Catalysis Letters Vol. 108, Nos. 3–4, May 2006 (© 2006)
DOI: 10.1007/s10562-006-0048-4

Activation of a Au/TiO_2 catalyst by loading a large amount of Fe–Oxide: Oxidation of CO enhanced by H_2 and H_2O

Masashi Shou,[a] Hiroyuki Takekawa,[a] Dong-Ying Ju,[a] Tokio Hagiwara,[a] Da-ling Lu,[b] and Ken-ichi Tanaka[a,*]

[a] *Advanced Scientific Research Laboratory, Saitama Institute of Technology, 1690 Fusaiji, Okabe, Saitama, Japan*
[b] *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

Received 9 January 2006; accepted 15 February 2006

Catalytic activity of a 1 wt% Au/TiO_2 catalyst is markedly improved by loading a large amount of FeO_x, on which the oxidation of CO in excess H_2 is selectively promoted at temperature lower than 60 °C. Oxidation of CO with O_2 on the $FeO_x/Au/TiO_2$ catalyst is markedly enhanced by H_2, and H_2O moisture also enhances the oxidation of CO but its effect is not so large as the promotion by H_2. We deduced that activation of Au/TiO_2 catalyst by loading FeO_x is not caused by the size effect of Au particles but a new reaction path via hydroxyl carbonyl intermediate is responsible for the superior activity of the $FeO_x/Au/TiO_2$ catalyst.

KEY WORDS: activation of Au/TiO_2 by loading FeO_x; oxidation of CO; enhancement by H_2; enhancement by H_2O; selective oxidation of CO in H_2.

1. Introduction

Although the fuel cells for practical use becomes a prime subject, large power fuel cells are still under the development. The proton exchange type hydrogen fuel cell is a most promising fuel cell for stationary and mobile systems. Therefore, it is a requirement to remove CO contaminant in H_2 fuel with minimum loss of H_2. A supported Ru catalyst has been developed as a selective oxidation catalyst of CO in H_2, but the oxidation reaction is usually performed with excess O_2 of $O_2/CO = 1.5$, so that the loss of H_2 becomes larger and larger as increasing the CO content in hydrogen. Therefore, it is desired to develop the catalyst on which the oxidation of CO in excess H_2 takes place selectively with O_2 of $O_2/CO = 0.5$. We developed a highly active and highly selective new catalyst [1], which was prepared by loading a large amount of Fe–oxide on 1 wt% Pt supported on TiO_2, Al_2O_3, and CeO_2. A feature of a Pt/TiO_2 catalyst loaded with 100 wt% FeO_x was shown by the DRIFT (Diffuse Reflectance IR-Fourier Transform) IR spectra, that is, linearly bonded CO is predominant on the Pt/TiO_2 catalyst but bridged CO on Pt–Fe site is a main adsorption on the FeO_x loaded Pt/TiO_2 [2]. This result is essentially different from the result reported on a 5% Pt/Al_2O_3 with a small amount of Fe–Oxide by Korotkikh and Parrauto [3,4]. It was proved that the bridge bonded CO reacts far faster than linearly coordinated CO with respect to O_2 on the $FeO_x/Pt/TiO_2$ catalyst, which is one important role of FeO_x which improves the activity of Pt catalysts [2]. More essential role of the FeO_x is to promote the oxidation of CO by H_2 on the $FeO_x/Pt/TiO_2$ catalyst, which is the mechanism for highly selective oxidation of CO in excess H_2 on the $FeO_x/Pt/TiO_2$ catalyst [5].

Considering the intrinsic activity of the catalyst, the activity will be improved by either enhancing the rate determining step or opening a new reaction path. We supposed that a new reaction path involving H_2O is responsible for the improvement of the oxidation of CO by H_2 on the Pt/TiO_2 loaded with FeO_x [5].

