

## Au/CeO<sub>2</sub>에서의 일산화탄소의 산화반응

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### CO oxidation over Au/CeO<sub>2</sub>

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#### **Introduction**

Before Haruta *et al.* [1] reported that gold particles smaller than 10nm could be formed on Co<sub>3</sub>O<sub>4</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, NiO, and Be(OH)<sub>2</sub> through coprecipitation, and that these Au catalysts were active in the oxidation of CO at a temperature as low as 200 K, gold has been regarded as far less active as a catalyst than platinum-group metals because of its chemically inert character and of low dispersion on common support materials. A number of nano-sized gold catalysts have been prepared by different preparation methods and have been reported to have extraordinary activities for various reactions such as oxidations and hydrogenations. Among them, Au/CeO<sub>2</sub> catalyst has attracted interests due to its potential applications for some reactions. Flytzani-Stephanopoulos's group have studied the water-gas shift reaction over gold-cerium oxide catalysts and found some advantages over commercial Cu-ZnO [2]. Carrettin *et al* [3] reported that nanocrystalline CeO<sub>2</sub> could increase the activity of Au for Co oxidation by two orders of magnitude compared with conventional ceria. Bera and Hegde [4] prepared ceria-supported gold catalyst where Au was dispersed as Au<sup>0</sup> and Au<sup>+3</sup> states on CeO<sub>2</sub> of 20~30 nm crystallites by the solution combustion method and conducted various reactions such as CO and hydrocarbon oxidation and NO reduction. They found different activities between as-prepared and the heat-treated 1%Au/CeO<sub>2</sub>. Centeno *et al* [5] studied catalytic oxidation of n-hexane, benzene, and 2-propanol on Au/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Au/Al<sub>2</sub>O<sub>3</sub> catalysts prepared from the deposition-precipitation method and found that ceria improved the activity of gold particles in the oxidation of the tested volatile organic compounds resulting from the enhanced fixation and final dispersion of gold particles. Recently, some interesting works for the application of ceria-supported gold catalysts on preferential oxidation of carbon monoxide in hydrogen-rich gas mixture for the polymer electrolyte fuel cell have been reported [6-8].

In this study, Au/CeO<sub>2</sub> was prepared with a coprecipitation method and was applied to CO oxidation. CO oxidation as a model reaction has been studied intensively for twenty years over supported gold catalysts. To enhance oxidation activity in dry and wet conditions, a number of pretreatment conditions were tested and different tendencies were observed. Some characterization techniques to find out electronic states and structures of gold catalysts were applied to explain these different catalytic activities.

#### **Experimental**

##### **Preparation of catalysts**

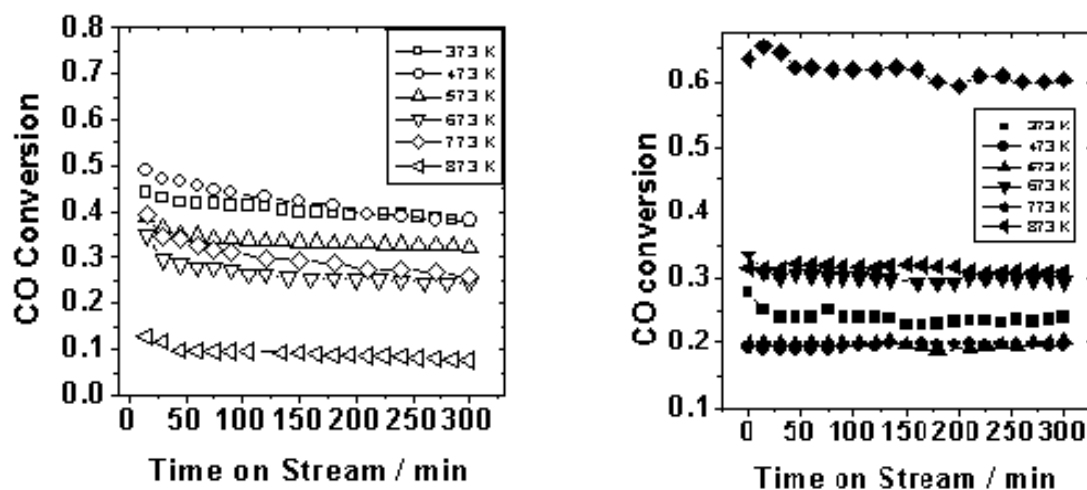
Au/CeO<sub>2</sub> catalysts were prepared by coprecipitation. Two aqueous solutions, one containing AuCl<sub>3</sub> (Aldrich) and the other containing Ce(NO<sub>3</sub>)<sub>3</sub> (Aldrich) were mixed under continuous stirring. The pH of this solution was raised to 10 by adding an aqueous solution of 1M NaOH drop by drop. After 1 h stirring at 343 K, precipitate was filtered, washed several times to remove residual chloride ion, dried at 353 K, and stored as fresh samples. The gold contents were determined by an ICP.

