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Highly reproducible syntheses of active Au/TiO_2 catalysts for CO oxidation by deposition–precipitation or impregnation

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Abstract

Gold catalysts supported on TiO_2 were prepared by a deposition–precipitation (DP) method to investigate how highly reproducible performance of the gold catalysts in CO oxidation can be achieved. A protocol was established for synthesizing identically performing catalysts by different operators. The results show that for this synthesis route, the calcination step is not needed to form highly active Au/TiO_2 catalysts, but leads to decreased activity. Improved catalytic activity was observed when a high solution pH was adjusted during the precipitation. Surprisingly, wet impregnation followed by ammonia steam treatment and a washing step with water also leads to Au/TiO_2 with 2- to 4-nm individual gold particles highly dispersed on the TiO_2 surface. In addition, this catalyst is active for room temperature CO oxidation. The temperature for 50% conversion of CO is below 25 °C, which is comparable to that of the gold catalyst prepared by the DP method. Therefore, contrary to reports in the literature, the impregnation method can be used in the preparation of high-activity gold catalysts.

Keywords: Gold catalysts; CO oxidation; Reproducibility; Deposition–precipitation; Impregnation

1. Introduction

A tremendous increase in research on gold catalysis was triggered by Haruta's first reports on the unexpectedly high catalytic activity of supported gold nanoparticles in CO oxidation [1,2]. Several methods for the preparation of highly active gold catalysts have been developed. Besides classical deposition–precipitation (DP) proposed by Haruta [3], other methods, including co-precipitation [4], co-sputtering [5], chemical vapor deposition [6], grafting [7], and adsorption of gold colloids on metal oxides [8] have been investigated. Usually these preparation methods can produce small (<10 nm) Au particles that are strongly attached to the supports. Despite the numerous methods developed, however, the DP method still seems to be the most efficient method of preparing highly active gold catalyst. In particular, using TiO_2 as a support, small, highly dispersed gold nanoparticles on the support can be achieved. Notably absent in the list of synthetic methods is the classical impregnation, because this pathway typically results in the formation of large gold particles with correspondingly low activity.

It has been pointed out that the nature of the support materials, as well as the physical state of the support, can strongly influence the activity of the resulting gold catalysts [9,10], although recent reports have demonstrated that "naked" gold particles can exhibit activity in aerobic glucose oxidation, which is comparable with supported particles [11]. Various metal oxides, including TiO_2 [3], Al_2O_3 [12], ZrO_2 [13], MgO [14], Fe_2O_3 [15], and Co_3O_4 [16], have been investigated as gold supports, with the goal of creating high catalytic activity. In addition, ordered porous silicas, such as SBA-15 [17] and MCM-48 [18], have been successfully used for the synthesis of active gold-based catalysts. Besides the preparation methods and the types of the supports, various other synthetic conditions, including pH value in the DP method, pretreatment, and calcination temperature, significantly influence the properties of the gold catalysts [13,19].

Despite the numerous studies published on supported gold catalysts, there is still no clear picture of the origin of the catalytic activity. In fact, the results reported in literature concerning gold catalysis are often contradictory, due to difficul-

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ties in reproducing the synthesis of the catalysts as well as problems with the catalytic tests. Thus the nature of the active species of the gold catalysts remains unclear. One reason behind the difficulty in elucidating the origin of catalytic activity is probably the unusual sensitivity of small gold particles to the environment, which leads to difficulties in synthesizing gold catalysts reproducibly. Because reproducibility of preparations and methods is crucial to gaining insight into catalytic systems, we have made a great effort to develop a robust synthesis protocol for the preparation of highly active gold-based catalysts. As reported previously [13], a consistent series of catalysts could normally be produced in one synthesis session, but day-to-day variability in catalyst performance for nominally identical catalysts could be as much as a 100-K difference in $T_{50\%}$, the temperature for 50% CO conversion.