We found similar enhancement effect of H_2 and H_2O on the Au/TiO_2 catalyst loaded with a large amount of FeO_x. It has been accepted that activity of the oxide supported Au catalyst seriously depends on the size of Au particles as proposed by Haruta *et al.* [4], and this curious phenomenon has been confirmed by many investigators by using the TEM (transmission electron microscopy) [6–10], the STM (scanning tunneling microscopy) [11], and the Mossbauer spectrum of ^{197}Au [12]. On the other hand, Chen *et al.* [13] showed that the array of Au atoms in (1×3) structure with two atomic layers formed on a TiO_2 monolayer gives a specific high activity for the oxidation of CO, which perhaps contradicts the particle size dependent activity. On the other hand, Fu *et al.* [14] claimed that nano-size metallic Au particles on Au/CeO_2–La do not promote the water–gas shift reaction but non metallic Au ions contribute to the catalysis, and they claimed a similar phenomenon for Pt/CeO_2–La.

---

*To whom correspondence should be addressed.
E-mail: ktanaka@sit.ac.jp

As discussed in this paper, unusual activity of the FeO_x loaded Au/TiO_2 catalyst may not be explained by the size of Au particles or the array of Au atoms, but the kinetic enhancement via a new reaction path on the specific Au site, which is so far ignored, is perhaps responsible for extraordinary activity of the $FeO_x/Au/TiO_2$ catalyst.

2. Experimental

About 1 wt% Au/TiO_2 was prepared by immersing anatase TiO_2 powder in a AuCl solution instead of $HAuCl_4$. The impregnated $AuCl/TiO_2$ was dried for 3 h at 140 °C, and then calcined in air at 400 °C for 2 h. The TiO_2 used in this paper was the same TiO_2 (Waco Pure Chem. Co) used for the $FeO_x/Pt/TiO_2$ catalyst in our previous paper. Haruta [7] suggested that pH of the solution of $HAuCl_4$ should be controlled to be higher than 6 to prepare Au particles smaller than 4 nm. We did not control the pH value of the AuCl solution in preparation of 1 wt% Au/TiO_2 catalyst. In fact, we found a lot of large Au particles in the TEM image as shown in figure 1. The result suggests that few small Au particles are formed so that this Au/TiO_2 catalyst has poor activity as shown in figure 2. The calcinated 1 wt% Au/TiO_2 catalyst was suspended in a solution of $Fe(NO_3)_3$ containing about equal weight of Fe^{3+} ion to TiO_2. All Fe^{3+} ion was loaded on the Au/TiO_2 by evaporation of water, and then the catalyst was dried at 120 °C and calcined in air at 400 °C for 2 h. As the weight % depends on the form of FeO_x, 150% in the form of Fe_2O_3 but 160% in the form of Fe_3O_4, so we described by the weight % of Fe atom as 100% $FeO_x/Au/TiO_2$. As shown in figure 2, activity for the oxidation of CO in H_2 is markedly improved by loading a large amount of Fe–oxide on the 1 wt% Au/TiO_2 catalyst. It is worthy of note that a stable activity for the oxidation of CO in H_2 can be attained by pre-heating in O_2 at 100 °C for 30 min on either Au/TiO_2 or $FeO_x/Au/TiO_2$, but the activity is suppressed by heating in H_2 at 200 °C for 60 min as shown in figure 3. Therefore, the $FeO_x/Au/TiO_2$ catalyst was pre-treated in O_2 at 100 °C for 30 min in advance of the reaction. It is difficult to get stable activity at 40 °C because of the effect of H_2O, but a steady activity is attainable at higher than 60 °C. Reactant gas was composed of CO (3 mL/min), O_2 (1.5 mL/min) and H_2 (20 mL/min), where a 5% CO containing N_2 was used by flowing 60 mL/min. The total flow rate was adjusted to be 100 mL/min by adding N_2. Reaction was performed by a fixed bed glass tube flow reactor (14 mm of diameter) mounting 1.5 g

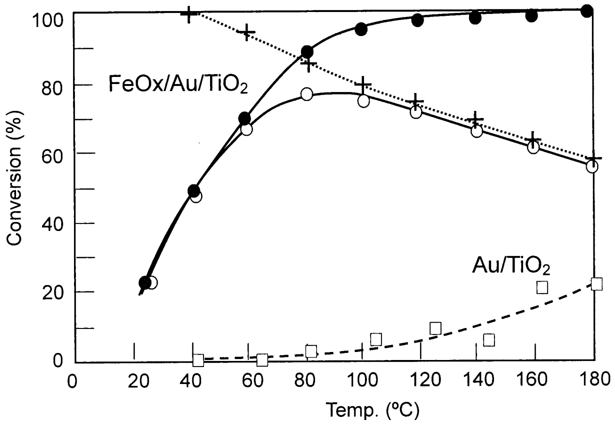


Figure 2. Conversion of CO and O_2 ($CO:O_2:H_2$ = 3:1.5:20) on a 100 wt.% $FeO_x/Au/TiO_2$ and 1 wt% Au/TiO_2. CO conversion (○), O_2 conversion (●), and selectivity (+) on the $FeO_x/Au/TiO_2$, and CO conversion (□) on a 1 wt% Au/TiO_2.

