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Performance of Au/TiO_2 catalyst under ambient conditions

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Abstract

The catalytic activity and stability of Au/TiO_2 have been examined under ambient conditions. The best performance was obtained for a catalyst calcined at 473 K and left at room temperature for a few days. The activity for CO oxidation was greatly influenced by moisture in the reactant gas and a maximum was observed at around 200 ppm. We have also succeeded in regenerating the catalysts exposed to various environments, such as rest room, using irradiation with light. The above results show that the Au/TiO_2 catalysts are very useful for indoor air quality control at room temperature without using thermal energy for regeneration. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gold catalysts; Carbon monoxide oxidation; Moisture; Calcination temperature; Regeneration

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1. Introduction

Since the discovery that gold in the form of nanoparticles supported on transition metal oxides is a novel catalyst, gold catalysis has attracted a number of researchers [1–3]. The catalysts are effective at low reaction temperatures even below 300 K for the oxidation of CO [4,5] and the decomposition of trimethylamine [6]. They have a preference for an oxidising atmosphere [4]. This indicates that gold catalysts will have advantages for application in residential situations. Therefore it is of great importance to determine the catalytic performance of gold under ambient conditions, and this is the subject of this paper and has been examined by studying the CO oxidation reaction. This paper consists of three parts: (1) the stability of Au/TiO_2 catalysts calcined at various temperatures, (2) the effect of moisture in the reactant gas on the catalytic activity of Au/TiO_2 and (3) the regeneration of the Au/TiO_2 catalyst kept under ambient conditions.

The particle size of gold on the metal-oxide supports can be controlled by the selection of a suitable calcination temperature. The fact that the smaller-sized gold particles give the higher activity [1] suggests the advantage of a lower calcination temperature. However the performance and stability of catalysts prepared by calcination at lower temperatures are still unknown. As one of the important parameters for controlling the nanometer scale catalyst structures is the calcination temperature, its effect was studied first and the information obtained will be useful for optimising catalyst preparation for practical use.

Moisture is one of the major components in the practical environment, but there have previously been only qualitative studies on the effect of moisture in the reactant gas on CO oxidation catalysed by gold [7–14]. We have therefore investigated the moisture effect for Au/TiO_2 over a range of four orders of magnitude by employing a reaction line particularly designed and constructed for ultraclean technology measurements in extremely dry conditions [15,16].

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This study might be helpful when comparing the activities measured under various experimental conditions, especially those for well-defined surfaces measured under ultrahigh vacuum.

Under practical conditions, gold catalysts may be deactivated by various impurity gases in air or occasionally by the accumulation of products on their surface [17]. Although the catalysts can be regenerated by heat treatment in the presence of oxygen, the heating temperature is strictly limited below that of calcination (typically 673 K). Since the smaller particle size gives the higher activity [1,2], the agglomeration of gold particles by heating might decrease the catalytic activity. In addition, it is unrealistic to use a heater or furnace for regenerating catalysts used in a residential environment. Consequently, a non-thermal method for the regeneration of Au/TiO_2 catalyst has been investigated: the use of irradiation by light in practical environments.

2. Experimental

Au/TiO_2 (P-25, JRC-TIO-4) catalyst samples were prepared by the deposition–precipitation method [18]. After being calcined at 473, 573, 673 and 873 K in air for 4 h, the samples were kept in a refrigerator in order to reduce any change by heat or light. For the investigation of moisture effects and photo-regeneration, only "standard" samples calcined at 673 K were used for the comparison with the previous results. The actual loading of gold in the catalyst samples analysed by ICP (inductively coupled plasma) spectroscopy was 1 wt.%. The average diameter of the gold nanoparticles was calculated from TEM (H-9000, Hitachi) photographs, using the image analyser for about 100–200 particles.

