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Adsorption of CO on gold supported on TiO_2

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Abstract

The adsorption of CO on TiO_2 supported gold has been investigated both under a constant pressure static system and under a closed recirculation system with liquid nitrogen cooled trap. Au/TiO_2 with 3.3 wt% loading and 3.5 nm mean particle diameter of Au was prepared by deposition–precipitation. Adsorption of CO on Au/TiO_2 was 90% reversible and satisfied the Langmuir isotherm. The amount of CO_2 produced during CO adsorption agreed well with the amount of irreversible CO adsorption. TiO_2 powder produced only 1/185th the amount of CO_2 at 273 K compared to gold powder, even though the amount of CO adsorbed per unit surface area was similar to that of gold powder. The results indicate that a reaction between oxygen adsorbed on the surface of small gold particles with CO is one of the major reaction pathways in forming CO_2.

Keywords: CO adsorption; Gold catalyst; TiO_2 support; CO_2 production

1. Introduction

Gold has long been regarded in the literature, perhaps unfairly as being catalytically far less active than platinum group metals. Recently groups led by Haruta amongst others have, however, found that gold is very active for the low temperature oxidation of CO, if dispersed on metal oxides such as TiO_2 [1–7], α-Fe_2O_3 [1,8,9], Co_3O_4 [1,8,9], MnO_x [10,11] and ZrO_2 [12,13]. The reason for the enhancement of catalytic activity seen upon the addition of ultra-fine dispersions of gold to metal oxides is still not well understood and many questions remain concerning the site of the reaction and chemical nature of gold. In an attempt to clarify the mechanism of the catalytic oxidation of CO with O_2 over supported gold catalysts, we have initiated a study on the adsorption of CO on gold supported on TiO_2 [14]. This catalyst was chosen because the combination between Au and TiO_2 exhibits the highest known synergy [15]; with standard titanium dioxide showing no detectable activity at temperatures below 573 K [16] and the activity of gold powder for CO oxidation being two orders of magnitude smaller than that of Au/TiO_2 [15].

Some data has already been reported for CO adsorption on poorly dispersed gold on TiO_2, which was reduced prior to the adsorption [5,6,17,18]. As highly dispersed Au/TiO_2 catalyst shows higher activities after an oxidizing pretreatment [2], the catalyst was fully oxidized in advance of CO adsorption. In the present

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study, CO_2 produced during CO adsorption was also measured to obtain some insight into the mechanism of the catalytic oxidation of CO. Furthermore, ultra fine gold powder not supported on a TiO_2 carrier and TiO_2 powder not loading gold particles were examined for comparison.

2. Experimental

2.1. Preparation and characterization of catalysts

The Au/TiO_2 catalyst used in this study was prepared by the deposition–precipitation method [19]. The TiO_2 powder used was Japan reference catalyst JRC-TIO-4, a predominantly anatase system with specific surface area of 44 m^2/g (supplied from the Catalysis Society of Japan). After calcination in air at 673 K, the specific surface area of the catalyst obtained was measured at 45 m^2/g. The gold loading was determined by X-ray fluorescence to be 3.3 wt%. and the mean particle diameter of gold to be 3.5 ± 0.8 nm, from TEM.

TiO_2 powder with no gold loading was prepared by treating the JRC-TIO-4 in the same manner as that for Au/TiO_2, except that a HCl solution was used instead of $HAuCl_4$ solution. Fine gold powder not supported on TiO_2 was manufactured by evaporating ultra high purity gold metal ($> 99.99\%$) in inert gas (Vacuum Metallurgical Co., Ltd.). The specific surface area of the fine gold powder was determined to be 4.1 m^2/g.

2.2. Adsorption measurement

Absorption measurements were made using two different glass apparatus; The first was a constant pressure static system (dead volume 84 cc), which was also used for determining the BET specific surface area of the catalyst. The second was a closed recirculation system (dead volume 187 cc), which was used to measure the catalytic activity [20]. Both system could be evacuated to a pressure of 1.3×10^{-3} Pa by means of an oil diffusion pump.

