

TiO₂ supported nano-Au catalysts prepared via solvated metal atom impregnation for low-temperature CO oxidation

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TiO₂ supported nano-Au catalysts were prepared by solvated metal atom impregnation (SMAI) method. The catalysts were characterized by means of AAS, TPD, H₂ reduction desorption (H₂-RD), XRD, TEM, XPS and tested for low-temperature CO oxidation. XRD and TEM results showed that the pretreatment temperature had an influence on the particle size of Au/TiO₂ catalysts. The average particle size increased with the increase in pretreatment temperature. XPS indicated that gold in the catalysts was presented in the form of metallic state clusters. Catalytic studies showed these catalysts were very active and stable in low-temperature CO oxidation. The CO oxidation activity of the catalysts increased as the Au particle size decreased. The measurement results of AAS, TPD and H₂-RD revealed that there were some organic fragments on the surface of Au particles which might be responsible for the high stability of the Au/TiO₂ catalysts.

KEY WORDS: CO oxidation; nano-particles of gold; TiO₂; solvated metal atom impregnation; stability.

1. Introduction

Gold supported on reducible oxides is well known to be active for CO oxidation at low temperature [1,2]. This reaction is of considerable concern since it plays an important role in CO safety gas masks [2], purification of air in CO₂ lasers [3], CO sensors [4], and so forth. It is therefore of interest to develop highly active CO oxidation catalysts to remove trace amounts of CO. Since Haruta and co-workers [5] discovered that highly dispersed gold catalysts are extremely active for CO oxidation even at subambient temperature, there have been a number of investigations dealing with gold-based catalysts for CO oxidation [6–11].

The CO oxidation activity is strongly influenced by the catalyst preparation methods. Usually, supported gold catalysts were prepared by co-precipitation, deposition-precipitation and chemical vapor deposition methods. These preparation methods can produce small Au particles below 10 nm in size and these Au particles exhibit high catalytic activity in CO oxidation.

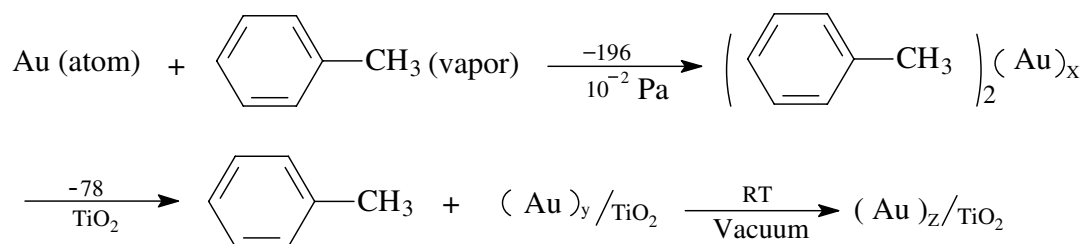
Co-precipitation is generally carried out by adding an aqueous solution of HAuCl₄ and a metal nitrate into an aqueous solution of Na₂CO₃. This preparation route is not easy to control. For example, extent of mixing, order and mode of adding various compounds, temperature, aging period of precipitate in mother liquor and washing procedures all affect the precipitation process [12]. In addition, co-precipitation of Au and transition metal oxide consumes large amounts of Au solution and creates low surface area support [13].

Deposition-precipitation (DP) have been known to be an useful method for the preparation of supported gold catalysts such as Au/ γ -Al₂O₃ and Au/TiO₂ [14–17]. Bamwenda *et al.* [14] observed that the CO oxidation activity of Au/TiO₂ synthesized by the DP method was four orders of magnitude greater than that of Au/TiO₂ synthesized by the photodeposition method. In Au/ γ -Al₂O₃ catalysts, it was found that gold oxides and gold chloride were presented on the surface of supported gold crystallites after oxidation treatment at 300 °C [15]. It was reported in the same paper that addition of Mg citrate to preparation solutions has a significant effect on properties of the Au/ γ -Al₂O₃ catalysts. In Au/TiO₂ catalysts, CO oxidation activity and Au particle size depended on the pH value of gold chloride solution and the variation of n values in [Au(OH) _{n} Cl_{4- n}]^{–1} formed by the partially hydrolyzation of HAuCl₄. The most active Au/TiO₂ catalyst was obtained after calcination at 300–400 °C. Below these temperatures, Au particles were metallic and larger than 5 nm in size. In addition, Au particle decreased to smaller than 4 nm above pH 6 of HAuCl₄ solution.

