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Enhancement of catalytic activity of Au/TiO_2 by thermal and plasma treatment

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Abstract−A significant enhancement in the catalytic activity of Au/TiO_2 in CO oxidation and preferential oxidation reaction by creating the active sites on the catalyst surface by thermal treatment as well as by producing small gold particles by plasma treatment has been studied. Au/TiO_2 catalyst (Au (1 wt%) supported on TiO_2) was prepared by conventional deposition-precipitation method with NaOH (DP NaOH) followed by washing, drying and calcination in air at 400 °C for 4 h. Thermal treatment of Au/TiO_2 was carried out at 550 °C under 0.05 mTorr. A small amount of Au/TiO_2 catalyst was taken from the untreated and thermally treated Au/TiO_2 and both kinds of catalysts were treated with plasma sputtering at room temperature. The activity of the catalysts has been examined in the reaction of CO oxidation and preferential oxidation (PROX) at 25-250 °C. Thermally treated Au/TiO_2 showed better catalytic activity as compared to the untreated catalyst. There is also an additional enhancement in the catalytic activity due to plasma sputtering on the both kinds of catalysts. Thermally treated Au/TiO_2 followed by plasma sputtering Au/TiO_2 showed higher conversion rates for CO oxidation reaction compared with untreated, thermally treated and plasma sputtered Au/TiO_2 catalysts. It may be concluded that the enhancement of catalytic activity of thermally treated Au/TiO_2 followed by plasma sputtering is owing to the generation of active sites such as oxygen vacancies/defects in TiO_2 support using thermal treatment as well as by producing small gold particles using plasma treatment.

Key words: Catalytic Activity, Au/TiO_2 Catalyst, CO Oxidation, Thermal and Plasma Treatment

INTRODUCTION

Since the discovery in the late 1980s that gold is catalytically active when it is dispersed as small particles on an oxide support, the preparation of gold-based catalysts has been widely studied [1-5]. They are active in many reactions of both industrial and environmental importance. The most remarkable catalytic properties of supported gold have been obtained for the reaction of CO oxidation at ambient temperature [3-6]. The catalytic activity strongly depends on the dimensions of gold particles and is the highest in the range of 1-3 nm [7-11], the material used as support, the synthesis method, parameters of the preparation (contact time, pH, temperature (T)) and the catalyst activation procedure [7,9,12,13].

Titanium oxide has attracted a great deal of research interest among the commercially employed catalysts over the past 30 years. Additional research interest has arisen for TiO_2 as a support for metal catalysts, particularly since Haruta et al. demonstrated that Au acts as a catalyst for low-temperature CO oxidation when dispersed as nanoclusters on a TiO_2 support [14]. It has been proven that the catalytic activity of Au/TiO_2 catalyst is mainly affected by two factors [15,16], the particle size of Au and the interaction between Au and TiO_2, in which the latter is more important than the former. Many researchers [16-20] are of the opinion that Au is the active site for CO adsorption and TiO_2 is the active site for O_2 adsorption, and the strong interaction between Au and TiO_2 can accelerate a spillover of the reaction species between Au and TiO_2, resulting in an increase in the catalytic activity.

Most of the highly active catalysts reported to date are prepared using precipitation methods, either co-precipitation or deposition-precipitation. It has been proposed that new adsorption sites are created at the interface, and some synergism between gold nanoparticles and support is responsible for the high activity [18,21]. Furthermore, it has been speculated that surface defects may alter the electronic configuration of Au nanoparticles to enable catalytic reactions [22]. However, only negligible research has been conducted so far to increase the activity of gold catalysts by creation of oxygen vacancies/defect sites. In view of fulfilling this research deficiency, we have selected to study the effect of oxygen vacancies/defect sites in gold catalysts for CO oxidation and preferential oxidation reactions. The goal of this work was to prepare Au/TiO_2 catalysts to study their catalytic performance and stability as a function of time in the CO oxidation reaction and PROX reaction. In this study, we have reported that nano-crystalline gold catalysts for CO oxidation and PROX reactions at low temperatures may be promoted by the creation of oxygen vacancies/defects on the support surface due to thermal treatment as well as by producing small gold particles using plasma treatment.