Prior to CO adsorption, all three samples underwent an oxidizing pretreatment which comprised of first oxidizing under 1 atm. O_2 at 523 K for 10 h. After cooling to room temperature, the catalyst samples were then aged while still under O_2 for a further 2 h at the adsorption temperature; after which the line was evacuated for 30 min before introducing CO. Both oxygen and carbon monoxide were obtained commercially and were fractionally distilled at liquid nitrogen temperature for purification. When the closed recirculation apparatus was used for the measurement of the adsorption isotherm of CO_2 the trap in the circulation line was cooled with liquid nitrogen in order to condense any CO_2 produced during adsorption. After measuring the adsorption isotherm, CO in the circulation line was evacuated. The CO_2 in the trap could then be evaporated at room temperature and the amount determined volumetrically. Subsequently, He (circa 6.7 kPa) was introduced into the circulation line and the trap cooled again to liquid nitrogen temperature. While circulating He, the catalyst temperature was then raised from room temperature to 473 K at a rate of 10 K/min after which the system was maintained at the temperature for a further 30 min. The total amount of CO_2 desorbed thermally during heating, which relates to the amount of CO_2 irreversibly adsorbed on the surface of the catalyst, was then determined volumetrically.

3. Results

3.1. Characterization of Au/TiO_2

Fig. 1 shows the TEM photograph of Au/TiO_2 (×200.000 magnifications) taken after calcination at 673 K. Deposited gold particles which appear as small black spots in the TEM photograph are uniformly dispersed on the surface of TiO_2 and have almost uniform diam-

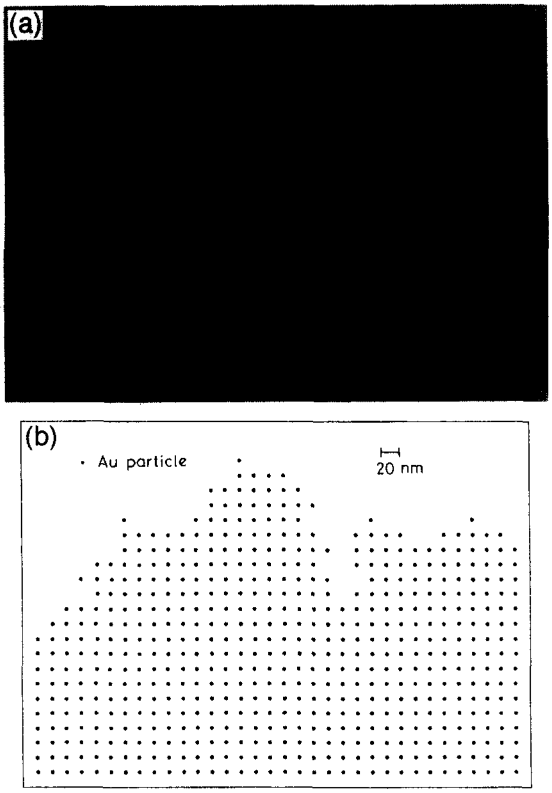

Fig. 1. TEM photograph of Au/TiO_2 (magnification 200000×) and the surface model of Au/TiO_2. The model was calculated based on the mean diameter of gold, viz. 3.5 nm, the loading of gold, viz. 3.3 wt%, and the BET specific surface area of Au/TiO_2, viz., 45 m^2/g. The calculated mean distance between two adjacent gold particles is 17 nm.

eter. A two dimensional model for Au/TiO_2 which can be drawn based on specific surface area, the loading and the mean particle size of gold is also presented in Fig. 1. The surface model expresses well the feature for gold particles dispersed on TiO_2 imaged in the TEM photograph.