The catalytic activities of the samples were measured mainly in fixed-bed flow reactors. Reactant gas of 1 vol.% CO in air was fed at 10^5 Pa, and the effluent gas was analysed using a TCD gas chromatograph (GC-8A, SHIMADZU). Moisture was added to the reactant gas (1 vol.% CO in air) by using wet molecular sieves and a water bubbler. The H_2O concentration was monitored by either cryoptical (HYCOSMO II, Osaka Sanso Kogyo) or electric capacitance dew-point hygrometers. Prior to the measurements, the catalyst samples calcined at 473 K and the other temperatures were heated in an air stream at 453 and 523 K for 30 min, respectively, except for the thorough drying at 0.1 ppm H_2O at 623 K for 5 days.

Investigation of the photo-regeneration was carried out as follows. After the heating in air at 523 K for 4 h, standard samples were kept for a month in glass tubes in three environmental conditions, i.e. office room, rest room and smoking area, while the unexposed reference sample was kept in a glass bottle with a screw cap. The catalyst samples were introduced into a photocatalytic reactor and evacuated at room temperature for 40 min to 10^{-4} Pa. The reaction was conducted in the dark at 280 K with the equivalent mixture of CO and O_2 at 10^3 Pa. The CO_2 produced was collected with a liquid-nitrogen trap and analysed by a TCD gas chromatograph (GC-8A, SHIMADZU). Irradiation was carried out with a high-pressure mercury lamp (100 W, 200–500 nm) at 280 K under oxygen atmosphere at 1 kPa. In order to measure the changes in the adsorption property caused by the exposure to the ambient air and by photo-regeneration, FT-IR spectra were taken with Perkin-Elmer 1760 and 2000 under a controlled atmosphere and temperature (90–300 K). The spectra of the different samples have been normalised by the pellets weight.

3. Results and discussion

3.1. Effect of calcination temperature

Fig. 1 shows CO conversion as a function of the catalyst temperature for Au/TiO_2. The catalyst samples were kept in a refrigerator after calcination and were taken out just before the activity measurements. Except for the catalyst sample calcined at 473 K, the mean diameters of gold particles are directly reflected in the catalytic activities (Table 1). The grey colour of the catalyst sample after drying was almost unchanged after calcination at 473 K, while it turned purple after calcination at temperatures above 573 K. It can be assumed that oxidic gold precursors are not completely decomposed into metallic particles at 473 K. This is confirmed by FT-IR spectra taken at 90 K, where the band at $\sim 2100\ \mathrm{cm}^{-1}$ for CO adsorbed on the metallic particles of gold is more intense for the catalyst calcined at 573 K than at 473 K [19]. The catalyst calcined at 873 K shows lower but fair activity for CO

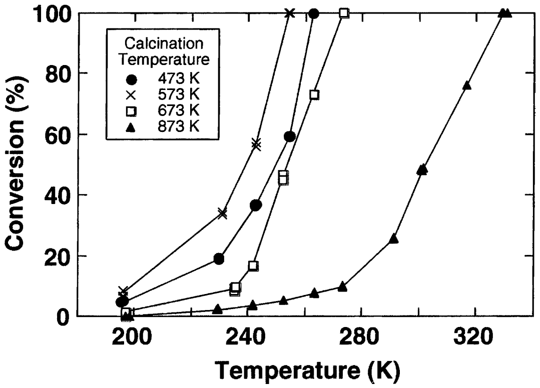

Fig. 1. Conversion of CO as a function of reaction temperature for Au/TiO_2 catalysts calcined at 473, 573, 673 and 873 K. Catalyst sample: 100 mg of 1 wt.% Au/TiO_2. Reactant gas: 1 vol.% CO in air, 33 ml/min.