EXPERIMENTAL

1. Synthesis of Au/TiO_2 Catalysts

The Au/TiO_2 catalyst with nominal gold loading of 1 wt% supported on TiO_2 was prepared by deposition-precipitation (DP) under

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complete control of all parameters: temperature, pH, and stirrer speed using solid $HAuCl_4 \cdot 3H_2O$ (Acros) as gold precursor and Titania (Degussa P25) was used as support (45 m^2 g^{-1}, nonporous, purity >99.5%). The gold precursor solution was neutralized slowly with vigorous stirring to pH 7 at 70 °C with a NaOH solution and mixed with a TiO_2 suspension that was kept at 35 °C. The resulting mixture was maintained at pH 7 at 35 °C for two hours. The mixture was filtered, and the solid was washed twice with room temperature deionized water and then once with 70 °C water. The solid was suction filtered and dried at room temperature.

The half amount of prepared Au/TiO_2 catalyst was followed by thermal treatment at 550 °C under 0.05 mTorr for 4 hr. The two catalysts (without and with thermal treatment) were treated with plasma sputtering at room temperature in 26 mTorr Ar for 20 min. In this study, catalysts of Au/TiO_2 (without thermal treatment), Au/TiO_2 (thermally treated), Au/TiO_2 (plasma treatment), and Au/TiO_2 (thermally treated followed by plasma treatment) are referred as AuTi-1, AuTi-2, AuTi-3 and AuTi-4 respectively.

2. Catalysts Characterization

The structure and surface composition of the different catalysts (AuTi-1, AuTi-2, AuTi-3 and AuTi-4) were obtained by different techniques. X-ray diffraction (XRD) measurements were performed on a Bruker D8 advance diffractometer by using CuKα radiation (within the 2θ range going from 10 to 85) to evaluate the catalyst structure. The size and particle distribution of the Au nanoparticles were derived from transmission electron microscopy (TEM) images. TEM examination of Au/TiO_2 catalysts was performed with a Hitachi HF-2000 TEM with a field emission gun at 200 keV. The Raman spectra were recorded on a Renishaw MicroRaman Invia spectrometer, equipped with an argon laser source. The laser excitation line was 514 nm, and the power was of 25 mW. The catalysts were further characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements, and thermal plasma deposition (TPD).

3. Activity Measurements

The catalytic activity tests were carried out in a conventional flow reactor system. The products were analyzed by a Varian 3400 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD), flame ionization detector (FID) and a carbosphere column. 0.05 g of Au/TiO_2 was used in each activity test, and the gas compositions were 1 vol% CO with air balance with a gas hourly space velocity (GHSV) of 120,000 h^{-1} for the oxidation of CO, and 50% H_2, 1% O_2, 1% CO and 48% N_2 with a GHSV of 120,000 h^{-1} for the preferential oxidation (PROX) of CO. After CO oxidation, the catalyst bed was purged with Ar for approximately 15 min at 195 K to remove CO and O_2 before warming up to room temperature for subsequent H_2 pulse reduction. This step is critical because it has been noted previously that as-prepared Au/TiO_2 catalyst can be rapidly reduced by the reaction mixture at room temperature.

RESULTS AND DISCUSSION

1. Catalysts Surface Properties

In the following, we present and discuss results on the structure and surface composition of the various catalysts (AuTi-1, AuTi-2, AuTi-3 and AuTi-4). XRD powder patterns of all catalysts were recorded on a Bruker D8 Advance diffractometer by using CuKα radiation (within the 2θ range going from 10 to 85). XRD patterns of all catalysts show the formation of anatase as the main crystalline TiO_2 phase for the entire catalysts as shown in Fig. 1. It seems that the incorporation of Au restricts the transformation of the TiO_2 anatase phase to the rutile TiO_2 crystalline phase [23]. Normally,

