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***In situ* IR, pulse reaction and TPD – ITD study of catalytic performance of room-temperature carbon monoxide oxidation on supported gold catalysts**

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Abstract: With *in situ* IR, two different CO adsorption bands were detected on various chemical state gold catalysts. One band is attributed to the linear CO on an oxidized gold catalyst (2100 cm^{-1}), the other one is ascribed to the bridged CO on metallic gold (2085 cm^{-1}). CO pulse reaction showed that Au/Fe₂O₃ catalyst had a room-temperature activity even in the presence of moisture. The produced CO₂ was detained and more easily desorbed from supported gold catalyst than support oxide. TPD-IDT results indicated that the O₂⁻ superoxide ions are the possible active oxygen species.

Keywords: supported gold catalyst; room-temperature CO oxidation; pulse reaction; TPD-IDT technique

Introduction

Owing to its chemical inertia, gold has long been regarded as a much less active catalyst than platinum group metals. However, the pioneering work conducted by Haruta (Haruta, 1993a) had clearly shown that gold is extraordinarily active for low-temperature CO oxidation, and stimulated extensive studies in this area. Nowadays research and development on gold catalysts are extended to not only catalytic behaviors but also some applications. Supported gold catalysts, such as Au/TiO₂, Au/MnO_x, Au/ZnO, Au/Fe₂O₃, Au/Al₂O₃ and Au/NiFe₂O₄, have been identified as promising catalysts used in chemical sensors (Kobayashi, 1990; Gardner, 1991; Ando, 1997), scaled CO₂ lasers (Hao, 1995a; Haruta, 1997) and air purification devices (Hutchings, 1996; 1997). Some of them are also employed for hydrogen elimination from CO₂ feed gas for urea synthesis (An, 1996; Hao, 1996a). Recent efforts have concentrated on the reason for the remarkable activities of these supported gold catalysts (Bond, 1999), perhaps related to the gold activation and the CO oxidation reaction mechanism.

Based on the structure characterizations of gold catalysts by XPS, TEM, XRD, TPR and XAFS techniques (Valden, 1998; Haruta, 1989; Hao, 2000; Epling, 1996; Cunningham, 1998; Kozlova, 1998; Bassi, 1976), it seems clear that the size of gold particle and its electronic structure appear important in understanding their catalytic behaviors. Although some insight into the catalytic mechanism was proposed (Bocuzzi, 1996; Liu, 1999; Hao, 1996b), it is not yet understood clearly. However, few results about relationship between catalytic activities, active phase structure and absorption-desorption characters are available, and the ongoing study is therefore very desirable to understanding the reaction mechanism.

In the study described in this paper, we have examined CO adsorption by *in situ* IR, catalytic performances of room-temperature CO oxidation on Au/Fe₂O₃ and Au/ZnO catalysts had been investigated by pulse reaction and TPD-IDT techniques. It aimed to correlate the catalytic activities, active phase structure and absorption-desorption characters, and to explore the reaction mechanism.

1 Experimental section

Gold catalysts were prepared by coprecipitation. A mixed aqueous solution of HAuCl_4 (0.1M) and nitrate of support metals (0.1M) was added dropwise into 1M Na_2CO_3 under vigorous stirring. The precipitate was alternatively centrifuged and washed several times until it was free of chloride ions, dried at 110°C , and then treated in an oxygen atmosphere. The preparation procedure in detail was as described in previous works (Hao, 1995b; 1996b; 1997). The gold loading was 1.23% and 6.09% respectively. The support oxide sample was also prepared by coprecipitation method. The preparation procedure was similar to gold catalyst as described above.

IR spectra of CO adsorbed on $\text{Au/Fe}_2\text{O}_3$ was recorded in the range of $1200\text{--}2400\text{ cm}^{-1}$ on a Hitachi 270 – 30 infrared spectrophotometer with a 2 cm^{-1} resolution at room temperature. The catalyst was pressed in pellet, and then placed into a special vacuum cell with double beams, that allowed catalyst evacuation and sequential CO adsorption. The samples were evacuated at 200°C and then cooled down room temperature, IR spectra were in situ scanned at room temperature after sequential CO adsorption. The spectra were obtained by subtracting the background of the sample prior to the CO adsorption and IR absorption of CO in gas phase.

Pulse reaction was performed in the continuous flow quartz micro-reactor with an on-line Ion-Trap Detector MS (Finning MAT 700) for analyzing exit gas. The pulse volume of carbon monoxide was 0.3 ml, catalyst (0.2 ml) was purged with a He flow (20 ml/min) for 30 min at room temperature or 200°C respectively, and then the CO pulse reaction was conducted at room temperature, and carbon monoxide was continuously monitored by using the Ion-Trap Detector.