Compared with DP method, conventional impregnation has not been so successful in producing active gold catalyst. It was reported that Au/TiO₂ catalysts prepared by impregnation had low CO conversion, owing to the fact that it was difficult to prepare Au particles in nanometer size by impregnation [14]. In other studies, the authors concluded that reasons for the low activity of gold catalysts prepared by impregnation were the residue chlorine ions on the catalytic surface, which originate from the HAuCl₄ solution, and weak interaction between gold particles and the support [18]. The residual chloride was found to affect the activities in two

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Scheme 1. *x*, *y* and *z* represent the number of Au atoms.

different ways. It facilitates the agglomeration of Au particles during heat treatment, and it inhibits the catalytic activity by poisoning the active site [19]. Recently Iwasawa *et al.* [20,21] improved impregnation to obtain highly active Au/TiO₂ catalysts by using gold phosphine complexes as precursor compounds. The authors pointed out that by using a gold compounds, a strong interaction between gold complex and the support can be produced and the effect of residue chlorine ions on the catalyst activity can be avoided.

In this study, we report the successful synthesis of highly dispersed Au catalysts (< 5 nm) using solvated metal atom impregnation (SMAI) method on TiO₂ supports. One of the features of the SMAI technique is that it can directly obtain highly dispersed zero-valent metals on the supports without high-temperature calcination and reduction processes which might cause small metal particle to aggregate to form larger ones [22]. The SMAI method is especially useful for preparing Au catalysts because it does not use HAuCl₄ as precursor compound, the effect of residue chlorine ions on the catalyst activity can be avoided.

2. Experimental

2.1. Preparation of catalysts

The procedures for preparing Au/TiO₂ catalysts by SMAI method are as shown in Scheme 1.

The TiO₂ support were dehydrated under vacuum (1.3×10^{-2} Pa) at 400 °C for 8 h. Toluene used as the solvating medium was carefully dehydrated and degassed by “freeze–thaw” process. The design of the static metal atom reactor for the preparation of the precursor solution of bis(toluene) gold (0) has been described elsewhere [23]. In a typical experiment, approximately 1 g of gold chop (99.99%) was evaporated and co-condensed with 130 mL of toluene at –196 °C under a dynamic vacuum of less than 1.33×10^{-2} Pa over a period about 2 h. After finishing the co-condensation, the co-condensate was allowed to be warmed up to –78 °C and melted down to the bottom of the reactor. the bis(toluene) gold (0) complex prepared in this way is extremely air sensitive and thermally unstable, which decomposes into gold (0) and toluene at about –100 °C. The precursor solution was transferred

to the precooled (–78 °C) TiO₂ through a stainless steel tube. The TiO₂ was impregnated with solvated Au atom (cluster) solution for 5 h at –78 °C under stirring. Then the Au–toluene/TiO₂ slurry was gradually warmed to room temperature. The colorless excess toluene was removed by a syringe and the Au/TiO₂ catalysts were dried under vacuum at room temperature, 300 and 600 °C respectively for 6 h. The dry samples were stored and handled in the nitrogen filled glovebox. The obtained catalysts are symbolized as Au/TiO₂ (RT), Au/TiO₂ (300) and Au/TiO₂ (600), respectively.

2.2. Temperature programmed desorption (TPD)

Temperature programmed desorption experiments were carried out using a standard apparatus. The desorption temperature could be up to 600 °C. The heating rate is 0.5 °C per second. A quadruple mass spectrometer was employed to monitor the desorbing species.

2.3. H₂ reduction desorption (H₂–RD)

H₂ reduction desorption experiments were performed on a double way microreactor. All samples were thoroughly degassed in vacuum at 100 °C prior to the hydrogen treatments. The reduction was carried out at 200 °C under H₂ of 2.3×10^4 Pa. Desorption products were analyzed by a SP-502 gas chromatograph.

2.4. Atomic absorption spectroscopy (AAS)

The gold loading was determined by using an atomic absorption spectroscopy (AAS). Before the measurements, the machine was calibrated with Au standard solution (Sigma–Aldrich). Gold in the catalysts was dissolved in aqua regia. The mixture was heated to gentle boiling while stirring continuously. After significant reduction of the solution volume, the slurry was filtered and diluted with deionized water to a concentration in the calibrated range. During the measurements, the wavelength was set to 243 nm and acetylene gas mixed with air was utilized for the flame source.

2.5. X-ray diffraction (XRD)

X-ray diffraction of the supported gold particles was performed on a D/MAX- IIIA X-ray diffraction spec-

trometer. Diffraction patterns were recorded with $\text{CuK}\alpha$ radiation and graphite monochromator over a 2° – range of 20° – 70° . The working voltage and current of X-ray tube were 45 kV and 170 mA.

2.6. X-ray photoelectron spectra (XPS)

The X-ray photoelectron spectra were taken before each catalytic run. XPS were recorded on a PHI-5300 spectrometer using $\text{AlK}\alpha$ radiation (1486.6 eV). The instrument was operated at pressure below 1×10^{-8} Pa. Samples were mounted on the holder using double sided type. The XPS binding energies were referenced to the graphite C_{1s} peak at 284.2 eV and the system was occasionally checked using the $\text{Fe } 2p_{3/2}$ peak at 706.8 eV of a sputtered cleaned pure iron foil.