3.2. Effect of temperature on the adsorption isotherm of CO on Au / TiO$_2$

After oxygen in the system was evacuated from 1 atmosphere pressure to an O_2 pressure between 2–3 Pa at a temperature of 273 K, a slow increase in the O_2 pressure at a rate of approximately 0.1 Pa/min was observed under the absence of evacuation. The pressure finally stabilized at 50 Pa. This increase in pressure we ascribe to the desorption of weakly adsorbed O_2 on the surface of Au/TiO_2. A continuous evacuation for 30 min could lower the pressure in the system down to 5.0×10^{-3} Pa.

Fig. 2 shows the adsorption isotherms of CO on Au/TiO_2 measured in the static system at 253, 263, 273 and 303 K. At all temperatures studied adsorption occurred instantaneously after the introduction of CO. The adsorption isotherms shift significantly with temperature. The volume of CO adsorbed shows a tendency of saturation with increasing CO pressure and that at 303 K passes through a break at a CO pressure near 15–20 kPa.

3.3. Reversibility of adsorption of CO on Au / TiO$_2$

By repeating twice at 273 K the adsorption isotherm for CO, the reversibility of CO adsorption on Au/TiO_2 was examined in the static system. Curve (a) in Fig. 3 shows the adsorption isotherm of CO measured soon after the oxidizing pretreatment. After measuring the isotherm, CO in the system was evacuated at 273 K to remove adsorbed CO from the catalyst surface.

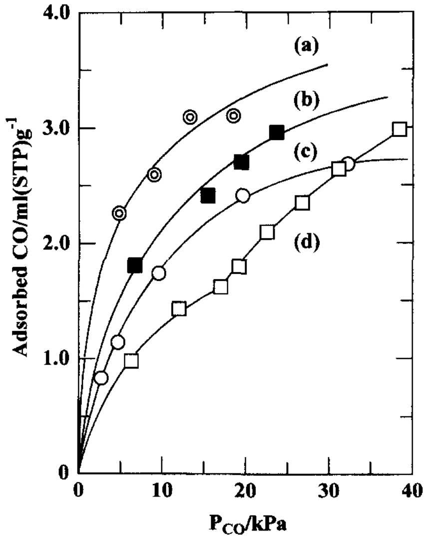

Fig. 2. Adsorption isotherms of CO on Au/TiO_2 measured in the static system: (a) 253 K; (b) 263 K; (c) 273 K; (d) 303 K.

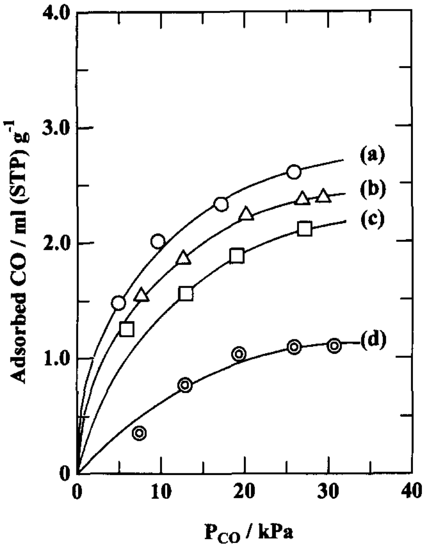

Fig. 3. The reversibility of adsorption isotherm of CO on Au/TiO_2 at 273 K in the static system. Curve(a); the 1st run measured after the oxidizing pretreatment, Curves (b) and (c); the 2nd run measured after evacuating for 2 h and 1 min, respectively, after 1st run, Curve (d); the 2nd run measured after reducing the CO pressure down to 1.3 kPa after 1st run.

The extent of evacuation was then varied in order to examine the reversibility of the adsorption of CO on Au/TiO_2. Curves (b) and (c) are the isotherms obtained on a 2nd run measured after evacuating the catalyst for 2 h and 1 min, respectively. Curve (d) was obtained by reintroducing CO after the CO pressure was decreased to 1.3 kPa.

Adsorption isotherms taken in the 1st run, i.e., after the oxidizing pretreatment were measured 3 times and were reproducible. Adsorption isotherm in the 2nd run, however, depends significantly upon the evacuation condition and approaches towards curve (a) with increasing evacuation time, however, even with prolonged evacuation time curve (a) could not be reproduced.