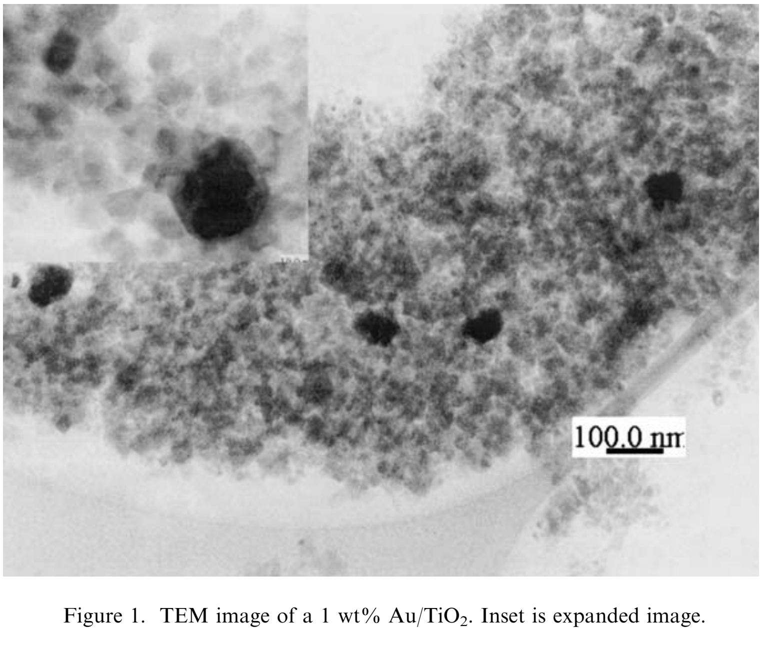


Figure 1. TEM image of a 1 wt% Au/TiO_2. Inset is expanded image.

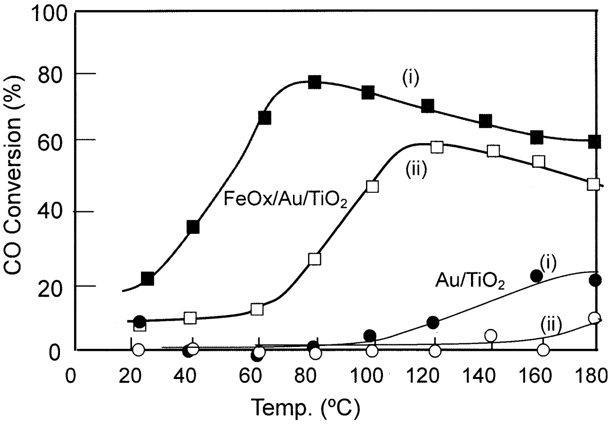


Figure 3. Catalytic activity of 1 wt%Au/TiO_2 and 100 wt% FeO_x/Au/TiO_2 improved by pretreatment. (i) Treated with O_2 at 100 °C for 30 min, and (ii) heated in H_2 at 200 °C for 1 h after the treatment with O_2. CO conversion on 100 wt% FeO_x/Au/TiO_2 (■) (□), and on Au/TiO_2, (●) and (○).

catalyst. To attain a steady state activity, the reactant gas was flowed for more than 30 min at each reaction temperature. Effect of H_2 on the oxidation of CO was examined by adding H_2 (20 mL/min) to a steady reaction of CO (3 mL/min) + O_2 (1.5 mL/min) + N_2, where the N_2 flow rate was adjusted to be 100 mL/min in total.

Effect of H_2O moisture on the oxidation of CO was observed by changing dry N_2 to N_2 containing H_2O moisture, that is, N_2 flow was bubbled through water at room temperature (estimated about 3% of H_2O of moisture). Analysis of the gas was performed by on-line gas chromatography.

