

Supported Au Catalysts for Low-Temperature CO Oxidation Prepared by Impregnation

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Gold catalysts supported on γ -Al₂O₃ powder were prepared by impregnation with solutions of HAuCl₄ which were aged in pH ranging from 5 to 11 for 15–720 min. During aging, hydrolysis of the AuCl₄⁻ complex gave rise to various species as observed by UV/vis spectroscopy. Au loading and particle size were determined by AAS and XRD. Activity of the catalysts was evaluated at room temperature under stoichiometric as well as excess oxygen concentrations. Au particle size and loading were influenced by the precursor speciation, demonstrating that intermediate values of aging pH and time are required for maximum CO conversion. The state of support, wet or dry before impregnation, did not seem to influence catalyst activity, while an excess of oxygen improved conversion. The preparation method was extended to washcoated monoliths and similar high activity was observed. © 2002 Elsevier Science (USA)

Key Words: gold catalysts; CO oxidation; impregnation; alumina support.

INTRODUCTION

Gold supported on reducible oxides is known to catalyze CO oxidation at low temperatures (cf. 1, 2). This reaction is important for CO safety gas masks (2), purification of air in CO₂ lasers (3), and CO sensors (4, 5). Supported gold catalysts have been primarily prepared by coprecipitation (6–9), and deposition–precipitation (10–13). These preparation methods can produce small Au particles below 10 nm in size which are strongly attached to metal oxide supports.

Coprecipitation is usually performed adding an aqueous solution of HAuCl₄ and a metal nitrate into an aqueous solution of Na₂CO₃. This manufacturing route is not easy to control. For example, extent of mixing, as well as order and mode of addition of the various compounds, temperature, aging period of precipitate in mother liquor, filtering and washing procedures all affect the precipitation procedure (14). In addition, coprecipitation of Au and transition metal oxide consumes large amounts of Au solution and creates low surface area supports (15). High surface area

supports provide better utilization of expensive catalysts. Thus, various researchers prepared supported Au catalysts on preformed high surface area supports. Hoflund *et al.* (6) attempted to mount Au/MnOx coprecipitates on a monolith by immersing it in a mixture of HAuCl₄ and Mn(NO₃)₂ solutions while adjusting the pH, but the resulting monolith was not active at temperatures below 100°C. A possible reason was suggested to be low loading of Au/MnOx, since Au/MnOx coprecipitates were observed in the solution but not on the monolith.

Deposition–precipitation (DP) has been used to prepare supported gold powder catalysts such as Au/TiO₂ (10, 12) and Au/ γ -Al₂O₃ (11–13). The pH of a gold chloride solution is raised to a value between 6 and 10 depending on the isoelectric point of support, and the partially hydrolysed species [Au(OH)_nCl_{4-n}]⁻ ($n = 1-3$) then react with the surface of the support to form Au(OH)₃ (2). In Au/TiO₂ catalysts, CO oxidation and Au particle size depended on the values of n in [Au(OH)_nCl_{4-n}]⁻ varying with pH (1). Furthermore, the most active Au/TiO₂ catalyst was obtained after calcination at 300–400°C. Below these temperatures, Au particles were present in oxidic form, while above them, Au particles were metallic and larger than 5 nm in size. In addition, Au particle size decreased to smaller than 4 nm above pH 6 of HAuCl₄ solution. In Au/Al₂O₃ catalysts, after oxidation treatment at 300°C, gold oxides and gold chloride were found to be present on the surface of supported gold crystallites (11). In the same study, it was reported that addition of Mg citrate to preparation solutions had a significant effect on properties of the Au/Al₂O₃ catalysts. For example, Au particle size decreased when adding Mg citrate during preparation and thus catalytic performance was enhanced. In addition, Au/Al₂O₃ prepared by adding Mg citrate exhibited better selectivity for CO oxidation in hydrogen stream (13). Au/Mg(OH)₂ catalysts also showed an improvement of activity by adding Mg citrate in the preparation (10). It was suggested that citrate ions were adsorbed on support and they suppressed migration of Au particles during heat treatments.

Even though noble metal catalysts are mostly prepared by impregnation methods, conventional impregnation has

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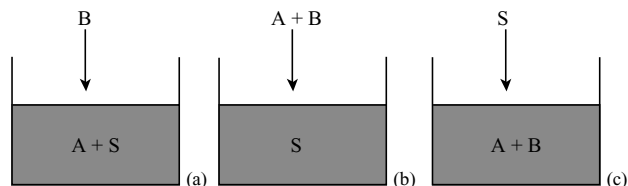


FIG. 1. Schematics of preparation procedures (a) conventional deposition-precipitation, (b) wet impregnation, (c) dry impregnation; A: HAuCl_4 solution, B: base solution (e.g., Na_2CO_3), S: support material.

not been particularly successful in producing active gold catalysts. Bamwenda *et al.* (16) reported that Au/TiO_2 powder catalysts prepared by impregnation had low CO conversion compared with other catalysts prepared by deposition-precipitation. The authors concluded that it is difficult to prepare Au particles in nanometer size by impregnation, which is responsible for low-temperature CO oxidation. In other studies, reasons for the low activity of supported gold catalysts prepared by impregnation were suggested to be residue chlorine ions on the catalytic surface, which originate from the HAuCl_4 solution, and weak interaction between gold particles and substrate (8, 17). Recently, Iwasawa's group (18) improved impregnation by using hydroxides as support and gold phosphine complexes as precursor compounds. These catalysts were as active as gold catalysts prepared by coprecipitation. It was proposed that hydroxyl groups of the hydroxide react with gold complexes, and that produces a strong interaction between gold complexes and the support. Furthermore, Iwasawa's group pointed out that by using a gold phosphine solution, the detrimental effect of residue chlorine ions on the catalyst activity can be avoided.

