

# The Activation of Supported Au Catalysts prepared by Impregnation

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## Abstract

**In this study, Au/TiO<sub>2</sub>, Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Au/C catalysts were prepared by an incipient-wetness impregnation method. The CO oxidation activity after different pretreatment was analyzed. Two pretreatments are found possible to activate these catalysts for CO oxidation: (i) high-temperature hydrogen reduction and (ii) aqueous base treatment using NH<sub>3(aq)</sub>. The high-temperature hydrogen reduction is effective for Au/TiO<sub>2</sub> and Au/C, but not Au/Al<sub>2</sub>O<sub>3</sub>. The base treatment is effective for Au/Al<sub>2</sub>O<sub>3</sub> and Au/TiO<sub>2</sub>, but not Au/C. Small Au particles of ca. 2 nm size were observed in activated Au catalysts from both pretreatments; however, the high-temperature H<sub>2</sub> reduction procedure also resulted in large Au particles of ca. 25 nm size which makes it a less efficient pretreatment than the base treatment. The activated Au/TiO<sub>2</sub> catalysts show comparable turnover frequency as the Au/TiO<sub>2</sub> catalyst prepared by a deposition precipitation method. The effective pretreatments were found to be accompanied by a reduced acidity, which is measured by the pH of aqueous catalyst suspension. Reasons for such activation are discussed.**

## Keywords

Au/TiO<sub>2</sub>, Au/Al<sub>2</sub>O<sub>3</sub>, Au/C, impregnation, incipient wetness, pretreatment, base treatment

## 1 Introduction

Supported Au catalysts are very active for CO oxidation reaction. However, active Au catalysts are overwhelmingly prepared by the deposition-precipitation (DP) method first described by Haruta and coworkers [1]. Active Au catalysts can be otherwise prepared by coprecipitation [2] or vapor deposition [3,4]. Conventional impregnation (IMP) methods for supported metal catalysts failed to yield active Au catalysts [5], though some earlier reports [6,7] showed that they may be applicable. Recently, a modified IMP method is reported by Bowker and coworkers [8,9] which can lead to high CO oxidation activity as catalysts prepared by the DP method. The IMP methods have advantages of being simple and easy to control and have been used effectively for preparing different metal catalysts. Conventional IMP catalysts require gas treatment at elevated temperature to activate the catalysts. If effective activation methods are available, supported Au catalysts can be prepared by an IMP method for all kinds of applications.

For the activation of Au catalysts prepared by a DP method, calcination seems to work better than a hydrogen reduction at elevated temperatures. [10] However, a high-temperature hydrogen reduction (H<sub>2</sub>, 773 K, expressed as HTR hereafter) seems the best way to activate Au/TiO<sub>2</sub> catalysts prepared by an IMP method while a subsequent calcination resulted in even higher activity. [6] The activity of HTR-activated IMP Au catalyst and that of the calcined DP catalyst have not been carefully compared, not to mention the Au morphology evolution during these activation procedures. Furthermore, a HTR treatment seems effective when calcination failed to activate supported Au catalysts. [11-13] For example, Choudhary et al. prepared Au/TiO<sub>2</sub> from [Au<sub>6</sub>(PPh<sub>3</sub>)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (in CH<sub>2</sub>Cl<sub>2</sub>) and HTR resulted in smaller Au particles and higher CO oxidation activity than using calcinations pretreatment. [11] It is noteworthy that all Au compounds decompose to metallic Au at temperatures no more than ca. 523 K. [14] The need of different pretreatment for differently prepared Au catalysts seems less relevant to the extent of Au reduction. Thus, understanding the pretreatment effect on Au catalysts may provide insight to the active Au morphology.

The as-prepared IMP Au catalysts are essentially inactive for CO oxidation. This study explores applicable activation procedures for Au catalysts prepared by an IMP method, and related changes in catalyst morphology are examined. Three different supports, namely, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and carbon black, are used such that the effect of support on the activation method can be learned.

## 2 Experimental

Supported Au catalysts of nominally 1% Au loading are prepared by an incipient wetness impregnation method from AuCl<sub>3</sub> (Aldrich) and three supports, TiO<sub>2</sub> (Degussa, P25),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (Strem, low soda) and C (Cabbot, XC72R). Table 1 uses

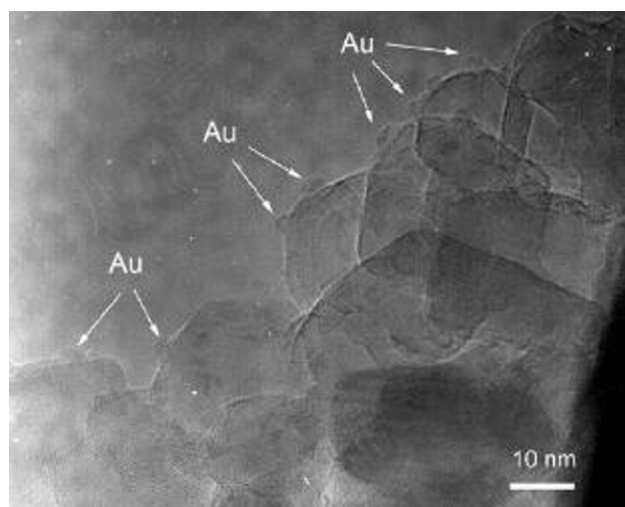
**Table 1**

Suffix used to name Au/Al<sub>2</sub>O<sub>3</sub> prepared by different base treatments