3.4. Adsorption of CO on Au/TiO_2, Au and TiO_2 and the simultaneous production of CO_2

Fig. 4 shows the adsorption isotherms of CO on Au/TiO_2, Au and TiO_2 as measured at 273 K in the closed recirculation system with use of a liquid nitrogen trap. In the diagram the adsorption isotherm of CO on Au/TiO_2 measured at 273 K in the static system without use of a liquid nitrogen trap is also presented to show the influence of CO_2 production on the adsorption isotherm. These two isotherms almost overlap with one another.

Table 1 summarizes the amount of CO_2 produced at 273 K during CO adsorption and that thermally desorbed from the catalyst surface following heat treatment in circulating He. The amount of CO_2 produced during CO adsorption on Au/TiO_2 (94 μl/g) and that thermally desorbed in circulating He (130 μl/g) amounts to 3.5% and 5.0% of the volume of CO adsorbed at the equilibrium CO pressure of 26.6 kPa (2.6 ml(STP)/g).

Prior to CO adsorption on TiO_2 powder, O_2 in the system was evacuated gradually at 273 K. When evacuation was stopped just after the O_2 pressure was lowered to 2–3 Pa, an increase in O_2 pressure was again observed as was previously seen in Au/TiO_2. Fig. 4 shows that TiO_2 adsorbs almost the same amount of CO as Au/TiO_2. However, the amount of CO_2 pro-

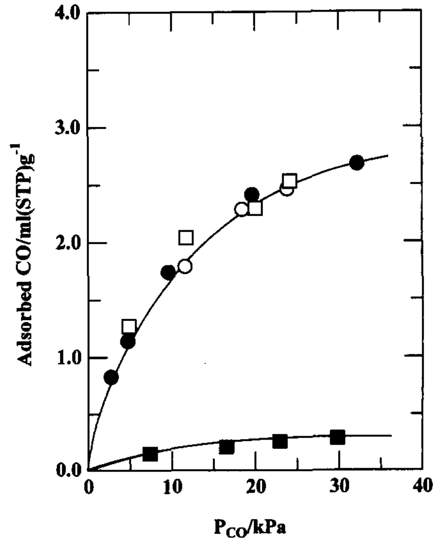

Fig. 4. Adsorption isotherms of CO on Au/TiO_2 (○), Au(■) and TiO_2 (□) at 273 K measured in the closed recirculation system with liquid nitrogen cooled trap. Adsorption isotherm of CO on Au/TiO_2 measured in the static system (●) is presented for comparison.

Table 1
The amount of CO_2 produced during CO adsorption on Au/TiO_2, Au, and TiO_2

	Desorbed at 273 K in circulating CO		Desorbed thermally in circulating He during the heat treatment up to 473 K	
	μl/g	μl/m^2	μl/g	μl/m^2
Au/TiO_2	94	2.1	130	3.0
Au	98	24	24	5.9
TiO_2	0.57	0.013	28	0.62

duced during CO adsorption (0.57 μl/g) is negligibly small compared to the volume of CO adsorbed on TiO_2 at the equilibrium CO pressure of 26.6 kPa (2.5 ml/g). The amount of CO_2 desorbed thermally during heating from TiO_2 surface (28 μl/g) is much larger than that produced at 273 K.

In the case of gold powder, no increase of O_2 pressure was, however, observed after evacuation was stopped under O_2 pressure below 1 Pa. The volume of CO adsorbed on Au (0.3 ml(STP)/g at 26.6 kPa) is very small compared to those on Au/TiO_2 and TiO_2 (Fig. 4). However, the amount of CO_2 produced at 273 K per unit surface area during CO adsorption (24 μl/m^2) is much larger than that produced on TiO_2 (0.013 μl/m^2).