In this study, $\gamma\text{-Al}_2\text{O}_3$ support is impregnated with Au solution adjusted in pH by alkali solution. While in DP, alkali solution is added in Au solution containing the support (Fig. 1a), in our impregnation procedure Au solution mixed with alkali solution is added in wet or dry $\gamma\text{-Al}_2\text{O}_3$ powder, where the first is wet impregnation (Fig. 1b) and the second is dry impregnation (Fig. 1c). In dry impregnation, the solution fills the pores of the support and initially convective transport dominates over diffusion. In wet impregnation, however, pores filled with pure solvent are immersed in impregnating solution and thus no convective solute transport takes place in the pores. In both wet and dry impregnation, the pH of Au solution and aging time prior to impregnation are carefully controlled. Experiments were performed with $\gamma\text{-Al}_2\text{O}_3$ powder, as well as $\gamma\text{-Al}_2\text{O}_3$ washcoated monoliths.

EXPERIMENTAL

Catalyst Preparation

Au/ $\gamma\text{-Al}_2\text{O}_3$ powder catalysts. 20 ml of 2.5×10^{-3} M HAuCl_4 (Alfa) aqueous solution was aged at pH from 5

to 11 for 15–720 min. Aqueous solution, 0.1 M Na_2CO_3 (Alfa), was used to adjust the pH during aging. $\gamma\text{-Al}_2\text{O}_3$ powder was prepared by crushing $\gamma\text{-Al}_2\text{O}_3$ pellets (cylindrical shape with 1/8" diameter and length, Engelhard) and sieving with mesh No. 22 (opening of 0.710 mm). A set of samples was prepared by wet impregnation (see Fig. 1b). One gram of $\gamma\text{-Al}_2\text{O}_3$ powder was dispersed in 100 ml of water. The aged Au solution (20 ml) was added into the slurry of $\gamma\text{-Al}_2\text{O}_3$ powder under vigorous stirring and then impregnation was allowed to continue for 30 min. The $\gamma\text{-Al}_2\text{O}_3$ powder was subsequently filtered and washed with 500 ml of hot water (95°C) to remove chlorine ions that might affect catalytic activity (3). Finally, the powder was dried in air at 120°C overnight, followed by calcination at 300°C for 4 h. The samples prepared by this method are shown in Table 1. Another sample was prepared by transferring 1 g of $\gamma\text{-Al}_2\text{O}_3$ powder into 100 ml of water mixed with 20 ml of 2.5×10^{-3} M HAuCl_4 (Alfa) aged at pH 9 for 4 h (see Fig. 1c; dry impregnation). Three samples were prepared by dry impregnation under the same conditions.

Au/ $\gamma\text{-Al}_2\text{O}_3$ monolith catalysts. A cordierite monolith coated with $\gamma\text{-Al}_2\text{O}_3$ (cell density 250 cells per square inch, Johnson Matthey) was cut to 6–7 mm in diameter and 50 mm in length. This monolith was immersed in 100 ml water mixed with 20 ml 2.5×10^{-3} M HAuCl_4 aged at pH 9 for 4 h (dry impregnation). After stirring the mixture of $\gamma\text{-Al}_2\text{O}_3$ monolith and Au solution for 1 h, the monolith was washed with 500 ml of hot water (95°C). Finally, it was dried in air at 120°C overnight, followed by calcination at 300°C for 4 h. Three $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ monolith catalysts were prepared by the above procedure at the same conditions in order to examine reproducibility of preparation.

UV/vis Spectroscopy

Complexation of Au during aging of Au solution was investigated using UV/vis spectroscopy (Shimadzu UV-2401 PC). The pH of 20 ml 2.5×10^{-3} M HAuCl_4 aqueous solution was adjusted to 5, 7, 9, and 11 with 0.1 M Na_2CO_3 solution and Au solution at each pH was sampled at 15, 60, 240, and 720 min of aging time. UV/vis absorption spectra were taken using 0.1 cm path length quartz cuvettes.

TABLE 1

pH during aging	Aging time			
	15 min	60 min	240 min	720 min
5	AuAlO5_15	AuAlO5_60	AuAlO5_240	AuAlO5_720
7	AuAlO7_15	AuAlO7_60	AuAlO7_240	AuAlO7_720
9	AuAlO9_15	AuAlO9_60	AuAlO9_240	AuAlO9_720
11	AuAlO11_15	AuAlO11_60	AuAlO11_240	AuAlO11_720

Atomic Absorption Spectroscopy (AAS)

The gold loading was determined by using an atomic absorption spectrometer (Philips PU9100). Before the measurements, the machine was calibrated with 0.5–20 mg/ml of Au standard solutions which were prepared from 1000 mg/ml of Au standard solution (Sigma–Aldrich). Gold in the catalysts was dissolved in aqua regia which was prepared by mixing 18 parts concentrated HNO_3 with 82 parts concentrated HCl . At the same time, 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. Au in 0.1 wt% of $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ powder prepared by incipient wetness was dissolved in aqua regia to confirm the efficiency of the Au extraction. This experiment showed that 93–95 wt% of Au used in the preparation was recovered by the extraction method. During the measurements, the wavelength was set to 243.2 nm and acetylene gas mixed with air was utilised for the flame source.