Suffix	Description
-IMP	Fresh AuCl <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> prepared by an incipient-wetness impregnation, dried at 298 K under vacuum.
-la	The Au/Al <sub>2</sub> O <sub>3</sub> -IMP catalyst is further impregnated to incipient wetness with 25% NH <sub>4</sub> OH <sub>(aq)</sub> and then oven dried.
-lb	Al <sub>2</sub> O <sub>3</sub> is impregnated with 25% NH <sub>4</sub> OH <sub>(aq)</sub> and oven dried, then impregnated with AuCl <sub>3(aq)</sub> and vacuum dried.
-lc	The Au/Al <sub>2</sub> O <sub>3</sub> -lb catalyst is further impregnated to incipient wetness with 25% NH <sub>4</sub> OH <sub>(aq)</sub> and then oven dried
-ld	A mixture of NH <sub>4</sub> OH <sub>(aq)</sub> and AuCl <sub>3(aq)</sub> is impregnated to incipient wetness over Al <sub>2</sub> O <sub>3</sub> and then vacuum dried.
-le	The Au/Al <sub>2</sub> O <sub>3</sub> -IMP is dispersed in H <sub>2</sub> O and NH <sub>4</sub> OH <sub>(aq)</sub> was added to keep pH~10.5, aged, then filtered and vacuum dried.

Au/Al<sub>2</sub>O<sub>3</sub> as an example to illustrate the names and details of the post-impregnation base treatments used in this study. The supported Au catalysts prepared by a deposition method will use the suffix '-DP' in this paper. Two reference catalysts are used for comparison in this study, i.e., 1.5% Au/TiO<sub>2</sub> and 0.8% Au/C (both from World Gold Council, marked with suffix '-WGC'). These catalysts were subjected to different in-line gas treatment prior to reaction analysis. The frequently used gas pretreatment includes oxygen calcination at 573 K (C), hydrogen reduction at 773 K (HTR), and hydrogen reduction at 473 K (LTR). The gas pretreatment is carried out as: (i) purging the catalyst with He at 298 K for 30 min, (ii) introducing either H<sub>2</sub> or O<sub>2</sub>, (iii) heating at ca. 10 K/min up to the target pretreatment temperature, (iv) holding at target temperature for 1hr, and (v) cooling the catalyst under He purge. Sequential pretreatment, e.g., HTR/C or HTR/C/LTR, is also used which follows the conditions described earlier [6].

The CO oxidation activity is measured at 1% CO and 10%

**Figure 1**

TEM image of 1% Au/TiO<sub>2</sub>-IMP catalyst after HTR/C/LTR pretreatment

O<sub>2</sub> (balance He) with a home-made flow reactor system. All gases were controlled by mass flow controllers and further treated with dryer column whenever applicable. Typically, 100 or 250 mg of catalyst was loaded into a pyrex U-tube reactor and a space velocity of ca. 30 or 12 μmol CO/sec/g catalyst was used. The reactor is connected to the system via a 4-way valve such that the reactor can be isolated from the system when needed, e.g., when monitoring entrance gas composition. After in-line gas treatment, the reaction gases were admitted and the effluent composition was monitored with respect to onstream time using a GC (Shimadzu, GC8A). The steady-state conversion was recorded, which is typically observed after 30 min onstream. Thereafter, the reactor temperature was raised (or cooled) under He to the next reaction temperature and again the steady state conversion was recorded. The reaction test was carried out through a stepwise temperature-ascending-descending sequence, such that the stability of the catalyst can be monitored by comparing data at the ascending sequence and that at the descending sequence.

### 3 Results and discussion

#### 3.1 High-temperature H<sub>2</sub> pretreatment

It has been reported that a HTR pretreatment can effectively activate Au/TiO<sub>2</sub> catalysts prepared by an incipient-wetness impregnation method. [6,7] However, there are two important issues remained unanswered, i.e., (i) what the Au morphology is in such activated catalysts, and (ii) how active it is comparing to Au/TiO<sub>2</sub>-DP, prepared by a deposition method. Earlier report [6] showed that the Au particle size in HTR-activated Au/TiO<sub>2</sub>-IMP (including HTR, HTR/C, or HTR/C/LTR pretreatment) is around 25 nm from XRD peak broadening analysis. On the other hand, XPS analysis indicates that the activated 1% Au/TiO<sub>2</sub>-IMP (HTR/C/LTR) has a dispersion of 30%. [15] A bimodal Au particle distribution is indicated, but the morphology of smaller Au particles in this HTR-activated Au/TiO<sub>2</sub>-IMP has not yet been imaged. With HRTEM, we found that Au particles of ca. 2 nm size are presented in 1% Au/TiO<sub>2</sub>-IMP (HTR/C/LTR) as shown in Figure 1. The small Au particles at the edge of TiO<sub>2</sub> grains have a large interface with TiO<sub>2</sub>, similar to the morphology of similar size Au in Au/TiO<sub>2</sub>-DP catalysts [1]. This indicates that small Au particles in HTR-activated Au/TiO<sub>2</sub>-IMP have strong interaction with TiO<sub>2</sub>.