Gold supported on TiO_2 prepared by DP for CO oxidation was selected as target catalyst because this system has been widely investigated. As a result of this study, a synthesis procedure with well-controlled steps that allows the preparation of active catalysts with a high level of reproducibility could be developed. In addition, because impregnation is a rather straightforward and simple catalyst synthesis procedure compared with the DP method, we attempted to develop an impregnation method for the synthesis of active gold catalysts. Impregnation has not been considered a good method for producing active gold catalysts, due to the difficulty in creating individual Au particles <10 nm by this method [20]. Our studies led to the discovery that wet impregnation followed by ammonia gas-phase treatment and a final washing step with water results in the formation of gold catalysts containing 2-nm gold particles. Consequently, these gold catalysts show similar catalytic activity in CO oxidation as those materials prepared by the DP method.

2. Experimental

Reproducible catalysts were obtained through the following procedure. First, 1.8 g of TiO_2 (Degussa P25) was suspended in 75 ml of deionized water under vigorous stirring for 0.5 h. Then the pH value of this suspension was adjusted with 0.1 M NaOH solution to the desired value, using a computer-based pump system connected to a pH meter. The suspension was maintained at this pH under stirring for additional 1.5 h. In parallel, 15 ml of deionized H_2O and 1.4 ml of 0.1 M NaOH solution were mixed in another beaker. Then 2.048 ml of 0.2 M $HAuCl_4$ aqueous solution ($HAuCl_4$: Alfa-Aesar, 99.99%) was added, and the mixture was shaken once. This solution was kept statically for 1 h. Subsequently, the gold aqueous solution was added into the TiO_2 suspension under stirring. During addition of the gold solution, the pH was maintained at the same value as before the addition via adjustment with 0.1 M NaOH solution using a computer-controlled pump system. The suspension was vigorously stirred for another 2 h. All of the steps described previously were carried out under exclusion of light by covering all containers with a layer of alumina folia. The solids were collected by centrifugation (10,000 rpm for 5 min), washed in 20 ml of deionized water, and then centrifuged again. This washing step was repeated once. Finally, the solids were dried for 16 h under a 10^{-2}-mbar vacuum in a desiccator (174 mm diameter, 2.4 l volume), with 45 g of P_2O_5 as a drying agent scattered on the bottom. The freshly dried samples typically were pale yellow and were used directly to perform the catalytic test. The gold amount used should have resulted in a nominal gold loading of 4.48%. Chemical analysis revealed loadings of 1.22% at pH 10; that is, the gold was not completely precipitated onto the support. The gold loading was somewhat higher at lower pH (1.62% at pH 8 vs. 2.06% at pH 7).

To prepare Au/TiO_2 catalyst by the impregnation procedure, 0.2 ml of $HAuCl_4$ aqueous solution was added dropwise to 0.75 g of TiO_2 support (Degussa P25) under manual stirring. This sample was then treated with ammonia in the gas phase to obtain stable $Au(OH)_3$. The ammonia treatment was performed in a closed glass container in which an ammonia solution (30 wt%) was kept in an open beaker and the sample was kept in another beaker. The glass container with the sample and the ammonia solution was heated in an oven at 50 °C for 4 h. The sample was finally washed with deionized water to completely remove the residual chloride ions. After filtration, the Au/TiO_2 catalyst was dried at 50 °C for 16 h to prepare it for the catalytic test. The concentration of the $HAuCl_4$ solution was tuned from 0.1 to 0.5 M to vary the gold loading on the TiO_2 support.

Transmission electron microscopy (TEM) investigations were performed in a Hitachi HF2000 microscope equipped with a cold-field emission gun at a beam energy of 200 kV. Samples were dispersed on a copper grid. The gold content of the catalysts, including possible contamination of chloride ions, was determined by energy-dispersive X-ray analysis (EDX) performed on a Hitachi S-3500N scanning electron microscope equipped with an OXFORD EDX system.

The activity of the catalyst for CO oxidation was measured in a plug flow reactor using 50 mg of sieved catalyst (250–500 µm). The operation temperature controlled with a thermocouple could be adjusted in the range of -100 to 300 °C. Before each experiment, the reactor was cooled to -40 °C under a flow of high-purity nitrogen, which was replaced by a gas mixture of 1% CO in air (purity 99.9999%) at a flow rate of 67 ml/min, corresponding to a space velocity of 80,000 ml/(h g_{cat}), to start the experiment. In typical runs, the temperature was ramped at a rate of 2 °C/min. Control experiments under steady-state conditions revealed no significant deviations in activity at the corresponding temperatures.