X-Ray Diffraction (XRD)

In order to obtain Au particle size, XRD was carried out with a Philips powder diffractometer PW3040 with $\text{Cu K}\alpha$ radiation in the 20° to 90° range of 2θ at 40 kV and

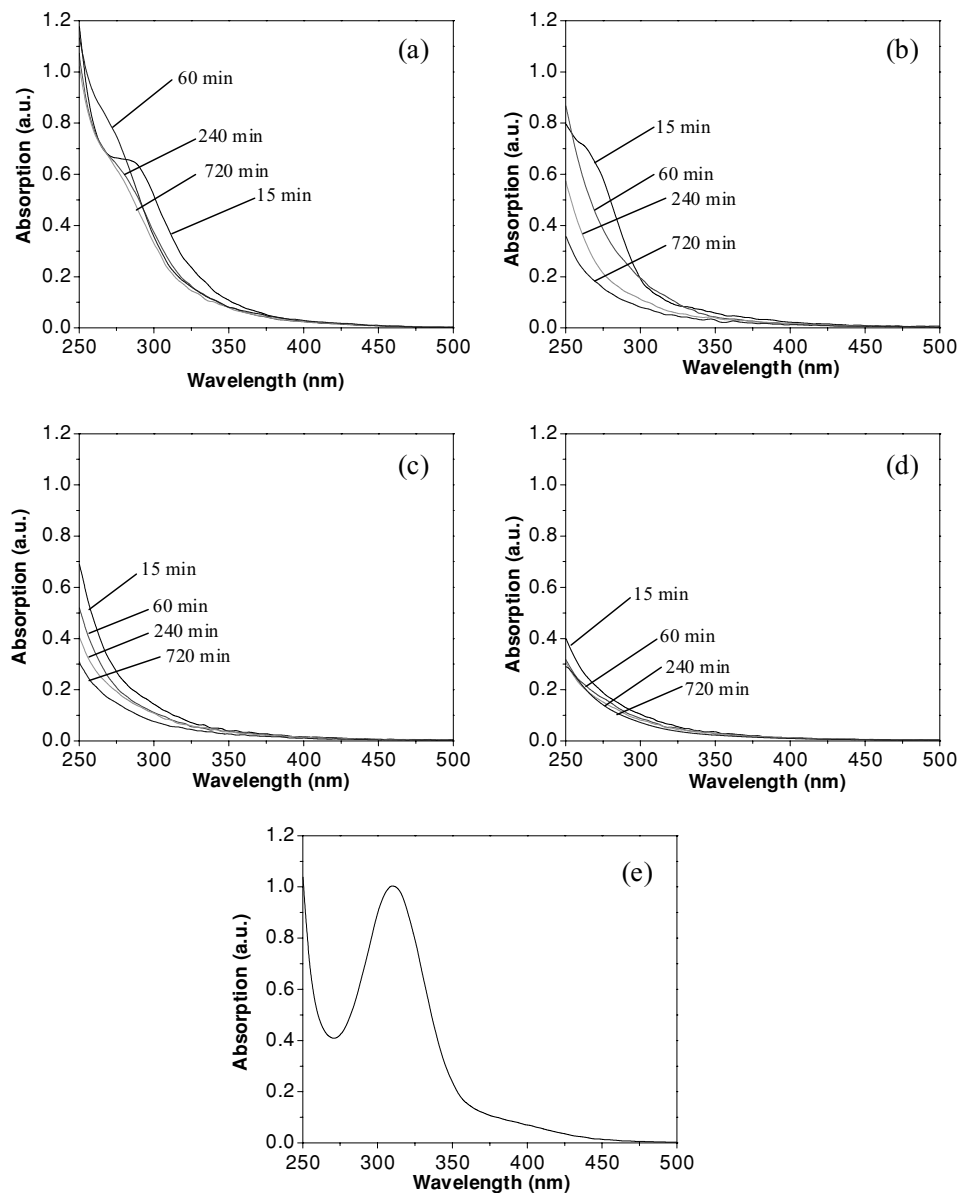


FIG. 2. UV/vis spectra of 2.5×10^{-3} M HAuCl_4 solutions at (a) pH 5, (b) pH 7, (c) pH 9, (d) pH 11 with aging time and (e) pH 2 without adding Na_2CO_3 solution.

TABLE 2
Au Loading and Au Particle Size of Au/ γ -Al₂O₃ Powder Catalysts, along with Corresponding Conversions and Reaction Rates Observed

	Au loading (wt%)	Au particle size ^b (nm)	CO conversion ^d (%)	Rate of CO oxidation ^d ($\mu\text{mol s}^{-1} \text{g Au}^{-1}$)
AuAlO5_15	0.668	7.5	0	0
AuAlO5_60	0.478	6.8	0	0
AuAlO5_240	0.714	7.3	0 (0)	0 (0)
AuAlO5_720	0.429	6.1	0	0
AuAlO7_15	0.428	7.5	0	0
AuAlO7_60	0.149	n.d. ^c	18	3
AuAlO7_240	0.420	n.d. ^c	40 (56)	2.36 (3.31)
AuAlO7_720	0.386	4.3	16	1.03
AuAlO9_15	0.128	n.d. ^c	18 (52)	3.49 (10.1)
AuAlO9_60	0.202	n.d. ^c	44 (71)	5.4 (8.72)
AuAlO9_240	0.430	n.d. ^c	57 (97)	3.29 (5.59)
AuAlO9_240_D ^a	0.501	n.d. ^c	-(95)	-(4.70)
AuAlO9_720	0.170	n.d. ^c	42 (63)	6.13 (9.19)
AuAlO11_15	0.089	n.d. ^c	0	0
AuAlO11_60	0.065	n.d. ^c	17	6.49
AuAlO11_240	0.005	n.d. ^c	0 (0)	0 (0)
AuAlO11_720	0.007	n.d. ^c	0	0

^a The sample was prepared by dry impregnation under the same conditions as those of AuAlO9_240.

^b Measured by XRD.

^c Not detectable.

^d CO conversion and rate of CO oxidation were obtained in stoichiometric ratio of CO and O₂ at 24 ± 1°C after 1 h of reaction time. Numbers in parenthesis are CO conversion and rate of CO oxidation in air.

30 mA. A Ni filter was used to remove the Cu K_{β} radiation. Gold particle size was calculated based on Scherrer's equation at 77.55° where the Au peak was clearer than other Au peaks.