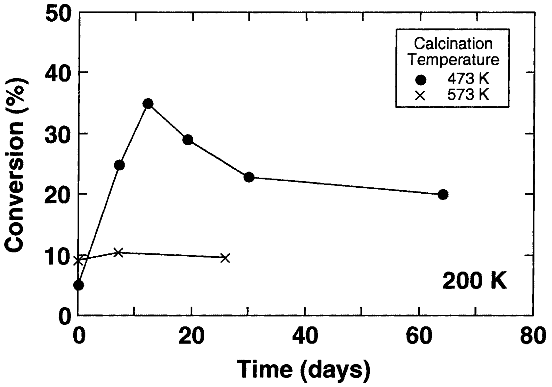

Fig. 2. Time-on-stream change in the conversion of CO at 200 K over Au/TiO_2 catalyst exposed to the ambient conditions. Prior to each measurement, the catalyst was pretreated by heating at 453 K in air for 30 min. Catalyst sample: 100 mg of 1 wt.% Au/TiO_2. Reactant gas: 1 vol.% CO in air, 33 ml/min.

oxidation (Fig. 1), in spite of the absence of the CO species adsorbed on the metallic gold surfaces. Consequently, the activity for CO oxidation observed at 90 K for the sample calcined at 573 K is attributed to the steps, edges and corners of the metallic particles of gold [19].

When the catalyst calcined at 473 K was kept in a glass reactor at room temperature, as shown in Fig. 2, the activity was considerably increased in a few days and then decreased but remained higher than the initial state after 2 months. It is even more active than the catalysts calcined at higher temperatures (Fig. 1), which means the best performance is obtained by calcination at lower temperatures followed by exposure to ambient conditions. The same catalyst was continuously used and pretreated by heating at 453 K prior to each measurement. The colour of the catalyst gradually changed from grey to purple. On the contrary, neither colour nor activity changed for the catalysts calcined at higher temperatures (Fig. 2). These results indicate that the decomposition of the oxidic gold precursors into metallic gold particles has been completed during the exposure to ambient conditions. However, TEM photographs showed no significant change in structure after the increase in activity. Because it is relatively difficult to detect gold particles smaller than 2 nm by TEM in the heterogeneous structures, it is probable that among oxidic gold clusters, chemical and morphological changes proceed mainly at a smaller scale.

Table 1
Mean diameter of gold particles estimated from TEM photographs and temperature for 50% conversion of CO over Au/TiO_2 catalysts calcined at various temperatures

	Calcination temperature (K)			
	473	573	673	873
Mean diameter of Au particles (nm)	2.4	3.5	3.4	7.9
Temperature for 50% of conversion (K)	245	235	250	300

These results are consistent with the evidence obtained from FT-IR experiments at 90 and 300 K on the sample calcined at 473 K [19]. The spectra clearly indicate that on this sample, a significant fraction of gold is in a non-metallic oxidised state with a high dispersion, which is not active towards CO adsorption at low temperatures [19]. Although these gold species can be reduced by interaction with CO at room temperature giving rise to a strong and broad band assigned to CO adsorbed on amorphous, disordered gold phase [19], the change in apparent colour of the catalyst was not significant after its use for CO oxidation at 273 K in an oxidising atmosphere.

3.2. *Effect of moisture*

Fig. 3 shows the reaction rates of CO oxidation over the Au/TiO_2 catalyst at 273 K as a function of the logarithmic moisture concentration in the reactant

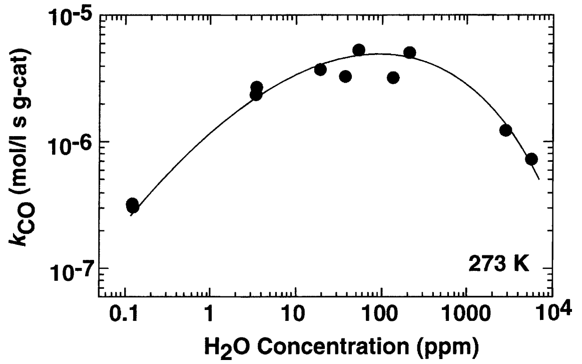

Fig. 3. Dependence of CO oxidation rate at 273 K over Au/TiO_2 on the moisture concentration of the reactant gas. Catalyst sample: 50 mg of 1 wt.% Au/TiO_2. Reactant gas: 1 vol.% CO in air, 67 ml/min.

gas. Catalytic activities are influenced by moisture by more than 10 times and a maximum was observed at ~200 ppm. It is noted that the concentration of the residual moisture in a commercial gas cylinder is about 3 ppm [2] and the activities did not change so much between 3 and 200 ppm. At this ordinary concentration in laboratory experiments, the activity for the Au/TiO_2 catalyst is relatively high, whereas it is appreciably low under dry or wet conditions. Except for the decrease in the activity at ~6000 ppm, which is probably due to the blockage of active sites by a thick layer of adsorbed water from the reactant gas saturated with moisture, supported gold catalysts generally prefer the “wet” condition.

