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Applied Catalysis A: General 299 (2006) 52–57

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Poisoning effect of SO_2 on the catalytic activity of Au/TiO_2 investigated with XPS and in situ FT-IR

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Received 20 July 2005; received in revised form 22 September 2005; accepted 3 October 2005

Abstract

The suppression of the CO oxidation activity by SO_2 treatment in Au/TiO_2 catalyst was investigated by means of reaction experiments, in situ IR and XPS. The CO oxidation activity over Au/TiO_2 catalyst decreased after SO_2 treatment. The oxidation state of Au particles did not change after SO_2 treatment. The XP spectra in the S 2p region showed that sulfate was formed on TiO_2 supports after SO_2 treatment. The IR experiment revealed that SO_2 treatment increased the adsorption strength between Au and CO. Carbonate peak was absent for the SO_2-pretreated sample in the presence of CO. The migration of CO was completely blocked by surface sulfate compound. Strong and irreversible formation of sulfate at the perimeter is the main reason of the loss of CO oxidation activity at low temperature CO oxidation.

Keywords: Au/TiO_2; CO oxidation; SO_2 poisoning; XPS; In situ IR

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1. Introduction

Supported gold catalysts are well known to be highly active at low temperatures in several oxidation reactions [1–4]. One major application is the selective oxidation of CO in H_2-rich gases (preferential oxidation of carbon monoxide), which is currently the most attractive method for the removal of CO impurities from feed gas streams for polymer electrolyte fuel cells.

Although it is generally accepted that the high catalytic activity of supported gold catalysts in low temperature CO oxidation can be attributed to the presence of small gold particles, which are stabilized by the support [5–7], the nature of the active species remains under discussion. While some authors believe ionic gold provides the active sites for CO oxidation [8,9], others claim metallic gold to be the active species [5,6]. However, according to many papers, the gold/support interface plays an important role [10–12]. But the mechanism and the various properties of supported gold catalysts are still unclear. Haruta and co-workers reported that the SO_2 treatment has great impact on CO oxidation activity of supported Au catalysts [12]. However, the detailed characterizations for sulfate formation were not reported. Hence, we would like to report the poisoning effect of SO_2 treatment on Au/TiO_2 investigated with XPS and in situ IR.

2. Experimental

2.1. Catalyst preparation

The Au/TiO_2 catalysts were prepared by deposition precipitation method using $HAuCl_4{\cdot}3H_2O$ (Aldrich Co.) as a Au precursor. The pH value of the solution was maintained at 7 with 1 M NaOH and the solution was stirred vigorously with a magnetic stirrer at 70 °C for 1 h. After stirring, the catalyst was washed with cold distilled water and dried for 1 day in an oven at 100 °C. After drying, the catalyst was calcined at 400 °C for 4 h under O_2 flow. The BET surface area of the TiO_2 support was 57 m^2/g. Pt/TiO_2 catalyst was prepared by impregnation method for comparison. The metal loadings measured by ICP-AES were 0.5 wt.% for the Pt/TiO_2 and 0.92 wt.% for the Au/TiO_2 prepared at pH 7.

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doi:10.1016/j.apcata.2005.10.030

2.2. Reaction studies

The catalytic reaction tests were carried out at a gas hourly space velocity of 15,000–120,000 cc/h g cat in a quartz tubular reactor with simulation gas containing 1 vol.% CO with air balance. Before each experiment, the catalyst was pretreated in O_2 at 250 °C for 1 h. In case of SO_2 poisoning experiments, 0.5 vol.% SO_2/He gas was fed with a flow rate of 15 cc/min for 1 h before the simulation gas was fed. SO_2 was introduced at room temperature and at 300 °C, respectively. The products were analyzed using a GC (HP 5890, molecular sieve 5A column for CO) equipped with a thermal conductivity detector.

2.3. XPS measurements

The X-ray photoelectron spectra were acquired with a surface analysis system (LHS-10, SPECS GmbH) equipped with a multiplate channel detector using Mg Kα radiation (200 W). The pass energy was 71 eV. Each pelletized catalyst was treated with SO_2 at room temperature and at 300 °C for 30 min in the high-pressure reaction cell. The SO_2 gas was introduced into the high-pressure reaction cell through the mass flow controller (MFC). After the temperature was cooled down to room temperature, the catalysts were pumped down to transfer into the analysis chamber via the preparation chamber without exposure to air. Binding energies were referenced to C 1s at 284.5 eV.