CO Oxidation at Room Temperature

Au/ γ -Al₂O₃ powder catalysts. The activities of the catalysts were measured by CO oxidation at room temperature (24 ± 1°C) in a continuous flow reactor for at least 1 h without pretreatment or preactivation. The reactor was an 8-mm i.d. quartz tube. A mixture 1% CO (CP grade, BOC) and 0.5% O₂ (zero grade, BOC) balanced by N₂ (zero grade, BOC) at a total flow rate of 50 ml/min (stoichiometric test) and 0.15 g of catalyst was used. Also, catalysts prepared with Au solution aged at pH 9 were tested with 1% CO in dry air at the same total flow rate as in stoichiometric test (excess test). The CO concentration at the reactor outlet was analysed online by N.D.I.R. CO analyser (AAL model 401).

Au/ γ -Al₂O₃ monolith catalysts. Au/ γ -Al₂O₃ monolith catalysts (6–7 mm in diameter and 50 mm in length, 1.5 g) were tested for CO oxidation at room temperature (24 ± 1°C) in a continuous flow reactor for at least 4 h without pretreatment or preactivation. The reactor was an 8-mm i.d. quartz tube. The monolith catalysts prepared were tested in a mixture of 1% CO in dry or wet air at a total flow rate of 50 ml/min. The wet air was prepared by bubbling dry air

in boiling water and then condensing water vapor at 24°C prior to mixing with CO gas.

RESULTS

Au/ γ -Al₂O₃ powder catalysts. UV/vis spectroscopy was used to investigate the speciation of Au chloride

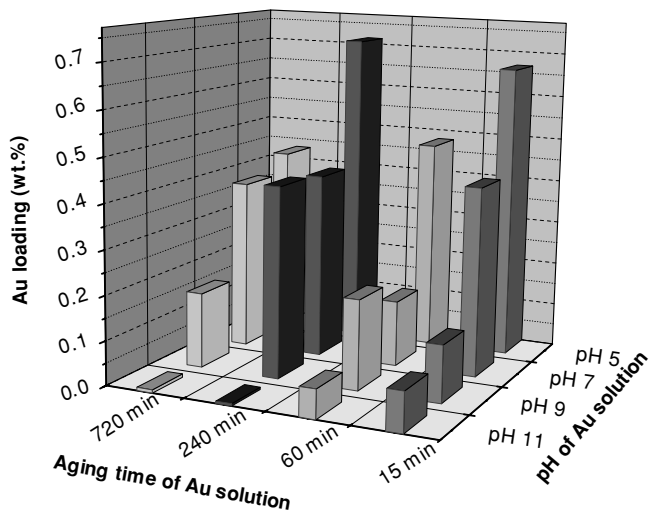


FIG. 3. Au loading of Au/ γ -Al₂O₃ powder catalysts with aging conditions of HAuCl₄ solution.

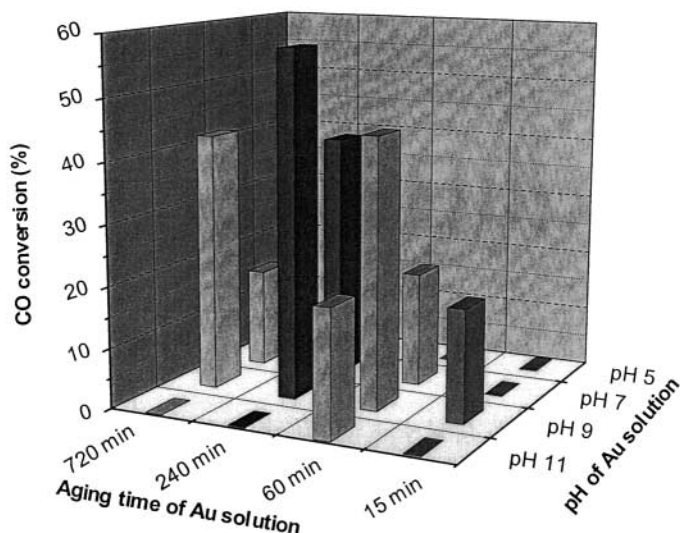


FIG. 4. CO conversion of Au/ γ -Al₂O₃ powder samples after 1 h of reaction time in stoichiometric test as a function of aging conditions of Au precursor solution.

complexes during aging of HAuCl₄ solution. UV/vis absorption spectra obtained at different aging time and pH are shown in Fig. 2. At pH 5, a shoulder is observed at \sim 288 nm after aging the Au solution for 15 min. This shoulder shifts to \sim 275 nm at 60 min and disappears at 240 and 720 min. At pH 7, a shoulder is obtained at \sim 275 nm when Au solution was aged for 15 min. The shoulder disappears

after 60 min and also total absorption decreases with aging time. At pH 9, no shoulder is observed during aging and total absorption decreases with aging time. Finally, at pH 11, absorption is much smaller than that at pH 9 and after 60 min of aging time the absorption did not change.

A summary of Au loading and particle size of Au/ γ -Al₂O₃ powder catalysts used in this work is shown in Table 2. Figure 3 shows Au loading of samples prepared with solutions of different pH and aging time. In general, Au loading decreases with increasing pH at same aging time. These results are in agreement with Chang *et al.* (11) and Grisel *et al.* (19) who prepared Au/Al₂O₃ catalysts by deposition-precipitation. Furthermore, dependence of Au loading on aging time seems to be nonmonotonic, apart from pH 11.