Fraction of reacted O_2 with CO and H_2 is given $X_{O}2 = \Delta\mathbf{O_2}/\ \mathbf{a_0}$, and the fraction of oxidized CO is given by $X_{CO} = \Delta\mathbf{CO}/\mathbf{b_0}$, where $\mathbf{a_0}$ and $\mathbf{b_0}$ are the initial composition of O_2 and CO of the reactant gas (CO + H_2 + O_2) and Δ**CO** and $\Delta\mathbf{O_2}$ are the reacted CO and O_2. Selectivity (**S**) is given by the fraction of reacted CO to reacted O_2, that is, $\mathbf{S} = 1/2(\Delta\mathbf{CO}/\Delta\mathbf{O_2}) = \mathbf{1/2}(\mathbf{b_0}X_{CO}/\mathbf{a_0}X_{O}2)$. Therefore, $\mathbf{S} = X_{CO}/X_{O2}$ for the reaction of a stoichiometric composition of CO and O_2 ($\mathbf{a_o}/\mathbf{b_o} = 1/2$). In our flow system, the ratio of $\mathbf{a_o}/\mathbf{b_o}$ is difficult to adjust exactly in 1/2, which means the selectivity obtained in this experiment is not so accurate value but it is enough for our discussion.

3. Results

Since Haruta *et al.* [6] showed that catalytic activity of oxide supported Au particles depends on the particle size, it has been confirmed that the Au particles smaller than 4 nm have extremely activity for the oxidation of CO. Haruta recommended the preparation of active Au catalyst in alkaline solution, but the ! wt% Au/TiO_2 catalyst used in this paper was prepared by immersing TiO_2 in a AuCl solution without pH adjustment. Therefore, the 1 wt% Au/TiO_2 used in this paper had rather low activity as show in figure 2. By loading a large amount of FeO_x (100 wt% in Fe atom to TiO_2) on this poorly active Au/TiO_2 catalyst, the activity is extremely improved, on which the conversion of O_2 and CO ($CO/O_2 = 2/1$) at 60 °C in the presence of excess H_2 is elevated to nearly 100 and 80%, respectively. We confirmed that FeO_x has poor activity for this reaction which gives less than 20% conversion of O_2 at 170 °C. This phenomenon is very similar to the Pt/TiO_2 catalyst enhanced by loading FeO_x. As discussed in a previous paper [5], enhancement effect of H_2 and/or H_2O on the oxidation of CO is responsible for the unexpected activity of the FeO_x/Pt/TiO_2 catalyst, because no such enhancement was observed on the Pt/TiO_2 catalyst. Considering the promoting effect of H_2 and H_2O on the oxidation of CO observed on the FeO_x/Pt/TiO_2 catalyst, we expect similar promoting effect of H_2 and H_2O on the FeO_x/Au/TiO_2 catalyst.

As shown in figure 4 (a), when H_2 (20 mL/min) was added to a flow of CO (3.0 mL/min) + O_2 (1.5 mL/min) + N_2 (95.5 mL/min) by lowering the N_2 to 75.5 mL/min at 60 °C, a steady conversion of 20% was enhanced to about 60%, which is almost equal to a steady conversion of CO in the presence of H_2 at 60 °C in figure 3. This improvement by H_2 is very similar to that observed on the FeO_x/Pt/TiO_2 catalyst [3]. When the H_2 flow was stopped, the conversion of CO was down to around 40% as shown in figure 4(b). It should be pointed out that 40% is higher than the initial conversion of 20% attained by a flow of CO + O_2. We presumed that the conversion higher than 20% is due to the effect of H_2O remained after the stop of H_2 flow. To confirm the effect of H_2O on the oxidation of CO, after a steady oxidation of CO was attained in the presence of H_2 at 60 °C, H_2O moisture was added to N_2 flow. As shown in figure 5, a steady conversion of 60% was suppressed to ca. 50% by adding H_2O, and the conversion was down to about 42% by stopping the H_2 flow. We could say that the conversion of 42% attained in the presence of H_2O moisture is undoubtedly higher than the conversion of 30% attained in the presence of neither H_2O nor H_2 (20% in figure 4(a) was given by a catalyst of different version). To know the effect of H_2O on the oxidation of CO, H_2O moisture was introduced to a flow of CO + O_2 + N_2, and a steady conversion of about 40% was attained at 60 °C as shown in figure 6. A notable fact is that this steady CO conversion attained in the presence of H_2O moisture takes little influence of H_2, and the conversion is in good agreement with 40–43% attained by adding H_2O in figure 5. Accordingly, we could say that the improvement of the Au/TiO_2 catalyst by FeO_x is very similar to that of the FeO_x/Pt/TiO_2 catalyst although the promoting effect of H_2 and H_2O on the FeO_x/Pt/TiO_2 catalyst is more pronounced.