4. Discussion

4.1. Surface model of Au / TiO_2

The number of Au atoms contained in one deposited gold particle and the number of Au atoms exposed at the surface of one gold particle were calculated on the assumption that all deposited gold particles are hemi-spherical shaped close-packed structures [1] and have the same diameter (3.5 nm) (see Table 2). Using these assumptions nearly 40% of all Au atoms exist on the surface. The mean distance between two adjacent gold particles and the coverage of TiO_2 surface by gold particles were calculated to be 17 nm and 3%, respectively.

4.2. Langmuir adsorption of CO on Au / TiO_2

Fig. 5 shows the Langmuir isotherm plots of the data obtained in Fig. 2. The experimental data give linear plots at all temperatures, indicating that CO is chemically adsorbed as a monolayer on Au/TiO_2 surface at these temperatures [21]. Although the plots at 303 K breaks at a CO pressure near 15–20 kPa, the four straight lines have almost the same slope in the low CO pressure region. Lin et al. measured CO adsorption on the Au/TiO_2 (2.0%) sample after reduction at low and high temperatures and reported that the plots satisfy well the Langmuir isotherm [6,17].

According to the Langmuir isotherm theory, the slope of the line created by plotting Pco/Vco versus Pco and the intercept give us the saturation volume of CO and the adsorption coefficient (the ratio of the rate constant of desorption

Table 2
Numbers and amounts relating to the model for Au/TiO_2

Number of Au atoms in a single Au particle	660
Number of surface Au atoms in a single Au particle	270
Number of Au particles on Au/TiO_2	1.5×10^{17}/g-cat
Number of surface Au atoms on Au/TiO_2	4.0×10^{19}/g-cat
Volume of CO adsorption calculated on the assumption of stoichiometry surface Au:CO = 1:1	1.5 ml (STP)/g-cat

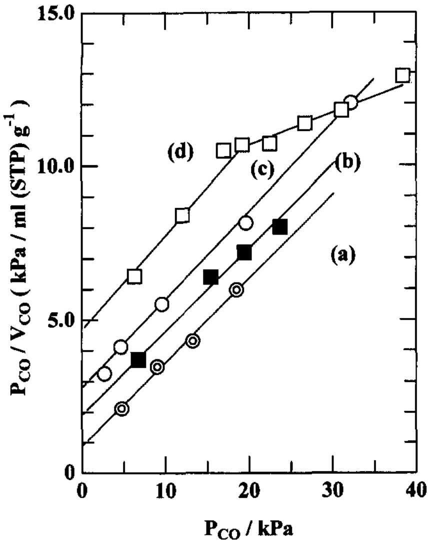

Fig. 5. Langmuir adsorption isotherm plots for the CO adsorption on Au/TiO$_2$ presented in Fig. 2: (a) 253 K; (b) 263 K; (c) 273 K; (d) 303 K.

to that of adsorption). Table 3 summarizes the saturation volume of CO and the adsorption coefficient at 253, 263, 273 and 303 K. The adsorption coefficient increases rapidly with temperature, reflecting the rapid decrease in the amount of CO adsorbed on Au/TiO$_2$ with an increase in temperature. The saturation volume of CO is almost independent of the adsorption temperature. The volume of N$_2$ required for the complete monolayer coverage of the surface of Au/TiO$_2$ was calculated to be 10.3 ml(STP)/g from the BET plots for the physical adsorption of N$_2$ at liquid nitrogen temperature. The molecular cross sectional area of N$_2$ is 16.2 Å^2, while that of CO is 16.3 Å^2 [22]. If one assumes that CO covers the entire surface of Au/TiO$_2$ with monolayer thickness, the volume required is 10.2 ml(STP)/g. Since the saturation volume of CO on Au/TiO$_2$ is nearly 3.5 ml(STP)/g, as presented in Table 3, this means that about 1/3 of the surface area of Au/TiO$_2$ exists as active sites for CO adsorption.