Au/ γ -Al₂O₃ powder catalysts were characterized by X-ray diffraction. Peaks corresponding to metallic gold and γ -Al₂O₃ were obtained. The peak of Au (111) overlapped with γ -Al₂O₃ peaks, and thus Au particle sizes were calculated from the Au (311) peak ($2\theta = 77.55^\circ$) using Scherrer's equation. The particle sizes are summarized in Table 2. Au/ γ -Al₂O₃ samples prepared with HAuCl₄ solution aged at pH 9 and 11 contain smaller gold particles than those prepared with HAuCl₄ solution aged at pH 5 and 7. This observation agrees with Haruta (1) who prepared Au/TiO₂ catalysts by deposition-precipitation and observed that Au particle size decreased with increasing Na₂CO₃ concentration used in the preparation. Comparing samples prepared by dry and wet impregnation, Au loading

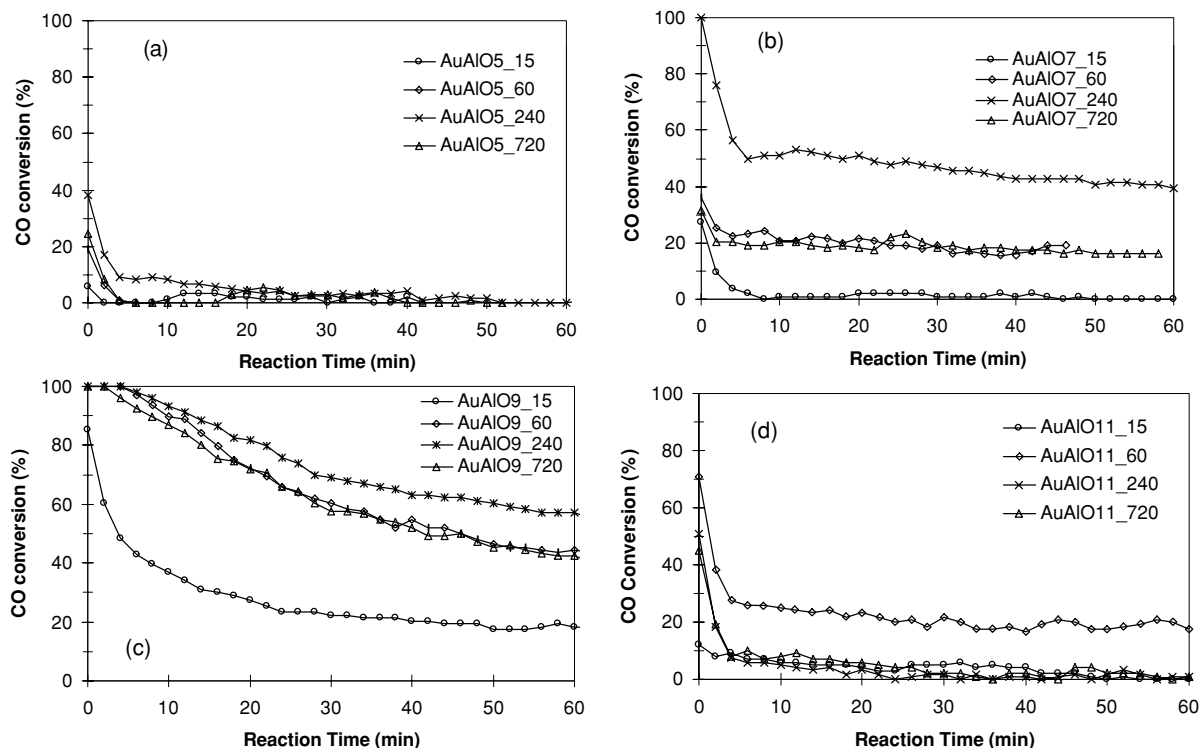


FIG. 5. CO conversion of Au/ γ -Al₂O₃ powder catalysts at $24 \pm 1^\circ\text{C}$ with reaction time (stoichiometric test).

and Au particle size of AuAlO9_240_D are similar to those of AuAlO9_240.

CO conversion of Au/ γ -Al₂O₃ samples after 1 h, under stoichiometric ratio of CO and O₂ are shown in Fig. 4 as a function of preparation conditions, while CO conversion is shown with reaction time in Fig. 5. The highest CO conversion after 1 h of reaction time is observed for AuAlO9_240. Deviation of preparation conditions from pH 9 and aging time 240 min leads to decrease of CO conversion. The rate of CO oxidation per unit mass of Au is displayed in Table 2. The highest rate of CO oxidation in stoichiometric reactants is observed for AuAlO11_60. Even though this catalyst shows the best utilization of Au, it exhibits relatively low conversion. All samples show that deactivation is present during the experiments, and the deactivation behavior depends on the preparation conditions. Many catalysts show a strong decrease in activity during the first 10 min on stream. Such behavior is not clearly understood, but it cannot be attributed to CO adsorption, whose concentration is so large that it would cover all available Au particles in a very short time. The slow decrease in conversion after 10 min is probably due to carbonate induced deactivation (2).

Samples prepared with Au precursor aged for 240 min were tested for CO oxidation in excess oxygen (see Fig. 6). Similar to the results of the stoichiometric test, AuAlO9_240 exhibits the highest CO conversion. However, deactivation behavior is improved. Indeed, excess of oxygen is beneficial for CO conversion, as demonstrated in Fig. 7, where the performance of samples prepared at pH 9 and various aging times is shown. The effect of type of impregnation, dry or wet, was assessed by comparing the performance of AuAlO9_240 and AuAlO9_240D. As shown in Fig. 8, CO conversion behavior with time is similar. Reproducibility of the preparation procedure was checked for both wet and dry impregnation, by measuring CO conversion vs time for 3 sets of powder samples and 1 set of mono-

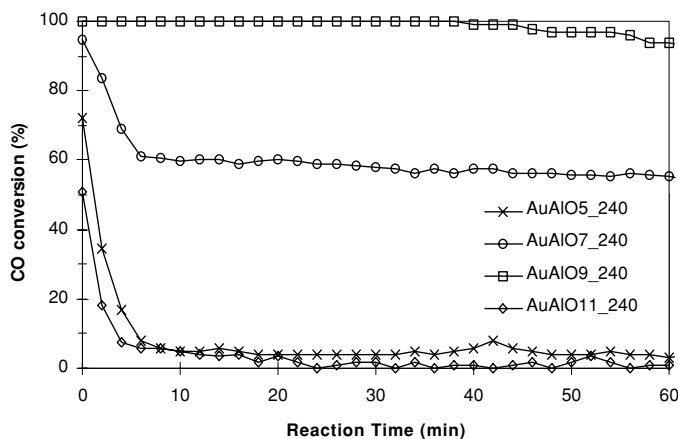


FIG. 6. CO conversion of Au/ γ -Al₂O₃ powder catalysts at 24 ± 1°C with reaction time (excess test).

