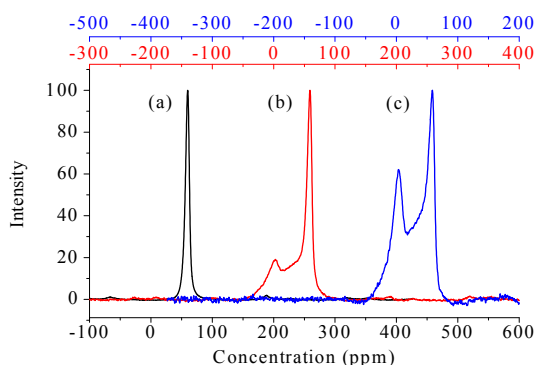


Figure 2. ^{29}Al -MAS Solid-state NMR of (a) NaY, (b) HY and (c) H(Na)Y.

In this research, NaY, HY and H(Na)Y (surface modified HY) were used as supports for loading gold species in the solution. It is necessary to explore their differences, especially of surface properties, before gold loading. In the spectra of ^{29}Al -MAS NMR, as shown in Figure 2, only one peak in 60ppm for NaY sample indicates that all Al species were inside the framework of zeolite [11]. As NaY was converted to HY, outeraframework Al species was found based on the growing intensity in 0ppm. After surface modification of HY with sodium hydroxide,

proportion of outeraframework Al significantly was increased. On the other hand, in comparison between ^{27}Si -MAS NMR and ^{27}Si -CPMAS NMR spectra, as shown in Figure 3, it is undoubted that nearly no Si-OH, which is from defect sites in the framework, was found in NaY [12]. In contrast, the presences of Si-OH groups in HY and H(Na)Y were evident. In summary, the examination by using solid state NMR indicates that NaY possesses most complete zeolite framework structure, and significant amount of defects are formed in the framework of HY and H(Na)Y.

From the results of XPS characterization, Al(2p) peak of NaY sample appeared in 74.25eV and Si(2p) peak in 102.37eV, corresponding to the results in the literature [13, 14]. However, for those of HY and H(Na)Y, both Al and Si peaks became broader. After the de-convolution, at least two peaks appeared. One was with higher binding energy and the other with lower. According to the literature, as more Al-O units was inserted into the silica-type framework, both of binding energy of Al(2p) and Si(2p) peaks progressively reduced [13-15]. As a result, it is estimated that two types of aluminosilicate structures were present on the exterior

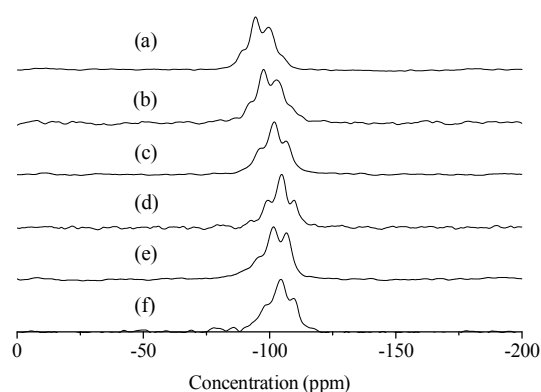


Figure 3. ^{27}Si -MAS Solid-state NMR of (a) NaY, (c) HY, (e) H(Na)Y and ^{27}Si -CPMAS of (b) NaY, (d) HY, (f) H(Na)Y

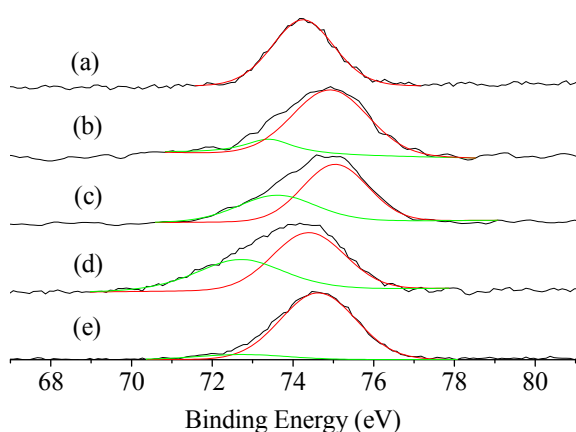


Figure 4. Deconvolution of Al peak in ESCA characterization of (a)NaY, (b)HY, (c)H(Na)Y, (d)Au/H(Na)Y and (e)H(Na)Y-w