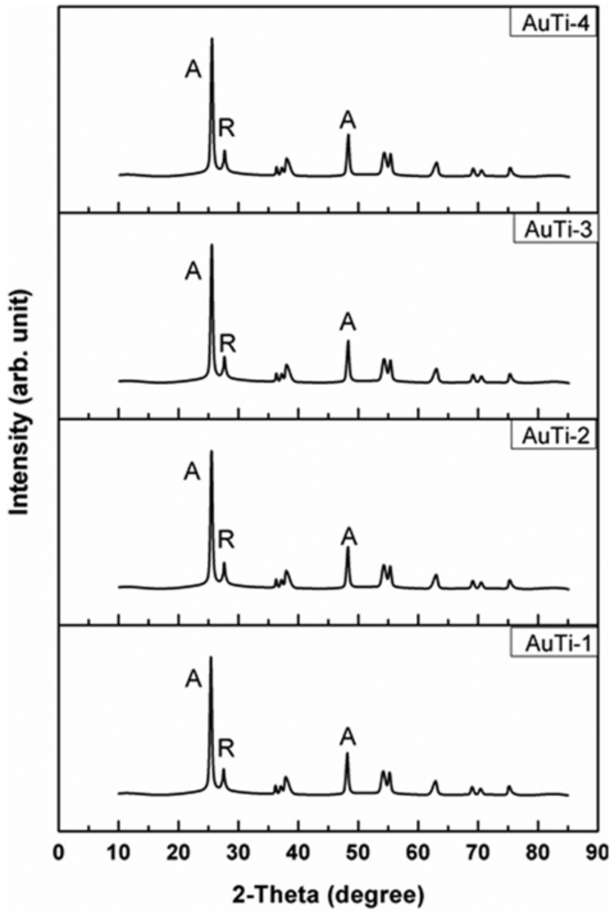


Fig. 1. X-ray diffraction patterns of the studied Au/TiO_2 catalysts.

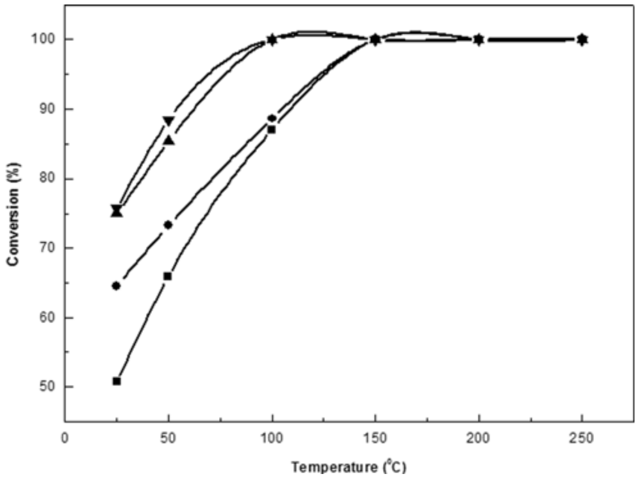


Fig. 2. CO oxidation at 25, 50, 100, 150, 200, 250 °C over Au/TiO_2 catalysts. AuTi-1 (■), AuTi-2 (●), AuTi-3 (▲), AuTi-4 (▼).

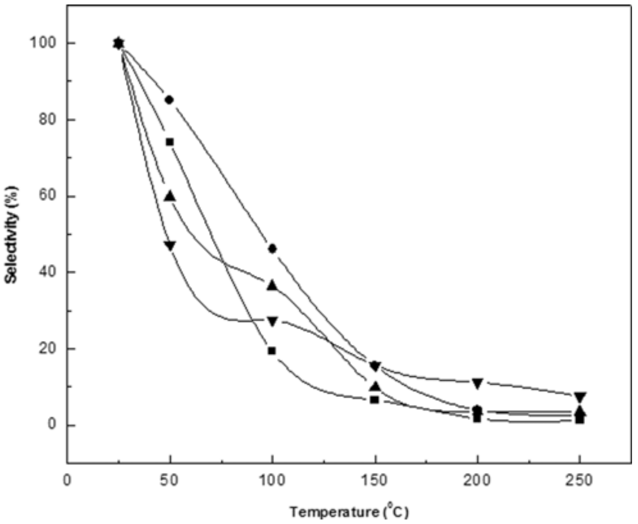


Fig. 3. **CO selectivity at 25, 50, 100, 150, 200, 250 °C over Au/TiO_2 catalysts for PROX reaction. AuTi-1 (■), AuTi-2 (●), AuTi-3 (▲), AuTi-4 (▼).**