2.7. Transmission electron microscope (TEM)

The electron microscopy study was performed using a Phillips 400ST transmission electron microscope. The samples for TEM were prepared by ultrasonic dispersion after the catalyst powder was ground and added to *n*-butanol. The suspension was left for 1 min to cause the large support particle to settle out. One drop of the suspension was then placed on a carbon coated copper grid. The sample was dried and operated at 100 kV.

2.8. Activity measurements

A steady-state catalytic test was carried out in a fixed-bed flow microreactor. The catalyst powder was sandwiched between glass wool plugs in an 8 mm i.d. glass reactor tube. Experiments were performed in the temperature range 273–393 K at atmospheric pressure. For each experiment 200 mg catalyst was used which was transferred into the reactor under the protection of N_2 gas flow. The reaction gases contain 1.0% CO balanced with air, purified through a molecular sieve column and passed through the catalyst bed at a flow rate of 67 mL/min ($sv = 20,000 \text{ h}^{-1}$). Kinetic data were taken after 10 or 20 min on stream at specified conditions. The products were analyzed by a SP-502 gas chromatograph.

3. Results and discussion

3.1. Elemental analyses and products of TPD and H_2 -RD

Table 1 Summarizes the Au loadings (AAS) and the C, H contents measured using Perkin-Elmer 240 elemental analyser. It can be seen that the catalysts prepared by SMAI method incorporate carbonaceous fragments.

Qualitative analysis of the products of the TPD at various temperatures for Au/TiO_2 (RT) catalyst was carried out. At lower temperatures (25 and 100 $^\circ\text{C}$), the

Table 1
Au loadings and C, H contents of Au/TiO_2 catalysts

Catalyst	Pretreatment temperature ($^\circ\text{C}$)	Au loading (wt%)	C (wt%)	H (wt%)
Au/TiO_2 (RT)	RT	3.1	0.9	0.16
Au/TiO_2 (300)	300	3.1	0.3	0.05
Au/TiO_2 (600)	600	3.1	0.05	0.01

Table 2
Products evolved during H_2 reduction desorption of Au/TiO_2 (RT) catalysts

Product	Content (mol%)	Product	Content (mol%)
CH_4	75	C_5H_{12}	1
CO_2	8	C_6H_6	6
C_2H_6	1	$\text{C}_6\text{H}_5\text{CH}_3$	3
C_3H_8	2	$\text{C}_6\text{H}_{11}\text{CH}_3$	1
C_4H_{10}	2	C_8H_x	1

main product desorbed is toluene with a small amount of benzene. At 200 $^\circ\text{C}$, CO_2 desorption started. CH_4 and H_2 desorbed only at temperatures = 280 $^\circ\text{C}$. Only small amount of CH_4 and H_2 were evolved upon heating the sample up to = 400 $^\circ\text{C}$.

In order to determine the composition of organic species adsorbed on the metal surface, hydrogen was added to the catalyst samples to displace surface alkyl fragments by the formation of the corresponding alkanes. For example, adsorbed methyl or methylene species would be desorbed as methane. The qualitative analysis results of the products desorbed during H_2 treatment for Au/TiO_2 (RT) catalyst are shown in table 2. It is clear that the predominant product is methane.

3.2. Catalyst characterization

XRD was used to measure the average Au particle size and to identify the crystalline phases presented on the catalysts. Figure 1 shows the XRD patterns of the three kinds of Au/TiO_2 catalysts pretreated at different temperature. For Au/TiO_2 (RT) catalyst, no distinct diffraction of gold could be identified due to small particle size. For Au/TiO_2 (300) and Au/TiO_2 (600) catalysts, a maximum in diffraction was detected at $d = 0.2335 \text{ nm}$, which is characteristic of metallic Au. The intensity of the diffraction peaks at $2\theta = 38.2^\circ$ for $\text{Au}(111)$, $2\theta = 44.4^\circ$ for $\text{Au}(200)$ and $2\theta = 64.6^\circ$ for $\text{Au}(220)$ depends on the pretreatment temperature. The intensity of the diffraction peak increased with increase of the pretreatment temperature. Small increase of the crystallite size was observed after heating to 300 $^\circ\text{C}$. Only sample heated to 600 $^\circ\text{C}$ resulted in significant particle size increase. The average crystallite diameter can be calculated according to Scherrer's equation $d = K\lambda/\beta\cos\theta$. The results are listed in table 3 along with TEM data.

