

SELECTIVE CO OXIDATION OVER SILVER COBALT COMPOSITE OXIDE CATALYSTS

Akkarat Wongkaew*

*Department of Chemical Engineering, Faculty of Engineering, Burapha University,
Bangsaen, Chonburi 20131, Thailand.*

Received March 2003; accepted October 2003.

ABSTRACT

The removal of CO containing in the reformed gas to ppm level has been extensively studied via selective CO oxidation method. This method is useful for fuel cell applications because the trace amount of CO containing in the reformed gas poisons the Pt anode at the electrode of PEM fuel cells. This leads to the lowers of the fuel cell efficiency. In this study, the activity of silver cobalt composite oxides as a catalyst to CO oxidation and selective CO oxidation in the simulated reformed gas were reported. It was found that the molar ratios of silver to cobalt of 1 to 3 and 1 to 5 were very active to CO oxidation at low temperatures (<50°C). These catalysts to selective CO oxidation were further investigated. The optimal O₂ concentration that added into the gas stream was 3%. It was also found that the presence of H₂O increased CO conversion but slightly changed selectivity to CO oxidation. Finally, the stability and the deactivation process were tested. It was shown that this catalyst was deactivated when methane formation occurred. The deactivation is an irreversible process due to carbon deposition.

Keywords : CO poisoning, silver cobalt composite oxide, PEM fuel cells, deactivation.

INTRODUCTION

Steam reforming of methanol (Amphlett et al., 1994) or partial oxidation of hydrocarbons (Houseman and Cerini, 1974) followed by water gas shift reaction (Bunluesin et al., 1998) are commonly used methods to produce H₂ for polymer

electrolyte fuel cells (PEFC). The gas composition from these processes contains 40-75% H₂, 15-20% CO₂, ~10% H₂O, 0-25% N₂, and 0.5 to 1% CO. CO contained in the gas stream seriously depresses the performance of PEM fuel cell by poisoning

the Pt-based anode electrode of PEM fuel cells (Schmidt et al., 1997; Lemons, 1990). Palladium-based membrane purification, methanation and selective catalytic CO oxidation are the methods of reducing CO in the gas stream to 10 ppm or less, necessary for operation of the fuel cell, with minimum loss of hydrogen. Of these three methods, selective CO oxidation is the most promising and economical approach. Many catalysts, especially noble metal supported oxide catalysts, such as Pt/ Al_2O_3 (Vlastnik et al., 1987), Ru/ Al_2O_3 (Oh and Sinkevitch, 1993), Rh/ Al_2O_3 (Kahlich et al., 1997), Au/ Mn_2O_3 (Sanchez et al., 1997) and Au/ Fe_2O_3 (Kahlich et al., 1999) were studied for the removal of CO contained in the gas stream to ppm level. The study of selective catalytic CO oxidation over transition metal catalysts is rare even though they are cheaper than noble metal supported catalysts.

This study describes the results of silver cobalt composite oxide for the CO oxidation and selective CO oxidation reaction.

EXPERIMENTAL DETAILS

Catalyst preparation

Composite oxides of silver/cobalt with different molar ratios (1:1, 1:3, and 1:5) were prepared by the coprecipitation method. AgNO_3 (Aldrich, 99.8%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka, 99.0%) were dissolved in deionized water. The total metal concentration of this solution was 0.1M. Na_2CO_3 solution (1.0M) was added to the metal solution with stirring at a rate of 2-3 ml/min. The resulting precipitate in the solution was aged at pH 8 for 3 hours. After aging, the precipitate was washed with hot deionized water several times for removing excess ions and then dried in a conventional oven at 110°C overnight. The obtained powder was ground and then sieved to 140 mesh. Finally, the catalyst was calcined in air at 200°C for 3 hours.