TPD was also carried out on this flow micro-reactor, the samples were purged with a He flow (20 ml/min) at 200°C for 30 min, and allowed to cool down to room temperature. Then the samples adsorbed CO_2 or O_2 respectively in a pure CO_2 or O_2 flow (20 ml/min) for 5 min and flushed by He flow until no CO_2 or O_2 was detected. The temperature of reactor was then raised at a rate of $5^\circ\text{C}/\text{min}$ to 350°C . The gases evolved during the TPD runs were analyzed with the Ion-Trap Detector.

2 Results and discussion

2.1 CO absorption

IR measurements readily distinguish between carbon monoxide adsorbed on support and gold. In the former case, CO absorption band on iron oxide occur near 2186 cm^{-1} which is attributed to CO adsorbed on Fe^{3+} ions (Ji, 1996). CO was adsorbed on two $\text{Au/Fe}_2\text{O}_3$ catalysts with different gold loading and an $\text{Au/Fe}_2\text{O}_3$ catalyst treated by CO at room temperature (Fig. 1 – 3), (a) 1.23% $\text{Au/Fe}_2\text{O}_3$ (300°C O_2 30 min); (b) 6.09% $\text{Au/Fe}_2\text{O}_3$ (300°C O_2 30 min) and (c) 6.09% $\text{Au/Fe}_2\text{O}_3$ (300°C O_2 30 min) treated by CO two times for 2h. It was shown that no difference was found between the positions of the CO absorption bands on these two catalysts. These $\text{Au/Fe}_2\text{O}_3$ (300°C O_2 30 min) samples (a) and (b) have the 2100 and 1628 cm^{-1} . No 1628 cm^{-1} band was found on $\text{Au/Fe}_2\text{O}_3$ sample (c), it indicates that no active oxygen species occurred on catalyst surface after lengthy CO reaction. It is similar to result of CO pulse reaction discussed below.

To elucidate the electronic effects of catalyst on its adsorption properties, we recorded the IR spectra of CO adsorbed on different $\text{Au/Fe}_2\text{O}_3$ catalysts at room temperature (Fig. 2 and 4). CO was adsorbed on two freshly prepared samples: (b) 6.09% $\text{Au/Fe}_2\text{O}_3$ (300°C O_2 30 min) and (d) 6.09% $\text{Au/Fe}_2\text{O}_3$ (400°C air 4h). Positions of the CO absorption bands depend on surface structure, the $\text{Au/Fe}_2\text{O}_3$ treated in oxygen at 300°C has the 2100 and 1628 cm^{-1} , on the $\text{Au/Fe}_2\text{O}_3$ calcined at 400°C , the bands are at 2085 and 1620 cm^{-1} . Bands at 2100 and 2085 cm^{-1} are ascribed to the form of adsorbed CO, the bands

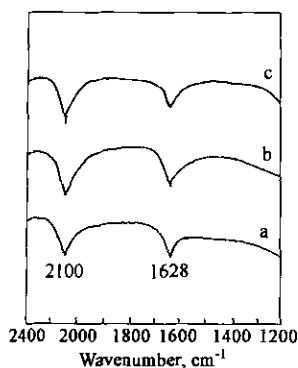


Fig.1 IR spectra of CO adsorbed on 1.23% Au/Fe₂O₃ (300°C O₂ 30 min) catalyst; 70 torr CO at room temperature; a. 1 min; b. 5 min; c. 20 min

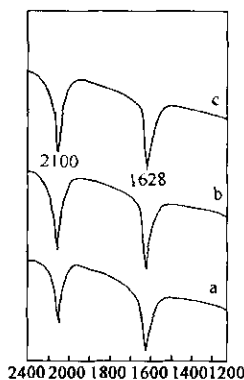


Fig. 2 IR spectra of CO adsorbed on 6.09% Au/Fe₂O₃ (300°C O₂ 30 min) catalyst; 70 torr CO at room temperature; a. 1 min; b. 5 min; c. 20 min

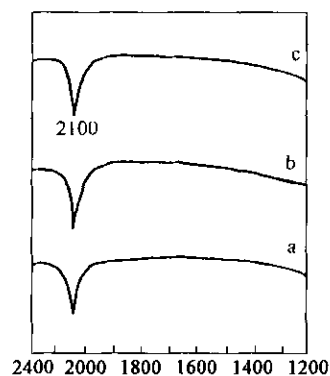


Fig.3 IR spectra of CO adsorbed on 6.09% Au/Fe₂O₃ (300°C O₂ 30 min) catalyst; treated by CO for two times for 2h, 70 torr CO at room temperature; a. 1 min; b. 5 min; c. 20 min