The concentrations of CO_2 and CO were analyzed at the outlet of the reactor with nondispersive infrared spectroscopy using two URAS 3E devices (Hartmann and Braun). The temperature for 50% conversion ($T_{50\%}$) as an index was used to evaluate the activity of the catalysts.

3. Results and discussion

3.1. Reproducibility of Au/TiO_2 catalyst

To investigate the reproducibility of gold catalysts, gold supported on TiO_2 prepared by the DP method was selected as a model system. Basically, we followed Haruta's standard prepa-

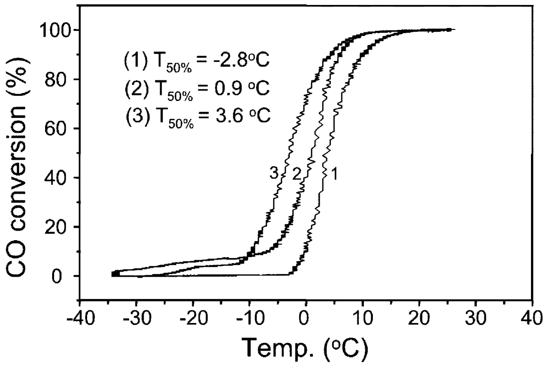


Fig. 1. Reproducibility of catalytic tests. CO conversion as a function of temperature for equal amounts of uncalcined samples from the same batch, measured at different times.

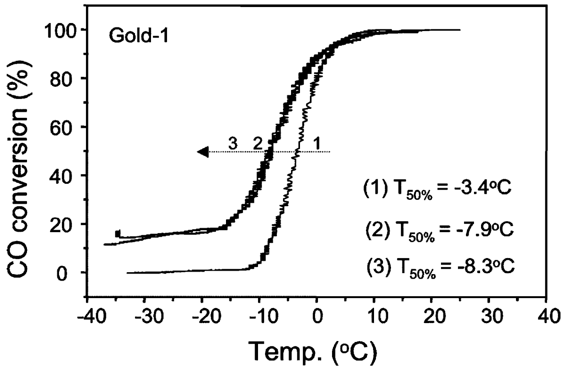


Fig. 2. Catalytic activity of one representative catalyst (gold-1) precipitated at pH 10 in CO oxidation. The three curves represent the results of three individual test cycles, the numbers indicates the sequence of the tests.

ration procedures; however, we provide more details of the synthesis compared with Haruta's report [2]. In addition, the synthesis differs with respect to the calcination step. In Haruta's approach, gold catalysts were calcined at temperatures $>200\,^\circ\mathrm{C}$ to obtain stable metallic species and strong metal–support interaction. In the present study, the calcination step was eliminated to reduce the number of parameters. Catalysts were still found to be highly active even without calcination.

To check the reproducibility of the catalyst synthesis, we must first make sure that the catalytic measurements themselves give reliable and reproducible data. Consequently, we checked whether identical samples would give identical catalytic results. A plug flow reactor was used to carry out the catalytic tests. One sample precipitated at pH 10 was divided into three parts, with each part then catalytically evaluated separately. For the tests, after the samples were mounted, the system was cooled directly to $-40\,^\circ\mathrm{C}$ as quickly as possible under nitrogen flow at a rate of 67 ml/min. At this temperature, the nitrogen was replaced by reactant gas (1% CO in air; 67 ml/min), and the temperature of the system was increased to $40\,^\circ\mathrm{C}$ at a ramping rate of $2\,^\circ\mathrm{C/min}$ while CO and CO_2 concentrations were monitored. With increasing temperature, CO was gradually converted into CO_2 over the Au/TiO_2 until full conversion was reached. The results of the three tests are shown in Fig. 1. Satisfactorily, one batch sample essentially shows the same $T_{50\%}$ within an error margin of $<\pm 5\,^\circ\mathrm{C}$, indicating a sufficiently high degree of reproducibility of the catalytic tests. Similar test reproducibility was also observed in related studies with other catalysts.