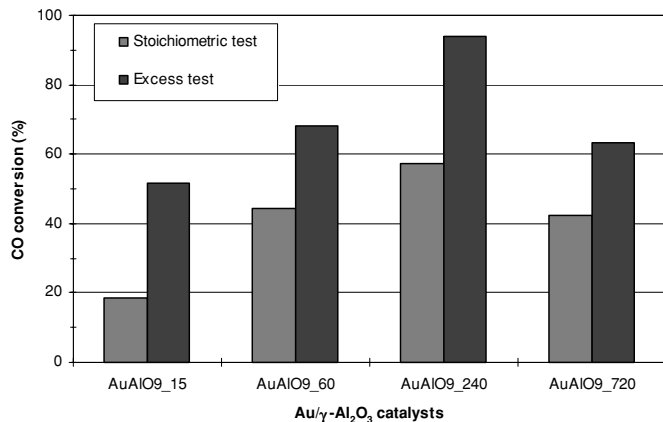


FIG. 7. Comparison of CO conversion at 60 min of reaction time in stoichiometric and excess tests for Au/ γ -Al₂O₃ powder catalysts prepared with Au precursor aged at pH 9 for various aging times.

lith samples, each set comprising 3 catalysts. Deviation of CO conversion from its average value was small and never exceeded 6%.

Au/ γ -Al₂O₃ monolith catalysts. Figure 9 shows CO conversion for Au/ γ -Al₂O₃ monoliths with reaction time at 24 ± 1°C in dry and wet air (excess test). The conversion of the 0.082 wt% fresh Au/Al₂O₃ monolith in dry air stabilized after ca. 200 min of reaction time at about 80%.

However, conversion decreased in the presence of water vapor. Comparing conversions of 0.082 wt% Au/ γ -Al₂O₃ monolith at 200 min of reaction time in dry and wet air, the 80% conversion in dry air dropped to ca. 10% in wet air. In order to investigate whether deactivation in wet air is reversible, the Au/ γ -Al₂O₃ monolith after CO oxidation in wet air was heated at 120°C in oven overnight, and then it was tested for CO oxidation in wet air again. The

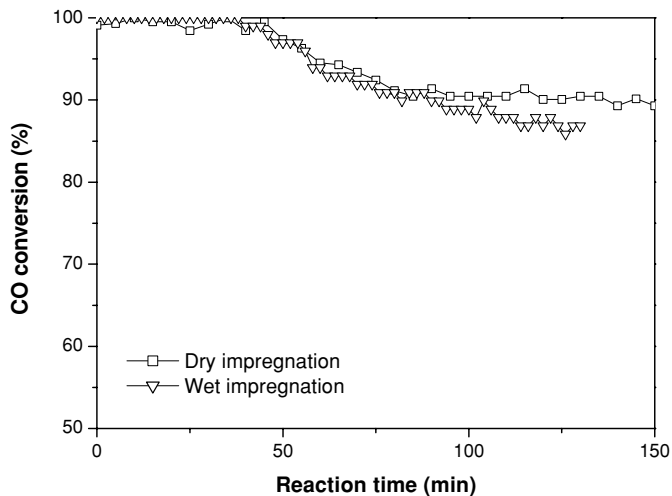


FIG. 8. CO conversion of Au/ γ -Al₂O₃ powder catalysts prepared by dry and wet impregnation at 24 ± 1°C (excess test).

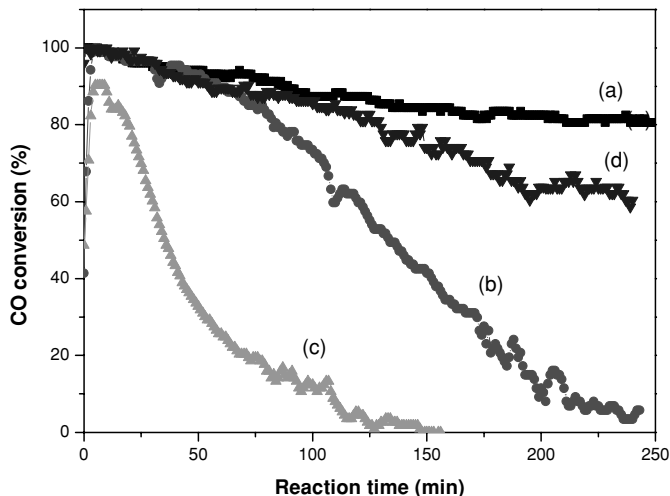


FIG. 9. CO conversion of Au/ γ -Al₂O₃/cordierite monoliths at 24 ± 1°C with reaction time (excess test) (a) fresh 0.082 wt% Au in dry air; (b) fresh 0.082 wt% Au in wet air, (c) 0.082 wt% Au after CO oxidation for 4 h in wet air and then heat treatment at 120°C in oven overnight, (d) fresh 0.142 wt% Au in wet air.

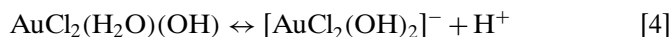
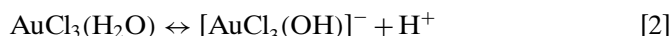
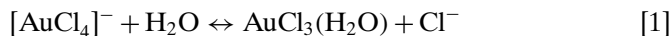
conversion of used catalyst was lower than that of the fresh catalyst, even though the used catalyst showed initially similar conversion to the fresh catalyst.