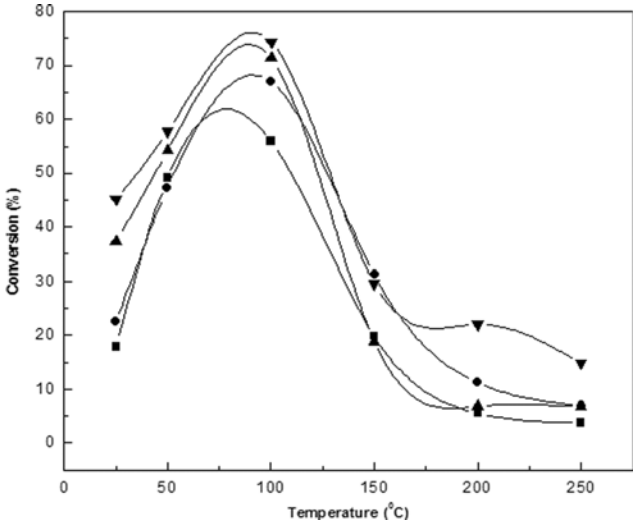


Fig. 4. **CO Oxidation at 25, 50, 100, 150, 200, 250 °C over Au/TiO_2 catalysts in PROX reaction. AuTi-1 (■), AuTi-2 (●), AuTi-3 (▲), AuTi-4 (▼).**

the rutile phase starts to grow at 450 °C in sol gel materials, which means that Au doping favors the retention of the anatase phase on these sol gel materials. In Fig. 1, there are main peaks of anatase-type TiO_2, but peaks for gold did not appear in Au/TiO_2. There may be two reasons for the disappearance of Au: one is good dispersion of Au in TiO_2 [24] and the other one may be due the amorphous behavior of Au [23].

2. Effects of Thermal and Plasma Treatment on CO Oxidation Activity

Fig. 2 shows the catalytic activity of Au/TiO_2 catalysts for CO oxidation prepared by DP method. The catalysts were evaluated for the low temperature oxidation of CO using 1 vol% CO with air balance and total flow rate was 120,000 h^{-1}. AuTi-3 and AuTi-4 catalysts showed higher catalytic activity as compared to AuTi-1 and AuTi-2 catalysts up to 100 °C, but all the catalysts showed 100% CO conversion with the increase of temperature up to 150 °C. Thermally treated Au/TiO_2 followed by plasma sputtering Au/TiO_2 catalyst has also demonstrated an additional enhancement of catalytic activity.

Fig. 3 shows that all the catalysts showed 100% selectivity at room temperature, but it is gradually decreased with the increase of temperature. The simulation gas contained 50% H_2, 1% O_2, 1% CO and 48% N_2, and the flow rate was fixed at 120,000 h^{-1} in all experiments. The reduction of the selectivity with the increase of temperature is expected for two main reasons. First, when the temperature increases, H_2 adsorption on catalyst is favored compared to that of CO [25]; second, the amount of oxygen in order to oxidize the CO is insufficient due to its consumption by H_2 oxidation at higher temperatures.