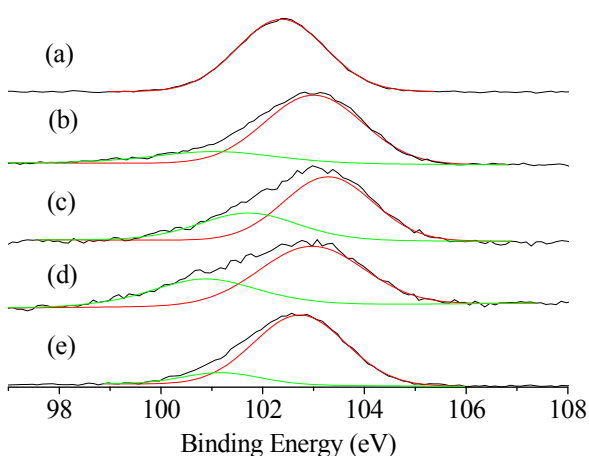


Figure 5. Deconvolution of Si peak in ESCA characterization of (a)NaY, (b)HY, (c)H(Na)Y, (d)Au/H(Na)Y and (e)H(Na)Y-w

surface of HY and H(Na)Y samples. The Si and Al peaks of higher binding energy indicated zeolite structure with the presence of vacancies replacing the ion-exchange sites (Al-O units). Meanwhile, those with lower binding energy indicated amorphous aluminosilicate structure which was newly formed by the Al and Si species outside the zeolite framework. The latter structure was considered having more Al species inside and, also, more defect sites.

However, the reduced intensity for peaks with lower binding energy of H(Na)Y-w sample, as shown in figure 4(e) and figure 5(e), indicated that the amorphous aluminosilicate structure was quite loose and could be easily washed away through the flushing process. As to Au/H(Na)Y sample, higher gold solution temperature not only strengthened the structure but also promoted the formation of amorphous aluminosilicate. Larger intensity of both Al and Si peaks with lower binding energy is observed in figure 4(d) and figure 5(d).

Zeta potential of zeolite supports

Table 2. Zeta-potential of zeolite supports

sample	With the Presence of NaNO ₃ salts	Measured zeta potential (mV) *
NaY	X	-35.3
HY	X	-32.1
H(Na)Y	O	35.5
H(Na)Y-w	X	-10.8
H(Na)Y-w-NaNO ₃	O	34.8

*0.3g of each sample (water excluded) immersed in 5.7g D. I. water

Because most of gold species, except of Au(OH)₃ precipitate, in the solution possessed negative charge, zeta-potential of zeolite supports is an essential factor which would significantly affect the progress of gold loading. Table 2 lists zeta-potential of NaY, HY, H(Na)Y, H(Na)Y-w and H(Na)Y-w-NaNO₃. According to the literature, the existence of electrolyte ions, which is also named indifferent electrolyte, would compress the electrical double layer and gradually reduce the zeta-potential of zeolite surface with the increasing concentration [16]. On the other hand, Al species is considered as specifically adsorbed ions, which could be adsorbed in the stem layer around zeolite surface through some specific and nonelectrostatic affinity. The presence of specifically adsorbed ions could reverse the sign of zeta potential [16,17].

As a result, it is not surprising why the zeta potential of H(Na)Y could be dramatically affected after surface modification with NaOH. With the increasing amounts of extraframework Al as shown in figure 2, there exists strong possibilities that some Al species left their original sites in the zeolite structure and got into the solution. As to H(Na)Y-w and H(Na)Y-w- NaNO_3 , it is clear that the sign of zeta potential could be effectively reversed with the presence of NaNO_3 salts.

Gold loading temperature and flushing process

Table 3. AA, ICP and ESCA characterization of Au/[H(Na)Y]-80, Au/[H(Na)Y]-80-f, Au/[H(Na)Y]-30, Au/[H(Na)Y]-30-f

Sample No.	AA/ ICP		ESCA		
	Au (wt%)	Al/Si (wt%)	Au/Si (wt%)	Al/Si (wt%)	Au/Al (wt%)
Au/[H(Na)Y]-80	0.98	0.37	0.57	1.55	0.36
Au/[H(Na)Y]-80-f	0.82	0.37	0.48	1.36	0.35
Au/[H(Na)Y]-30	0.91	0.37	0.24	0.98	0.24
Au/[H(Na)Y]-30-f	0.45	0.36	0.18	0.69	0.26

From table 3, it is found that gold loading temperature and flushing process possesses significant effects on the gold loading amounts. Compared to 30°C gold loading temperature, 80°C increased gold contents in both of bulk catalysts and exterior surface. Al/Si ratio was also promoted. Through the flushing process, both of gold and aluminum contents apparently reduced. However, less proportion of these two species was washed away for Au/Y samples prepared at 80°C. This result indicated that higher gold loading temperature not only promoted dehydration between Al-OH and Si-OH, but also caused chemical bonds between gold species in the solution and surface defects.

From the last column shown in table 3, no matter gold loaded at temperature of 30°C or 80°C, Au/Al ratio remained nearly the same before and after flushing process. Therefore, it is evident that gold species in the solution tended to approach Al on the exterior surface. Chemical bond between these two species was therefore formed through the dehydration process.