Abrupt switching of the moisture concentration is always followed by a gradual change in the catalytic activity, which suggests that the activity is mainly influenced by the amount of water absorbed by the catalyst [20]. Both apparent activation energy and reaction orders are similar under ~100 and ~3 ppm H_2O [20]. This indicates that the reaction mechanism is not significantly influenced by moisture, but only the pre-exponential factor in the rate law is changed. Thus it is likely that the moisture effect does not originate from the direct interaction of the catalyst with H_2O in the gas phase. Actually, the difference in concentration of H_2O (for example, 200 ppm) from that of CO or O_2 (1 and 21 vol.%, respectively) indicates that H_2O is not stoichiometrically consumed during the reaction. Instead it is more likely that the H_2O-derived species, e.g. –OH, on the catalyst surfaces is involved in the reaction. The species may activate the O_2 molecule or modify the electronic state of the gold atoms exposed at surface. A recent FT-IR study revealed that the presence of moisture markedly enhances CO oxidation over Au/TiO_2 at 90 K [19].

3.3. Regeneration by light irradiation

The catalytic activities of the Au/TiO_2 samples for CO oxidation after exposure to various environments for a month are shown in Fig. 4. No heat treatment was applied before the measurements of catalytic activity. The catalysts were deactivated but still active under the ambient conditions. In order to recover the initial catalytic activity, photo-cleaning of the samples was carried out using irradiation by light at 280 K after the introduction of oxygen into the reactor. During the photo-cleaning, a liquid-nitrogen trap was used to collect the products, e.g. CO_2, H_2O, etc., and the pressure in the reactor was monitored. It was found that oxygen was gradually consumed over 10 h. After the steady state of the pressure was confirmed, the activities for CO oxidation were measured. As shown in Fig. 5, the activities were almost comparable with that for the unexposed catalyst. Although the regained activities were less than that for the catalyst pretreated by heating, it can be said that the photo-cleaning was sufficiently effective at lower temperatures.

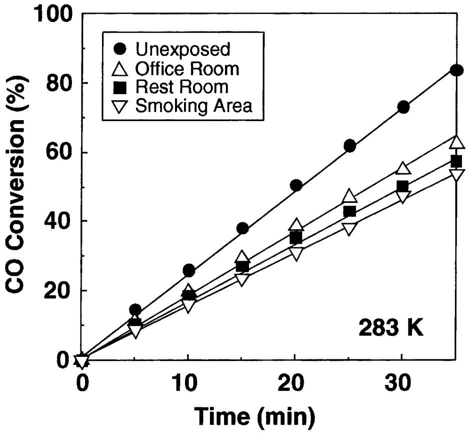

Fig. 4. Conversion of CO as a function of reaction time for Au/TiO_2 catalysts exposed to the various environmental conditions, as well as the unexposed one. The catalyst samples were not pretreated by heating but evacuated.

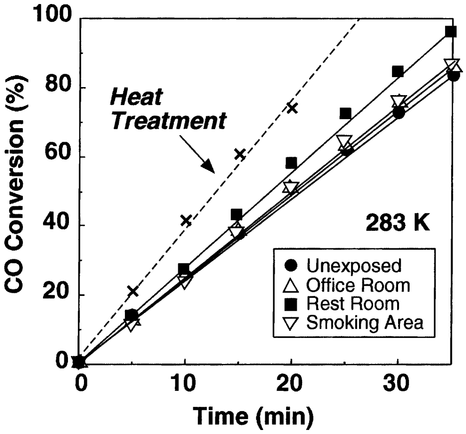

Fig. 5. Conversion of CO as a function of reaction time for the photo-cleaned Au/TiO_2 catalysts exposed to the various environmental conditions, as well as the unexposed one. The catalyst samples were not pretreated by heating but evacuated. The dashed line represents the activity of the catalyst pretreated by heating at 520 K in air for 30 min.