3. Effects of Thermal and Plasma Treatment on PROX Reaction

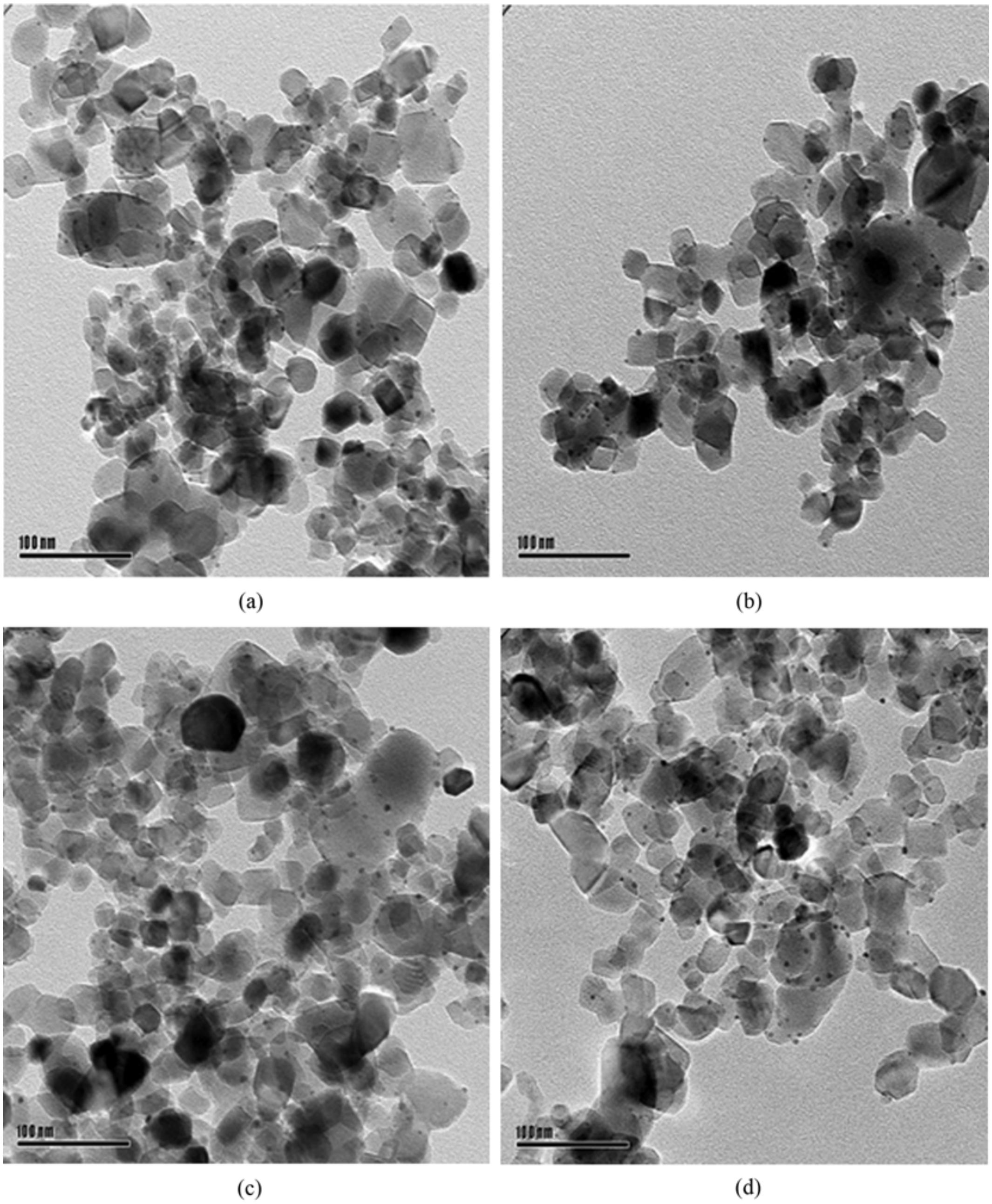
Fig. 4 shows the catalytic activity for PROX reaction using same catalysts. The activity also increased for the PROX reaction after oxygen vacancies/defect generation. The order of activity was the same as in case of CO oxidation below 100 °C, but the difference in the activity between catalysts was small. Above 100 °C, the efficiency order of the catalysts in the PROX reaction is different from that in the CO oxidation reaction. However, it is clear for all the catalysts that in the presence of H_2, the conversion of CO reaches a maximum at 100 °C followed by an abrupt decrease, which is attributable to the same reasons responsible for the reduction in selectivity with the increase of temperature.

4. Effects of Plasma Treatment on the Au/TiO_2 Catalysts

It is well-known that the particle size of Au has a significant impact on the catalytic activity in supported gold catalysts [26]. To investigate the particle size of Au prepared by DP method, TEM observations were performed as shown in Fig. 5(a)-(d). The number of gold particles increased for AuTi-3 and AuTi-4 as compared to AuTi-1 and AuTi-2, although the same amount of gold was deposited during the preparation of catalysts.