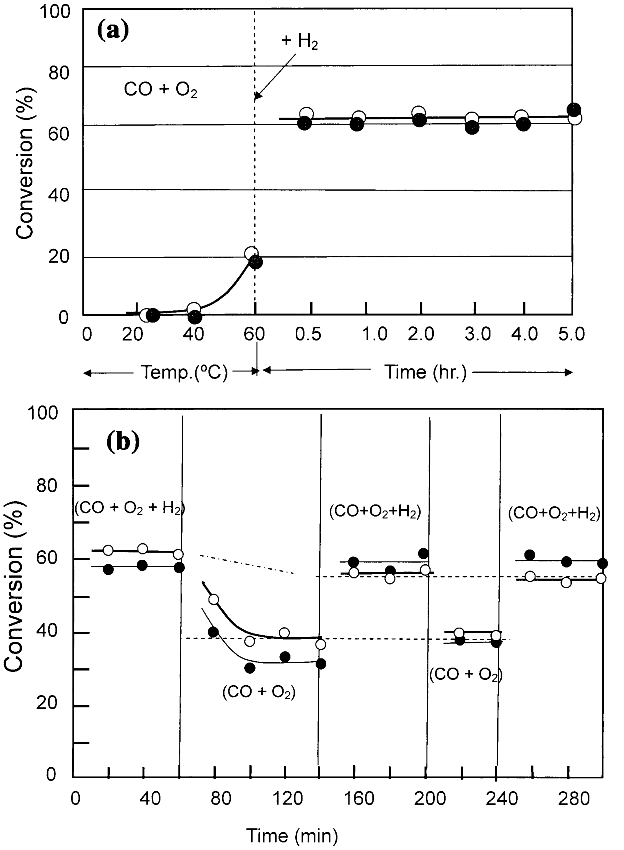


Figure 4. Enhancement of the oxidation of CO by H_2. (a) H_2 (20 mL/min) was added to a flow of CO (3.0 mL/min) + O_2 (1.5 mL/min) on the FeO_x//Au/TiO_2 catalyst at 60 °C. The total flow was adjusted to be 100 mL/min by N_2. (b) Reproducible enhancement of H_2 for the oxidation reaction of CO at 60 °C. Conversion of CO (○) and O_2 (●).

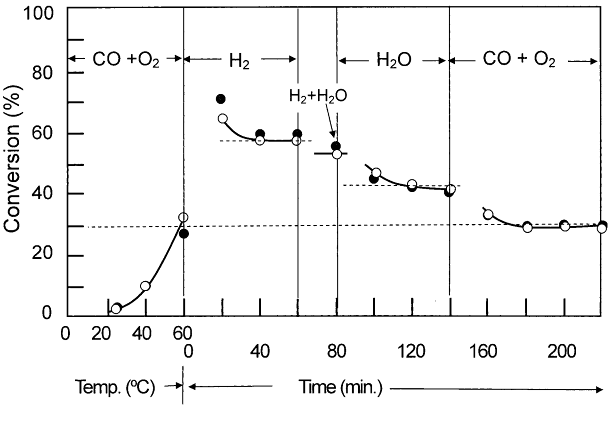


Figure 5. Enhancement of the oxidation of CO by H_2 and H_2O at 60 °C. H_2O moisture was added at 60 min in the presence of H_2.and the conversion was measured at 80 min, and then the H_2 flow was stopped to measure the effect of H_2O. When H_2O moisture was removed at 140 min, the conversion of CO (○) was down to the initial value of the CO + O_2 reaction.

