Chemical vapor deposition of gold on Al_2O_3, SiO_2, and TiO_2 for the oxidation of CO and of H_2

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In order to clarify the effect of metal oxide support on the catalytic activity of gold for CO oxidation, gold has been deposited on SiO_2 with high dispersion by chemical vapor deposition (CVD) of an organo-gold complex. Comparison of Au/SiO_2 with Au/Al_2O_3 and Au/TiO_2, which were prepared by both CVD and liquid phase methods, showed that there were no appreciable differences in their catalytic activities as far as gold is deposited as nanoparticles with strong interaction. The perimeter interface around gold particles in contact with the metal oxide supports appears to be essential for the genesis of high catalytic activities at low temperatures.

Keywords: chemical vapor deposition, gold catalysts, CO oxidation, hydrogen oxidation

1. Introduction

We have already reported that gold turns out to be surprisingly active at low temperatures for CO oxidation when it is deposited as nanoparticles on select metal oxides [1,2]. Coprecipitation [2–4], deposition–precipitation [1,5] and co-sputtering [6] can produce highly dispersed gold catalysts, which exhibit unique catalytic nature in many different reactions depending on the type of metal oxide supports [7]. In CO oxidation, the oxides of 3d transition metals, especially of group VIII, and hydroxides of alkaline earth metals [8,9] lead to high activities even at a temperature as low as 203 K. The requirements to the size of gold particles differ between the former and the latter supports. With TiO_2, Fe_2O_3, and Co_3O_4 supports, for example, gold particles in the range of 2–10 nm in diameter can exhibit high activity, but by contrast only gold clusters smaller than 1.5 nm [10] can exhibit high activity with $Be(OH)_2$ and $Mg(OH)_2$ supports.

It was previously reported that unsupported gold wires and sponge could catalyze the oxidation of CO at temperatures of 273–573 K in a closed recirculating reactor with apparent activation energies around 0 kJ/mol [11,12]. The reaction of CO with preadsorbed oxygen atoms on a Au(110) surface was also reported to take place at 125 K with an activation energy of 8.4 ± 4 J/mol [13]. Such low activation energies imply that CO oxidation could be detected even at room temperature if unsupported gold particles are small enough to give larger surface area. A recent work by Iizuka et al. [14] using gold fine powder prepared by evaporation in an inert gas with the least contamination (specific surface area 4.1 m^2/g, diameter of primary gold particles 30–50 nm) has proven that the reaction rate of CO oxidation could be measured even at 273 K in a closed recycle reactor with an apparent activation energy of 13 kJ/mol. These results have proved that even on the surface of unsupported Au, CO oxidation can take place at low temperatures.

When gold is deposited on the oxides of other metals by liquid phase methods, the catalytic activity is remarkably enhanced and can be measured in a fixed-bed flow reactor. Metal oxides suitable as a support are limited to a group of reducible metal oxides having p-type or n-type semiconductivities. In fact, gold supported on insulating, covalent bonded metal oxides like Al_2O_3 and SiO_2 was less active than Au/TiO_2, Au/Fe_2O_3, Au/Co_3O_4, and Au/NiO. It should also be noted that the catalytic activity of Au/TiO_2 for CO oxidation markedly changes depending on preparation methods. Turnover frequency differs by about four orders of magnitude between deposition–precipitation and photodeposition [15]. An impregnation method usually yields poorly active gold catalysts [15], however, it has been reported that a specific sequence of pretreatments (H_2 reduction at 773 K, calcination in 20 vol% O_2 at 673 K, and H_2 reduction at 473 K) appreciably enhances the catalytic activity of Au/TiO_2 [16]. Based on our experiences [17–19], the above pretreatments are considered to be effective to evaporate chloride ions and sinter gold particles resulting in a stronger contact (wetting), to oxidize $Au–TiO_2$ interface, and to moisten the catalyst surface by H_2O produced by low temperature H_2 reduction.

Taking these results into account, we have been allured to think that for the genesis of high activity of Au catalysts, the contact structure between Au particles and support is more important than the mean diameter of Au particles. Liu and Vannice have recently reported that the deposition of TiO_2 onto the surface of gold markedly enhances the catalytic activity for CO oxidation [17].

