

## Thermal Treatment Effect on Catalytic Activity of Au/TiO<sub>2</sub> for CO Oxidation

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**Abstract.** A novel and well-organized study for the synthesis and enhanced catalytic activity of Au/TiO<sub>2</sub> catalysts has been developed. A momentous improvement in the catalytic activity of Au/TiO<sub>2</sub> in CO oxidation and preferential oxidation reaction by thermal treatment has been studied. Au/TiO<sub>2</sub> catalyst (Au (1 wt.%) supported on TiO<sub>2</sub>) was prepared by conventional deposition-precipitation method with NaOH followed by washing, drying and calcination in air at 400 °C for 4 h. Thermal treatment of Au/TiO<sub>2</sub> was performed at 450 °C under 0.05 mTorr. The activity of the catalysts has been examined in the reaction of CO oxidation and preferential oxidation (PROX) at 25-250 °C. The catalytic performance was found to be strongly affected by thermal treatment of the prepared catalyst prior to the reaction. Heat treatment after Au deposition has a positive effect on the CO oxidation performance. This is attributed to the introduction of a stronger interaction between the oxide and Au which improves the catalytic activity.

### Introduction

The use of Au as a catalyst has become the hot topic for CO oxidation. after the discovery from Haruta *et al.* [1] in which they showed that Au supported catalysts exhibit high catalytic activity for CO oxidation, Many studies have been performed to reveal the role of the support during the reaction. The most attractive choice for supports is typically metal oxides, such as TiO<sub>2</sub>, CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> [2]. The preparation of gold-based catalysts has been widely studied [2-6] and the most significant catalytic properties of gold supported catalysts have been achieved for CO oxidation reaction at ambient temperature [4-7]. The dimensions of gold particles, support material, synthesis method, parameters for the preparation and the catalyst activation procedures are major factors to augment the catalytic activity [7-11]. Haruta *et al* [2] and Goodman *et al* [3] reported that, for CO oxidation, the catalytic activity has great impact on the particle size whereas the most favorable particle size range is from 2-4 nm. However, the nature of support on which the gold is dispersed also plays a critical part in the CO oxidation reaction. Au/TiO<sub>2</sub> is one of the most active gold based catalysts for CO oxidation. Recently Asif *et al* [12] reported that the thermal and plasma treatment of Au/TiO<sub>2</sub> catalyst can play a vital role to improve the catalytic activity in CO oxidation.

The present work highlights the catalytic behavior after the thermal treatment of a gold containing TiO<sub>2</sub> catalyst prepared by the deposition-precipitation method. Oxidation of CO was used as a test reaction using oxygen (from the air) as an oxidizing agent.

## Experimental

**Synthesis of Catalyst.** The sample was prepared under the controlled parameters: temperature, pH, stirrer speed, and reactant feed flow rates. All chemicals used were “analytical grade”. The Au/TiO<sub>2</sub> catalyst (Au (1 wt.%) supported on TiO<sub>2</sub>) was prepared by deposition-precipitation (DP) using solid HAuCl<sub>4</sub>·3H<sub>2</sub>O as gold precursor and Titania was used as support. The gold precursor solution was neutralized slowly with vigorous stirring to pH 7 (using NaOH solution) at 60 °C and mixed with a TiO<sub>2</sub> suspension that was kept at 35 °C. The resulting mixture was aged for 1 hr at 60 °C, filtered and washed carefully until complete elimination of Cl<sup>-</sup> anions. The sample was dried under vacuum at  $T = 80$  °C and calcined in air at 400 °C for 2 hr. The sample contained 1 wt.% of gold. The half amount of prepared Au/TiO<sub>2</sub> catalyst was followed by thermal treatment at 450 °C under 0.05 m Torr for 1 hr.

**Characterization.** As-synthesized resulting Au/TiO<sub>2</sub> catalysts were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman Spectroscopy for measuring various properties (phase, structure etc).

**Catalytic Activity Measurement.** Conventional flow reactor system was used to observe the catalytic activity of Au/TiO<sub>2</sub> catalyst. The products were analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD), flame ionization detector (FID) and a carbosphere column. The calculated amount of AuTiO<sub>2</sub> was around 80 mg. The experiments were carried out with a total gas flow of 100 ml/min in the range from room temperature to 250 °C. The gas mixture contained 1 vol.% CO with air balance for the oxidation of CO, and 50% H<sub>2</sub>, 1% O<sub>2</sub>, 1% CO and 48% N<sub>2</sub> for the preferential oxidation (PROX) of CO. Before activity measurement, the samples were thermal treated at 450 °C under 0.05 m Torr for 4 hr. Besides that no further treatments of the catalysts were performed prior to the activity measurements.