Consequently, we could tackle the problem of achieving a reproducible preparation of gold catalysts. Following the procedure described in Section 2, four gold samples, denoted as gold-1, gold-2, gold-3, and gold-4, were prepared under the same conditions but independently of each other on different days. These samples were synthesized at a pH of 10. The freshly prepared, noncalcined samples, typically yellowish in color, were used directly for the catalytic test. For each sample, three catalytic cycle tests were normally performed; cooling and heating were repeated three times as described in Section 2. To avoid changes in the state of the catalysts investigated, the starting and the ending temperature of every test were kept identical.

Table 1
Reproducibility of Au/TiO_2 catalysts deposited at pH 10. Explanation given in text

Sample	$T_{50\%}$-1 (°C)	$T_{50\%}$-2 (°C)	$T_{50\%}$-3 (°C)
Gold-1	−3.4	−7.9	−8.3
Gold-2	−2.1	−7.7	−13.7
Gold-3	0.7	−8.9	−10.3
Gold-4	−3.0	−11.8	–
Gold-5	4.9	−4.4	−9.5
Gold-6	7.2	−0.2	−1.2
Gold-7	6.2	1.7	−0.5

The four samples exhibited very similar activity, demonstrating the possible ability to reliably synthesize gold catalysts in a reproducible manner. A representative curve for sample gold-1 is shown in Fig. 2; results for the other samples are compiled in Table 1. The catalysts were very active for the oxidation of CO, showing a $T_{50\%}$ of about $-10\,^\circ\mathrm{C}$ and 100% conversion below room temperature (Fig. 2). Interestingly, in the first cycle the catalyst always showed a somewhat higher $T_{50\%}$; in contrast, the catalyst reached stable activity at a higher level in the two sequential tests. In addition, there seems to be some residual activity of the catalysts in the second and third cycles even at very low temperature, approaching $-40\,^\circ\mathrm{C}$, which was consistently observed throughout the whole study for the DP samples. The reason for this effect is not yet clear. Regardless of this formation process in the first cycle, analyzing the results given in Table 1 clearly reveals good reproducibility of Au/TiO_2 catalyst prepared by the DP method in the manner described in Section 2. Furthermore, in catalyst synthesis, tiny details that can be very difficult to communicate often affect the reproducibility of the synthesis. Therefore, to confirm independence of the catalyst performance of the operator who synthesized the material, three new Au/TiO_2 catalysts—gold-5, gold-6, and gold-7—were prepared by a different operator following the procedure described in Section 2 and tested under the same conditions by another investigator. The resultant activities are also given in Table 1. These new samples showed similar catalytic activity to the catalysts prepared earlier, although the average activity seemed to be slightly lower. The calculated mean $T_{50\%}$ for all of the catalysts considered in this work was $-6.4\,^\circ\mathrm{C}$ with a standard deviation of ±4 °C (calculated for the second and third runs, whereas activity is unstable in the first run), which we consider satisfactory overall, especially considering the difficulties normally encountered for gold-based catalysts.

We can identify several key factors as crucial to achieving good reproducibility in catalyst synthesis. These are physicochemical and operative parameters related to some of the preparation steps. The molarity of the NaOH solution seems to play a crucial role. In the present study, a 0.1 M NaOH solution was used to adjust the pH value of the TiO_2 suspension. This molarity is lower than that used in our previous work [13], allowing better pH control and avoiding high local alkali concentrations. It is important that the pH be as homogeneous as possible in the suspension. This also implies that pH should be strictly controlled during the entire preparation sequence.

Maintaining a fixed volume of the final suspension in the first step of the preparation, deposition, is also important. In particular, different volumes reached after the deposition could lead to changes in the loading of gold, particle size, and distribution on the TiO_2 support. Another sensitive step is the drying of Au/TiO_2 in the desiccator. The catalytic activity of gold is very sensitive to water or moisture; moisture at even the ppm level can improve the activity of gold in CO oxidation [21]. The rate at which water is removed from the as-made samples also has an affect. Thus changing the amount of P_2O_5 in the desiccator leads to a lower degree of catalyst reproducibility. In our study, the fresh samples with no pretreatment were used directly to perform catalytic tests. To prepare samples with identical water content, the drying conditions (e.g., the vacuum, the amount of drying agent, the drying time) were kept constant.