In order to make it sure whether Al_2O_3 and SiO_2 are really not effective as a support or the inferior activities are simply caused by the weak interaction of the gold particles with the supports and accordingly by poor dispersion, we have attempted to deposit gold on Al_2O_3 and SiO_2 by chemical vapor deposition of an organo-gold complex, which has already been proved to be effective to prepare Au/TiO_2 catalysts [18]. It was difficult to deposit gold on SiO_2 by coprecipitation and by deposition–precipitation mainly because the point of zero charge (PZC) of SiO_2 is around pH 2 and the large negative charge of SiO_2 at pH 7 does not allow the deposition of $Au(OH)_3$ on its surface. When the impregnation method was applied to deposit gold on SiO_2, the mean particle diameter of gold becomes very large (20 nm) and no detectable catalytic activity for CO oxidation is observed at temperatures below 500 K.

Recently, organo-gold complexes are also used for the preparation of highly dispersed gold catalysts in the liquid phase [19,20]. Chemical vapor deposition (CVD) [21,22] of gold has previously been applied to the formation of thick films in connection with electronic devices. This communication is the second part of a series of our work to prepare supported gold catalysts by CVD.

2. Experimental

2.1. Catalyst preparation

The metal oxides used as a support are SiO_2 powder (Fujisilycia Chemical, Ltd., type G, specific surface area 310 m^2/g), Al_2O_3 powder (a reference sample of the Catalysis Society of Japan, JRC-ALO7, specific surface area 180 m^2/g) and amorphous TiO_2 (Idemitsu Kosan Co., Ltd., specific surface area 113 m^2/g). As a gold precursor, $(CH_3)_2Au(CH_3COCH_2COCH_3)$, abbreviated to $Me_2Au(acac)$, was used without further purification of the reagent available from Tri Chemical Laboratory, Inc. Its vapor pressure at room temperature is about 8.5×10^{-3} Torr.

The CVD experimental setup made of hard glass was described elsewhere [18]. The lowest pressure that could be reached in the apparatus was about 10^{-3} Torr. Support metal oxides were evacuated at 473 K for 4 h to remove physically adsorbed water and were then treated with 20 Torr oxygen gas at 473 K for 30 min to remove organic residue and to oxidize the surface. The precursor vessel was heated to a fixed temperature of 306 K to gradually evaporate a measured amount of $Me_2Au(acac)$. The precursor adsorbed on the metal oxide supports which were mounted in the reaction vessel was calcined in air at a fixed temperature in the range of 473–773 K to decompose into metallic gold particles on the support surface.

For comparison, Au/Al_2O_3, Au/SiO_2, and Au/TiO_2 catalysts were also prepared by the liquid phase methods, coprecipitation (CP), impregnation (IMP), or deposition–precipitation (DP) using $HAuCl_4$ as a starting reagent. The Au/SiO_2 catalyst prepared by IMP was washed with hot water to remove the chloride ions and then dried at 393 K.

2.2. Characterization and catalytic activity measurements

The dispersion of gold particles was observed with a transmission electron microscope (TEM, Hitachi H-9000). At least 1000 particles were chosen to determine the mean diameter of gold particles and the diameter distribution was obtained by using a computerized image analyzer (EXCEL, Nippon Avionics Co., Ltd.).

All the catalytic activity measurements for CO oxidation and H_2 oxidation were carried out by using a conventional fixed-bed flow reactor and by passing the reactant gas through a molecular sieve column cooled at –77 °C to remove moisture down to 1 ppm. A powder sample (100 mg) sieved between 70 and 120 mesh (212–125 μm) was placed on a ceramic wool plug in a quartz tube with an inner diameter of 6 mm. After the pretreatment of the catalyst samples in an air stream at 523 K for 30 min, the reactant gas (1 vol% CO in air or 1 vol% H_2 in air) was passed through the catalytic bed at a flow rate of 33 ml/min ($SV = 20{,}000\ h^{-1}$ ml/g-cat). The catalyst temperature was monitored with a quartz-tube covered thermocouple contacting with the inlet part of the catalyst bed. It was raised or lowered stepwise and maintained at each temperature for more than 40 min until steady state conversions were obtained. Oxygen, nitrogen, and carbon monoxide in the inlet and the outlet were analyzed by a gas chromatograph (Shimadzu GC-8A) with a thermal conductivity detector (TCD) and with a column of molecular sieve 13X(5m) at 333 K. Calibration was done with a standard gas containing known concentrations of the components.