Shastri et al. have reported that the uptake of CO on blank TiO$_2$ decreased with increasing temperature becoming negligible at 323 K, and that CO adsorption on Au/TiO$_2$ at 323 K was close to monolayer coverage on gold at a CO pressure of 0.93 kPa or higher with the stoichiometry of Au/CO equal to 1:1 [18]. In the present study, the total number of Au atoms exposed to the surface corresponds to 1.5 ml CO(STP)/g under the assumption of the stoichiometry of Au/CO = 1 (see Table 2) and the saturation volume of CO on Au/TiO$_2$ (3.5 ml(STP)/g is about 2.3 times larger than this. Therefore, chemical adsorption of CO should occur on both gold and the TiO$_2$ support, or only on the support surface. FT-IR measurements have clearly shown that CO adsorbs on Au as a linearly bonded carbonyl and on TiO$_2$ as a bidentate carbonate and others [1,23].

Fig. 4 shows that the adsorption isotherm of CO on TiO$_2$ powder closely coincides with that of CO on Au/TiO$_2$ catalyst. Langmuir isotherm plots for the adsorption of CO on TiO$_2$ follow a straight line and gave the same saturation volume of CO (3.5 ml(STP)/g). Cant et al. measured CO adsorption on Au/TiO$_2$ (2 wt%) under transient condition and stated that CO uptake occurs primary on the support, though adsorption is strongly dependent on the pretreatment condition [5]. Lin et al. also described that the TiO$_2$ support surface rather than the exposed gold surface, contributes primarily to the adsorption results for CO [6,17]. The rapid increase of the adsorption coefficient in Table 3 would reflect the decrease of the amount of CO adsorbed on TiO$_2$ support surface with increasing temperature [18].

Fig. 4 shows that gold powder also adsorbs CO, though the volume of CO adsorbed is

Table 3
The saturation volume of CO on Au/TiO$_2$ and the adsorption coefficient

Temperature (K)	Saturation volume (ml(STP)/g)	Adsorption coefficient (k_d / k_a)
253	3.66	22
263	3.66	51
273	3.38	64
303	3.44	127

smaller than those of Au/TiO_2 and TiO_2 by one order of magnitude. However, the specific surface area of gold powder is smaller than those of Au/TiO_2 and TiO_2 by a factor of about 10. The amount of CO adsorbed per unit surface area of gold powder should be almost equal to that of TiO_2 powder. As calculated from the surface model, nearly 97% of the surface of Au/TiO_2 is occupied by TiO_2. Therefore, a large portion of CO is chemically adsorbed on the support surface [5,6,17], while only a small portion is adsorbed on the surface of gold particle. This assumption is almost consistent with the Langmuir-type adsorption based on the homogeneity of the adsorption sites [21].

4.3. *Reversibility of the adsorption of CO on Au/TiO_2 and the simultaneous production of CO_2*

The volume of CO adsorbed in the 1st run was 2.6 ml(STP)/g at the CO pressure of 26.6 kPa and that in the 2nd run after 2 hr evacuation was 2.4 ml(STP)/g at the same equilibrium CO pressure (Fig. 3). Accordingly, more than 92% of CO adsorption in the 1st run can proceed reversibly, but the remainder may be irreversible. Lin et al. reported similar results on the adsorption of CO on 2% Au/TiO_2 after reduction at low and high temperatures, though the irreversible part is much smaller than that in the present fully preoxidized Au/TiO_2 [6,17].

The production of CO_2 at 273 K shown in Table 1 indicates a reaction occurs between CO and an oxygen of yet unknown chemistry on Au/TiO_2 during CO adsorption. On the other hand, the presence of CO_2 thermally desorbed during heat treatment of the catalyst in circulating He indicates that a small part of CO is adsorbed so strongly on some surface oxygen on Au/TiO_2, that can not be removed by the evacuation at 273 K. This we have previously ascribed to carbonate and carboxylate formation on TiO_2 [1,23].