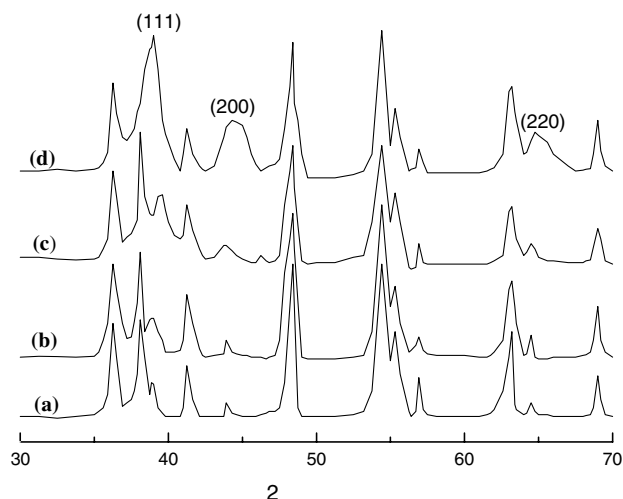


Figure 1. XRD patterns of Au/TiO₂ catalysts. (a) Support TiO₂; (b) Au/TiO₂ (RT); (c) Au/TiO₂ (300); (d) Au/TiO₂ (600).

Representative transmission electron micrographs for Au/TiO₂ catalysts are shown in figure 2. Smaller Au particles with diameter less than 1 nm are difficult to be distinguished accurately from the supports. At least 100 particles for each sample were counted, and particle size distributions were obtained by tabulating the number of the particles in a specific size range, i.e., 1.2–2.2 nm. Histograms were obtained by determining the percentage of the particles. The volume average diameter was calculated from the crystallite size distribution by using the following equation:

$$d\bar{v} = \frac{\left(\sum_i n_i d_i^4 \right)}{\left(\sum_i n_i d_i^3 \right)}$$

where n_i is the number of the particles having a characteristic diameter d_i (within a given diameter range). The histograms of the crystallite size distributions are presented in figure 3. The Au particle sizes obtained from TEM are listed in table 3 along with

Table 3
Average Au particle sizes of Au/TiO₂ catalysts

Catalyst	Pretreatment temperature (°C)	TEM (nm)	XRD (nm)
Au/TiO ₂ (RT)	RT	1.8	< 2.5
Au/TiO ₂ (300)	300	2.2	2.8
Au/TiO ₂ (600)	600	7.3	8.0

XRD results. It can be seen from table 3 that for all the catalysts the average Au particle sizes determined from TEM agree with those obtained from XRD line broadening. It is apparent that the SMAI method results in a high dispersion of gold particles on TiO₂. A major fraction of the gold particles were in the range of 1–3 nm of Au/TiO₂ (RT) and Au/TiO₂ (300) catalysts and exhibited an average particle size of 1.8 nm and 2.2 nm, respectively. However, larger gold particles were observed after high temperature (600 °C) treatment procedure. In the case of Au/TiO₂ (600) catalyst, most of the particles were concentrated in the 4–10 nm region and the average particle size was estimated to be 7.3 nm. It is note worthy that the Au particle size distribution of all Au/TiO₂ catalysts prepared by SMAI technique was narrow.

The XP spectra of Au 4f level for Au/TiO₂ catalysts under various treatments temperature are shown in figure 4. The absence of any appreciable binding energy differences between RT, 300 °C and 600 °C treatment conditions precludes any appreciable electronic structural change for the gold particles due to the different pretreatment temperatures. The detected Au 4f peaks did not exhibit any appreciable shift in the binding energies from those of bulk gold, indicating that the gold particles of all the samples were in metallic state.

3.3. Catalytic activity in CO oxidation

In general, the TOF is a convenient parameter to compare the activity of catalysts. Although the quantitative comparison of TOF is not yet possible because there is no good way to obtain an accurate dispersion of

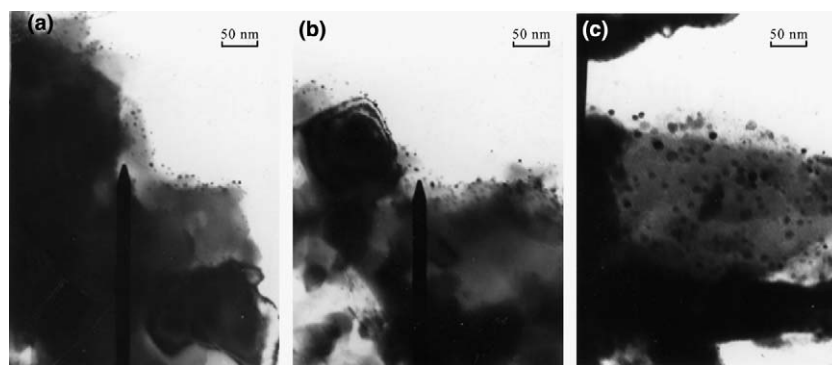


Figure 2. TEM photographs of Au/TiO₂ catalysts (10,000×). (a) Au/TiO₂ (RT); (b) Au/TiO₂ (300); (c) Au/TiO₂ (600).

