

Preparation of Au/TiO₂ for catalytic preferential oxidation of CO under a hydrogen rich atmosphere at around room temperature

Wen-Yueh Yu, Chien-Pang Yang, Jiunn-Nan Lin, Chien-Nan Kuo and Ben-Zu Wan*

Received (in Cambridge, UK) 9th August 2004, Accepted 13th October 2004

First published as an Advance Article on the web 30th November 2004

DOI: 10.1039/b412312n

Au/TiO₂ prepared in a pH adjusted gold solution by a deposition–precipitation method can possess high activity and stability for selective CO oxidation in a H₂ rich stream at ambient temperature.

Recently CO preferential oxidation in a H₂ rich stream (PROX) has drawn much attention in relation to the development of a fuel cell with a proton exchange membrane (PEMFC).^{1–4} In the past, three kinds of catalysts, platinum, copper and gold, were often used for PROX.^{3–6} The reaction temperature usually used for a platinum catalyst system was around 150 °C, that for copper was around 180 °C and that for gold was around 80 °C. These suggest that gold catalysts possess a better activity than platinum and copper at lower reaction temperatures. Moreover, based on relatively low, stable prices and more availability, gold catalysts show better economic competitiveness than platinum.⁷ Therefore, from the catalytic performance and the economic considerations, the gold catalyst is a promising candidate for PROX combined with PEMFC technology.

In general, the premise for good PROX performance is to choose a catalyst with more oxidation activity for CO than for H₂, even in the H₂ rich environment. It is required for practical application that the concentration of CO at the reactor outlet is reduced to below 100 ppm,³ in other words, almost 100% conversion of CO should be achieved in the reaction system. The stability of the catalyst system is as important as the reaction activity and selectivity. Moreover, for the complete removal of CO in the feed stream, the molar ratio of O₂ to CO at the reactor inlet should be equal to or higher than 0.5. The lower ratio is preferred, due to avoiding the possibility of higher H₂ consumption.

Several reports in the literature have described the preferential oxidation of CO in a H₂ rich stream over gold supported on TiO₂. Among them, Haruta *et al.*⁸ used a deposition–precipitation (DP) method, Choudhary *et al.*⁹ used a grafting method, Schubert *et al.*¹⁰ and Schumacher *et al.*^{11,12} used impregnation and DP methods for the preparation of gold on the support. It was shown from their data that only a portion of CO in the feed stream was selectively oxidized to CO₂, and none of the catalyst systems can achieve close to the expected 100% CO conversion. Moreover, their catalytic stabilities were uncertain. Recently Qiao and Deng¹³ prepared Au/Fe₂O₃ catalysts by a co-precipitation method. Without doing any pretreatment, their catalysts showed much better activity than those reported in the past. They can convert 100% CO in a hydrogen rich stream at a temperature as low as 8 °C. Nevertheless, the high O₂ to CO ratio (O₂/CO = 4) used was

a drawback; moreover, the effects of the presence of CO₂ and H₂O in the reaction system were not examined. Therefore, it is the objective of this research to prepare Au/TiO₂ catalyst with high activity and good stability for completely removing CO in a hydrogen rich stream. The low ratio of O₂/CO = 1 was used for the reaction, and the effects of CO₂ and H₂O were examined.

The method for the preparation of Au/TiO₂ in this research was deposition–precipitation. An aqueous solution of chloroauric acid (HAuCl₄·3H₂O, Merck) was used as gold precursor, which was prepared following the same procedures for preparing Au/Y (Y represents Y-type zeolite) reported in our previous papers.^{14,15} The following are the detailed procedures. A suitable amount of HAuCl₄ was dissolved in 230 ml deionized water. The concentrations of gold in the solution were 1.46×10^{-3} M. A solution of 0.1 M NaOH_(aq) was added for adjusting the pH of the gold solution to 6. The total pH adjusting time was taken as 24 h. During the first two hours, the pH was constantly adjusted to 6; later, due to the slower decrease of pH, only once every half an hour was the opportunity taken to adjust the solution back to pH 6. Because the chlorine content or the molecular size of gold precursors in the solution should be different using a different pH adjusting time, which would definitely influence the catalytic activity of the supported gold, the detailed results of the effect of pH adjusting time on the properties of Au/TiO₂ will be presented in a later publication. After adjusting the pH of the gold solution, 2 g TiO₂ powder (JRC-TIO-4, a Japanese reference catalyst) were added into the solution, followed by heating the solution to 80 °C, and maintaining it at this temperature for 1 h. After cooling, filtration, washing with 500 ml de-ionized water and drying at 60 °C in air, the resulting samples were designated as Au/TiO₂. From the analysis by atomic absorption, the gold loading in Au/TiO₂ was 1.3 wt%; in other words, 39% gold in the solution had been deposited on TiO₂ during the preparation process.