## Results and Discussion

**X-ray Diffraction Analysis.** XRD powder patterns of all catalysts were recorded on a Bruker D8 Advance diffractometer by using CuK $\alpha$  radiation (within the range  $2\theta$  going from 10 to 70). XRD patterns of all catalysts show the formation of anatase as the main crystalline TiO<sub>2</sub> phase for the entire catalysts as shown in Fig. 1. It seems that the incorporation of Au restricts the transformation of the TiO<sub>2</sub> anatase phase to the rutile TiO<sub>2</sub> crystalline phase. Normally, the rutile phase starts to grow at 450 °C in sol gel materials indicating that Au doping favors the retention of the anatase phase on these sol gel materials.

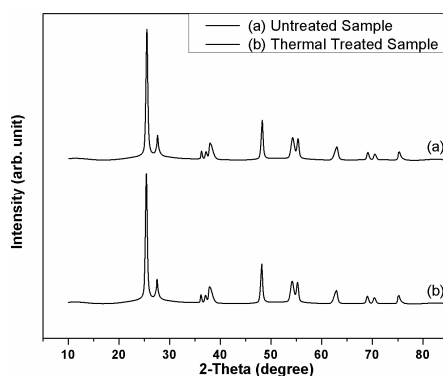


Fig. 1. X-ray diffraction patterns of the studied Au/TiO<sub>2</sub> catalysts

**Catalytic Activity Measurement.** Fig. 2 shows the catalytic activity of Au/TiO<sub>2</sub> 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. Thermal treated catalyst showed higher catalytic activity as compared to untreated catalyst up to 100 °C but the both catalysts were found to exhibit 100% CO conversion with the increase of temperature up to 150 °C. Moreover, both catalysts showed 100% selectivity (Fig. 3) at room temperature but gradually decreased with the increase of temperature. The reduction of the selectivity with the increase of temperature is

attributed to couple of reasons; first, when the temperature increases,  $H_2$  adsorption on catalyst is favored compared to that of CO [13], second, the amount of oxygen in order to oxidize the CO which is insufficient due to its consumption by  $H_2$  oxidation at higher temperatures.

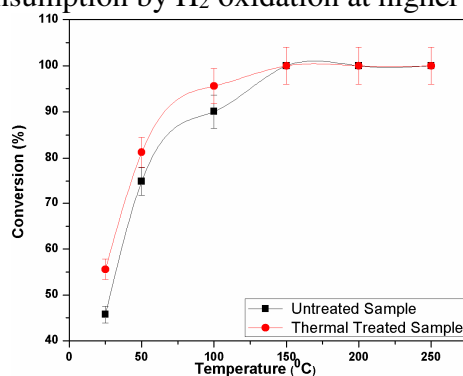


Fig. 2. CO Oxidation at 25-250 °C over Au/TiO<sub>2</sub> catalysts. Untreated Sample (■), Thermal Treated sample (●)

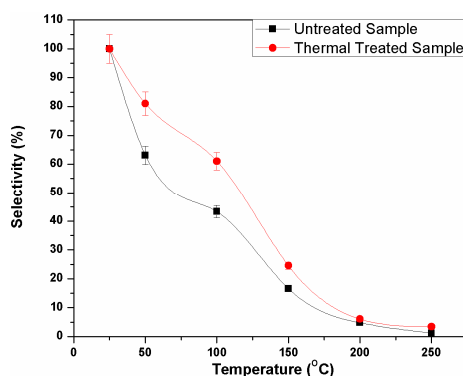


Fig. 3. CO selectivity at 25-250 °C over Au/TiO<sub>2</sub> catalysts for PROX reaction. Untreated Sample (■), Thermal Treated sample (●)

Fig. 4 shows the catalytic activity for PROX reaction using same catalysts. The activity also increased for the PROX reaction after thermal treatment. 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 the both 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.