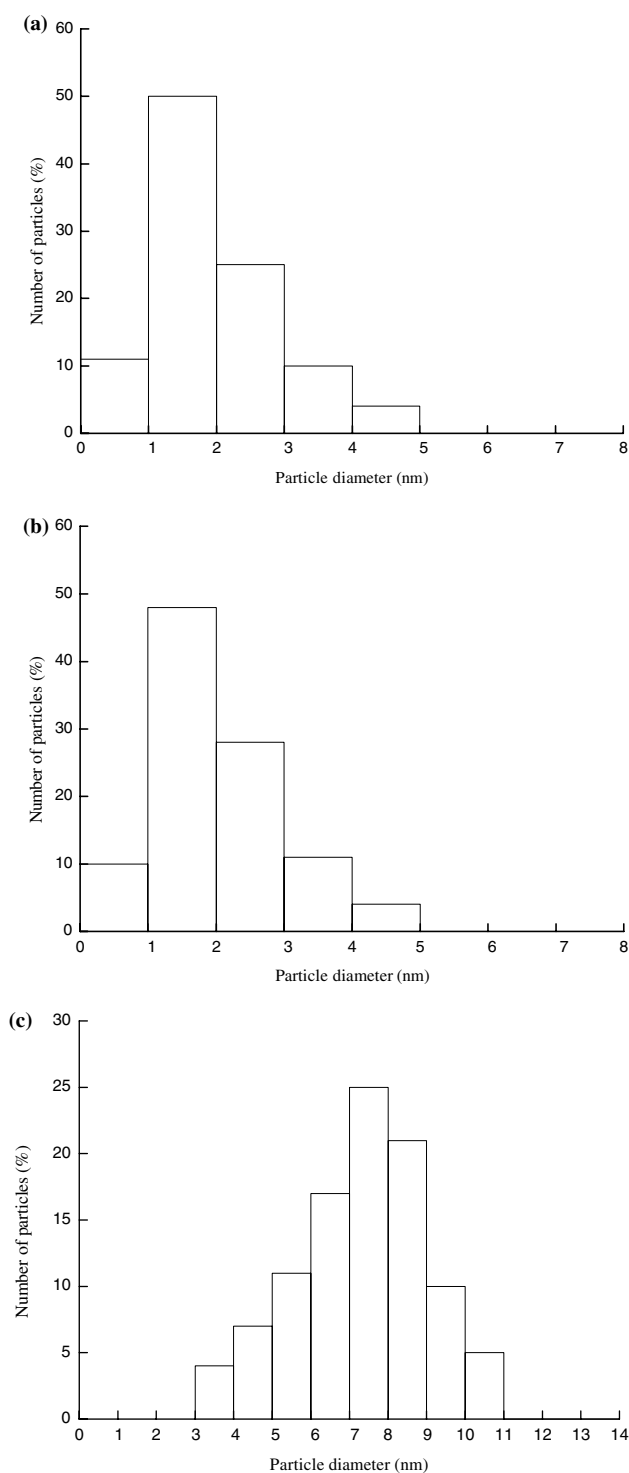


Figure 3. Particle size distribution for Au/TiO₂ catalysts. (a) Au/TiO₂ (RT); (b) Au/TiO₂ (300); (c) Au/TiO₂ (600).

Au sample, semi-quantitative comparison is still very valuable. Table 4 showed the comparison of CO oxidation activities on some catalysts prepared by different methods. It was noted that the TOF of the Au/TiO₂ catalysts prepared by SMAI is obviously higher than that of some other catalysts.

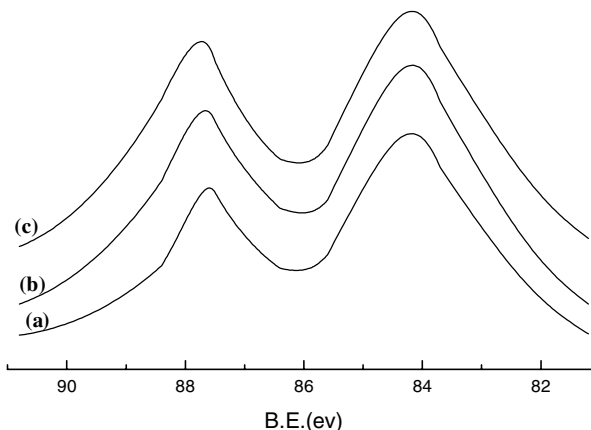


Figure 4. Au 4f peaks XP spectra of Au/TiO₂ catalysts. (a) Au/TiO₂ (RT); (b) Au/TiO₂ (300); (c) Au/TiO₂ (600).