After the reproducibility problem was solved and the pH during precipitation was identified as a crucial parameter, our obvious next step was to study the exact effect of pH value during precipitation on catalytic activity. To do this, we precipitated different Au/TiO_2 catalysts at various pH values; the results are shown in Fig. 3. An increase in pH from 7 to 10 during precipitation leads to a more active catalyst, consistent with previously reported results [13]. However, for samples precipitated at pH 11, $T_{50\%}$ increases to 15 °C, corresponding to an appreciably reduced catalytic activity. The best catalysts were produced at pH 10.

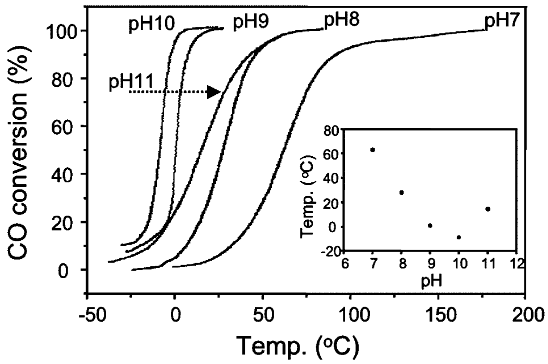
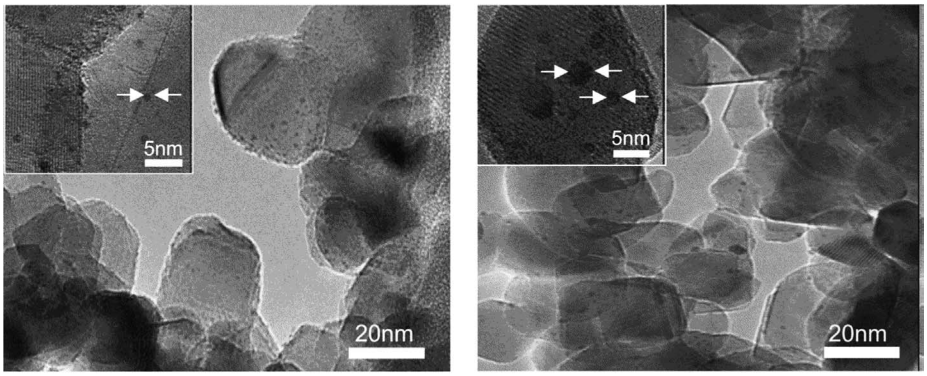


Fig. 3. pH dependence of catalytic activity of Au/TiO_2 catalysts (insert is temperature for 50% conversion as a function of deposition pH value).

Interestingly, after CO oxidation, the yellowish color of the fresh Au/TiO_2 changed to purple, a typical feature of metallic gold. This clearly indicates that the gold precursor (Au^{3+} and/or Au^{+}) reduced to Au^0 under reaction conditions. To check whether this reduction process was related to morphological changes in the gold particles, catalysts were investigated by TEM before and after the catalytic experiments. Au/TiO_2 (gold-2) was selected for these measurements. As shown in Fig. 4, the fresh sample shows a very homogeneous dispersion of gold particles <2 nm in size. After reaction, gold particles 3–4 nm in size are discernible, indicating that the gold particles grew during the CO oxidation. Because the catalytic tests were always carried out below 40 °C, this particle growth is likely caused not by the temperature effect, but rather by the reduction during the first catalytic run. In subsequent runs after the first reduction run, no further change in particle size was seen; the average size was still <4 nm, which, according to literature data, seems to be a critical size for active catalysts [22,23]. Rousset et al. also observed an increase in gold particle size during the CO oxidation reaction. The gold-supported catalysts that they used in their study were prepared by laser vaporization. Because the catalytic properties varied appreciably only between the first and second catalytic cycles, these authors deduced that the increase had already occurred during the first annealing treatment and not during the following reaction cycles [24], in agreement with our observations.



before reaction

after reaction

Fig. 4. TEM images of the Au/TiO_2 catalyst (gold-2) prepared at pH 10 (left: before reaction; right: after reaction).

