Activity promotion of Au/TiO₂ catalyst by defect generation for oxidation and preferential oxidation of CO

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Introduction
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 TiO₂ 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 TiO₂ support[1]. 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. Furthermore, it has been speculated that surface defects may alter the electronic configuration of Au nanoparticles to enable catalytic reactions.

In this work, we have reported that nano-crystalline gold catalysts for CO oxidation and PROX reactions at low temperatures can be promoted by the creation of oxygen vacancies on the support surface by thermal and plasma treatment.

Materials and Methods
Titania Degussa P25 was used as support (45 m² g⁻¹, nonporous, 70% anatase and 30% rutile, purity >99.5%) and solid HAuCl₄·3H₂O (Acros) as gold precursor. The thermal treatment of TiO₂ was carried out at 550 °C under 0.05 mTorr for 4 hr before Au deposition. After Au deposition on untreated and thermally treated TiO₂, both kinds of catalysts were treated with plasma sputtering in 26 mTorr Ar for 20 min at room temperature. 1 wt.% Au/TiO₂ catalysts were prepared by conventional deposition-precipitation (DP) method under complete control of all parameters: temperature, pH, stirrer speed, and reactant feed flow rates. The sample contained 1 wt.% of gold.

In this study, catalysts of Au/TiO₂ (Au deposited on untreated TiO₂), Au/TiO₂ (Au deposited on untreated TiO₂) followed by plasma treatment, Au/TiO₂ (Au deposited on thermally treated TiO₂) and Au/TiO₂ (Au deposited on thermally treated TiO₂) followed by plasma treatment are referred as AuTi-1, AuTi-2, AuTi-3 and AuTi-4 respectively.

Results and Discussion
Fig. 1 shows the catalytic activity of various Au/TiO₂ catalysts for CO oxidation prepared by DP method. The catalysts were evaluated for low temperature CO oxidation using 1 vol% CO with air balance and total flow rate was 120,000 ccm g⁻¹ cat. 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. Plasma sputtering treatment, after Au deposition on untreated and thermally treated TiO₂ has also resulted in the additional enhancement of catalytic activity. However, plasma sputtering showed lower effect on the AuTi-4 than on AuTi-2, since it is relatively more difficult to generate oxygen vacancies in thermally treated TiO₂ as compared to untreated TiO₂ with the help of plasma sputtering treatment.

Fig. 2 shows the catalytic activity for PROX reaction using same catalysts. The activity also increased for the PROX reaction after 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. In our study, it is suggested that additional number of gold particles were distributed on the support surfaces by the thermal and/or plasma treatment, which validates the creation of active sites. Therefore, it can be concluded that the enhancement in the catalytic activity of the thermal and/or plasma treated catalysts is attributable to the creation of oxygen vacancies. In order to verify the generation of oxygen vacancies sites by thermal and/or plasma treatment, Raman spectra were taken (Fig. 3). In the Raman spectra, the shifts of peak positions to the lower wave numbers were observed for the anatase TiO₂ bands. This result reveals that bond strength between Ti and O increased by the creation of the oxygen vacancies.

Significance
Oxygen vacancies of catalyst enhanced the catalytic activity of Au/TiO₂ in CO oxidation and PROX reaction.

References