FT-IR spectra are shown in Fig. 6 for the catalyst sample left in a rest room for a month before and after photo-cleaning, as well as the unexposed one. It is noted that the band around 2100 cm^{-1} disappears on the deactivated sample, while the band at 2176 cm^{-1} is much weaker in intensity. The former is assigned to the CO species adsorbed on the corner and/or step sites of the metallic particles of gold [19]. At room temperature, these species react with oxygen adsorbed at the perimeter interface around gold particles. The latter can be ascribed to the isolated carbonyl peroxo species bound to atomic gold species dispersed on the TiO_2 support surfaces [19]. It is noted that the intensity of CO band at 2100 cm^{-1} for the photo-cleaned sample was similar to that observed for the unexposed catalyst. This shows that CO adsorption sites serving as a reservoir for CO oxidation at the perimeter interface are readily blocked by the exposure of the catalyst to the atmosphere and that they become available again after the photo-cleaning. Although no direct information about a trace amount of deactivation species was obtained by FT-IR, they can be assumed to be the organic components of house dust, amines, alkaloids, etc. Whatever species they may be, they must have been decomposed on the catalyst surface by photo-cleaning. The band at 2150 cm^{-1}, which is assigned to CO interacting with the surface –OH groups on TiO_2 and correlated with the band at 3550 cm^{-1} [19], became significantly stronger after photo-cleaning. It seems however that this is not directly reflected in the catalytic activity.

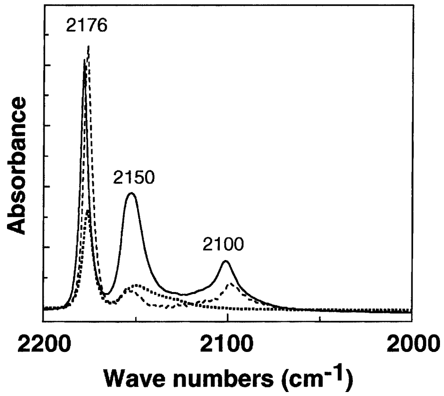

Fig. 6. FT-IR spectra taken in 200 Pa of CO at 90 K for Au/TiO_2 catalyst left in a rest room for a month before (dotted line) and after (solid line) photo-cleaning, as well as for the unexposed catalyst (dashed line).

Since it took over 10 h for the photo-cleaning, intermittent irradiation by light is not sufficient for the regeneration. This method may however be applied for usage of the catalyst under light. It should be stressed that this method has been found to be applicable for the catalysts deactivated under various domestic conditions.

4. Conclusions

Although calcination at temperatures above 573 K is necessary for decomposing oxidic gold species in the dried precursors of Au/TiO_2 prepared by the deposition–precipitation method, the catalytic activity of the catalyst calcined at 473 K increases after exposure to ambient conditions for a few days and exceeds those for the catalysts calcined at 573 K. The reduction of the precursors to metallic gold particles can also be completed by exposure to ambient conditions for a long time, and this is indicated by the change of the sample colour from grey to purple.

The moisture effect on CO oxidation rate is more than 10 times in the range 0.1–6000 ppm, yielding a maximum reaction rate at ~200 ppm. The activity is determined mainly by the amount of moisture accumulated in the catalyst sample, although the reaction mechanisms are not significantly influenced by moisture. This suggests that moisture is involved in the reaction at any moisture concentration.

Exposure of the catalyst samples to environmental conditions results in partial deactivation caused by the blocking of the active sites for CO adsorption. However, the catalysts can be regenerated by the irradiation of light without heat treatment.

All these results clearly show the good performance of Au/TiO_2 catalysts under ambient conditions and the effectiveness of photo-cleaning for recovering their catalytic activities.

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