The average size and size distribution of each catalyst were manually calculated from TEM images (Fig. 5(a)-(d)). According to the size distribution histogram, shown in Fig. 6(a)-(d), the average size of the gold particles (manually calculated) was 2.85 nm for the AuTi-4 catalyst, which was much smaller compared to the catalyst AuTi-1 (4.46 nm). To calculate the size distribution, we kept a margin of ±1 to remove the human error.

The results obtained from ICP-AES (OPTIMA 4300 DV (Perkin-Elmer, USA), Power: 1300 W Amount of catalyst=0.2 g) confirmed that the Au particles increased for AuTi-3 and AuTi-4 as compared to AuTi-1 and AuTi-2 (see Table 1). This implies that the creation of oxygen vacancies/defects on the support surface leads to a greater number of Au particles deposited on the TiO_2 surface since a single oxygen vacancy can bind three Au atoms on average [27]. Lopez et al. reported that the adhesion energy of gold particles on a defect-free TiO_2 surface is negligibly small and defects are required to obtain stable gold particles for gold deposition on rutile-TiO_2 (110) surface, which they have proved using DFT calculations [28]. They proposed that oxygen vacancies contribute towards the interface energy and determine the size and shape of the gold particles along with the number of active sites. In case of plasma sputtering treatment, it was reported that catalytic active species could be distrib-



(a) (b)

(c) (d)

Fig. 5. TEM micrograph of Au/TiO$_2$ catalysts. (a) AuTi-1, (b) AuTi-2, (c) AuTi-3, (d) AuTi-4.

uted more uniformly when compared to the catalyst prepared without plasma treatment [29]. It can be seen in Fig. 7 that there may be two main possibilities by sputtering plasma: one is that after sputtering plasma, the gold particles can be pressed and increase the contact area, and the second reason is that plasma sputtering can break down the Au particles into small particles; due to that reason, plasma treatment can increase the active sites.

5. Generation of Oxygen Vacancies/Defects by Thermal Treatment

In our study, it is suggested that additional number of gold particles were distributed on the support surfaces by plasma treatment. Therefore, it can be concluded that the enhancement in the catalytic activity of the thermally treated catalysts is attributable to the creation of oxygen vacancies/defects.

To verify the generation of oxygen vacancies/defects sites by thermal treatment, Raman spectra were taken as shown in Fig. 8. In the Raman spectra, the shifts of peak positions to the lower wave numbers were observed for the anatase TiO$_2$ bands. This result reveals that bond strength between Ti and O increased by the creation of the oxygen vacancies/defects.

Activation of oxygen at interface of Au and support is proposed to be the crucial factor in the synergism of gold and Titania [30]. Therefore, the increase in the CO oxidation activity after oxygen vacancies/defects generation is expected to result partly from the increase in the amount of O$_2$ adsorption on the TiO$_2$ support as shown in Fig. 9. As the amount of O$_2$ adsorption increases, the amount of active oxygen adsorbed at room temperature for 1 hr. The temperature increased from 30 °C to 500 °C with temperature increasing