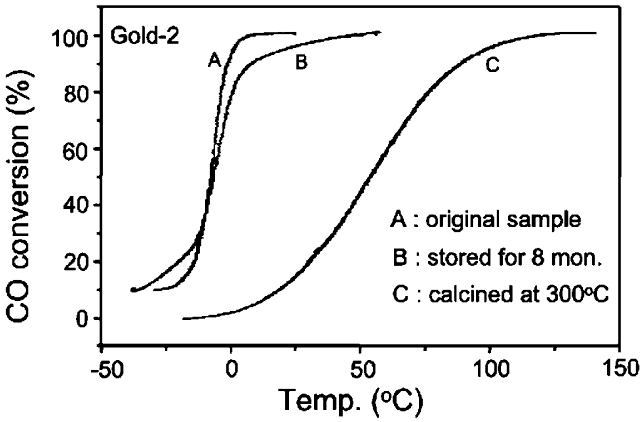


Fig. 5. Stability of Au/TiO_2 catalyst (gold-2) prepared at pH 10 (curve A: freshly prepared catalyst; curve B: after storage for 8 months; curve C: after calcination at 300 °C for 2 h).

3.2. *Stability of Au/TiO_2*

It has been reported that calcination at temperatures > 200 °C to remove residual water and transform the oxidic Au precursor into metallic Au is a fundamental step to obtaining stable, highly active gold catalysts [2]. In our case, calcination always led to a loss of activity. An example is presented in Fig. 5; when one sample (gold-2) precipitated at pH 10 was calcined at 300 °C for 2 h, $T_{50\%}$ rose to 50 °C (curve C in Fig. 5), in contrast to the very low $T_{50\%}$ (−7.7 °C) for the as-made uncalcined sample (curve A in Fig. 5). This result is consistent with what we pointed out in previous work—namely, that calcination at 300 °C leads to agglomeration of gold particles resulting in an average particle size of 4–8 nm [13]. Therefore, for the synthesis route described in this paper, using uncalcined samples for CO oxidation is preferable if high activity is the goal. Moreau et al. [25] reported a similar finding; in their case calcination was disadvantageous, because activity was reduced substantially after calcination at 400 °C. However, they found that activity was essentially unchanged by calcinations at 100, 200, and 300 °C [25].

To check for any loss of activity in the highly active samples of this study, the catalysts were stored in a vial in darkness at ambient atmosphere for 8 months at room temperature and subsequently catalytically reevaluated. The catalytic activity of gold-2, as a representative sample, was found to be unchanged compared with the original sample (curve B vs. curve A in Fig. 5).

To our knowledge, all of the preparations of Au/TiO_2 catalysts using the DP method reported in the literature were carried out in the dark (in cases where this point was addressed at all), because TiO_2 is able to photoreduce oxidic Au to metallic Au, which can lead to poor reproducibility of the catalyst synthesis. However, no detailed report on the effect of light on the catalytic activity has been published to date. Hence one fresh sample prepared at pH 10 (gold-2) was exposed to daylight on purpose. After 1 week, the sample color changed completely to purple, suggesting reduction of the gold species. Surprisingly, as shown in Fig. 6a, the catalytic tests show almost identical activity to a sample handled completely in the dark (Table 1). TEM (Fig. 6b) revealed similar particle sizes in the Au/TiO_2 reduced by daylight and the sample stored in darkness (Fig. 4a). Nevertheless, this experiment does not necessarily mean that excluding light is unnecessary. Particularly in the earlier stages of catalyst synthesis or during long-term exposure to light, activity may be influenced by light exposure. This effect is presently being studied in our laboratories.