### CO Oxidation

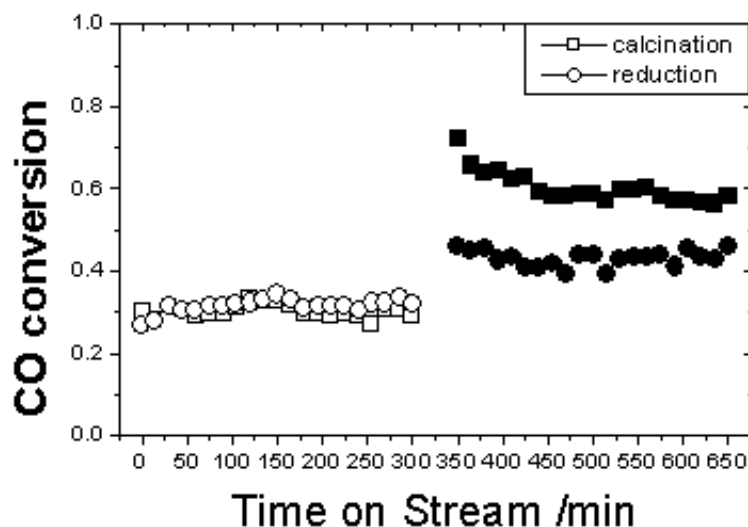
Experiments were carried out in a small fixed bed reactor with catalysts that had been retained between 45 and 80 mesh sieves. A standard gas of 1.0 vol% CO and 1.0 vol% O<sub>2</sub> balanced with helium was passed through the catalyst bed at atmospheric pressure. For activity tests under the wet condition, the reaction gases were directed through a water vapor saturator immersed in a constant temperature bath and fed to a reactor through a glass line warmed by a heating tape. The conversion of CO was determined through gas chromatographic analysis (HP5890A, molecular sieve 5A column) of the effluent from the reactor.

### Results and Discussion

Catalytic activities for CO oxidation over Au/CeO<sub>2</sub> catalysts prepared at different calcinations temperature were compared in dry and wet condition as shown in Fig. 1. Similar to other supported gold catalysts, Au/CeO<sub>2</sub> catalyst showed higher CO conversions in wet condition than in dry condition at the same temperature. Au/CeO<sub>2</sub> catalyst calcined at 773 K showed the highest CO conversion in the absence or presence of water vapor. It is interesting that Au/CeO<sub>2</sub> catalyst just dried at 373 K had comparable catalytic activities with other calcined ones at higher temperatures. The promotional effect of water vapor on the catalytic activity was manifest on Au/CeO<sub>2</sub> catalyst calcined at 773 K. Some gold catalysts have been reported to have enhanced catalytic activity for CO oxidation when it reduced at low temperatures. The effect of a reductive pretreatment with hydrogen on CO conversion in dry and wet condition was investigated. Figure 2 shows that no noticeable difference in CO conversion was found between calcined and reduced Au/CeO<sub>2</sub> catalyst in dry condition. However, the CO conversion decreased in wet condition when Au/CeO<sub>2</sub> catalyst was pre-reduced. XRD patterns were obtained to determine if there was any change in bulk crystalline structures. For all catalysts prepared, peaks representing crystalline CeO<sub>2</sub> and metallic gold were

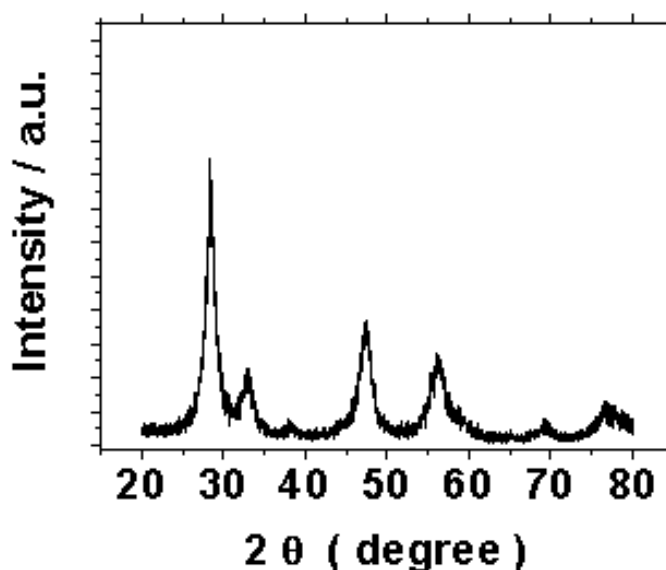


**FIG. 1.** CO conversions at 363 K in dry condition and 353 K in wet condition over Au/CeO<sub>2</sub> catalyst containing 0.95 wt% Au prepared at different calcination temperatures. The reactants, 1 vol% CO and 1 vol% O<sub>2</sub> in He, were fed directly to the catalyst (100mg) at a flow rate of 100 ml/min in dry condition (open points) and the reactants were directed to the catalyst (50 mg) at a flow rate of 100 ml/min through a water vapor saturator maintained at 283 K to obtain wet condition (filled points).



**FIG. 2.** CO conversions at 363 K over Au/CeO<sub>2</sub> catalyst containing 0.95 wt% Au calcined or reduced at 573 K. The reactants, 1 vol% CO and 1 vol% O<sub>2</sub> in He, were fed directly to the catalyst (100mg) at a flow rate of 100 ml/min in dry condition (open points) and the reactants were directed through a water vapor saturator maintained at 283 K to obtain wet condition (filled points).

obtained. Figure 3 shows that crystalline CeO<sub>2</sub> and metallic gold can be formed even through a drying process at 373 K. As the calcination temperature increased, the peak intensity corresponding to crystalline CeO<sub>2</sub> also increased. These results lead us to the conclusion that nano-sized metallic gold and strong interaction between gold and ceria contribute enhanced catalytic activity for CO oxidation in the absence and presence of water vapor.



**FIG. 3.** XRD patterns of Au/CeO<sub>2</sub> catalyst containing 0.95 wt% Au calcined at 373 K

### **Conclusions**

Pretreatment effects on Au/CeO<sub>2</sub> catalyst prepared by coprecipitation were studied for CO oxidation in dry and wet condition. Au/CeO<sub>2</sub> catalyst calcined at 773 K showed the highest CO conversion in the absence or presence of water vapor. Oxidizing environment appeared to be more favorable than reducing condition. Nano-sized metallic gold and strong interaction between gold and ceria appeared to be important for high catalytic activities in CO oxidation.

### **Acknowledgements**

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