In order to improve the catalyst performance in wet air, it was attempted to load more Au on the monolith. A 0.142 wt% Au/ γ -Al₂O₃ monolith catalyst exhibited about 60% conversion after 4 h of reaction time in wet air. Thus, deactivation behavior of the monolith catalysts can be improved by increasing metal loading.

DISCUSSION

Au/ γ -Al₂O₃ powder catalysts. Au solution at pH 5 showed shoulders at ~288 and 275 nm, while at pH 2 a peak appeared at ~310 nm (see Fig. 2e). These results are comparable with Peck *et al.* (20) who reported that at pH < 5, 10⁻⁴ M Au(III) chloride in 1 M NaCl solution exhibits a peak at ~314 nm, and the peak shifts to lower wavelength with increasing pH up to 6. Furthermore, absorption decreased with increasing pH, as also observed in Fig. 2. In the same study, Au chloride complexes were confirmed by Raman spectroscopy. The hydrolysis of the [AuCl₄]⁻ ion has been investigated in detail (cf. 21), and AuCl₃(H₂O), [AuCl₃(OH)]⁻, [AuCl₂(OH)₂]⁻, [AuCl(OH)₃]⁻, and [Au(OH)₄]⁻ have been postulated to form in a stepwise manner. Their relative concentrations are dependent on Cl⁻ and H⁺ concentrations as well as temperature. The relative concentrations of these species at the gold and chloride concentration used in this study are shown in Fig. 10 as a function of pH. They are obtained by considering the equilibrium equations between [AuCl₄]⁻, AuCl₃(H₂O), [AuCl₃(OH)]⁻, AuCl₂(H₂O)OH, [AuCl₂(OH)₂]⁻, [AuCl(OH)₃]⁻, and [Au(OH)₄]⁻, sug-

gested by Nechayev and Zvonareva (22):



The equilibrium constants are K₁ = 4 × 10⁻⁶ M, K₂ = 2.6 × 10⁻¹ M, K₃ = 3.6 × 10⁻³ M, K₄ = 2.8 × 10⁻⁵ M, K₅ = 9 × 10⁻⁹ M², and K₆ = 1 × 10⁻¹⁰ M². Calculated Cl⁻ concentrations were in the range 5.7 × 10⁻⁴ to 1.0 × 10⁻² M. The change of UV/vis spectra with pH and aging time is associated with hydrolysis of Au chloride complexes, although it is difficult to identify the solution composition. However, based on the UV/vis spectra and the speciation information presented, it is expected that the dominant species at equilibrium are [AuCl₂(OH)₂]⁻, [AuCl(OH)₃]⁻, [Au(OH)₄]⁻, and [Au(OH)₄]⁻ for pH 5, 7, 9, and 11, respectively, while at short aging times they are possibly AuCl₂(H₂O)OH, [AuCl₂(OH)₂]⁻, [AuCl(OH)₃]⁻, and [Au(OH)₄]⁻.

In general, deposition of Au complexes on γ -Al₂O₃ is accompanied by the following surface reactions (23, 24):

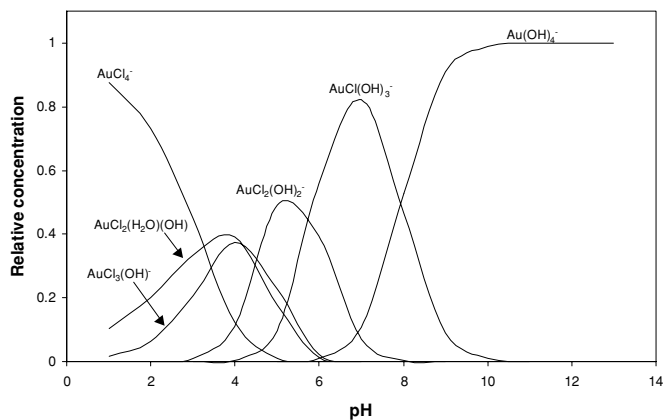
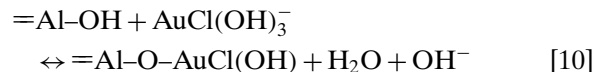
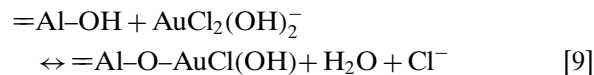
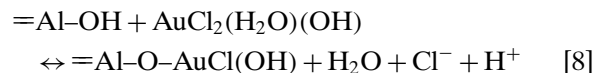
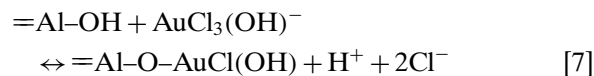
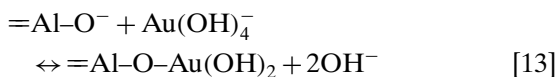
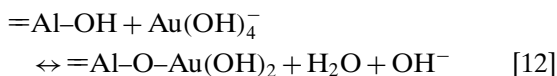
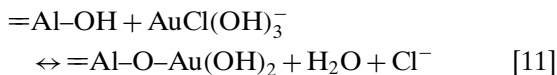


FIG. 10. Relative equilibrium concentration of gold complexes in 2.5 × 10⁻³ M HAuCl₄ solution, calculated with adsorption constants reported by Nechayev and Nikolenko (24).



It is worth noting that reactions [7]–[13] will disturb the hydrolysis reactions [1]–[6]. The values of adsorption constants for gold(III) chloride complexes on $\gamma\text{-Al}_2\text{O}_3$ are shown in Table 3 (24), according to which the strongest adsorbing species is $\text{AuCl}(\text{OH})_3^-$.

The adsorption constant for $\text{AuCl}_2(\text{H}_2\text{O})(\text{OH})$ is not available, but Machesky *et al.* (25) reported that even though this species has a neutral charge, it can be adsorbed as bidentate on goethite, since favorable steric factors dominate electrostatic effects. That is due to the fact that the bond distance between Cl or OH along the edge of Au(III)-chloride species is similar to the distance between hydroxyl groups on the goethite surface.