The activation energies were determined by Arrhenius plots. A powder catalyst sample (20–30 mg) mixed with quartz powder, both sieved between 70 and 120 mesh, was used for activity measurements. The flow rate of reactant gas (1 vol% CO in air) and catalyst temperature was varied to keep the CO conversion between 10 and 20%. As the rate of CO oxidation was almost independent of the concentrations [1] of CO and O_2, it was calculated based on a zeroth order reaction.

The number of gold atoms exposed to the surface was calculated from the mean diameter of Au particles and the actual Au loading obtained by inductively coupled plasma spectrometry (made by Sumika Chemical Analysis Service Co., Ltd.). The turnover frequency was calculated by dividing the reaction rate with the number of surface gold atoms.

3. Results and discussion

Figure 1 shows conversion versus temperature curves for CO oxidation over Au/Al_2O_3, Au/SiO_2, and Au/TiO_2 prepared by CVD and the liquid phase methods. The Au/SiO_2 catalyst prepared by IMP was poorly active and catalyzed CO oxidation only at temperatures above 500 K. Table 1 lists the catalytic properties of all the above catalysts including temperatures for 50% conversion ($T_{1/2}$) of CO and

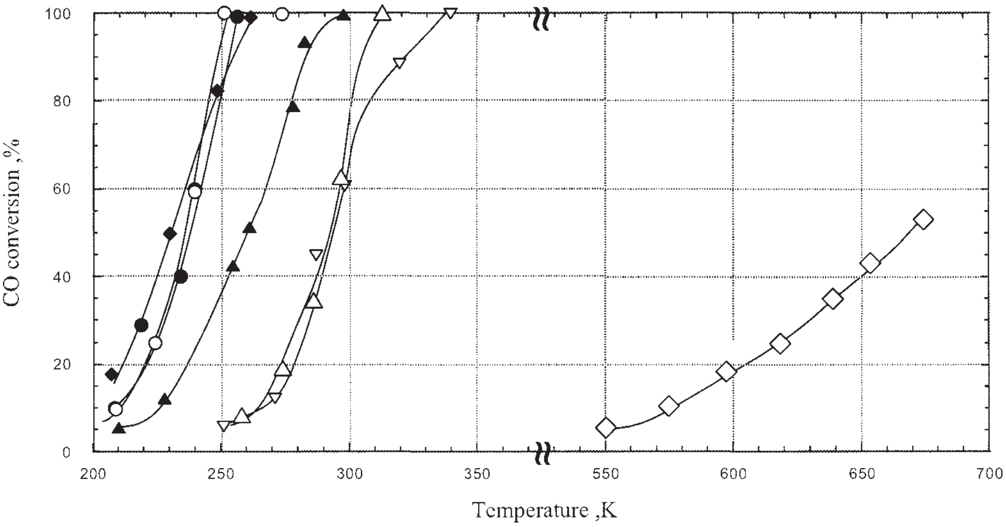

Figure 1. Conversion of CO as a function of catalyst temperature in CO oxidation over gold catalysts prepared by CVD and by liquid phase methods. The temperature for calcination is given in parentheses. (▲) 5.3 wt% Au/Al_2O_3 by CVD (573 K), (△) 0.96 wt% Au/Al_2O_3 by DP (573 K), (▽) 4.2 wt% Au/Al_2O_3 by CP (673 K), (♦) 6.6 wt% Au/SiO_2 by CVD (673 K), (◇) 14.7 wt% Au/SiO_2 by IMP (673 K), (•) 4.7 wt% Au/TiO_2 by CVD (573 K), (○) 2.0 wt% Au/TiO_2 by DP (573 K). Reactant gas; CO 1 vol% in air, SV = 20,000 h^{-1} ml/g-cat.