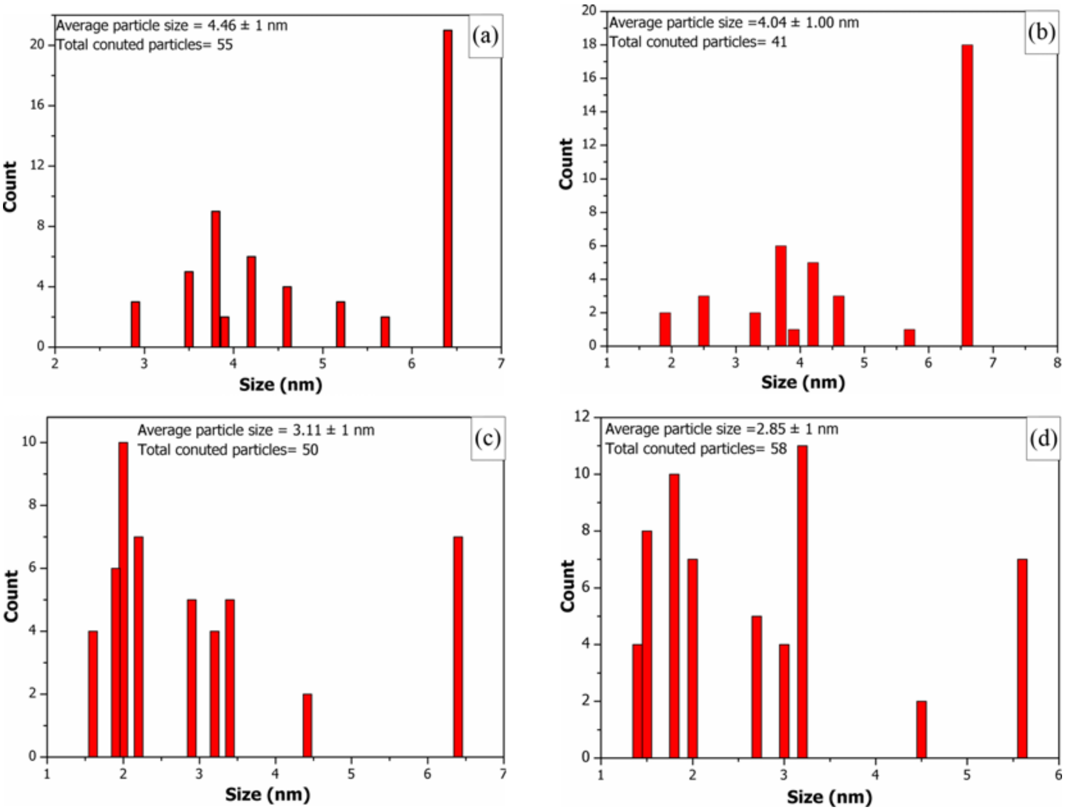


Fig. 6. Size distribution histograms of Au/TiO_2 catalysts. (a) AuTi-1, (b) AuTi-2, (c) AuTi-3, (d) AuTi-4.

Table 1. ICP-AES results of Au/TiO_2 catalysts

No.	Au (wt%)
AuTi-1	0.94
AuTi-2	0.95
AuTi-3	0.98
AuTi-4	0.99

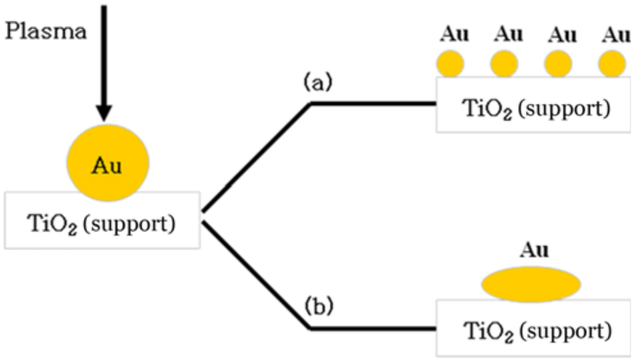


Fig. 7. Plasma effect on Au/TiO_2.

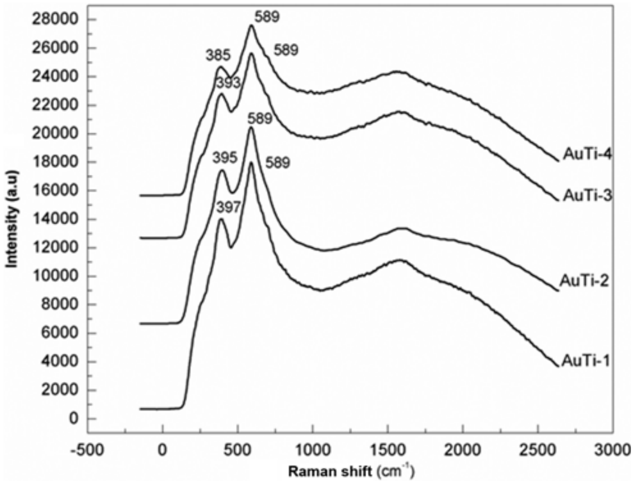


Fig. 8. Raman spectra of the studied Au/TiO_2 catalysts.