X-ray diffraction was used to identify the phases present in the samples. A Rigaku Rotating

anode X-ray diffractometer system generating $\text{CuK}\alpha$ radiation was used to obtain the XRD patterns. The BET surface area and average pore radius of catalysts were measured by an Autosorb-1 Gas Sorption System (Quantachrome Corporation).

Activity measurements

Catalytic carbon monoxide oxidation was performed in a tubular microreactor. The amount of the catalyst used was 70 mg. Reaction temperatures were measured with a K-type thermocouple in contacting the top of the catalyst bed. The activity was tested for CO oxidation with 1% CO in air and for selective CO oxidation in a mixture of 1% CO, 2% and 20% CO_2 , 0.5-5% O_2 , 0-2.6% H_2O , 40% H_2 and N_2 as balance. The total gas flow rate was 40 ml/min. Prior to the activity test, catalysts were purged with air at 120°C for 6 hours to eliminate the condensed water in the catalyst pores.

Outlet gas compositions from the reactor were analyzed by using a HP 5890 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). An 80/100 mesh carbosphere column was used to detect H_2 , CO, and CO_2 . To measure carbon dioxide, the oven temperature of GC was increased to 80°C. An ice cooled water condenser was used to trap excess water downstream of the reactor, before the outlet gas entered the GC.

Selectivity to CO oxidation is defined as the ratio of the amount of oxygen used for CO oxidation reaction to the total amount of oxygen consumed by the reactions.

RESULTS AND DISCUSSION

Catalyst characterization

The specific surface area of these catalysts was measured by BET method. It was found that with silver cobalt oxide molar ratios of 1 to 1, 1 to

3, and 1 to 5, surface area were 77, 127, and 89 m^2/g , respectively. The results from XRD showed that AgCoO and AgCoO_2 forms were present in the samples along with Ag_2O , Co_2O_3 , and CoO . This is due to the preparation technique (Gulari et al., 1999).

Catalytic CO oxidation activity

The molar ratio of silver to cobalt was varied in order to obtain the best catalysts for CO oxidation. As can be seen that from Figure 1, catalysts with molar ratios of silver to cobalt of 1 to 3 and 1 to 5 were highly active to CO oxidation at low temperatures ($\sim 50^\circ\text{C}$). For 1 to 1 molar ratio of silver to cobalt catalyst, CO conversion increased from 16% at 50°C to 100% at 110°C with $T_{1/2}$ of 78°C , where $T_{1/2}$ is defined as the temperature which reactants convert to products by 50%. These results imply that the amount of cobalt present in silver cobalt oxide catalyst strongly affects the activity of the catalyst. Gulari et al. (1999) investigated the activity of Co_2O_3 , Ag_2O and composite oxide of silver and cobalt on CO oxidation and found that Co_2O_3 ($T_{1/2} \sim 40^\circ\text{C}$) was more active to CO oxidation than Ag_2O ($T_{1/2} \sim 90^\circ\text{C}$), while the presence of both silver and cobalt elements showed the best performance for CO oxidation ($T_{1/2} \sim 38^\circ\text{C}$). These results were in agreement with the findings of Gulari et al. (1999) and Simonot et al. (1997) that the presence of cobalt in the catalyst enhances CO oxidation.

Selective CO oxidation

The performance of silver cobalt oxide catalysts was further investigated for 1 to 3 and 1 to 5 molar ratios for selective CO oxidation because both catalysts showed very good performance to CO oxidation at low temperature. The feed gas contained 1%CO, varying amounts of O_2 , 2-20% CO_2 , 0-2.6% H_2O , 40% H_2 and N_2 as balance.