The TEM (Hitachi H7100) pictures of Au/TiO₂ were taken under 75 kV. The detection of chlorine was by SEM (Hitachi S-2400) with KeveX Delta 80000 EDS. The catalytic measurements were carried out in a packed bed within a shell and tube quartz reactor (7 mm id) under atmospheric pressure. The reactor temperature was controlled at between 25 and 70 °C by the fluid in the shell from a thermostat. 0.04 or 0.2 g of Au/TiO₂ mixed with 0.2 g of silicon carbide (SiC, Strem Chemical) was used for the reaction tests. No catalyst pretreatment processes were applied before the reaction tests. The feed ratio was CO/O₂/H₂/N₂ = 1/0.5 or 1/50/balance (in vol%). The total flow rate was 110 ml min⁻¹ (space velocity = 165000 or 33000 h⁻¹ ml g-cat⁻¹). When the effects of CO₂ and H₂O on the reaction were examined, 15% CO₂ and 3% H₂O were further added into the reactor. The

*benzuwan@ntu.edu.tw

concentrations of CO, CO₂ and O₂ in the effluent gas were analyzed by two gas chromatographs (Shimadzu GC-8A with Carboxen[®] 1000 column and Shimadzu GC-14A with molecular sieve 5A column).

Fig. 1 presents the conversions of CO and O₂, and the selectivity for CO oxidation at 25 °C, while only 0.04 g Au/TiO₂ (space velocity = 165000 h⁻¹ ml g-cat⁻¹) and O₂/CO = 1 in the feed were used. The selectivity is defined as the ratio of O₂ consumed with CO to total amount of O₂ consumed in the reactor. Since only the oxidations of CO and H₂ occurred in the Au/TiO₂ system, the value of the selectivity can represent the preferential activity for CO oxidation in the reaction system. The higher value is preferred in this research. Moreover, because the presence of CO₂ and H₂O is inevitable in the hydrogen rich stream from reforming or water gas shift reaction, for the practical application of Au/TiO₂ in completely removing CO, the effects of CO₂ and H₂O on preferential oxidation were examined and the results are also shown in Fig. 1. Therefore, there are four regions in Fig. 1: Region A represents the results while CO₂ and water vapor were not present in the feed; Region B represents the presence of 3% water vapor in the feed; Region C represents the presence of 15% CO₂; and Region D represents the presence of both 15% CO₂ and 3% water vapor. From the time on stream results presented in Fig. 1, it can be observed that 100% CO conversion or close to 100% CO conversion (after 48 h various tests) was achieved at the reactor outlet, when there was no addition of CO₂ or H₂O (Region A). The oxygen conversion was about 52%, in which 80% was consumed with CO and 20% with H₂; in other words, the selectivity for the oxidation of CO was 0.8. The high value of the selectivity demonstrates the preferential oxidation of CO under a hydrogen rich atmosphere over Au/TiO₂ catalyst, while only a low ratio of O₂/CO = 1 was used. Moreover, the stability of the reaction system was good during the time on stream tests. The

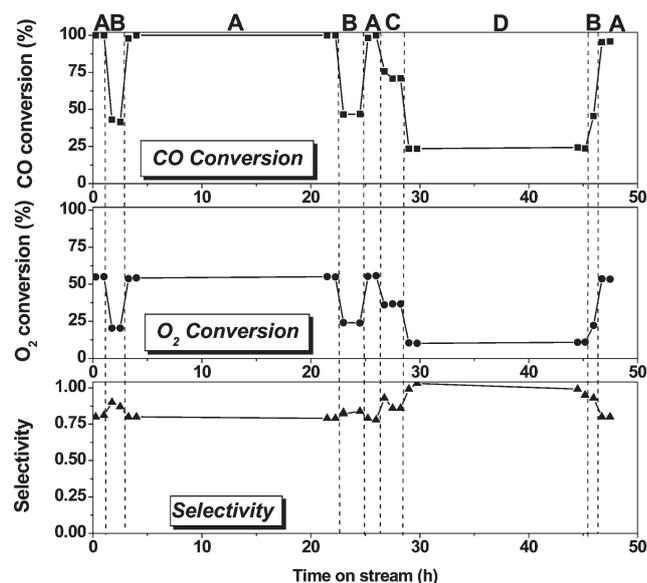


Fig. 1 Preferential oxidation of CO over 0.04 g Au/TiO₂ versus time on stream at 25 °C. Feed composition: CO/O₂/H₂/CO₂/H₂O/N₂ = 1/1/50/0 or 15/0 or 3/balance (vol%), total flow rate = 110 ml min⁻¹. A. without CO₂ and H₂O in the feed. B. with 3% H₂O in the feed. C. with 15% CO₂ in the feed. D. with 3% H₂O and 15% CO₂ in the feed.