occur in the 1628 and 1620 cm⁻¹ and are attributed to carbonate on support oxides. As reported in previous work (Hao, 2000; 2001a), catalyst (b) is gold of a partial oxidized state (Au^{δ+}), but sample (d) is gold of reduced state (Au⁰). A band at 2100 cm⁻¹ is detected, and ascribed to the linear CO on gold oxidized sites, on reduced sample a new band at 2085 cm⁻¹, and assigned to bridged CO on gold sites. With the increase of the treated temperature, the gold particles increase and the BET surface decreases, and results in different absorption types. Compared with the former, a slight frequency shift of adsorption band on the later catalyst corresponding to the CO form is caused by the increased ability to donate electron density due to the σ-π antidonation of CO. This observation is similar to the results reported by Salama (Salama, 1995), Schwank (Schwank, 1980) and Minico (Minico, 1997). The complex overlapping bands occur in the range 1200—1800 cm⁻¹ and are attributed to carbonate and carboxylate ions on support oxide (Bocuzzi, 2000). The linear CO chemisorbed on the highly dispersed oxidized gold catalyst has a high frequency shift compared to the reduced gold catalyst. The surface structure of gold catalysts is responsible to it. As shown in Table 1, the electronic properties of supported gold catalysts were studied to elucidate the reasons of remarkable activity for low-temperature CO oxidation, the oxidized gold catalysts were found to have higher activities than the reduced gold catalysts.

2.2 CO pulse reaction

In order to explore the reaction of CO with surface oxygen species in absence of gas phase oxygen, CO pulse reactions were conducted in various conditions. The interaction of CO with untreated Au/Fe₂O₃ and Au/ZnO catalysts were studied at room temperature by analyzing carbon monoxide, water and the formed carbon dioxide, and the profiles are depicted in Fig.5—7. The time interval of two pulses is 2 min. From Fig.5, it was seen that with 1st CO pulse, a certain amount of CO₂ exhaled, when the number of pulses increased, the conversion of CO decreased, until the 5th pulse, no more CO was oxidized. This indicates that the catalyst has the room-temperature activity of CO oxidation, and surface oxygen species were limited and used up steeply with increase of CO pulse, until 5th pulse they were consumed completely. Another important finding is that the produce of carbon dioxide was later than the consumption of carbon monoxide. Carbon dioxide was exhaled with the reaction running. Perhaps at first the CO₂ formed was absorbed on catalyst surface, and then desorbed with the reaction heat. A similar result was observed

on Au/ZnO catalyst. Fig. 7 shows the CO pulse profile of Au/Fe₂O₃, it can be observed that CO was oxidized even in presence of water, which is consistent with its good resistance to moisture. As shown above, the production of CO₂ in the pulse reactions was detected, so CO₂-TPD was performed. The results are shown in Fig. 8—9, the significant peaks of 44(CO₂) were observed at 79°C and 76°C over Au/Fe₂O₃ and Au/ZnO catalysts respectively.

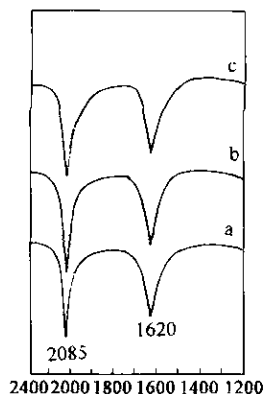


Fig. 4 IR spectra of CO adsorbed on 6.09% Au/Fe₂O₃ (400°C 4h) catalyst 70 torr CO at room temperature; a. 1 min; b. 5 min; c. 20 min

Table 1 Relationship between gold chemical state, bands of CO absorption and catalytic activity

Sample	Gold chemical state	BET, m ² /g	Bands of CO absorption, cm ⁻¹	Catalytic activity, (T _{1/2} , °C)
b	Au ⁸⁺	136.4	2100	- 22
	Bonding energy: Au _{4f7/2} : 84.2(e.V), Au _{4f5/2} : 87.9(e.V)	1628		
d	Au ⁰	40.1	2085	87
	Bonding energy: Au _{4f7/2} : 83.8(e.V), Au _{4f5/2} : 87.5(e.V)	1620		