To elucidate the distribution of large and small Au particles in HTR-activated Au/TiO<sub>2</sub>-IMP catalysts, we calculated the concentration of large (25 nm) and small (2 nm) Au particles based on the following equations:

$$Au/Ti = \frac{\pi}{2} (d_1^2 \cdot n_1 + d_2^2 \cdot n_2) \cdot \frac{1.2 \cdot 10^{19} Au/m^2}{7 \cdot 10^{18} Ti/m^2} \quad (1)$$

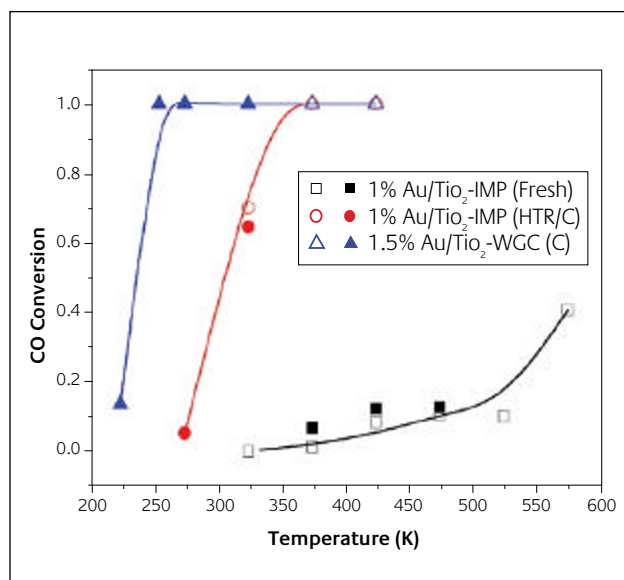
$$gram Au/m^2 = \frac{\pi}{12} (d_1^3 \cdot n_1 + d_2^3 \cdot n_2) \cdot \rho_{Au} \quad (2)$$

where  $n_1$  and  $n_2$  represent the number density per m<sup>2</sup> of catalyst surface of the two sizes ( $d_1$  and  $d_2$ ) of hemispherical Au particles.

The Au/Ti data was taken from XPS data [15] and the gram Au/m<sup>2</sup> data was calculated from Au loading and BET area. The resulting number density of 2 nm Au in the 1% Au/TiO<sub>2</sub>-IMP (HTR/C) catalyst is estimated as around 10<sup>13</sup>/m<sup>2</sup> while that of 25 nm Au is approximately 2 orders lower. The estimated number densities can be translated into that 2-nm-size particles constitute approximately 10 % (by wt) or 60 % (by exposed Au surface) of total Au in the 1% Au/TiO<sub>2</sub>-IMP (HTR/C). The low number density qualitatively explains, together with the low contrast of small Au particles [16], why only few Au particles are observed in TEM image (Figure 1).

Figure 2 compares the CO oxidation of fresh Au/TiO<sub>2</sub>-IMP, Au/TiO<sub>2</sub>-IMP (HTR/C), and Au/TiO<sub>2</sub>-WGC (C). The effect of HTR-activation is obvious but the activity seems lower than the catalyst prepared by DP method. Based on the 30% dispersion estimated from XPS [15], the 1% Au/TiO<sub>2</sub>-IMP (HTR/C) in Figure 2 has a calculated TOF (turnover frequency) of 0.043 s<sup>-1</sup> at 273 K. This is comparable to the 0.02 – 0.06 s<sup>-1</sup> for Au/TiO<sub>2</sub>-DP (C) at 273 K, 1 % CO + 20 % O<sub>2</sub>, and a space velocity of ca. 2.5 μmol CO/sec/g catalyst [4]. If the dispersion is based on the particle number density discussed above, the calculated dispersion is 9 % and the corresponding TOF would be higher. It is clear that the Au/TiO<sub>2</sub>-IMP (HTR/C) catalyst has a comparable specific activity (TOF) as the Au/TiO<sub>2</sub>-DP. This seems consistent with their similar morphology observed in TEM. However, the HTR-activated Au/TiO<sub>2</sub>-IMP catalyst is less efficient than a DP catalyst because ca. 90 % of its total Au is presented as large (ca. 25 nm) Au particles.

Since HTR is effective in activating Au/TiO<sub>2</sub>-IMP catalyst, we tested the same HTR treatment for the activation of 1% Au/Al<sub>2</sub>O<sub>3</sub>-IMP catalyst and 3% Au/C-IMP catalysts. Results



**Figure 2**

CO oxidation activity over 1% Au/TiO<sub>2</sub>-IMP (HTR/C) catalyst and 1.5% Au/TiO<sub>2</sub>-WGC (reference catalyst, after calcinations at 573 K). Reaction conditions: 1 % CO, 10 % O<sub>2</sub>, balanced He, space velocity = 12 μmol CO/sec/g catalyst. Open symbols represent data measured during temperature-ascending sequence while filled symbols represent those during temperature-descending sequence

shown in Figure 3 indicate that this HTR cannot activate 1% Au/Al<sub>2</sub>O<sub>3</sub>-IMP whereas it enhances the CO oxidation activity over Au/C-IMP catalysts. Neither can a calcination activate Au/Al<sub>2</sub>O<sub>3</sub>-IMP and Au/C-IMP catalysts. Obviously the effectiveness of the HTR treatment is support-dependent.

The reason why HTR is ineffective for Au/Al<sub>2</sub>O<sub>3</sub>-IMP is puzzling and is discussed here. The HTR activation of Au/TiO<sub>2</sub>-IMP was attributed to Cl removal [6]. The CO oxidation activity of differently prepared Au/TiO<sub>2</sub> catalysts was found to decrease with increase of Cl XPS intensity. [8,9] One possible explanation of the low activity of Au/Al<sub>2</sub>O<sub>3</sub>-IMP (HTR) is the poisoning by Au-Cl bond. We reported earlier that this Au/Al<sub>2</sub>O<sub>3</sub>-IMP fresh catalyst contains mainly Au-O bond but Au-Cl bond forms when treated under He up to 473 K. [17] This is attributed to residual Cl on Al<sub>2</sub>O<sub>3</sub> surface. [17] From Figure 3a, the fresh Au/Al<sub>2</sub>O<sub>3</sub>-IMP, Au/Al<sub>2</sub>O<sub>3</sub>-IMP (after He, 473K) and Au/Al<sub>2</sub>O<sub>3</sub>-IMP (HTR) catalysts show similar low CO oxidation activity. This implies that an initial state with Au-Cl morphology (e.g., after He 473K) is not the only detrimental factor to the catalytic activity. Furthermore, EXAFS analyses [17] show no Au-Cl bond in Au/Al<sub>2</sub>O<sub>3</sub>-IMP either after treatment at temperatures higher than 523 K or after a reaction test no matter what pretreatment was used. Only Au-Au bond was present in these cases. Therefore, neither a direct Au-Cl bonding nor the extent of reduction can explain the ineffective HTR activation for Au/Al<sub>2</sub>O<sub>3</sub>-IMP.

