Pt Catalyst Supported on Zeolite for Selective Oxidation of CO in Reformed Gases

Masahiro Watanabe,* Hiroyuki Uchida, Hiroshi Igarashi, and Miki Suzuki
Laboratory of Electrochemical Energy Conversion, Faculty of Engineering, Yamanashi Universiry, Takeda 4-3, Kofu 400

(Received September 27, 1994)

A new catalyst for the oxidative elimination of CO from the mixed gas with large excess H_2, in application to polymer electrolyte fuel cells, was developed. The catalyst consists of Pt nanocrystallites highly dispersed on A-zeolite. The catalyst is shown to exhibit a very high selectivity, for example, 10 times larger than Pt supported on alumina, under similar conversion levels. The possibility of achieving CO rejection to very small amounts is demonstrated with the proposed catalyst.

Polymer electrolyte membrane fuel cell (PEFC) has attracted a great interest as a power source of electric vehicles (EV) owing to the potential of high energy efficiency compared with the conventional combustion engines and to the zero-emission of air pollutants. The PEFC operates with pure hydrogen or reformed gases from methanol or natural gas as the fuel. Since the cell is operated at relatively low temperatures, *e.g.* 60–80°C, the anode catalyst is extremely sensitive to poisoning by carbon monoxide (CO) which remains in reformed gases to the extent of 100ppm.[1] Therefore, it is essential to develop a simple system which can accomplish low levels of CO (less than 100ppm) in large excess of H_2. One of the possibilities proposed was the oxidative elimination of CO using Pt catalyst supported on alumina (Pt/Al_2O_3)[2–5] in presence of 2% oxygen or air. However, this may lead to an accidental explosion since the O_2 content is close to the lower limit of explosion of mixed gas. Moreover, the amount of O_2 is much larger than the stoichiometric amount required for CO elimination. This would, in turn, result in wasteful consumption of H_2. Oh and Sinekevitch[6] recently reported that Ru/Al_2O_3 and Rh/Al_2O_3 were very active for the CO oxidation at 100 °C. Their results were obtained under relatively mild condition; gas composition of 900 ppm CO, 800 ppm O_2 and 0.85 vol% H_2 in N_2 background was used. Hence further experiments, in practical environments, are warranted.

Here we present a new catalyst comprised of highly dispersed metals such as platinum in A-zeolite. This is found to selectively oxidize CO with nearly stoichiometric amounts of O_2. Platinum catalyst supported on A-zeolite (denoted as Pt/AZE) was prepared as follows. Parent Na-A zeolite was ion-exchanged with aqueous solution of $[Pt(NH_3)_4]Cl_2$, filtered and washed well with distilled water. The resulting solid was dried by carefully increasing the temperature stepwise from room temperature to 50 °C, under vacuum using an aspirator and subsequently with a vacuum pump having a liq. N_2 trap. It was then ground and sieved with 80–100 mesh. The resulting powder was baked at 500 °C in air and H_2 for 1 h, respectively. As a reference to the Pt/AZE, Pt/Al_2O_3 was prepared by impregnating γ-Al_2O_3 (specific surface area; 160 m^2/g) with H_2PtCl_6 solution, followed by the processes similar to those for Pt/AZE to get the powder with 80–100 mesh. The powder was baked at 150 °C in air for 3 h and at 500 °C in H_2 for 15 h. Platinum loading on Pt/AZE and Pt/Al_2O_3, was determined to be 6.4%, by ICP analysis. X-ray diffraction did not reveal the presence of Pt nanocrystallites in the catalysts, both before and after the selective CO oxidation reaction. This could be due to the nanosized, probably less than 3 nm, nature of the Pt particles. The oxidation of CO was carried out in a flow reactor of 0.4 cm in diameter kept at desired temperatures ranging from 150 to 350 °C. The composition of the gaseous mixture used was 1% CO, 0.5–2.5% O_2 and the balance of H_2 and various contact times (W/F) of 0.06–0.24 g s cm^{-3} (the flow rates of 25–100 cm^3 min^{-1}) over 0.1 g of catalysts were used. The CO content was chosen based on the levels accepted for the reformed gases used conventionally in phosphoric acid fuel cells. The products were analyzed by gas chromatography after the steady state was achieved.

As shown in Figure 1, CO conversion increases proportionally with increasing contact time and approaches values of 95% and above, at temperatures lower than 250 °C. However, the maximum conversion is found to decrease with temperatures above 250 °C and this may be ascribed to the enhanced consumption of O_2 in the H_2 oxidation.