Table 4
Comparison of CO oxidation activities

Catalyst	Preparation methods ^a	<i>d</i> Au (nm)	<i>T</i> (K)	TOF (s ⁻¹)	References
Au/TiO ₂	CP	4.5	313	0.095	[24]
	DP	1.7	273	0.06	[25]
	CVD	3.8	273	0.02	[25]
	DP	2.5	300	0.15	[14]
	SMAI	1.8	293	0.068	^b
	SMAI	2.2	293	0.059	^b
Au/Ti(OH) ₄	IAH	3	300	0.05	[26]
Au/Fe ₂ O ₃	CP	3.6	203	0.021	[27]
Au/Al ₂ O ₃	CP	3.5	273	0.006	[25]
	DP, pH 7	4	298	0.004	[28]
Au/SiO ₂	CVD	6.6	298	0.02	[25]

^aCP, coprecipitation; DP, deposition-precipitation; CVD, chemical vapor deposition; IAH, impregnation of AuPPh₃NO₃ onto as-precipitated hydroxides.

^bPresent work.

Figure 5 shows the CO oxidation catalytic activity of the Au/TiO₂ samples pretreated at different temperature. The sample Au/TiO₂ (RT) pretreated at room temperature showed highest catalytic activity at temperature below room temperature (293 K), obtaining 50% CO conversion at 273 K. The sample pretreated at 600 °C Au/TiO₂ (600) showed no catalytic activity at 273 K. Although the sample Au/TiO₂ (300) pretreated at 300 °C exhibited lower catalytic activity Au/TiO₂ (RT) that pretreated at room temperature at reaction temperature below 293 K, it showed an appreciable activity for CO oxidation. The order of the activity at room temperature for different pretreatment temperature was Au/TiO₂ (RT) > Au/TiO₂ (300) > Au/TiO₂ (600). While 100% CO conversion was achieved at 303 and 313 K for Au/TiO₂ (RT) and Au/TiO₂ (300) catalysts, respectively, full CO conversion was obtained only at 493 K for Au/TiO₂ (600) catalyst.

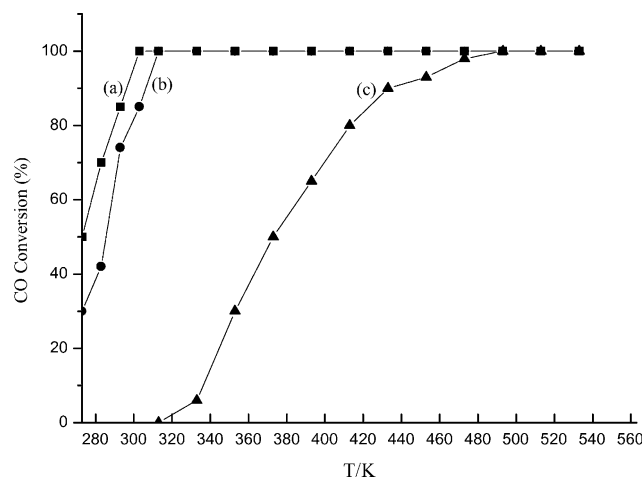


Figure 5. Catalytic activities of gold catalysts in CO oxidation as a function of reaction temperature. (a) Au/TiO₂ (RT); (b) Au/TiO₂ (300); (c) Au/TiO₂ (600).

It is known from the literature that long exposures to air cause sintering of the gold particles and thereby deactivation [8]. In order to see if the Au/TiO₂ catalysts prepared by SMAI method are stable, we carried out the stability/regeneration investigation on all the samples. Figure 6 depicted the variation of the CO oxidation catalytic activity of these catalysts as a function of reaction time. In these studies, the reaction temperature was kept at 293 K for both Au/TiO₂ (RT) and Au/TiO₂ (300) catalysts while it was kept at 373 K for Au/TiO₂ (600) catalyst. The deactivation rate for Au/TiO₂ (RT) and Au/TiO₂ (300) was very small and only dropped from 85% to 80% and from 80% to 78%, respectively. The activity of Au/TiO₂ (600) remained almost constant during this period until the reaction was stopped (20 h).

The results of catalytic test have demonstrated that the CO oxidation activity of the Au/TiO₂ catalysts by SMAI was comparable to that of the most active Au/TiO₂ catalysts reported in the literature [11,14,29]. In [29], the Au/Ti(OH)₄ catalyst was obtained by grafting Au(PPh₃)₃(NO₃) onto the as-precipitated Ti(OH)₄ followed by a temperature-programmed calcination treatment. The authors reported that the freshly prepared Ti(OH)₄ was essential for the synthesis of highly dispersed Au particles and the high activity of the catalysts while conventional TiO₂ and commercial Ti(OH)₄ were found to be inefficient for the successful synthesis and resulted in an inactive CO oxidation catalyst with a particle size greater than 15 nm. In [11], a highly active Au/TiO₂ catalyst was synthesized by the interaction of a [Au₆(PPh₃)₆](BF₄)₂ complex with conventional TiO₂ support. The authors reported that the most active catalyst among prepared catalysts using different pretreatment procedures was the HTR/LTC pretreated catalyst. This result is similar to that observed by Lin *et al.* [18] on Au/TiO₂ catalyst