Another possible explanation for the low activity of Au/Al<sub>2</sub>O<sub>3</sub>-IMP (HTR) is the surface acidity, possibly resulting from residual Cl on Al<sub>2</sub>O<sub>3</sub> surface. Gold catalysts are known to be relatively inactive when supported on acidic supports [18]. To examine if the surface acidity may be the reason why Au/Al<sub>2</sub>O<sub>3</sub>-IMP cannot be activated by HTR, we use the equilibrated pH of aqueous catalyst suspension as an index to the surface acidity. Table 2 shows the results of fresh IMP catalysts and those after HTR/C treatment. The fresh IMP catalysts are all acidic. The HTR treatment made Au/TiO<sub>2</sub>-IMP and Au/C-IMP to become neutral, but the Au/Al<sub>2</sub>O<sub>3</sub>-IMP (HTR/C) remained acidic. The change from acidic to neutral seems to coincide with effective HTR activation of these IMP catalysts. All the Au/Al<sub>2</sub>O<sub>3</sub>-IMP spent catalysts from Fig.3a show an equilibrated pH from 4.7 – 4.9, which suggests that the acidic surface may be the reason of their similarly low activity. When the hydrogen treatment temperature for Au/Al<sub>2</sub>O<sub>3</sub>-IMP was increased to 973 and 1273 K, the activity was still low (not shown) and the equilibrated pH of the spent catalyst was 4.8 and 5.9 respectively. Chlorinated Al<sub>2</sub>O<sub>3</sub> is known as a strong acid and a significant amount of Cl remained after TPD up to 973 K. [19] These results support the proposed Cl-removal as the reason of enhanced catalytic activity by high-temperature H<sub>2</sub> treatment [6], but the change in surface acidity is considered as the main effect. It will be shown later that the relatively inactive Au/Al<sub>2</sub>O<sub>3</sub>-IMP (HTR) can be activated by a further base treatment. This substantiates the proposed surface acidity effect and that residual Cl on Al<sub>2</sub>O<sub>3</sub> seems the most likely origin of surface acidity.

The effect of Cl on Au catalysts can be more than the surface acidity effect. Oh *et al.* [20] reported that the presence of surface Cl during pretreatment may cause Au sintering and suppressed activity. Several studies [11-13,20] have shown that calcinations resulted in larger Au particles and lower activity than H<sub>2</sub> pretreatment when the catalyst contained residual Cl. This seems to suggest that H<sub>2</sub> pretreatment can suppress the Cl-assisted Au sintering. If so, when and how the Au moiety became reduced during pretreatment may be critical in determining the eventual catalyst performance when residual Cl is present. The so-called procedure-sensitive HTR for Au/TiO<sub>2</sub>-IMP we reported earlier [21] may be related to this. It was found [21] that the HTR treatment with H<sub>2</sub> flow starting from room temperature resulted in a more active Au/TiO<sub>2</sub> than the HTR with H<sub>2</sub> introduction only at 773 K. In-situ XANES (x-ray absorption near-edge spectroscopy) of Au/TiO<sub>2</sub>-IMP [21] indicates that the HTR beginning with He had a faster Au reduction than that beginning with H<sub>2</sub>, although both showed a complete Au reduction at ca. 400 K. Though this may not be a direct evidence of the H<sub>2</sub>-suppression of Cl-assisted sintering, it certainly demonstrates that how and when the Au becomes reduced during pretreatment can affect the catalyst performance.

The HTR-activation is also observed with 3 % Au/C-IMP catalyst and 0.8 % Au/C-WGC catalyst as shown in Fig. 3b. However, the activity enhancement is not sufficient to make Au/C a good low-temperature CO oxidation catalyst. Table 2 indicates a reduced surface acidity after HTR. Although this is attributable to Cl-removal, it should be noted that the carbon surface acidity can be also related to surface oxygen. A hydrogen treatment at 773 K (HTR) may not be severe enough to completely remove surface oxygen, but its effect cannot be excluded. Furthermore, the 0.8 % Au/C-WGC catalyst is prepared by a sol deposition process, in which Cl residue is supposedly low. The acidity changes of Au/

**Table 2**

*Effect of HTR/C treatment on the equilibrated pH of catalyst suspension<sup>1</sup>*

Catalyst	Fresh	After HTR/C
1% Au/TiO <sub>2</sub> -IMP	3.5	8.7
1% Au/Al <sub>2</sub> O <sub>3</sub> -IMP	4.2	5.3
1% Au/C-IMP	4.3	7.0
1.5% Au/TiO <sub>2</sub> -WGC	7.8 <sup>2</sup>	-
0.8% Au/C-WGC	4.7 <sup>2</sup>	8.2 <sup>3</sup>

<sup>1</sup> The equilibrated pH was measured by dispersing 0.1 g catalyst in 10 ml DI water at room temperature.

<sup>2</sup> As received.