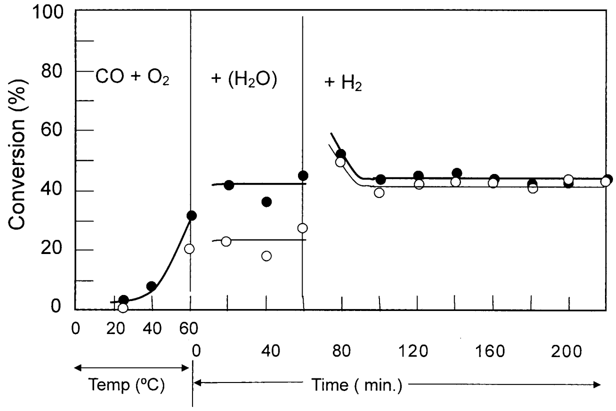


Figure 6. Effect of H_2O moisture on the conversion of CO (○) and O_2 (●) at 60 °C. When a steady conversion was attained at 60 °C, H_2O moisture was added to N_2, and H_2O moisture was removed from N_2 at 60 min and H_2 was added.

4. Discussion

Catalytic oxidation of CO with O_2 on precious metal catalyst (Pt, Pd, Rh) has been explained by the reaction of adsorbed CO with adsorbed oxygen on the metal surface or with oxygen at the perimeter of the support. For example, selective oxidation of CO in H_2 has been explained by the competitive adsorption of CO, H_2, and O_2 on the metals. In fact, the oxidation reaction of CO on Rh catalysts [15–17] takes an inverse order (−0.8) of CO pressure in a wide pressure range of CO, but the reaction on the Rh/CeO_2 catalyst takes the zero-th order in CO pressure. The 0^{th} order in CO pressure was explained by the reaction of adsorbed CO with lattice oxygen at the perimeter of metallic Rh particles with CeO_2. The reaction of CO with lattice oxygen at the perimeter, the activity will depend on the mobility of lattice oxygen, which has been proved on $Rh/Ce_{0.5}Zr_{0.5}O_2$ and Pt–Rh supported on CeO_2 or CeO_2–ZrO_2 [18,19]. According to the reaction mechanisms so far proposed on the precious metal catalysts, similar mechanism is tacitly presumed on the supported Au catalyst, that is, the slow rate determining step is the reaction of adsorbed CO with adsorbed oxygen atom although Haruta [7] claimed important contribution of the perimeter of Au particles with oxides. However, the activity of Au catalyst improved by particles size or array of Au atoms, and the role of Au ion shown by Fu *et al.* [14] may not be convinced by these explanations.

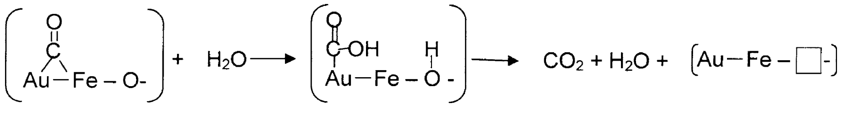
So far no new mechanism has been proposed for the oxidation of CO even if H_2 and/or H_2O would enhance the reaction. H_2O molecule, however, plays some times essential role in catalysis not only in the oxidation reaction but also in the reduction reaction. The reduction of WO_3 by H_2 is a good example. Firstly, it was reported that yellow WO_3 did not change to blue in H_2 even at 150 °C but the color changed to blue within 1 min when Pt/Al_2O_3 catalyst was mechanically mixed [20]. However, later it was claimed that the reduction of WO_3 is very slow even in the presence of Pt/Al_2O_3 catalyst when the catalyst is dried, that is, the yellow WO_3 is readily changed to blue in the presence of H_2 if H_2O

or alcohols is adsorbed on the surface [21]. The role of H_2O was explained by promotion of the ionization of H into H^+ and electron on the Pt surface, which is an essential process in hydrogen fuel cell. The hydrated H^+ rapidly diffuses over the surface to form H_xWO_3, where H_2O molecules is indispensable to transport intermediate species. Similar role of H_2O molecule may take place on the $FeO_x/Pt/TiO_2$, and the rust color of Fe_2O_3 changes to dark brown of Fe_3O_4 during the oxidation of CO in the presence of H_2, but the reduction of FeO_x to Fe_3O_4 is independent of the activity of the $FeO_x/Pt/TiO_2$ catalyst. We could say that the direct contribution of H_2O to the oxidation of CO is responsible for the superior activity of the Pt/TiO_2 loaded with FeO_x, where a new reaction path is opened. The contribution of H_2O is similar to the Wacher reaction of $C_2H_4 + 1/2\ O_2 \rightarrow CH_3CHO$, in which H_2O molecule does not appear but it is indispensable to form a key intermediate of $CH_2OH–CH_2–PdCl$. A large isotope effect ($k_H/k_D = 4.0$) is known for the formation of aceto-aldehyde in D_2O, and an isotope effect of $k_H/k_D = 1.4$ was obtained for the oxidation of CO promoted by H_2 and D_2 as well as the reaction promoted by H_2O and D_2O on the $FeO_x/Pt/TiO_2$ at 60 °C [22].