Table 1
Mean diameters of gold particles in Au supported on Al_2O_3, SiO_2, and TiO_2 and their kinetic parameters for the oxidation of H_2 and of CO.[a]

Support	Method	Au loading (wt%)	Calc. temp. (K)	Mean diameter of Au (nm)	$T_{1/2}(H_2)$ (K)	$T_{1/2}(CO)$ (K)	TOF(CO) (273 K) (s^{-1})	$E_a(CO)$ (kJ/mol)
Al_2O_3	CVD	5.3	573	3.5 ± 2.7^b	331	261	0.01	36
	DP	0.94	573	2.4 ± 1.1^b	362	290	0.02	32
	CP	4.2	673	3.5 ± 1.9^b	367	289	0.006	38
SiO_2	CVD	6.6	673	6.6 ± 3.8^b	329	227	0.02	17
	IMP	14.7	673	20^c	589	668	–	–
TiO_2	CVD	4.7	573	3.8 ± 2.7^b	321	239	0.02	41
	DP	2.0	573	1.7 ± 0.4^b	313	237	0.06	37

[a] DP: deposition–precipitation, CP: coprecipitation, IMP: impregnation, TOF(CO) (273 K): turnover frequency of CO oxidation at 273 K, E_a (CO): activation energy of CO oxidation.
[b] TEM observation.
[c] XRD measurement.

of H_2. Because the optimum calcination temperature depends on support metal oxides and preparation methods, the catalyst precursors were calcined in air at 573 or 673 K. Hydrogen oxidation takes place at lower temperatures than CO oxidation over unsupported gold powder [2] and appears to be much less influenced by metal–support interaction. Therefore, the catalytic activity for H_2 oxidation can be primarily related to the exposed surface area of gold. On the other hand, the catalytic activity for CO oxidation is markedly dependent on the preparation methods [15], the mean diameter of Au particles [1], and the contact structure between the Au particles and the support metal oxides [5,23].

For all the three supports, the CVD method can produce highly active catalysts for CO oxidation. While the coprecipitation method is advantageous in preparing powder catalysts with high Au loadings above 10 wt%, with an intermediate Au loading below 5 wt% it results in lower catalytic activity than the other methods; $T_{1/2}$ value of Au/Al_2O_3 prepared by CP is higher than that of the CVD sample and is similar to that of the DP sample with a much lower Au loading.

The TEM photograph in figure 2(a) shows that many small gold particles are dispersed on Al_2O_3 by CVD but a few large gold particles are also observed. In figure 3(a), which shows the distribution of the diameters of gold particles for the Au/Al_2O_3 by CVD, a peak is observed at a diameter between 2 and 3 nm and the mean diameter is calculated to be 3.5 nm with a standard deviation of 2.7 nm. While the mean diameter of gold particles is almost the same as that of the CP sample, this standard deviation of gold particles is much larger than those for Au/Al_2O_3 and Au/TiO_2 prepared by coprecipitation and deposition–precipitation.

In contrast to other supported gold catalysts, Au/SiO_2 (IMP), which is poorly active for both H_2 and CO oxidation (much higher $T_{1/2}$ values), exhibits a catalytic nature similar to that of unsupported gold particles; the catalytic activity for H_2 oxidation is higher than that for CO oxidation. Because the catalytic activities of Au/SiO_2 for both