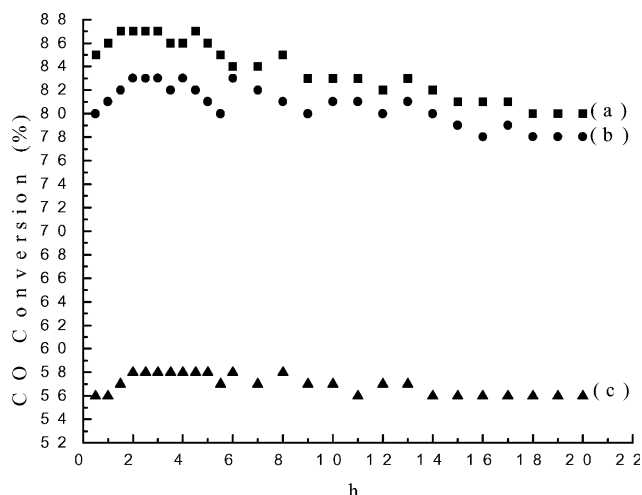


Figure 6. CO conversion over Au/TiO₂ catalysts as a function of reaction time. (a) Au/TiO₂ (RT) at 293 K; (b) Au/TiO₂ (300) at 293 K; (c) Au/TiO₂ (600) at 373 K.

prepared by the wet-impregnation method, wherein the highest activity catalyst was HTR/C/LTC catalyst which by following sequence, high-temperature reduction at 773 K followed by calcination at 673 K and finally low-temperature reduction at 473 K. Based on these results, Goodman *et al.* [11] suggested that the HTR/LTC pretreatments modify the TiO₂ supported so that there is an optimized interaction between Au (obtained from [Au₆(PPh₃)₆](BF₄)₂ complex) and TiO₂; this leads to a higher dispersion and an enhanced CO oxidation activity. The low-temperature CO oxidation activity of our Au/TiO₂ catalysts, especially Au/TiO₂ (RT) and Au/TiO₂ (300) prepared by SMAI method was much higher than that of the catalysts studied by Lin *et al.* [18], because of the enhanced Au dispersion (average particle size < 8 nm) in our case as opposed to that in their work (average particle size = 8 nm). Compared to Goodman *et al.*'s studies [11], our Au/TiO₂ catalysts also showed a little higher CO oxidation activity at room temperature. While 100% CO conversion was obtained at ~313 K for our Au/TiO₂ (RT) and Au/TiO₂ (300) catalysts, complete CO conversion was achieved only at 393 K for their most active HTR/C/LTC catalyst. The difference in CO oxidation activity is attributed to the different Au dispersion, which is related to the different decomposing condition and behavior of the Au precursors in these studies.

It is well known that high-temperature treatment usually results in catalyst sintering. Iwasawa and co-workers observed an average Au particle size of ca. 30 nm after high temperature calcination of Au-phosphine complex and conventional TiO₂. Interestingly, the high-temperature treatment sample Au/TiO₂ (600) in our study also showed good CO oxidation activity. The reason for this is that the high-temperature pretreatment did not cause serious sintering of the samples. After

treatment at 600 °C, the average particle size of the Au/TiO₂ (600) catalyst was smaller than 8.2 nm as determined by XRD and TEM. The possible explanation for this phenomenon is that in the process of SMAI catalyst preparation Au vaporizes monoatomically and cocondense with excess toluene. Upon warming, some Au clusters occur, but the cluster growth process completes with the reaction between the growing clusters and the toluene solvent. This also explained why there are some organic species adsorbed on the Au cluster surface. The predominant surface alkyl fragment is methyl, which is formed by insertion of Au and Au clusters into toluene and methyl C–C bond into toluene molecules. It is the organic fragments on the Au surface that decrease the degree of aggregation of Au particles during high-temperature treatment.

It is noteworthy, our samples showed little deactivation at 293 K [Au/TiO₂ (RT) and Au/TiO₂ (300)] and 373 K [Au/TiO₂ (600)], they were stable for 20 h during CO oxidation at below 100 °C. In contrast, studies on model catalyst systems [18] showed rapid deactivation at above ambient temperatures. The deactivation was also found to be rapid in Au/TiO₂ catalysts synthesized by the conventional wet-impregnation method [18]. Goodman *et al.* [11] reported the Au/TiO₂ catalyst synthesized from a [Au₆(PPh₃)₆](BF₄)₂ complex showed a high stability because of the stabilization effect of the HTR/LTC treatment of the Au clusters on the TiO₂ surface. The high stability for our samples may also be attributed to the stabilization effect of the organic fragment on the Au cluster surface.