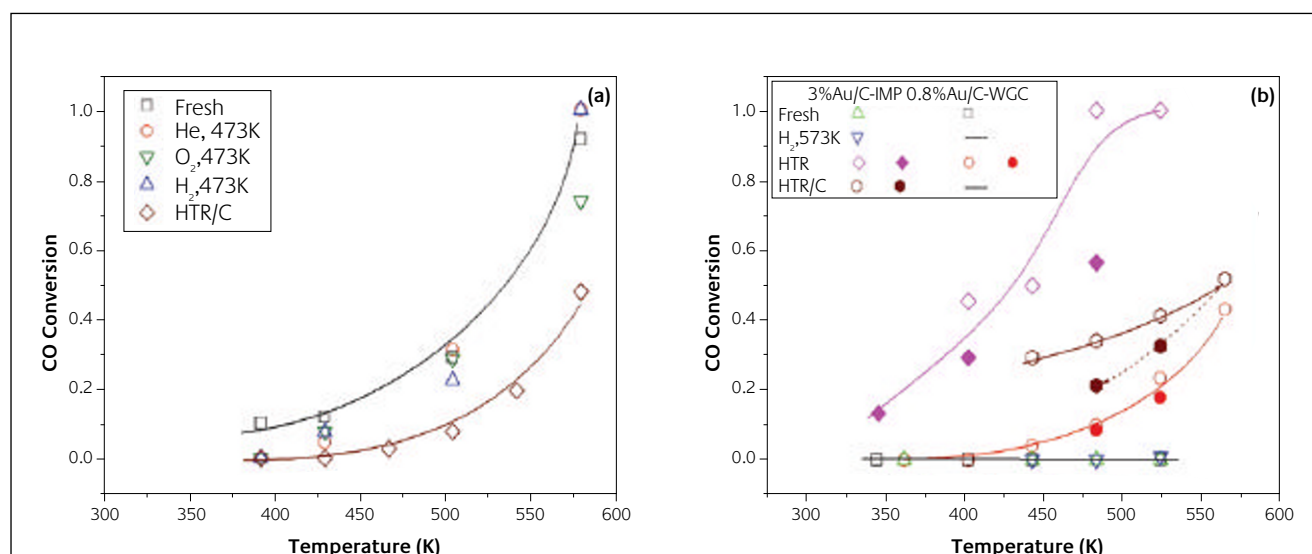
<sup>3</sup> This sample was pretreated with HTR and used for CO oxidation test prior to the pH measurement

C before and after HTR cannot be unequivocally attributed to Cl-removal at this moment. However, HTR is still the best pretreatment we found to activate Au/C-IMP and 0.8 % Au/C-WGC, and a decrease in surface acidity was observed at the same time.

The CO oxidation activity of both 3% Au/C-IMP (HTR) and 0.8 % Au/C-WGC (HTR) catalyst is far lower than that of Au/TiO<sub>2</sub>-IMP (HTR) shown in Figure 2. This is tentatively classified as the support effect. Unlike oxide-supported Au catalysts, the Au/C-IMP (HTR) is deactivated by a further calcination at 573 K (i.e., HTR/C treatment) or by CO oxidation reaction at temperatures above 523 K. The reason for such deactivation is not known at this moment.

### 3.2 Effect of base pretreatment

Gold catalysts prepared by a DP method comparatively use an additional ingredient, i.e., base, than IMP catalysts in their



**Figure 3**

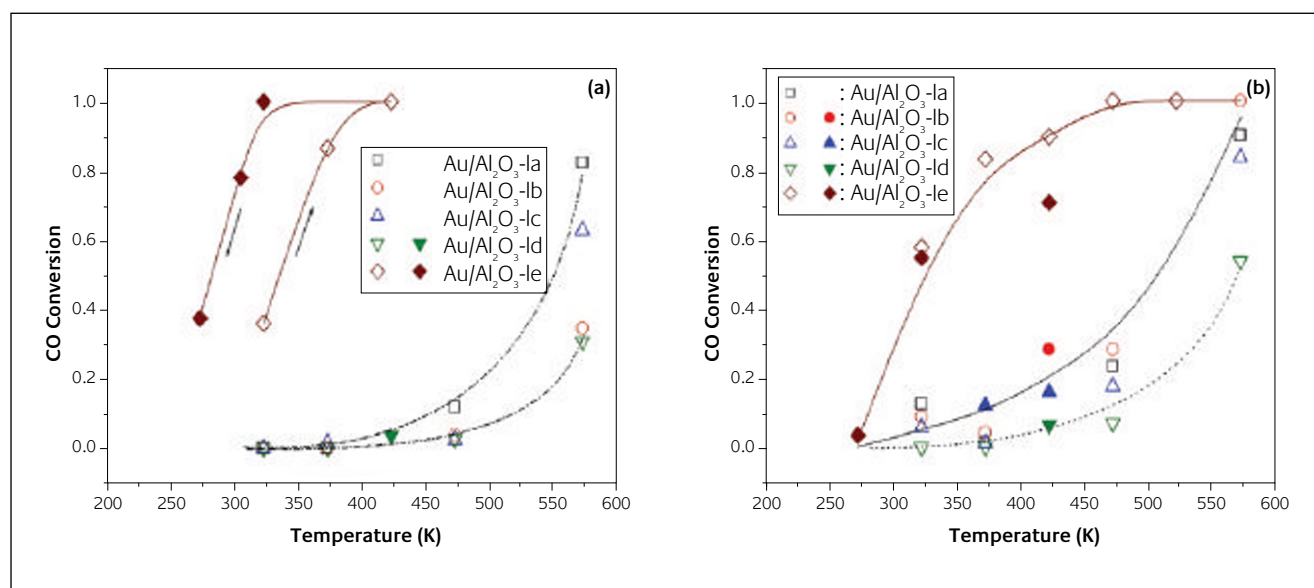
*Effect of pretreatment on the CO oxidation activity over (a) 1% Au/Al<sub>2</sub>O<sub>3</sub>-IMP and (b) 3% Au/C-IMP catalyst. Reaction conditions: 1 % CO, 10 % O<sub>2</sub>, balanced He, space velocity = (a) 12 and (b) 30 μmol CO/sec/g catalyst. Open symbols represent data measured during temperature-ascending sequence while filled symbols represent those during temperature-descending sequence*