In the case of the static system, CO irreversibly adsorbed on Au/TiO_2 during the 1st run could not be removed afterwards by evacuation at 273 K. This we believe originates from irreversibly adsorbed CO formed during the first run blocking the adsorption sites for CO adsorption during run 2. This would contribute to the decrease in the volume of adsorbed CO by 5.0% (Table 1). In addition, oxygen species removed as CO_2 from Au/TiO_2 during the 1st run can not contribute to CO_2 formation in the 2nd run. Thus the volume of adsorbed CO in the 2nd run should decrease by the volume of CO_2 produced at 273 K, or more specifically by 3.5% (Table 1). The total decrease amounts to 8.5% of the volume of adsorbed CO in run 1, and is almost equivalent to the irreversible part of CO adsorbed on fully oxidized Au/TiO_2.

As can be seen in Fig. 4, the adsorption isotherm of CO on Au/TiO_2 measured in the recirculation system closely overlaps with the isotherm measured in the static system in which the liq N_2 trap was not used. If CO_2 produced during CO adsorption at 273 K desorbs in the gas phase in the static system, it cannot contribute to the decrease of CO pressure. In this case, the difference should be observed between the two isotherms measured with and without use of liquid nitrogen trap. The coincidence between two isotherms suggests that CO_2 produced at 273 K during CO adsorption in the static system probably adsorbs weakly on the surface of Au/TiO_2.

4.4. *Production of CO_2 during the CO adsorption on Au and TiO_2 powders*

The slow liberation of O_2 from oxidized TiO_2 powder at 273 K indicates that loosely bound adsorbed oxygen must be present on the surface of TiO_2. Since TiO_2 only produced trace amounts of CO_2 during adsorption of CO (Table 1), this loosely bound oxygen could not react with adsorbed CO, at least at 273 K. Table 1 shows that a small amount of CO_2 desorbs from the TiO_2 surface during heat treatment in circulating He. Therefore a small amount of CO must adsorb strongly on some surface oxygens on TiO_2 at 273 K and then reduce to form CO_2 at higher temperatures.

It is notable in Table 1 that the amount of CO_2 produced at 273 K on Au powder measured per unit surface area is 185 times larger than that produced on TiO_2. The production of large amount of CO_2 indicates that active oxygen species, which could not be removed by evacuation for 30 min at 273 K, must be present on the surface of gold powder and that these oxygen species react with CO to form CO_2 at the same temperature. Fukushima et al. reported that adsorption of oxygen on gold supported on SiO_2, MgO and Al_2O_3 takes place above 473 K, though no detectable adsorption occurs at temperature below 443 K [24]. Also, Outka et al. reported that CO reacts with oxygen adatoms to form CO_2 on the Au(110) surface at 273 K [25]. We infer from this that some surface Au atoms in the gold particles adsorb oxygen during the oxidizing pretreatment performed at 523 K, after which the adsorbed oxygen species react with CO at 273 K.

Table 1 shows that a considerable amount of CO_2 is produced during CO adsorption on Au/TiO_2 at 273 K. Since oxygen adsorbed on TiO_2 reacts only with difficulty with adsorbed CO at 273 K, while oxidized gold powder produces large amount of CO_2 during CO adsorption, the CO_2 production observed during CO adsorption on oxidized Au/TiO_2 catalyst at 273 K must exclusively occur on the surface and/or the perimeter interface of gold dispersed on TiO_2 support.

5. Conclusion

Adsorption of CO on pre-oxidized Au/TiO_2 at 253–303 K takes place mainly as reversible Langmuir-type chemisorption. A large portion of CO is adsorbed on TiO_2 support, which contributes to the reversible part of chemisorption. The irreversible part of CO adsorption, which is about 10% of the total amount of adsorbed CO, is related to CO_2 formation on the surface of gold particles and the accumulation of carbonate-like species on the surface of TiO_2.

The results indicate that one of the major reaction pathways for CO oxidation to form CO_2 come from oxygen adsorbed on the surface of gold particles. Further work is now underway to determine the role of the $Au-TiO_2$ perimeter interface.

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