Taking these results into account, the effect of H_2 on the oxidation of CO was confirmed on the $FeO_x/Au/TiO_2$ catalyst as shown in figure 4(a) and (b). When the H_2 flow was stopped at 60 min in figure 4(b), the CO conversion was down to ca. 40% attained, but it was undoubtedly higher than 20% in figure 4(a). This may be the promoting effect of H_2O remained on the catalyst. However, a steady conversion in the presence of H_2 at 60 °C was slightly lowered by addition of H_2O moisture at 60 min, and the conversion of CO was down to about 50% at 80 min as shown in figure 5. When H_2 flow was stopped, the CO conversion was down to ca. 40%, which is a steady CO conversion in the presence of H_2O moisture. When H_2O moisture was removed from the N_2 flow, CO conversion was gradually lowered from 40 to 30% as shown in figure 5. Accordingly, we can conclude that the oxidation of CO over the $FeO_x/Au/TiO_2$ is promoted by H_2O moisture, but the promotion effect of H_2O is not so pronounced as that on the $FeO_x/Pt/TO_2$ catalyst. The effect of H_2O moisture on the oxidation of CO with O_2 in absence of H_2 is shown in figure 6. An interesting fact is that enhancement of the oxidation of CO adding H_2O moisture was little, and the reaction after the stop of H_2O moisture was took little effect of H_2.

So far the enhancement effect of H_2O and/or H_2 on the oxidation of CO has been reported on Au catalysts [10–13]. Date *et al.* [23] explained the effect of H_2O moisture by the electronic property of the support oxides, either insulator or semiconductor, but this explanation may have no scientific conviction. On the other hand, Daniells *et al.* [24] proposed a reaction of adsorbed CO with OH coordinated to Au ion on the Au/Fe_2O_3 catalyst, and explained a significant effect of H_2O by the formation of hydroxyl–carbonyl intermediate. Taking these facts into account, the catalytic activity of Au catalyst is not so simple as is explained by the particle size or the array of Au atoms, and we could say that the reaction mechanism via a specific intermediate is undoubtedly important. In this respect, the result shown by Fu *et al.* [14], no activity change of Au/CeO_2 catalyst by removing Au particles, is quite interesting phenomenon.

As shown in this paper, the inactive Au/TiO_2 catalyst is improved by loading a large amount of FeO_x. This improvement can not be explained by such the structure effects as the size of Au particles or the array of Au atoms. As discussed above, the promoting effect of H_2 and/or H_2O on the oxidation of CO is responsible for the superior activity of the $FeO_x/Au/TiO_2$. Costello *et al.* [23] reported the isotope effect of $H_2/D_2 = 1.4$ on the oxidation of CO enhanced by hydrogen on the Au/Al_2O_3 catalyst, but little isotope effect of H_2O/D_2O was observed on the oxidation of CO. If the reaction would proceed between the adsorbed CO and O over the catalyst, it is hard to explain the isotope effect of H_2 and D_2 by the reaction mechanism. Therefore, the isotope effect was explained by the population of active sites, that is, the population depends on the dynamic balance of poisoning and recovering of the carbonated ($Au–CO_3$) sites by H_2 and D_2. We wish to claim that a large isotope effect of H_2O/D_2O = 1.4 was on the oxidation CO on the $FeO_x/Pt/TiO_2$ at 60 °C [22], which supports our proposed reaction mechanism via hydroxyl–carbonyl intermediate. If the similar mechanism would be applicable to the oxidation of CO on the $FeO_x/Au/TiO_2$ catalyst enhanced by H_2 and H_2O, the catalysis is described as follows.