preparation. Therefore, we tried to activate the Au/Al<sub>2</sub>O<sub>3</sub>-IMP catalyst by introducing a base in the preparation procedures. Table 1 summarizes different ways of base introduction we tried. Aqueous NH<sub>3</sub> solution was used. Although a possible formation of fulminating gold was warned [22], we did not observe any symptom of its formation. Using NH<sub>3(aq)</sub> also serves an intention to the possible formation of volatile NH<sub>4</sub>Cl species, as a way to remove surface Cl. Figure 4 compares the activity of these base-treated 1% Au/Al<sub>2</sub>O<sub>3</sub>-IMP, as is and after a HTR treatment. The as-is base-treated Au/Al<sub>2</sub>O<sub>3</sub>-IMP catalysts, except Au/Al<sub>2</sub>O<sub>3</sub>-le, are slightly less active than the fresh Au/Al<sub>2</sub>O<sub>3</sub>-IMP (in Figure 3a), but a HTR treatment increased their activities higher than that of Au/Al<sub>2</sub>O<sub>3</sub>-IMP (HTR).

From Figure 4, it is obvious that only Au/Al<sub>2</sub>O<sub>3</sub>-le showed a significant activity enhancement which is overwhelmingly high comparing to all other treatments we did to Au/Al<sub>2</sub>O<sub>3</sub>-IMP. In addition, Figure 4a indicates the presence of in-line activation of the fresh Au/Al<sub>2</sub>O<sub>3</sub>-le catalyst where the activity measured during the temperature-descending sequence is higher than that in the temperature-ascending sequence. The activity developed through in-line activation is higher than the activity after a HTR treatment. We observed such an in-line activation in many of our Au catalysts prepared by a DP method [23], in which a calcination at 573 K can effectively activate the catalysts to match the activity developed in-line. This is also true for the Au/Al<sub>2</sub>O<sub>3</sub>-le catalyst. Figure 5 shows that the Au/Al<sub>2</sub>O<sub>3</sub>-le (C) has a stable enhanced CO oxidation activity. The calcination pretreatment resulted in higher activity than HTR for the Au/Al<sub>2</sub>O<sub>3</sub>-le, similar to the pretreatment effect of Au/Al<sub>2</sub>O<sub>3</sub>-DP [10]. The similar pretreatment effect suggests that the Au/Al<sub>2</sub>O<sub>3</sub>-le catalyst may assume a similar Au morphology as that prepared from a DP method. Using NaOH<sub>(aq)</sub> instead of NH<sub>3(aq)</sub> achieved similar high activity. [24]

This kind of base-treatment was reported effective to activate Au catalysts prepared by a wet impregnation method [25,26] and Au catalysts prepared by a DP method but at lower pH [27]. The incipient wetness impregnation method is not examined in these studies. Bowker and coworkers [8,9] reported a DIM (double impregnation) method to prepare active Au/TiO<sub>2</sub> for CO oxidation. The DIM method uses incipient wetness impregnation, but half of the pore volume was filled with Na<sub>2</sub>CO<sub>3(aq)</sub> solution; furthermore, the freshly prepared catalyst is washed several times with Na<sub>2</sub>CO<sub>3(aq)</sub> solution and water. The DIM method used Na<sub>2</sub>CO<sub>3(aq)</sub> solution as a media to remove residual Cl. [8,9] It was proposed [27] that a base treatment to DP catalysts prepared at lower pH can change adsorbed Au morphology probably via 'rapid equilibrium', in which Cl-removal is indicated. We analyzed the filtrate from Au/Al<sub>2</sub>O<sub>3</sub>-le preparation and found no Au but a significant amount of Cl (ca. 80% of Cl in precursor) [24]. A significant Cl removal is again attributable for the activation via this base treatment. Although the replaced Cl may be from ligand-exchange of the adsorbed Au moiety [27], we think it is more likely originated from Cl on support surface as discussed previously. This is supported by that this base treatment also enhanced the CO oxidation activity of the reduced but relatively inactive Au/Al<sub>2</sub>O<sub>3</sub>-IMP (HTR), as shown in Fig. 6.

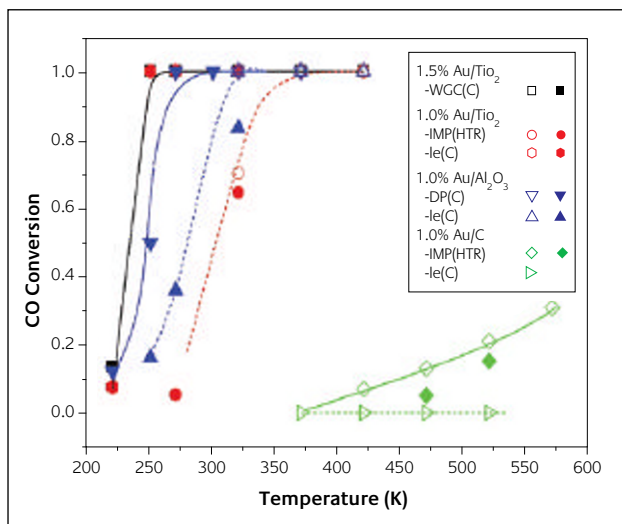
Table 3 shows the equilibrated pH of all these base-treated Au/Al<sub>2</sub>O<sub>3</sub>-IMP catalysts. Results indicate that the only active catalyst, i.e., Au/Al<sub>2</sub>O<sub>3</sub>-le, is the one that is not acidic. This suggests again the surface acidity effect. TEM images in Fig. 7 indicate that both Au/Al<sub>2</sub>O<sub>3</sub>-la and Au/Al<sub>2</sub>O<sub>3</sub>-le have Au particles around 1-2 nm size; Au particles larger than 5 nm were very few. This indicates both Au/Al<sub>2</sub>O<sub>3</sub>-la and Au/Al<sub>2</sub>O<sub>3</sub>-le have a higher Au dispersion than the Au/Al<sub>2</sub>O<sub>3</sub>-IMP catalysts [24]. However, Au/Al<sub>2</sub>O<sub>3</sub>-le showed an enhanced activity but