Varying O_2 concentration in the gas feed

As shown in Figures 2 and 3, an increase of O_2 concentration in the gas feed from 0.5% to 5.25% dramatically increases CO conversion. For 1:3 molar ratio of Ag:Co, CO conversion reached maximum $\sim 38\%$ at 200°C when 0.5% O_2 was added into the gas feed. It was observed that methane formation at temperatures higher than 160°C . The higher CO conversion at high temperatures may be due to methane formation together with CO oxidation. Further increase in O_2 concentration in the gas feed increased maximum CO conversion to 80% at 180°C for 2.0% O_2 and 100% at 140°C for 5.25% O_2 . Again, it was observed that methane formation from the run with 2.0% O_2 at temperatures higher than 160°C but no methane formation was observed for the run with 5.25% O_2 . The appearance of methane as a by-product may be caused by the presence of cobalt oxide (Satterfield, 1980) and the competition between CO oxidation, H_2 oxidation and methanation reactions in the presence of small amounts of O_2 . The silver cobalt catalyst with the molar ratio of silver to cobalt 1:5 showed better performance to CO oxidation in the presence of H_2 than that catalyst with molar ratio of 1:3 did. As can be seen that from Figure 3, with 0.5% O_2 in the gas feed, CO conversion reached a maximum of 58% at 200°C . Methane formation was observed at temperatures greater than 150°C . An increase in O_2 concentration from 2% to 5.25% increased maximum CO conversion to 95% at 180°C and 100% at 120°C , respectively. Interestingly, when the addition of O_2 was greater than 2%, there was no methane formation observed for both catalysts. Since I could not measure the O_2 consumption due to the overlapping of the peak area of O_2 and N_2 , it was assumed that O_2 was used up at the temperature which CO conversion reached maximum. According to this assumption, selectivity on CO oxidation of this catalyst was $\sim 20\text{-}30\%$.

Water effect

Investigation of water effect was conducted by humidifying the feed. Gas feed contained 1% CO, 2.0% and 3.0% O₂, 2% CO₂, 2.6% water, 40% H₂ and balance with N₂. It was found that the addition of water has a positive effect to CO oxidation. Schryer et al. (1991) reported the beneficial effect of water vapor on the CO oxidation activity of platinumized tin catalyst. They explained this observation as a regeneration of surface hydroxyls. With 2% O₂ containing in gas feed, CO conversion increased from 88% for the run without H₂O to 93% for the run with 2.6% H₂O at 180°C, while CO conversion for gas feed containing 3% O₂ increases from 87% for the run without H₂O to 99.7% for the run with 2.6% H₂O at 150°C. Further investigation on the effect of water on selective CO oxidation should be conducted in order to obtain the performance of this catalyst for the whole range of temperatures studied.

Deactivation test

The result of deactivation test was shown in Figure 4. Silver cobalt 1:5 molar ratio catalyst was tested in 1% CO, 3% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and N₂ as balance at 150°C for 76 hours. It was found that CO conversion was constant at 99.72% with selectivity of ~20% (assumed all O₂ consumed by oxidation reactions). No methane formation was observed under this condition. After 76 hours, the temperature was decreased to 130°C and kept to this temperature for 63 hours. CO conversion dropped to 40% and was constant. Again there was no methane formation observed. The temperature was increased back to 150°C for 24 hours. CO conversion was constant at ~99.89%. Then O₂ concentration was decreased to 2% at 150°C, and it was found that CO conversion decreased to 85% with methane formation (CO+3H₂→CH₄+H₂O). As can be seen from the

reaction, in the presence of CO and H₂ methane formation could happen. The temperature was further decreased to 145°C in order to understand conditions that methane was formed and it was noticed that below 145°C the peak of methane disappeared from GC. The catalyst was kept under this condition for 183 hours and it was found that CO conversion slowly decreased from 83% to 54%. O₂ concentration was increased to 3% and CO conversion was observed. CO conversion was ~88%. Then the catalyst was purged with air at 180°C for 7 hours in order to regenerate the catalyst activity. It was found that the catalyst activity was not recovered by regeneration under oxidizing environment. These results indicated that methane formation caused permanent loss of active sites to CO oxidation. This may be due to carbon deposition blocking the active sites for the reactions or metal sintering.