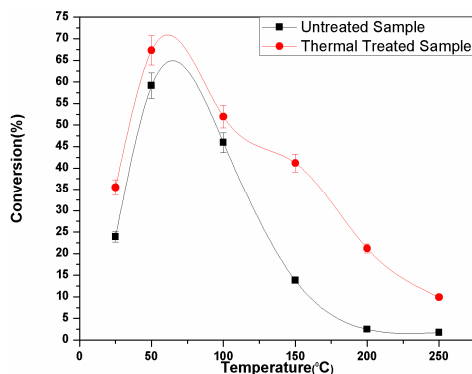


Fig. 4. CO Oxidation at 25-250 °C over Au/TiO<sub>2</sub> catalysts in PROX reaction. Untreated Sample (■), Thermal Treated sample (●)

To confirm the structural changes of the catalyst surface due to thermal treatment, XPS spectra of untreated and thermal treated Au/TiO<sub>2</sub> catalysts were recorded. The XPS spectra of the two used Au/TiO<sub>2</sub> samples show a shift (of about 0.3 eV) toward lower binding energies in comparison with

the thermal treated catalyst as shown in Fig. 5. This shift shows that there are changes in electronic structure with increasing size of the Au clusters deposited on TiO<sub>2</sub> support, consequently pointing out the agglomeration of the particles when the catalyst is working.

XPS spectra of untreated and thermally treated Au/TiO<sub>2</sub> catalysts were recorded to confirm the structural changes of the catalyst surface owing to thermal treatment. The XPS spectra of the two used Au/TiO<sub>2</sub> samples show a shift (of about 0.3 eV) toward lower binding energies in comparison with the thermal treated catalyst as shown in Fig. 5. In addition, this shift shows the changes in electronic structure with increasing size of the Au clusters deposited on TiO<sub>2</sub> support consequently pointing out agglomeration of the particles when the catalyst is working.

Raman spectra (Fig. 6) of the untreated and thermal treated Au/TiO<sub>2</sub> samples exhibit a clear shift in the signal at 397 cm<sup>-1</sup> for an anatase standard, although this could be attributed to a change in particle size. In either case, the Au is clearly highly dispersed though the titania matrix, which should maximize its effect on the surface properties of the support material.

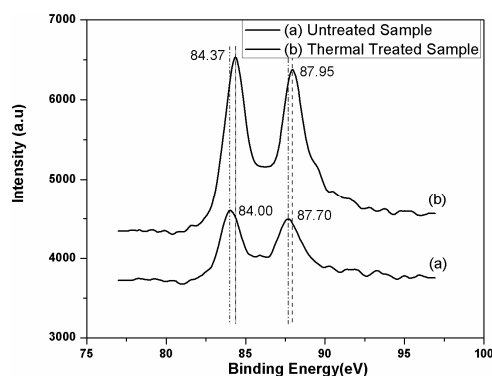


Fig. 5. XPS spectra of the untreated and thermal treated Au/TiO<sub>2</sub> catalyst

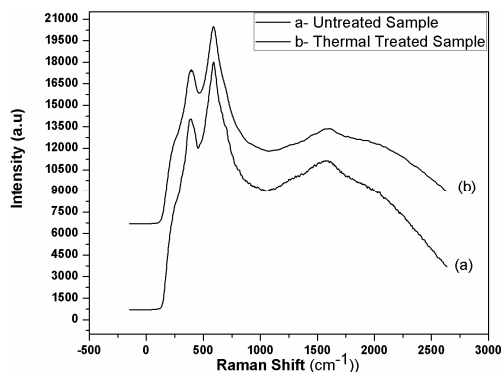


Fig. 6. Raman spectra for the untreated and thermal treated Au/TiO<sub>2</sub> catalyst

## Summary

Catalytically active Au/TiO<sub>2</sub> catalysts were fabricated by DP method. To gain further insight into the effect of thermal treatment and gold/Titania interface in the low temperature oxidation of CO, the samples were thermally treated consequently showing better catalytic activity than untreated Au/TiO<sub>2</sub> catalysts. The enhancement in the catalytic activity in CO oxidation and preferential oxidation of CO (PROX) can be attributed to the rise the number of gold particles by thermal treatment. The catalytic activity of the Au/TiO<sub>2</sub> catalysts showed size dependence where higher catalytic activity occurred on smaller gold nanoparticles. The improvements in the activity of Au/TiO<sub>2</sub> catalysts may be due to the increase in the amount of absorbed active oxygen at low temperature by thermal treatment.

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