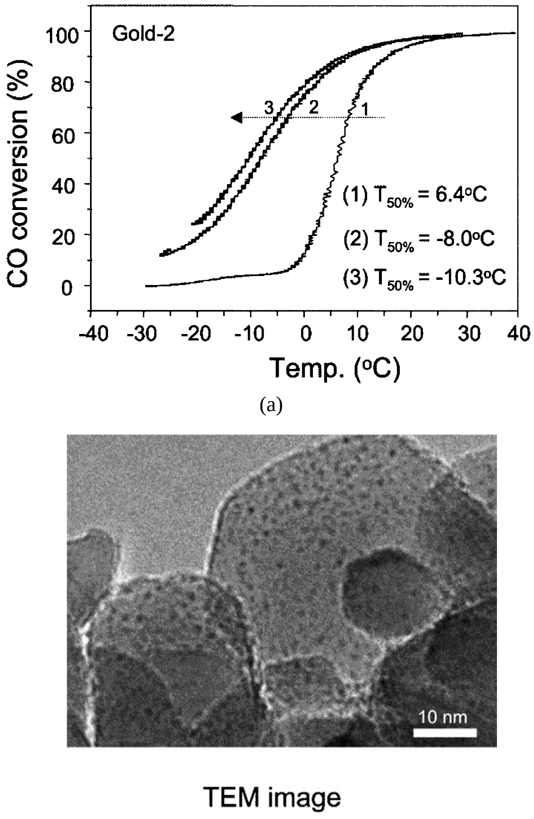


Fig. 6. Light effect on the Au/TiO_2 catalyst. Freshly prepared Au/TiO_2 deposited at pH 10 was exposed to daylight for one week. (a) Catalytic activity in CO oxidation measured in three cycles; (b) TEM image of this catalyst.

3.3. *Catalytic activity of Au/TiO_2 prepared by impregnation*

Compared with the DP method, conventional impregnation has several advantages, including simpler synthesis, more efficient use of gold precursors, fewer steps, lack of a filtration step, and shorter synthesis time. Impregnation thus appears more attractive for industrial applications. However, in the synthesis of highly active gold catalysts, impregnation creates several problems. Impregnation results in large gold particles with correspondingly low activity. In addition, it is not easy to remove residual chloride ions from the $HAuCl_4$, which act as poisons on the gold catalysts. To overcome these problems, Iwasawa's group improved the impregnation procedure using hydroxides as supports and gold phosphine complexes instead of gold chloride as precursor species [26]. Sodium boron hydride was used as the reducing agent during this synthesis to obtain highly active and stable CO oxidation catalysts with particle sizes of 2–5 nm [27]. An impregnation method using solvated metal atoms was also developed to achieve an active nano-Au catalyst [28].

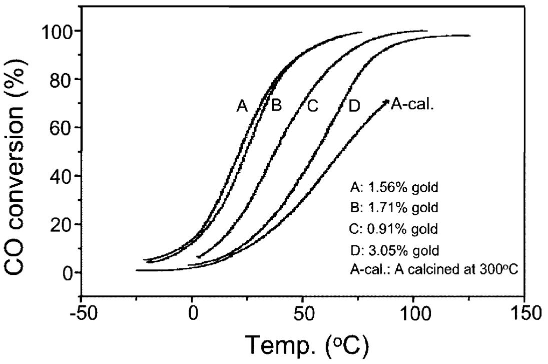


Fig. 7. Catalytic activities of Au/TiO_2 catalysts prepared by impregnation method having different gold loading.

However, both of these techniques are not very straightforward, and the availability of alternative impregnation processes for the production of active gold catalysts is highly desirable.