Scheme 1

In conformity with a new reaction route proposed here, the lattice oxygen or coordinated OH to Fe contributes to the oxidation of hydroxyl carbonyl intermediate. We could speculate that the pretreatment with H_2 may reduce the lattice oxygen forming OH.

So far the activity of Au catalyst has been explained by either the structure or the electronic state of Au particles, and few attention has been paid to the reaction mechanism. However, the result observed in this paper suggests the importance of the new reaction path via a specific intermediate formed in the presence of H_2 and/or H_2O.

Acknowledgments

Authors appreciate professor Masaki Haruta of Tokyo Metropolitan University for his variable discussion, and K. Tanaka appreciate Mr. Mitsushi Umino of the president of Astech Co. for his long time back up of our research works. This work was supported by the High-Tech Research Center of Saitama Institute of Technology, and a Grant-in-Aid for Scientific Research [(C) 17550136] of the Ministry of Education and Technology of Japan.

References

[1] K. Tanaka, Y. Moro-oka, K. Ishigure, T. Yajima, Y. Okabe, Y. Kato, H. Hamano, S. Sekiya, H. Tanaka, Y. Matsumoto, H. Koinuma, H. He, C. Zhang and Q. Fehg, Catal. Lett. 92 (2004) 115.

[2] Xiaoyan Shi, Changbin Zhang, Masashi Shou, Hong He, Shinichi Sugihara, and Ken-ichi Tanaka, Catal. Lett. (in press).

[3] X. Liu, O. Korotkikh and R. Farrauto, Appl. Catal. A 226 (2002) 293.

[4] O. Korotkikh and R. Farrauto, Catal. Today 62 (2000) 249.

[5] Ken-ichi Tanaka, Masashi Shou, Hong He and Xiaoyan Shi, submitted to publication.

[6] M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, J. Catal. 115 (1989) 301.

[7] M. Haruta, Catal. Today 36 (1997) 153.

[8] G.C. Bond and D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319.

[9] R. Grisel, K.-J. Weststrate, A. Gluhoi and B.E. Nieuwenhuys, Gold Bull. 35/2 (2002) 39.

[10] R.J.H. Grisel, P.J. Kooyman and B.E. Nieuwenhuys, J.Catal. 191 (2000) 430; F. Boccuzzi, A. Chiorina, M. Manzoli, P. Lu, T. Akita, S. Ichikawa and M. Haruta, J. Catal. 202 (2001) 258.

[11] M. Valden, X. Lai and D.W. Goodman, Science. 281 (1898) 1647.

[12] A. Goossens, M.W.J. Craje, A.M. van der Kraan, A. Zwijnenburg, M. Makkee, J.A. Moulin, R.J.H. Grisel, B.E. Nieuwenhuys and L.J. de Jongh, Hyperfine Interact. 139/140 (2002) 59.

[13] M.S. Chen and D.W. Goodman, Science. 306 (2004) 252.

[14] Q. Fu, H Saltsburg and M Flytzani-Stephanopoulos, Science. 301 (2003) 935.

[15] T. Bunluesin, E.S. Putna and R.J. Gorte, Catal. Letters. 41 (1996) 1.

[16] T. Bunluesin, H. Condatos and R.J. Gorte, J. Catal. 157 (1995) 222.

[17] S. Hiraite, X. Wang, T. Luo, R.J. Gorte and J.P. Wagner, Appl. Catal. A 215 (2001) 271.

[18] G. Vlaic, P. Fornasiero, S. Geremia, J. Kaspar and M. Graziani, J. Catal. 168 (1997) 386.

[19] Y. Zhang, S. Anderson and M. Muhammed, Appl. Catal. B6 (1995) 325.

[20] S. Khoobiar, J. Phys. Chem. 68 (1964) 411.

[21] R.B. Levy and M. Boudart, J. Catal. 32 (1974) 364.

[22] Unpublished data.

[23] M. Date, M. Okumura, S. Tsubota and M. Haruta, Angew. Chem. Intern. Edition 43 (2004) 2129.

[24] S.T. Daniells, M. Makkee and J.A. Moulijn. 100 (2005) 39.

[25] C.K. Costello, J.H. Yang, H.Y. Law, Y. Wang, J.-N. Lin, L.D. Marks, M.C. Kung and H.H. Kung, Appl. Catal. A. Gen. 243 (2003) 15.