**Figure 4**

CO oxidation activity over 1% Au/Al<sub>2</sub>O<sub>3</sub>-IMP after different base-treatments (a) as is and (b) after a HTR pretreatment. Reaction conditions: 1% CO, 10% O<sub>2</sub>, balanced He, space velocity = 12 μmol CO/sec/g catalyst. Open symbols represent data measured at temperature-ascending sequence while filled symbols represent those at temperature-descending sequence. Please refer to Table 1 for description about base treatment procedures



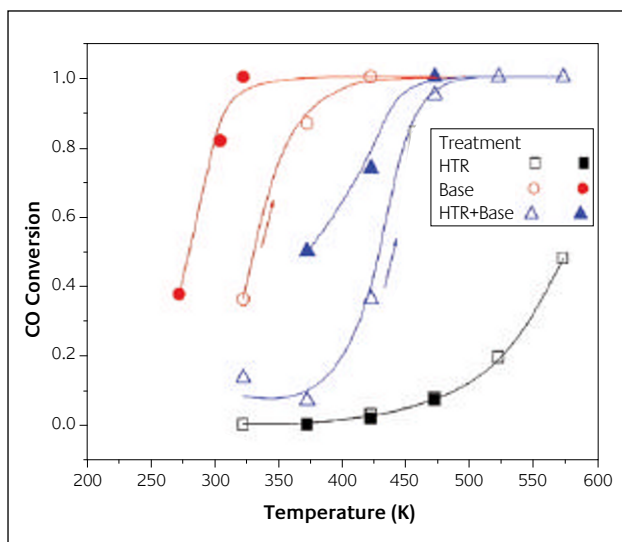


**Figure 5**

CO oxidation activity over Au/Al<sub>2</sub>O<sub>3</sub>-IMP, Au/TiO<sub>2</sub>-IMP, and Au/C-IMP catalysts after either base-treatment or high-temperature H<sub>2</sub> treatment. Reaction conditions: 1 % CO, 10 % O<sub>2</sub>, balanced He, space velocity = 12 μmol CO/sec/g catalyst (for Au/TiO<sub>2</sub> and for Au/Al<sub>2</sub>O<sub>3</sub>) or 30 μmol CO/sec/g catalyst (for Au/C). Open symbols represent data measured during temperature-ascending sequence while filled symbols represent those during temperature-descending sequence

Au/Al<sub>2</sub>O<sub>3</sub>-Ia did not. The results suggest that both ways of base treatment suppressed the tendency of Au sintering but the surface acidity seems the key factor determining how active the base-treated Au/Al<sub>2</sub>O<sub>3</sub>-IMP is.

As a base treatment can effectively promote Au/Al<sub>2</sub>O<sub>3</sub>-IMP catalyst to achieve high CO oxidation activity, we tried this activation procedure to 1% Au/TiO<sub>2</sub>-IMP and 1% Au/C-IMP catalysts. The results are included in Figure 5. The Au/TiO<sub>2</sub>-IMP can be effectively activated by this base treatment to show



**Figure 6**

The activation of 1% Au/Al<sub>2</sub>O<sub>3</sub>-IMP for CO oxidation using (i) base-treatment, (ii) high-temperature H<sub>2</sub> treatment (HTR), and (iii) HTR followed by base-treatment. Reaction conditions: 1 % CO, 10 % O<sub>2</sub>, balanced He, space velocity = 12 μmol CO/sec/g catalyst. Open symbols represent data measured during temperature-ascending sequence while filled symbols represent those during temperature-descending sequence

a comparable activity as the 1.5% Au/TiO<sub>2</sub>-WGC reference catalyst. Titration of the filtrate from the preparation of Au/TiO<sub>2</sub>-Ie indicated that almost 100% of Cl in precursor was removed by such a base treatment. [24] However, this base-treatment is not at all effective for Au/C-IMP catalyst. Reasons for such a difference are not known but it can still be classified as the support effect.

Figure 5 compares the activation by such a base-activation and that by high-temperature H<sub>2</sub> treatment to IMP catalysts. Both high-temperature H<sub>2</sub> treatment and base-treatment (followed by a calcination) can be effective in activating Au catalysts prepared by an incipient-wetness impregnation method. The base-treatment is more effective for Au/Al<sub>2</sub>O<sub>3</sub>-IMP and Au/TiO<sub>2</sub>-IMP, attributable to surface acidity effect and the absence of Au as large as 20-30 nm resulting from high-temperature H<sub>2</sub> treatment. Although Au/C can be activated by HTR its activity is still far lower than the activated Au/Al<sub>2</sub>O<sub>3</sub> and Au/TiO<sub>2</sub>. The Au/TiO<sub>2</sub>-IMP after base activation is more active than Au/Al<sub>2</sub>O<sub>3</sub>-IMP after base activation. We suspect that it is due to the remain of small amount of Cl in Au/Al<sub>2</sub>O<sub>3</sub>, which is indicated from our filtrate Cl analysis described above. It needs further study to confirm the correlation. However, results in this study indicate that the Au catalysts prepared by IMP method can be activated to have the same high CO oxidation activity as that prepared by DP method.