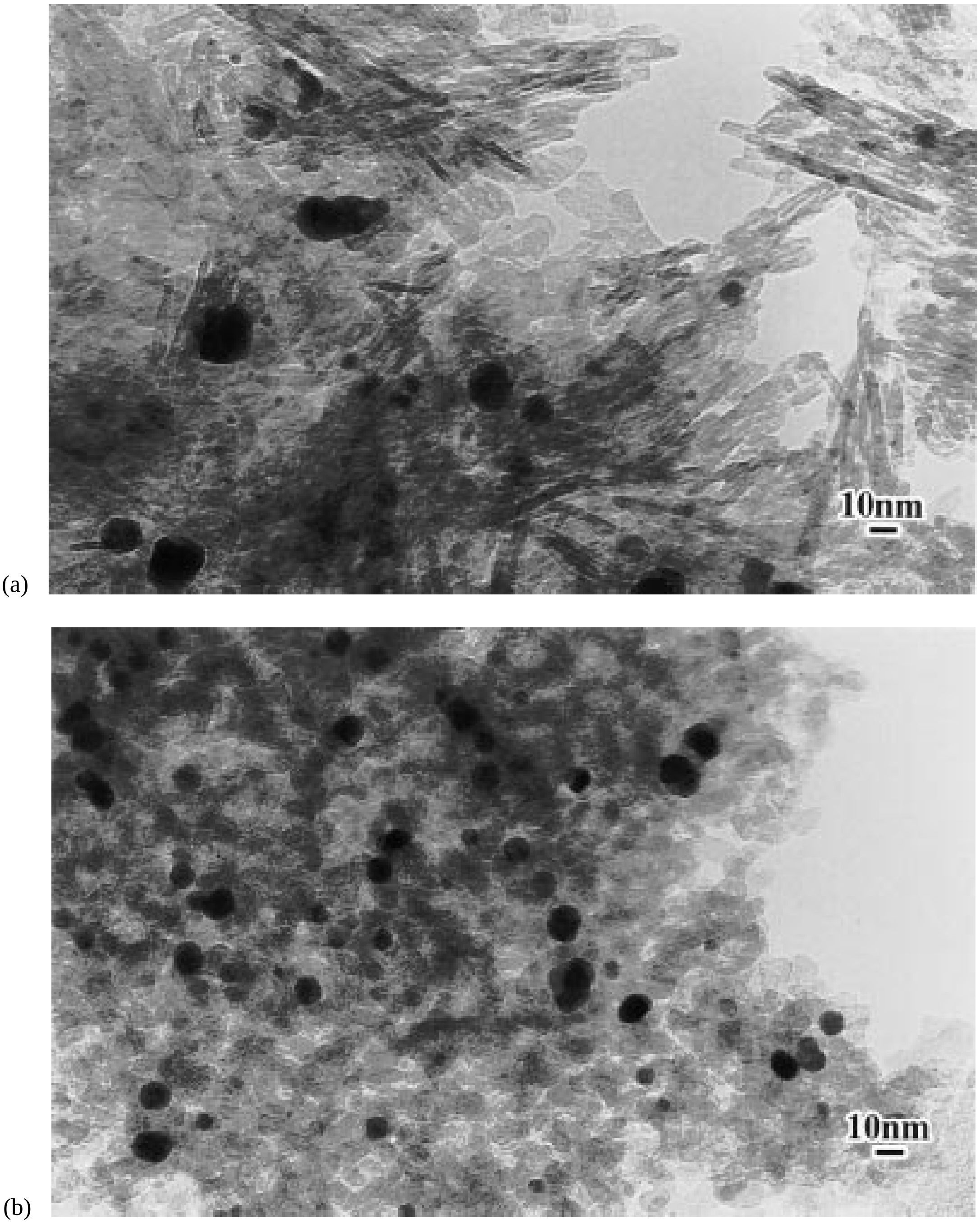

Figure 2. TEM photographs of supported gold catalysts prepared by CVD. (a) 5.3 wt% Au/Al_2O_3 calcined at 573 K for 4 h, and (b) 6.6 wt% Au/SiO_2 calcined at 673 K for 4 h.

the reactions were too low with small Au loadings, table 1 shows the data for the sample with a high Au loading. On the other hand, Au/SiO_2 (CVD) exhibits a high catalytic activity and $T_{1/2}$ value is lower by about 100 K for CO oxidation than for H_2 oxidation. By the CVD method, nanoparticles of Au can be deposited even on acidic SiO_2 support.

In the TEM photograph in figure 2(b) for Au/SiO_2 (CVD) calcined at 673 K, most of gold particles are smaller than 10 nm in diameter. From the bimodal size distribution of gold particles with a maximum around 2–3 nm shown in figure 3(b), the mean diameter is calculated to be 6.6 nm, which is smaller by three times than that of Au/SiO_2 (IMP).