high conversion of CO in the hydrogen rich stream and the good stability of the catalyst system are due to the lengthy pH adjustment (= 6) for the dilute gold chloride solution before addition of TiO₂ support. Because there was less chlorine content in gold precursors after 24 h solution pH (= 6) adjustment, the gold particle sizes deposited on TiO₂ (*i.e.*, can't be observed from TEM and no residual chlorine was detected from EDS) were less than those from the gold solution with shorter pH adjustment time (*e.g.*, around 5 nm gold particle sizes after 1 h adjustment and with residual chlorine detected from EDS). A similar chloride effect on the particle size and on the catalytic activity of Au/Al₂O₃ was reported by Oh *et al.*¹⁶ In contrast, for the preparation of Au/TiO₂ in the past, either because the lengthy pH adjustment for the gold solution was not carried out,⁸ because the TiO₂ support was added into the gold chloride solution before any pH adjustment,¹⁰⁻¹² or because a different gold complex was used for the deposition,⁹ the catalytic activities of the resulting Au/TiO₂ were not as good as ours. None of them can provide the activity for 100% CO conversion in a hydrogen rich stream.⁸⁻¹² These may be due to the chloride (or anion) contamination or the large gold particle sizes on the TiO₂ surface.

For the effect of H₂O on the reaction, it can be seen in Fig. 1 that the conversions of CO and O₂ were dramatically decreased and the selectivity for CO oxidation was increased, with the presence of 3% water vapor (Region B) in the feed. The process was reversible. When water vapor was removed, the conversions and the selectivity recovered to the originals. On the other hand, when 15% CO₂ was in the reaction system (Region C), the decreases of the conversions of CO and O₂ were also observed; however, they were not as pronounced as those resulting from the presence of water vapor. Nevertheless, when both 15% CO₂ and 3% water vapor were in the feed (Region D), the conversions were decreased to the least and the selectivity for CO oxidation was increased to the most, as shown in Fig. 1. They were gradually recovered after removing both CO₂ and water vapor from the reaction system. The results in Fig. 1 indicate that both CO₂ and H₂O are reversibly adsorbed on the surface of Au/TiO₂, which can reduce the reaction activity significantly and increase the selectivity for preferential oxidation of CO. By removing them, the reaction activity can be recovered.

For the moisture effect on CO oxidation over Au/TiO₂, Daté *et al.*¹⁷ have indicated that when the concentration of moisture is above 200 ppm, the catalytic activity is depressed, probably due to the blocking of the active sites. This is because there are water-derived active sites for the catalytic reaction on the surface of gold particles, which are hydrophilic and adsorb moisture easily. For the adsorption of CO₂ on nano-gold, carbonate or bicarbonate species may be formed on the active sites. It may be reversibly desorbed from the surface by the heat generated from the oxidation reactions; or by the decomposition of carbonate with the presence of water proposed by Daté *et al.*¹⁸

The results in Fig. 1 suggest that more Au/TiO₂ (or less space velocity) and higher reaction temperature have to be used in order to remove CO completely in a hydrogen rich stream with the presence of 15% CO₂ and 3% H₂O. Therefore, the space velocity = 33000 h⁻¹ ml g-cat⁻¹ in contrast to 165000 h⁻¹ ml g-cat⁻¹ in Fig. 1 was used for improving CO conversion, and the reaction results at different reaction temperatures are shown in Fig. 2. Two ratios of O₂ to CO (0.5/1 and 1/1) in the feed stream

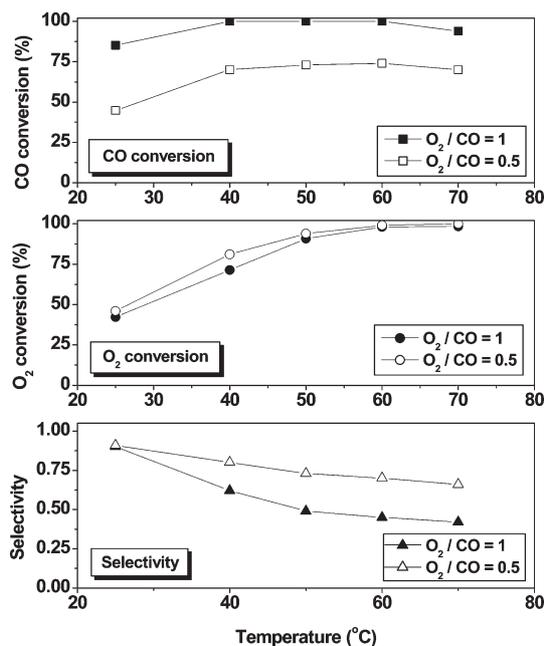


Fig. 2 Preferential oxidation of CO over 0.2 g Au/TiO₂ at different temperatures. Feed composition: CO/O₂/H₂/CO₂/H₂O/N₂ = 1/0.5 or 1/50/15/3/balance (vol%), total flow rate = 110 ml min⁻¹.