## 4 Conclusion

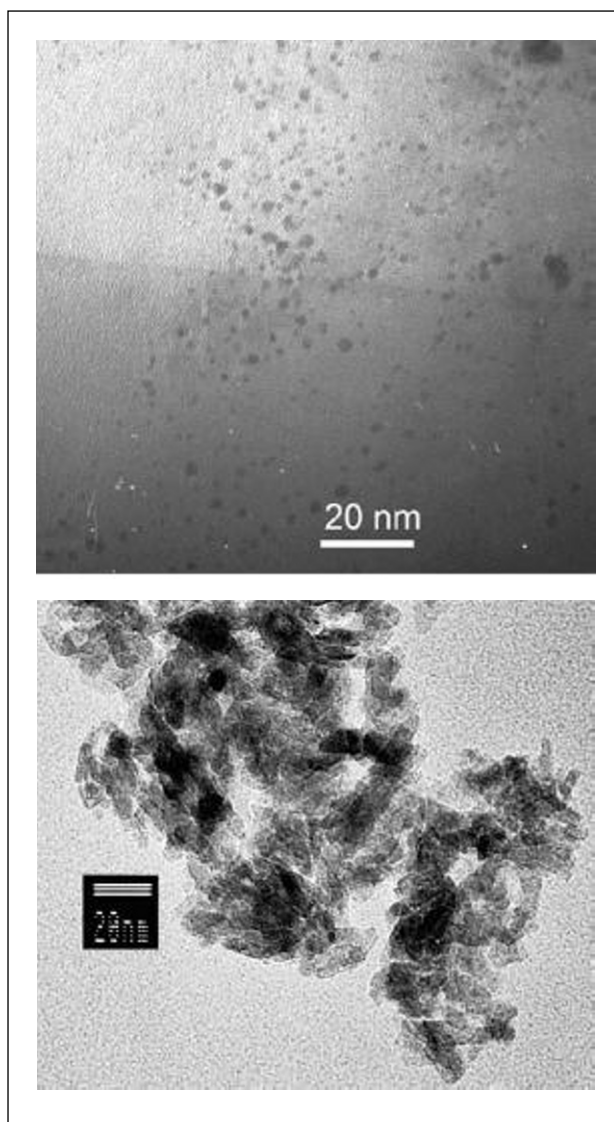
Supported Au catalysts prepared by an incipient wetness impregnation method can be activated for CO oxidation by either a high-temperature H<sub>2</sub> treatment or an aqueous base-treatment. The activated IMP catalysts have TOFs similar to that of Au catalysts prepared by a DP method. Small Au particles of ca. 2 nm size were present after both ways of activation. The latter method is considered more effective because the former method can cause the formation of large Au particles of around 25 nm during high-temperature treatment.

Support plays an important role in the activity development. A HTR (H<sub>2</sub>, 773 K) enhanced the CO oxidation activity of Au/C-IMP and Au/TiO<sub>2</sub>-IMP catalysts, but not Au/Al<sub>2</sub>O<sub>3</sub>-IMP catalyst. On the other hand, the base-treatment is ineffective for activating Au/C-IMP catalysts but it is good for both Au/TiO<sub>2</sub>-IMP and Au/Al<sub>2</sub>O<sub>3</sub>-IMP catalysts. The HTR-activated Au/C-IMP catalysts appear to be far less active for CO oxidation than activated Au/TiO<sub>2</sub>-IMP and Au/Al<sub>2</sub>O<sub>3</sub>-IMP catalysts.

The CO oxidation activity enhancement was observed when a reduced acidity was resulted by the activation pretreatment. The surface acidity effect is suggested as the main reason for the effectiveness of these activation treatments to the supported Au catalysts prepared by IMP. Residual Cl on oxide support may cause an increased acidity and consequently a lower activity. Thus, effectiveness of

**Figure 7**

TEM image of (a) 1% Au/Al<sub>2</sub>O<sub>3</sub>-Ia and (b) 1% Au/Al<sub>2</sub>O<sub>3</sub>-Ie catalysts. The 1% Au/Al<sub>2</sub>O<sub>3</sub>-Ia catalyst is prepared by sequential IMP of AuCl<sub>3(aq)</sub> and NH<sub>3(aq)</sub>. The 1% Au/Al<sub>2</sub>O<sub>3</sub>-Ie catalyst is obtained by treating a fresh Au/Al<sub>2</sub>O<sub>3</sub>-IMP with excess NH<sub>3(aq)</sub>. Please refer to Table 1 for description for catalyst preparation and pretreatment



**Table 3**

Effect of Base treatment procedure on the equilibrated pH of catalyst suspension<sup>1</sup>

Catalyst	Fresh	After HTR
1% Au/Al <sub>2</sub> O <sub>3</sub> -IMP	4.2	5.3
1% Au/Al <sub>2</sub> O <sub>3</sub> -Ia	4.2	4.7
1% Au/Al <sub>2</sub> O <sub>3</sub> -Ib	N.A. <sup>2</sup>	4.3
1% Au/Al <sub>2</sub> O <sub>3</sub> -Ic	5.0	5.0
1% Au/Al <sub>2</sub> O <sub>3</sub> -Id	N.A. <sup>2</sup>	4.8
1% Au/Al <sub>2</sub> O <sub>3</sub> -Ie	7.8	7.3

<sup>1</sup> The equilibrated pH was measured by dispersing 0.1 g catalyst in 10 ml DI water at room temperature. All samples are the spent catalysts after CO oxidation studies.

<sup>2</sup> Not analyzed.

different activation treatment seems attributable to the extent of Cl-removal.

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