Although gold loading differs in TiO_2-supported catalysts, judging from $T_{1/2}$ values for both CO oxidation and H_2 oxidation, CVD can be regarded as effective as DP in the preparation of highly dispersed gold. Au/TiO_2 prepared by photochemical deposition [15] or by mechanical mixing of Au colloids [5,23] with TiO_2 powder has spherical Au particles simply loaded on the TiO_2 support and exhibits poor catalytic activities for CO oxidation. However, calcination at higher temperatures gives higher catalytic activities for

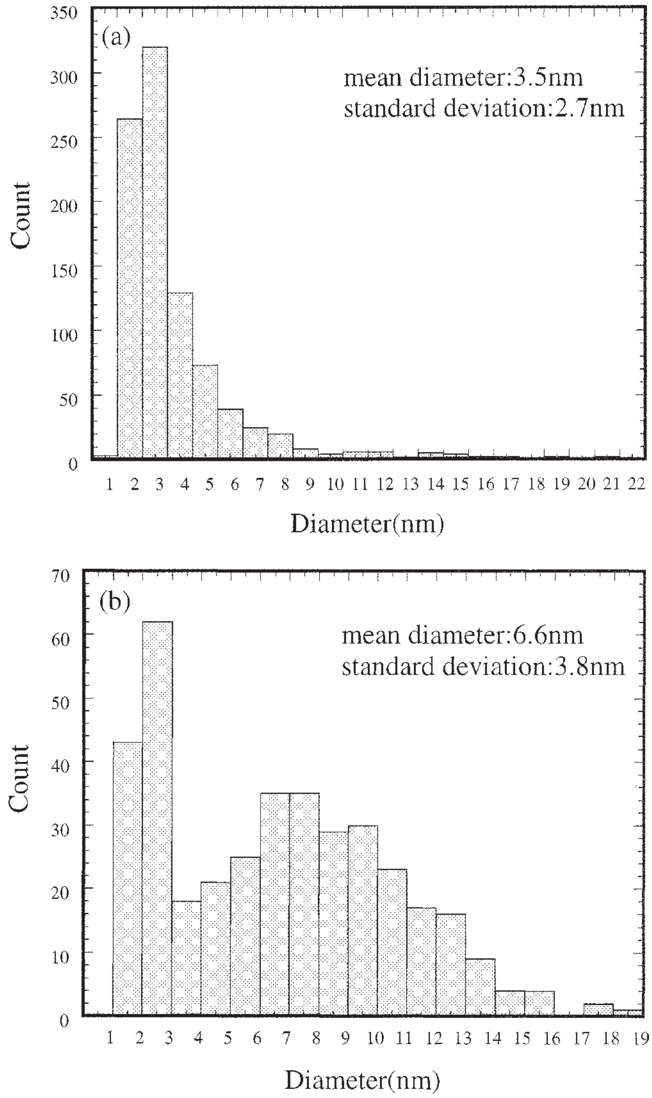

Figure 3. Size distribution of Au particles of (a) 5.3 wt% Au/Al_2O_3 prepared by CVD and by calcination at 573 K for 4 h, and (b) 6.6 wt% Au/SiO_2 prepared by CVD and by calcination at 673 K for 4 h.

the mechanically mixed Au colloid. Bollinger and Vannice have reported that the deposition of TiO_2 on large Au particles remarkably enhances the catalytic activity for CO oxidation [17]. These results suggest that the Au–support interaction and, more definitely, an increase in peripheral distance between Au particles and support may have a key role for the genesis of remarkably high catalytic activities in CO oxidation at low temperatures.