Considering the above speciation and adsorption information, the effect of increasing pH can be rationalized. As pH increases, concentration of Al–OH adsorption sites decreases and hence adsorbed Au species decrease, leading to lower catalyst loading as also shown in Fig. 3. However, by increasing solution pH (up to pH 7), concentration of strongly adsorbing complexes ($\text{AuCl}_2(\text{OH})_2^-$ and $\text{AuCl}(\text{OH})_3^-$) increases as shown in Fig. 10. Thus, an optimum value of pH is expected where the concentration of strongly adsorbed species is maximized. If we postulate that these species give eventually the small Au particles required for CO oxidation, the maximum at each aging time in Fig. 4 can be explained. Indeed, it is widely recognized that catalyst dispersion is strongly influenced by the affinity of precursor for the support (26).

The aging time of Au solution at fixed pH can influence the concentration of the various Au complexes, because equilibration of HAuCl_4 in alkaline solution is established slowly. Under nonequilibrium conditions, the composition of Au complexes is likely to be similar to that under equilibrium at lower pH. Therefore, the pH which gives rise

to maximum concentration of strongly adsorbed species is expected to depend on the aging time.

In order to investigate CO conversion in excess oxygen, CO oxidation was performed in air (excess test). Excess oxygen resulted in higher CO conversion as shown in Fig. 7. The beneficial effect of higher oxygen partial pressure has also been shown by Haruta *et al.* (8) for Au supported on TiO_2 , Co_3O_4 , and Fe_2O_3 . Since it is widely accepted that oxygen participates in the reaction through prior adsorption on the support (2), high oxygen concentration could increase the amount of adsorbed oxygen and eventually CO conversion.

The state of support (dry or wet) before impregnation does not seem to play a significant role. Au loading is slightly higher in dry impregnation than in wet impregnation, which is expected since no water is present in the pores to dilute the precursor solution, but in both cases Au particle size is below the XRD detection limit. Thus CO conversion is almost the same between the corresponding samples prepared by dry and wet impregnation (see Fig. 8).

Au/ $\gamma\text{-Al}_2\text{O}_3$ cordierite monoliths. In order to investigate if the preparation procedure developed for powder catalysts could be extended to supports more suitable for commercial applications, similar preparation conditions were employed for Au/ $\gamma\text{-Al}_2\text{O}_3$ cordierite monolith. Even though the monolith has different Au loading as compared to the corresponding powder catalyst (0.082 wt% vs 0.501 wt%), the space velocities used are different (2000 ml/h cat.-g vs 6000 ml/h cat.-g), and mass transport conditions during reaction are also different, similar conversion was obtained (80% vs 95%).

Since under realistic conditions CO oxidation catalysts may be operated in humid environment, the Au/ $\gamma\text{-Al}_2\text{O}_3$ monolith catalysts were examined for CO oxidation in wet air. The existence of water vapor (ca. 2 wt%) in feed gas suppressed CO oxidation. This result has been reported in several studies of Au/ TiO_2 catalysts (27–29). Bollinger and Vannice (27) reported that addition of 0.6% water vapor at 313 K deactivated an 1.0% Au/ TiO_2 catalyst. The authors suggested that the deactivation is possibly due to H_2O adsorption on TiO_2 blocking titania interfacial sites. Grunwaldt *et al.* (29) observed that existence of 0.1% of H_2O in reaction feed stream significantly decreased catalytic performance of Au/ TiO_2 in CO oxidation. They suggested that the reason could be adsorption on active sites or pore filling (capillary condensation). In contrast to these, Haruta *et al.* (30) and Liu *et al.* (31) found that CO oxidation on Au/ Fe_2O_3 catalysts was enhanced by the presence of water vapor or was insensitive to the coexistence of water vapor. It was reported that CO_2 formation was further enhanced when moisture is added to the reactant mixture of CO and air (32). FT-IR measurements indicated that CO adsorption on surface of gold particles is enhanced by moisture (30). This enhancement is not due to water gas shift

TABLE 3

Adsorption Constants of Au(III) Chloride Complexes on $\gamma\text{-Al}_2\text{O}_3$ (from Ref. 24)

Au(III) complex	Adsorption constant (l/mol)
AuCl_4^-	35
$\text{AuCl}_3(\text{OH})^-$	35
$\text{AuCl}_2(\text{OH})_2^-$	50 ± 3
$\text{AuCl}(\text{OH})_3^-$	59 ± 3
$\text{Au}(\text{OH})_4^-$	29.4 ± 2.6

reaction of CO and water because the shift activity is almost zero at 273 K (33). Our results show that saturated water vapor has an inhibiting effect similar to the Au/TiO₂ catalyst. For that system, catalyst activity could be partially recovered after heating at 393 K for 30 min, and complete reactivation was obtained after calcination at 673 K and then low temperature reduction (27). In our system, almost all the initial activity is restored after heating at 120°C in air, but deactivation of the regenerated catalyst is faster than the fresh catalyst, indicating that deactivation is at least partly reversible in nature. In an attempt to improve deactivation behavior, the Au loading was increased from 0.082 to 0.142 wt%. Indeed, suppression of CO oxidation by water vapor decreased and CO conversion at 200 min of reaction time increased from ca 10 to ca 70%.

CONCLUSIONS

Aging of precursor solution at different pH alters the concentration of the various gold species obtained by hydrolysis of HAuCl₄. Optimum aging conditions exist which give rise to strongly adsorbing species such as AuCl(OH)₃⁻, without decreasing substantially the adsorption capability of the support. In this way high loading and sufficiently small size of Au particles are obtained resulting to high conversion of CO at room temperature. Impregnation of washcoated monoliths with properly aged precursor solutions also demonstrated high activity. The state of support before impregnation did not affect catalyst characteristics. Excess oxygen was found to be beneficial while the presence of water vapor detrimental to catalyst activity.

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