4. Conclusions

Highly dispersed Au/TiO₂ catalysts were prepared by solvated metal atom impregnation method and tested for CO oxidation. These catalysts exhibited high catalytic activity in CO oxidation at low temperature. The pretreatment temperature played a crucial role in defining catalyst dispersion and activity. The average Au particle size increased and the activity decreased with the increase in pretreatment temperature. Gold existed in a metallic state in all the Au/TiO₂ catalysts synthesized by SMAI technique. The very finely dispersed metallic state Au are responsible for the high activity in low-temperature CO oxidation while the larger Au and high state Au contribute little to the activity. The Au/TiO₂ catalysts prepared via SMAI technique, especially those pretreated at below 300 °C are not only very active in low-temperature CO oxidation but also very stable.

Acknowledgments

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Reference

- [1] M. Haruta, *Catal. Today* 36 (1997) 153.
- [2] G.C. Bond and D.T. Thompson, *Catal. Rev. Sci. Eng.* 41 (1999) 319.
- [3] S.D. Gardner, G.B. Hoflund, D.R. Schryer, J. Schryer, B.T. Upchurch and E.J. Kielin, *Langmuir* 7 (1991) 2135.
- [4] M. Ando, T. Kobayashi and M. Haruta, *J. Chem. Soc. Faraday Trans.* 90 (1994) 1011.
- [5] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet and B. Delmon, *J. Catal.* 144 (1993) 175.
- [6] M.A. Bollinger and M.A. Vannice, *Appl. Catal. B* 8 (1996) 417.
- [7] Y. Yuan, A.P. Kozlova, K. Akasura, H. Wan, K. Tsai and Y. Iwasawa, *J. Catal.* 170 (1997) 191.
- [8] M. Valden, X. Lai and D.W. Goodman, *Science* 281 (1998) 1647.
- [9] S. H. Wu, W. P. Huang, S. M. Zhang, W. Wei, S. H. Zhang and X. C. Zheng, *Chin. J. Catal.* 21 (2000) 419.
- [10] R.J.H. Griesel and B.E. Nieuwenhuys, *J. Catal.* 199 (2001) 48.
- [11] T.V. Choudhary, C. Sivadinarayana, C.C. Chusuei, A.K. Datye, J.J.P. Fackler and D.W. Goodman, *J. Catal.* 207 (2002) 247.
- [12] J.W. Geus and J.A.R. van Veen, in: *Catalysis: An Integrated Approach to Homogenous, Heterogeneous and Industrial Catalysis*, eds. J.A. Moulijn, P.W.N.M. van Leeuwen and R.A. van Santen (Elsevier, Amsterdam, 1993) p. 335.
- [13] M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.* 115 (1989) 301.
- [14] G. R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, *Catal. Lett.* 44 (1997) 83.
- [15] C.K. Chang, Y.J. Chen and C.T. Yeh, *Appl. Catal. A* 174 (1998) 13.
- [16] E.D. Park and J.S. Lee, *J. Catal.* 186 (1999) 1.
- [17] G.K. Bethke and H.H. Kung, *Appl. Catal. A* 194 (2000) 43.
- [18] S.D. Lin, M. Bollinger and M.A. Vannice, *Catal. Lett.* 17 (1993) 245.
- [19] H.S. Oh, J.H. Yang, C.K. Costello, Y.M. Wang, S.R. Bare and H.H. Kung, *J. Catal.* 210 (2002) 375.
- [20] Y. Yuan, K. Akasura, H. Wan, K. Tsai and Y. Iwasawa, *Catal. Lett.* 42 (1996) 15.
- [21] A. Kozlov, A.P. Kozlova, H. Liu and Y. Iwasawa, *Appl. Catal. A* 182 (1999) 9.
- [22] S.M. Zhang, W.P. Huang, X.H. Qiu, B.Q. Li, X.C. Zheng and S.H. Wu, *Catal. Lett.* 80 (2002) 41.
- [23] K.J. Klabunde, *ACC Chem. Res.* 8 (1975) 399.
- [24] M.A. Bollinger and M.A. Vannice, *Appl. Catal. B* 8 (1996) 417.
- [25] M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma and M. Haruta, *Catal. Lett.* 51 (1998) 53.
- [26] A.I. Kozlov, A.P. Kozlova, H. Liu and Y. Iwasawa, *Appl. Catal. A* 182 (1999) 9.
- [27] A.M. Visco, A. Donato, C. Milone and S. Galvagno, *React. Kinet. Catal. Lett.* 61 (1997) 219.
- [28] S.-J. Lee and A. Gavrilidis, *J. Catal.* 206 (2002) 305.
- [29] Y. Yuan, K. Akasura, A.P. Kozlova, H. Wan, K. Tsai and Y. Iwasawa, *Catal. Today* 44 (1998) 333.