CONCLUSIONS

1. Silver cobalt composite oxides with 1:3 and 1:5 molar ratios were highly active to CO oxidation. CO conversion reached 100% at low temperature (~50°C).
2. The optimum O₂ concentration for this catalyst to remove 1% CO from the simulated reformed gas was 3%.
3. Water has a positive effect on selective CO oxidation.
4. For long-term activity, carbon deposition or sintering of the catalyst may cause loss of activity of the catalysts. Therefore, this catalyst should not be operated under methane forming conditions.
5. Silver cobalt composite oxide is a good catalyst for the removal of CO in the reformed gas. It can be used to eliminate 1% CO to a single digit ppm level of CO with ~20-30 selectivity.

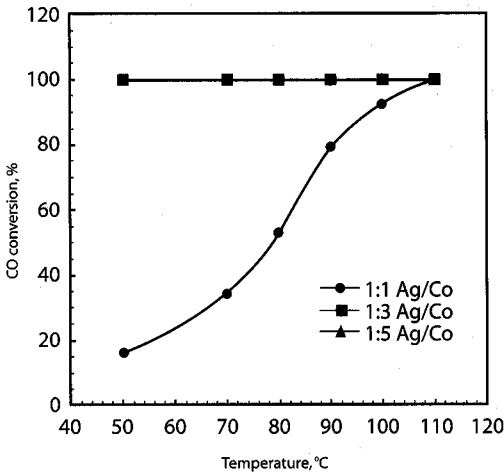


Figure 1. The activity of silver cobalt composite oxide with different molar ratios of silver to cobalt to CO oxidation as a function of temperature.

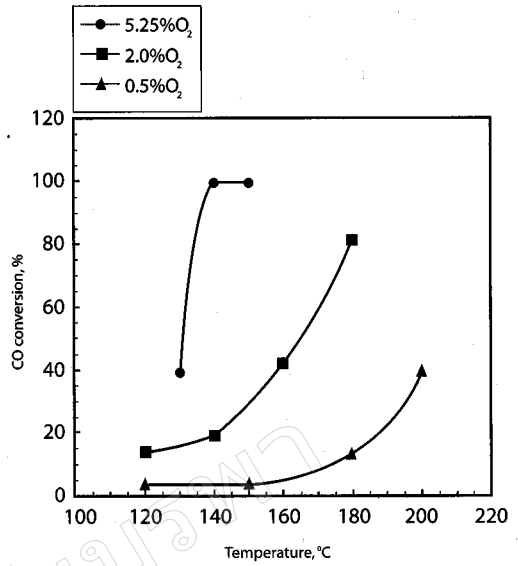


Figure 3. Dependence of CO conversion on O₂ concentration as a function of temperature for silver cobalt composite oxide with molar ratio of 1:5.

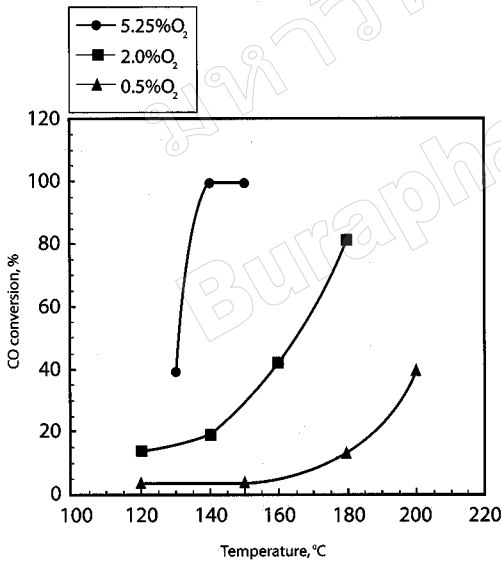


Figure 2. Dependence of CO conversion on O₂ concentration as a function of temperature for silver cobalt composite oxide with molar ratio of 1:3.