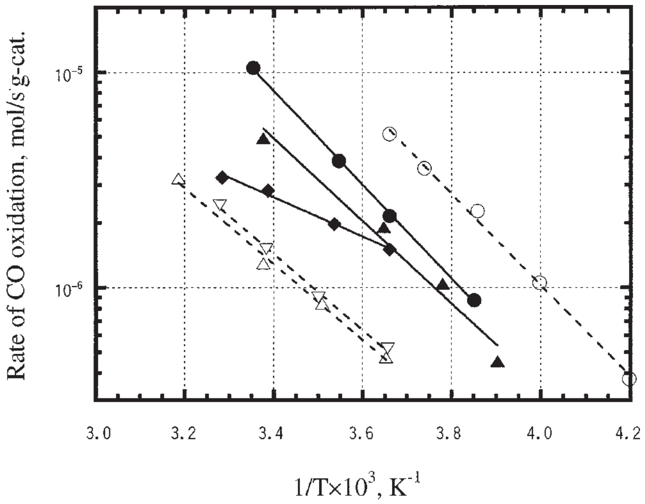

Figure 4. Logarithmic reaction rate of CO oxidation over Au/Al_2O_3, Au/SiO_2, and Au/TiO_2 as a function of reciprocal temperature. The temperature for calcination is the same as that in figure 1. (▲) 5.3 wt% Au/Al_2O_3 by CVD, (△) 0.96 wt% Au/Al_2O_3 by DP, (▽) 4.2 wt% Au/Al_2O_3 by CP, (◆) 6.6 wt% Au/SiO_2 by CVD, (●) 4.7 wt% Au/TiO_2 by CVD, (○) 2.0 wt% Au/TiO_2 by DP.

The Arrhenius plots are depicted in figure 4 and from the straight lines rates of reaction and turnover frequencies (TOF) for CO oxidation at 273 K are obtained. While the gas adsorption technique is generally used to determine the number of surface active sites of Pt, no reliable method is available for determining the exposed surface area of gold. TEM observation can be used instead of the above technique as far as the dispersion of gold particles is homogeneous. Because it was probable that we missed the existence of small gold particles which could not be clearly observed by TEM and therefore the mean diameters of gold particles were not always decisively correct, TOF values should be roughly compared with each other. A little larger TOF value for Au/TiO_2 (DP) can be ascribed to a smaller mean diameter of gold particles, which is in accordance with our previous results [1].

The apparent activation energies of Au/Al_2O_3 prepared by the three methods are almost identical. TOF values of the CVD and DP samples are also in the same order. While Au/Al_2O_3 catalysts prepared by CP and by CVD have almost the same Au loadings and mean diameters of Au particles, TOF values of the CVD sample are higher than that of the CP sample. It is likely that Au particles are partly embedded in the bulk of Al_2O_3 support in the CP sample.

The TOF and activation energy of Au/SiO_2 (IMP) were not obtained because the catalyst was inactive at 273 K. In contrast, Au/SiO_2 prepared by the CVD method exhibits catalytic activity for CO oxidation as high as Au/Al_2O_3 and Au/TiO_2, with an activation energy of 17 kJ/mol and TOF at 273 K of 0.02 s^{-1}. The activation energies and TOF at 273 K are similar for the two Au/TiO_2 catalysts prepared by CVD and by DP methods. As the activation energy for Au/SiO_2 is lower than those of Au/Al_2O_3 and Au/TiO_2, the nature of the metal oxide supports has some influence on the rate-determining step in the low-temperature CO oxidation, probably on the oxygen activation step.

From the results obtained for the Au catalysts prepared by CVD, the order of TOF among Au/TiO_2, Au/Al_2O_3, and Au/SiO_2 could be compared and was found to be nearly the same. The extremely low catalytic activity of Au/SiO_2 (IMP) for CO oxidation might be ascribed to the large Au particles simply loaded on SiO_2 without significant interaction.

4. Conclusions

From the comparison of the catalytic activities for the oxidation of CO and of H_2 among Au/Al_2O_3, Au/SiO_2, and Au/TiO_2 prepared by CVD and liquid phase methods, the following conclusions have been derived.

(1) Gold can be deposited on SiO_2 as small particles by the chemical vapor deposition of an acetylacetonate complex of gold. While liquid phase preparation methods are not applicable to acidic metal oxide supports, the CVD method can deposit Au as nanoparticles with relatively high dispersion even on acidic supports.

(2) Gold nanoparticles highly dispersed on SiO_2 is active for CO oxidation at temperatures below 273 K.

(3) The orders of TOF values for CO oxidation at 273 K are similar among Au/Al_2O_3, Au/SiO_2, and Au/TiO_2. This result indicates that the deposition of gold particles on the support with strong interaction is a major controlling factor for the evolution of catalytic activity and that the nature of the support is not a ruling factor for CO oxidation at 273 K (but not at 203 K).

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