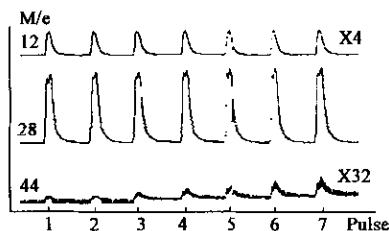


Fig. 5 CO pulse reaction over Au/Fe₂O₃ (300°C O₂ 30 min) catalyst



Fig. 6 CO pulse reaction over Au/ZnO (300°C O₂ 30 min) catalyst

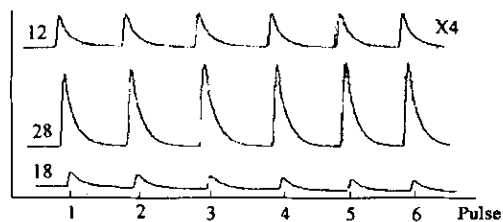


Fig. 7 CO pulse reaction over Au/Fe₂O₃ (300°C O₂ 30 min) catalyst

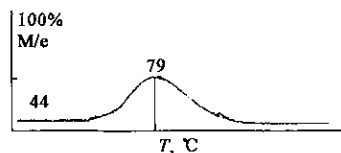


Fig. 8 CO₂ - TPD over Au/Fe₂O₃ catalyst after CO pulse reaction

2.3 CO₂ - TPD measurements

CO₂ TPD measurements were conducted on support oxides and correlative catalysts. The results are shown in Fig. 10—13. The significant peaks of 44 (CO₂) observed were approximate and in the temperature range of 70—90°C. This indicates that perhaps the product CO₂ exhaled from support oxides

in the CO oxidation over gold catalyst. It supported the reaction mechanism as follows.

Au and support (metal oxide) participate in the catalytic actions. The reaction takes place at the Au/support interface. It is most likely that CO adsorbed on the gold particles and O₂ adsorbed on the support oxide surface and produced O₂⁻ superoxide ions, and CO₃⁻ ions are possible reaction intermediates.

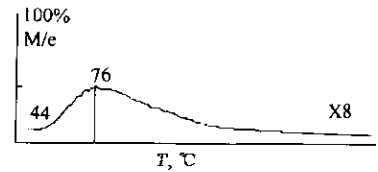


Fig.9 CO₂ – TPD over Au/ZnO catalyst after CO pulse reaction

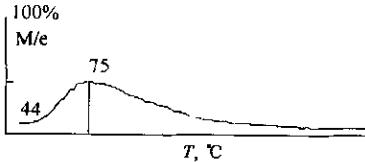


Fig. 10 CO₂ – TPD over Au/Fe₂O₃ catalyst

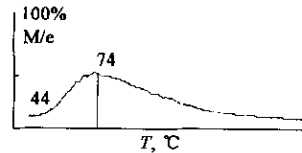


Fig.11 CO₂ – TPD over Au/ZnO catalyst

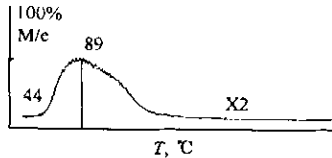


Fig.12 CO₂ – TPD over Fe₂O₃

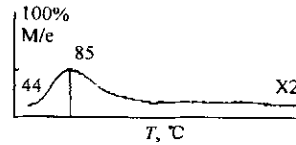


Fig.13 CO₂ – TPD over ZnO

Compared with the corresponding support oxides, the peak temperatures of CO₂-TPD on gold catalysts were lower than the oxides, this reveals that CO₂ is more easily exhaled from gold catalyst than oxide catalyst.

2.4 O₂ TPD measurements

O₂ TPD were performed on Au/Fe₂O₃ and Au/ZnO catalysts, as shown in Fig. 14—15. The significant peaks of 32(O₂) were observed at 281 °C and 285 °C respectively. When the peak temperature of O₂⁻ TPD occurred in the range of 200—300 °C, the surface active oxygen species were ascribed to O₂⁻ ions (Haruta, 1993b). Also we ascribed these signals to the O₂⁻ superoxide ions. In fact our previous work (Hao, 2001b) proved that the paramagnetic superoxide ions detectable by EPR can be generated on Au/ZnO catalyst by oxygen adsorption at room temperature. This O₂-TPD experimental overcomes the drawback of EPR and can be used to detect the surface active oxygen species over Au/Fe₂O₃ catalyst.

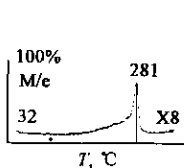


Fig.14 O₂-TPD over Au/Fe₂O₃ catalyst

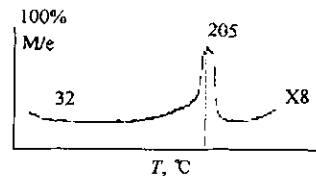


Fig.15 O₂-TPD over Au/ZnO

3 Conclusions

The following conclusions can be drawn from the results in this investigation: (1) CO pulse reaction showed that Au/Fe₂O₃ catalyst had a room-temperature activity even in the presence of moisture. The

produced CO_2 was more easily desorbed from supported gold catalyst than support oxide. (2) TPD – IDT results indicated that the O_2^- superoxide ions are the possible active oxygen species on $\text{Au}/\text{Fe}_2\text{O}_3$ and Au/ZnO catalysts, it is most likely that reaction takes place at the Au/support interface.

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