Gold loading onto zeolite supports with different surface compositions and zeta potentials

Properties of surface composition and zeta potential for

zeolite supports were illustrated in detail in the second and third section. It required further investigation on the effects of these properties on the gold loading progress. Table 4 listed gold contents in the bulk catalysts and Au/ Si ratio on the exterior surface. On the other hand, after adding zeolite into gold solution, solution pH changed significantly. Therefore, variation in the form of gold species should be taken into account.

In order to compare the gold loading amount on different types of zeolite based on the consistence of gold complex forms, Au/HY data should be excluded in advance because the dominant gold species, as shown in the third column of table 2, is completely different. In table 4, it is noticeable that nearly no gold species deposited onto NaY. For Au/H(Na)Y sample, about 1 wt% of gold is contained. However, gold loading onto H(Na)Y-w supports was only 0.46% left, with more than 10-time Au/Si ratio on the exterior surface as compared to that of Au/H(Na)Y. After immersing H(Na)Y-w into 1N NaNO_3 solution, that is, H(Na)Y-w- NaNO_3 sample, the amount of gold loading returned to around 1 wt%, together with similar Au/Si ratio by XPS.

Form the aspect of zeta potential, nearly no gold monomers could approach the surface of NaY and H(Na)Y-w, because the zeta-potential was negative. However, $\text{Au}(\text{OH})_3$ preprecipitate, with much larger size, could deposit onto exterior surface owing to the electroneutrality. Nevertheless, physical deposited gold nanoparticles were easily washed away by the flushing procedure. Chemical bond between Au-OH and surface defects of zeolite was required. The zeolite framework of NaY is so complete that nearly no gold particles could be anchored on the exterior surface. As to Au/H(Na)Y-w, surface defects promoted gold loading onto the supports, which is evidenced by the extremely high Au/Si ratio, as shown in table 4.

For Au/H(Na)Y and Au/H(Na)Y-w- NaNO_3 samples, zeolite surface with positive zeta-potential attracted gold monomers with negative charge in the solution. Because of the tiny size, they easily got into the interior of zeolite. On the other hand, the presence of surface defects also caused dehydration with Au-OH. Generally speaking, owing to the similar properties in zeta-potential and surface structure

Table 4. Properties of gold solution, gold loading in bulk catalysts and Au/Si ratio on the exterior surface of Au/NaY, Au/HY, Au/H(Na)Y, Au/H(Na)Y-w, Au/H(Na)Y-NaNO₃

Sample	pH value after adding zeolite into gold solution	dominant gold species	gold loading (wt%)	Au/ Si by XPS
Au/NaY	6.63	Au(OH) ₄ ⁻ , AuCl(OH) ₃ ⁻ , Au(OH) ₃	0.08	-
Au/HY	4.97	AuCl ₂ (OH) ₂ ⁻	0.94	0.1
Au/H(Na)Y	6.71	Au(OH) ₄ ⁻ , AuCl(OH) ₃ ⁻ , Au(OH) ₃	1.02	0.67
Au/H(Na)Y-w	6.75	Au(OH) ₄ ⁻ , AuCl(OH) ₃ ⁻ , Au(OH) ₃	0.46	9.26
Au/H(Na)Y-w-NaNO ₃	6.57	Au(OH) ₄ ⁻ , AuCl(OH) ₃ ⁻ , Au(OH) ₃	1.07	0.7

for H(Na)Y and H(Na)Y-w-NaNO₃, gold amounts in the bulk catalysts, as well as those on the exterior, are very much alike.

With differences in gold complex forms, the process of gold loading for Au/HY sample is quite dissimilar. In the pH5 gold solution, nearly no Au(OH)₃ precipitate formed; meanwhile, number of chlorides on gold atom increased. Chloride group, as an electron withdrawing group, caused uneven electron distribution around the gold monomers. Hydroxyl groups on Au atom tended to be slightly electroneutrality. This explained why the gold species with negative charge could still enter the interior of zeolite, together with few amount of gold on the exterior surface of HY, as shown in table 4.

Conclusions

In this study, effects of gold species and zeolite status on gold loading process were thoroughly explored. From the aspect of gold species, pH value of the solution significantly affected the gold complex form. In pH5 solution, they existed in the form of gold monomer with negative charge. As the pH value approached neutral, Au(OH)₃ species formed. They easily aggregated and became larger ones. Therefore, as the pH increased, amounts of gold loading decreased, together with much larger gold nanoparticles on the surface. From the aspect of zeolite status, surface composition and zeta-potential were essential factors which apparently affected the mechanisms of gold loading. Because most of gold monomers in the solution possessed negative charge, zeolite surface with positive zeta-potential helped them getting into cages. On the other hand, defects on the zeolite surface caused dehydration with Au-OH and helped anchor these gold species with larger size.

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