2.4. In situ FT-IR measurements

FT-IR spectra were acquired using an in situ cell installed in a Nicolet Magna 560 FT-IR spectrometer with an MCT detector. The cell was equipped with KBr windows. The catalyst was pressed into a self-supported disc and pretreated under O_2 flow at 300 °C for 1 h. It was then cooled down to room temperature in He flow. Both adsorption of CO and SO_2 was carried out for 0.5 h. Desorption was carried out in a He flow of 45 cc/min. For SO_2 adsorption, a gas mixture of SO_2 (0.5%)/He at a total flow of 70 cc/min was used. All spectra were recorded by accumulating 500 scans with a spectral resolution of 4 cm^{-1}.

3. Results

3.1. Reaction studies

Fig. 1 shows the CO oxidation activity of the Pt/TiO_2 catalyst and of Au/TiO_2 catalysts prepared at pH 3 and pH 7. The reactant flow rate was 30,000 cc/h g cat. For the Pt/TiO_2 catalyst, the conversion greatly increased above 150 °C and all reactant CO converted to CO_2 above 200 °C. The Au/TiO_2 catalysts showed different CO oxidation activity according to the pH of preparation condition. The Au/TiO_2 catalyst prepared at pH 7 showed 100% conversion at 25 °C. However, the catalyst prepared under pH 3 showed lower activity than Pt/TiO_2 catalyst. It is well-known that the particle size of Au has a great impact on the catalytic activity in supported gold catalysts [13]. To investigate the particle size of Au prepared by deposition precipitation method, TEM pictures were taken (figures not shown). The images showed that the catalyst prepared at pH 7 has a particle size below 5 nm, whereas the catalyst prepared at pH 3 has a much larger particle size. The Au/TiO_2 catalyst prepared at pH 7 showed 100% conversion at room temperature even after the flow rate was changed to 120,000 cc/h g cat, and the activity did not decrease after 24 h operation under the flow rate of 60,000 cc/h g cat. Therefore, the poisoning effect by SO_2 was investigated only with the Au/TiO_2 catalyst prepared at pH 7.

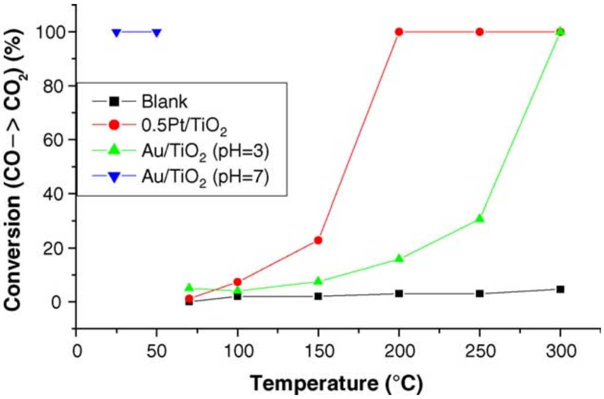

Fig. 1. CO oxidation over Pt/TiO_2, Au/TiO_2 (pH 3) and Au/TiO_2 (pH 7).

Fig. 2 shows the decrease in catalytic activity after SO_2 treatment. The flow rate of simulated gas was fixed to 60,000 cc/h g cat for all experiments. The fresh catalyst showed 100% CO conversion at room temperature and maintained its activity to 250 °C. However, the activity of the catalyst pretreated with 0.5 vol.% SO_2/He gas for 1 h at room temperature decreased significantly. It showed no activity until 50 °C and the activity increased sharply between 100 and 150 °C. The conversion reached 100% at 250 °C. The catalyst pretreated with SO_2 gas mixture at 300 °C showed no significant activity until 150 °C and the conversion did not reach to 100% even at 250 °C. These results indicate that the poisoning by SO_2 increased with increase in SO_2 treatment temperature.

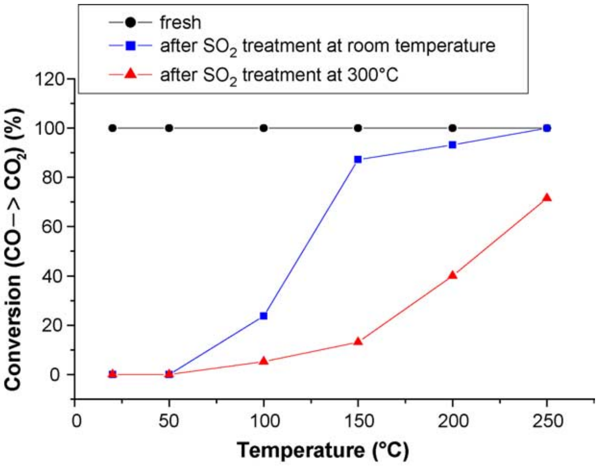

Fig. 2. CO oxidation over Au/TiO_2 before and after SO_2 treatment.