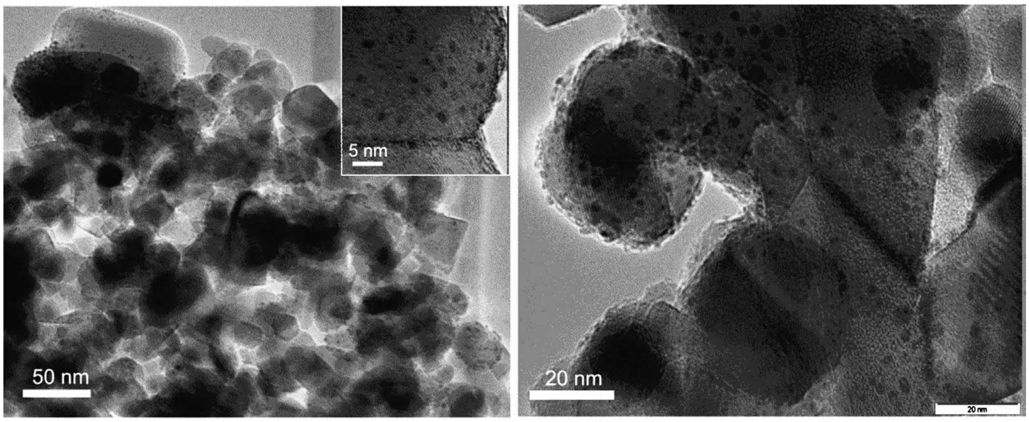
Consequently, we developed a wet impregnation technique, combined with subsequent NH_3 treatment, to provide a simple alternative method. The ammonia treatment step is important, because it results in the formation of $Au(OH)_3$ on TiO_2, allowing the removal of residual chlorine ions on the support by simple washing. As described in Section 2, a series of samples with varied gold loading was prepared. EDX measurement confirmed that no detectable levels of chloride ions were left on the catalysts. Similar to the catalysts prepared by the DP method, these samples were directly tested for catalytic activity in CO oxidation in the as-made, uncalcined state. To investigate the calcination effect, samples were also calcined at 300 °C for 2 h before the catalytic test; the results are reported in Fig. 7. All of the samples with different gold loadings were active for CO oxidation, although their activity did not quite reach the levels observed for the materials prepared by the DP method. Comparing the results from sample A and sample A-calcined clearly shows that calcination led to deactivation, as was also observed for Au/TiO_2 prepared by the DP method. At room temperature, sample A (1.56% Au) and sample B (1.71% Au) reached 50% conversion, whereas sample C with a lower Au loading (0.91%) demonstrated a small increase in $T_{50\%}$. Higher Au loading (sample D; 3.05%) led to an increase in $T_{50\%}$ to >50 °C. TEM investigations (Fig. 8) indicate that small, isolated gold particles can be dispersed on the TiO_2 support through the impregnation method. The particle sizes are dependent on the gold loading. With 1.56% Au loading (sample A), the particle size was around 2 nm. In contrast, an increase in Au loading (sample D; 3.05%) led to relatively large (3–4 nm) particles. This finding is in agreement with the decreased catalytic activity, confirming for this type of catalyst as well the clear correlation between particle size and activity described previously for other gold-based systems.

The foregoing results demonstrate that the impregnation method combined with ammonia treatment provides a simple alternative route for the synthesis of active catalysts for CO oxidation. But it remains difficult to synthesize catalysts with a homogeneous gold particle size distribution, which may lead to reproducibility problems. The development of optimized synthetic conditions for this pathway remains under investigation.

4. Conclusion

This study has demonstrated that Au/TiO_2 catalysts prepared by the DP method show good reproducibility under meticulously controlled synthesis conditions. The crucial factors influencing reproducibility are strict pH control during precipitation, which is facilitated by using a relatively dilute NaOH solution; maintenance of a fixed volume at the end of the synthesis; and exact control of the drying conditions. The catalytic activity of Au/TiO_2 depends strongly on the pH during precipitation, with the optimal pH value found to be 10. Calcination of the as-made material is not needed to achieve high activity; on the contrary, it causes an obvious drop in the activity of the Au/TiO_2 catalyst. Freshly prepared Au/TiO_2 catalysts showed very good long-term stability. Even after storage for 8 months, the Au/TiO_2 catalyst retained the same activity level as measured for the original sample at the beginning of the catalytic run.

Au/TiO_2 catalysts prepared by wet impregnation followed by ammonia treatment and washing consist of highly dispersed gold particles on the support. Particle size is usually <4 nm,



1.56% gold loading

3.05% gold loading

Fig. 8. TEM images of Au/TiO_2 catalysts with different gold loading prepared by impregnation.

with the actual size depending on the loading of the gold on the support. Such catalysts show an activity in CO oxidation almost as high as that of samples prepared by the DP method.

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