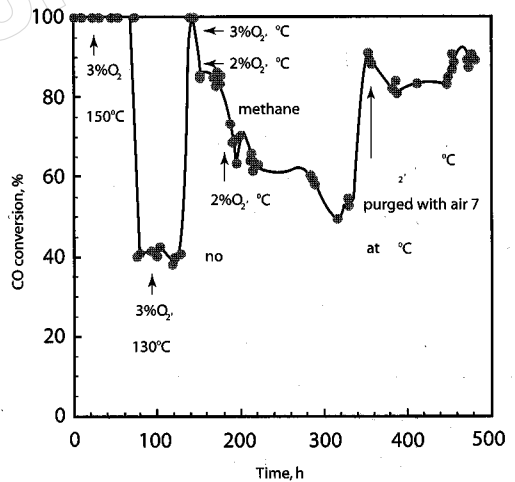


Figure 4. Deactivation test of silver cobalt composite oxide with molar ratio of 1:5. Gas composition: 1%CO, vary O₂, 2%CO₂, 2.6%H₂O, 40%H₂ and N₂ as balance.

REFERENCES

- Amphlett, J.C., Creber, K.A.M., Davis, J.M., Mann, R.F., Peppley, B.A., and Stokes, D.M. 1994. Hydrogen production by steam reforming of methanol for polymer electrolyte fuel cells. *International Journal of Hydrogen Energy* 19:131.
- Bunluesin, T., Gorte, R.J., and Graham, G.W. 1998. Studies of the water-gas-shift reaction on ceria-supported Pt, Pd, and Rh: Implications for oxygen-storage properties. *Applied Catalysis B: Environmental* 15:107.
- Gulari, E., Guldur, C., Srivannavit, S., and Osuwan, S. 1999. CO oxidation by silver cobalt composite oxide. *Applied Catalysis A: General* 182:147.
- Houseman, J., and Cerini, D.J. 1974, SAE Paper No. 740600.
- Kahlich, M., Schubert, M.M., Hutter, M., Noeske, M., Gesteiger, H.A., and Behm, R.J. 1997. Kinetics of the selective CO oxidation in H₂-rich gas on Pt/Al₂O₃. *Journal of Catalysis* 171:93.
- Kahlich, M.J., Gasteiger, H.A., and Behm, R.J. 1999. Kinetics of the selective low-temperature oxidation of CO in H₂-rich gas over Au/Fe₂O₃. *Journal of Catalysis* 182:430.
- Lemons, R.A. 1990. Fuel cells for transportation. *Journal of Power Sources* 29:251.
- Oh, S.H., and Sinkevitch, R.M. 1993. Carbon monoxide removal from hydrogen-rich fuel cell feed-streams by selective catalytic oxidation. *Journal of Catalysis* 142:254.
- Sanchez, R.M.T., Ueda, A., Tanata, K., and Manita, M. 1997. Selective oxidation of CO in hydrogen over gold supported on manganese oxides. *Journal of Catalysis* 168:125.
- Satterfield, C.N. 1980. "Heterogeneous Catalysis in Practice". McGraw-Hill Book Company, New York.
- Schmidt, V.M., Oetjen, H.-F., and Divisek, J. 1997. Performance improvement of a PEM using fuels with CO by addition of oxygen evolving compounds. *Journal of Electrochemical Society* 144:L237.
- Schryer, D.R., Upchurch, B.T., Hoflund, G.B., and Herz, R.K. 1991. Two-component catalysts for low-temperature CO oxidation: a Monte Carlo study. *Journal of Catalysis* 130:314.
- Simonot, L., Garin, F., and Maire, G. 1997. A comparative study of LaCoO₃, Co₃O₄ and LaCoO₃-Co₃O₄ I: Preparation, characterisation and catalytic properties for the oxidation of CO. *Applied Catalysis B: Environmental* 11:167.
- Vlastnik, V.J., Armellini, F.J., and Jordano, F.A. 1987. Preferential oxidation of CO over Pt/Al₂O₃ for fuel cell applications. Los Alamos National Laboratory.