ratio of 10 °C min^{-1}. Two distinctive adsorption sites exist for all catalysts (see Fig. 9). One is a weakly adsorbed site appearing at 120 °C, and the other is a strongly adsorbed site at about 200 °C, because O_2 adsorption energy at the interface is higher than at Au [31]. We assigned peaks at 200 °C to O_2 species desorbed from the interface of Au/TiO_2 catalyst. For the AuTi-1 catalyst, the desorption peak at 200 °C appeared as a shoulder. But for the defected catalysts, this peak can be seen clearly. The amount of strongly adsorbed oxygen species that desorbed above 200 °C increased for the thermal and/or plasma treated catalysts. It is thought that oxygen species desorbed at higher temperature participate in the CO oxidation reaction on the Au/TiO_2 catalyst. Therefore, the increase in CO oxidation activity after defects generation can be attributed to the increase of ability to adsorb these active oxygen species on Au/TiO_2 catalyst, particularly on the interface of Au and TiO_2. Fig. 9 shows the O_2 desorption spectra for the AuTi-1 catalyst, when O_2 was adsorbed

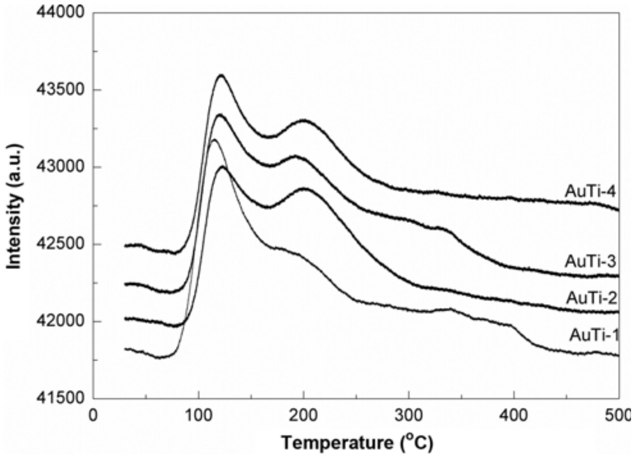


Fig. 9. Oxygen TPD spectra of Au/TiO_2 catalysts. AuTi-1, AuTi-2, AuTi-3, AuTi-4.

at 30 °C and 100 °C, respectively. The activity differences between catalysts at 100 °C were smaller compared to at room temperature. AuTi-1 catalyst also showed high activity at that temperature. Therefore, it was thought that if O_2 was adsorbed at high temperature, the amount of active oxygen species, which desorbs at high temperature, would increase. The increase of the amount of the desorbed O_2 at 200 °C in spite of high adsorption temperature means that these are chemisorbed species. It is expected that this species participate in the CO oxidation reaction more actively. On the other hand, AuTi-3 catalysts showed almost the same result regardless of the O_2 adsorption temperature. This means that AuTi-3 catalyst has ability to adsorb these active oxygen species on the interface of Au/TiO_2 catalyst even at the room temperature.

CONCLUSIONS

Catalytically active Au/TiO_2 catalysts were fabricated by DP method. To gain further insight into the role of the defects and gold/Titania interface in the low temperature oxidation of CO, we created oxygen vacancy/defects by thermal treatment and small gold particles by plasma treatment. After thermal and plasma treatment, catalysts showed better activity than untreated Au/TiO_2 catalysts. The enhancement in the catalytic activity in CO oxidation and preferential oxidation of CO (PROX) can be attributed to an increase in the number of gold particles by plasma treatment and to created oxygen vacancy/defects by thermal treatment. The catalytic activity of the Au/TiO_2 catalysts showed size dependence where higher catalytic activity occurred on smaller gold nanoparticles. The improvement in the catalytic activity of Au/TiO_2 catalysts may be due to increase in the number of gold particles by plasma treatment deposited on TiO_2 surface and the ability to absorb active oxygen in the low temperature by creating oxygen vacancies/defects by thermal treatment.

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