were examined. It can be found in Fig. 2 that O₂ conversion increased with the increase of reaction temperature; nevertheless, CO conversion did not change significantly when the reaction temperature was increased to higher than 40 °C. In fact, CO conversion started to decrease at 70 °C. These results indicate that more hydrogen oxidation occurred when the reaction temperature was increased, which reduced the possibility for CO oxidation. Therefore, it can be observed in Fig. 2 that the selectivity for CO oxidation was decreased along with the increase of reaction temperature. However, CO was still removed completely in the effluent at reaction temperatures between 40 and 60 °C, when the O₂ to CO ratio in the feed was 1 : 1, as shown in Fig. 2. Nevertheless, CO could not be removed completely when the O₂ to CO ratio was 0.5 : 1. Therefore, by adjusting the space velocity and the reaction temperature and using the ratio of O₂/CO = 1 in the feed,

Au/TiO₂ can be applied for removing CO completely in a hydrogen rich stream with the presence of CO₂ and H₂O.

In this research, a deposition-precipitation method for the preparation of Au/TiO₂ is presented. Without any high temperature pretreatment, the catalyst possesses high activity and stability for oxidizing CO completely in a hydrogen rich stream (50% H₂) at ambient temperature, even in the presence of 15% CO₂ and 3% H₂O. Only O₂/CO = 1 of low ratio is required for the reaction.

One of the authors, J.-N. Lin, appreciates the learning acquired in the research group of Professor H. H. Kung (Northwestern University, USA) during March to June 2002.

Wen-Yueh Yu, Chien-Pang Yang, Jiunn-Nan Lin, Chien-Nan Kuo and Ben-Zu Wan*

Department of Chemical Engineering, National Taiwan University, Taipei, 106, Taiwan. E-mail: benzuwan@ntu.edu.tw; Fax: (+886)-2-2362-3040; Tel: (+886)-2-3366-3021

Notes and references

- 1 C. Song, *Catal. Today*, 2002, **77**, 17.
- 2 T. V. Choudhary and D. W. Goodman, *Catal. Today*, 2002, **77**, 65.
- 3 D. L. Trimm and Z. I. Önsan, *Catal. Rev.-Sci. Eng.*, 2001, **43**, 31.
- 4 A. F. Ghenciu, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 389.
- 5 G. Avgouropoulos, T. Ioannides, C. Papadopoulou, J. Batista, S. Hočevar and K. Matralis, *Catal. Today*, 2002, **75**, 157.
- 6 M. M. Schubert, A. Venugopal, M. J. Kahlich, V. Plzak and R. J. Behm, *J. Catal.*, 2004, **222**, 32.
- 7 D. Cameron, R. J. Holliday and D. T. Thompson, *J. Power Sources*, 2003, **118**, 298.
- 8 M. Haruta, Japanese Patent 08,295,502 A2 12, 1996.
- 9 T. V. Choudhary, C. Sivadinarayana, C. C. Chusuei, A. K. Datye, J. P. Fackler, Jr. and D. W. Goodman, *J. Catal.*, 2002, **207**, 247.
- 10 M. M. Schubert, V. Plzak, J. Garcke and R. J. Behm, *Catal. Lett.*, 2001, **76**, 143.
- 11 B. Schumacher, V. Plzak, M. Kinne and R. J. Behm, *Catal. Lett.*, 2003, **89**, 109.
- 12 B. Schumacher, Y. Denkwitz, V. Plzak, M. Kinne and R. J. Behm, *J. Catal.*, 2004, **224**, 449.
- 13 B. T. Qiao and Y. Q. Deng, *Chem. Commun.*, 2003, 2192.
- 14 J.-N. Lin, J.-H. Chen, C.-Y. Hsiao, Y.-M. Kang and B.-Z. Wan, *Appl. Catal., B: Environmental*, 2002, **36**, 19.
- 15 J.-N. Lin and B.-Z. Wan, *Appl. Catal., B: Environmental*, 2003, **41**, 83.
- 16 H.-S. Oh, J. H. Yang, C. K. Costello, Y. M. Wang, S. R. Bare, H. H. Kung and M. C. Kung, *J. Catal.*, 2002, **210**, 375.
- 17 M. Daté and M. Haruta, *J. Catal.*, 2001, **201**, 221.
- 18 M. Daté, M. Okumura, S. Tsubota and M. Haruta, *Angew. Chem., Int. Ed.*, 2004, **43**, 2129.