The effect of O_2 concentration on the CO conversion is shown in Figure 2. It is clear that the CO conversion increases with increase in O_2 concentration in the feed, and the conversion at 250 °C is found to be larger than at 200 °C. A conversion of 95% was achieved at 2% O_2 concentration, at a temperature of 250 °C. The gross O_2 conversion are also shown in Figure 2. It can be seen that the gross O_2 conversions are approximately constant over different O_2 concentrations in the feed. However, the gross oxygen conversion at 250 °C is 100% while it is only 50% at 200°C. It becomes apparent that the excess O_2, over the stoichiometric amount needed for CO oxidation (0.5%), is consumed by H_2 oxidation, when the temperatures are sufficiently elevated.

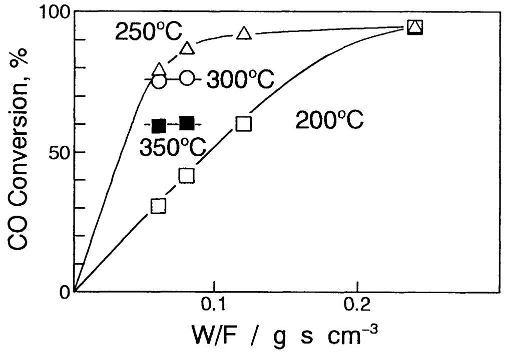

Figure 1. Contact-time dependencies of the catalytic oxidation of CO over Pt/AZE in a gas mixture (1% CO, 1% O_2 and the balance H_2) at a series of temperatures.

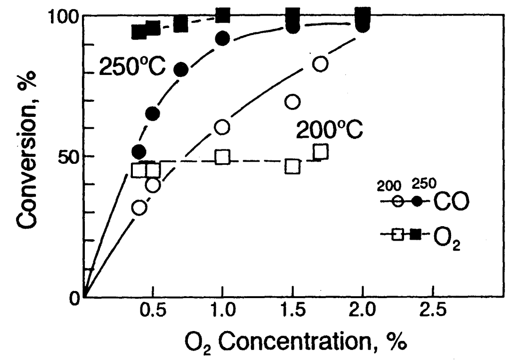

Figure 2. Effects of O_2 concentration in mixed gases (1% CO + H_2) on the CO conversion (○,●) and on the gross O_2 conversion (□,■) over Pt/AZE at 200 °C (○,□) and 250 °C (●,■) under W/F= 0.12 g s cm^{-3} (flow–rate; 50 cm^3 min^{-1}).

Enhanced H_2 consumption by the excess O_2 was observed on Pt/Al_2O_3 (Figure 3) compared to that on Pt/AZE. It is obvious, even at 150 °C, that the conversion of CO to CO_2 is *ca.* 80% while the gross O_2 conversion is 100%, resulting in the low selectivity for the CO oxidation. The fractions of O_2 used for CO and H_2 oxidation are plotted in the same figure. The former was smaller than the latter even at low reaction temperature. *i.e.* only 40% of O_2 was consumed for CO while the remaining 60% was consumed for H_2 oxidation at 150 °C.

The fractions of O_2 consumption for the oxidation of CO and H_2 on Pt/AZE, as a function of O_2 content in the feed, are shown in Figure 4(A) as a function of O_2 content. At 200 °C, about 90% of O_2 is consumed for CO oxidation at a concentration of 0.5% O_2 in the feed, while it is 62% at a concentration of 1% O_2 in the feed gas. It is clear that the conditions of low O_2 content and low temperatures favor selective CO oxidation. "Selectivity" of O_2 consumption to CO oxidation is defined as the ratio of (O_2 conversion to CO_2) to (O_2 conversion to H_2O). Figure 4(B) shows the CO selectivity as a function of O_2 content, for Pt/AZE and Pt/Al_2O_3 catalysts. The selectivity on Pt/Al_2O_3 is less than unity even at 150 °C, and this is almost independent of O_2 content. In contrast, an enhanced selectivity is obtained on Pt/AZE with decreasing O_2 content. It should be pointed out that exceptionally high selectivity is obtained for Pt/AZE catalyst at 0.5% O_2 in the feed and at 200 °C reaction temperature, despite the fact that the CO conversion, as predicted from the data at 1% O_2 and 200 °C (Figures 3 and 4(A)), is slightly lower than that of Pt/Al_2O_3. These results indicate that the selectivity and the conversion of Pt/AZE catalyst can be improved by lowering the reaction temperature and/or by supplying a small excess of O_2, preferably into integrated reaction zones of Pt/AZE. The disadvantage of lowering the temperature can be overcome by increasing the W/F and it is expected that nearly 100% conversion of CO could be achieved without sacrificing the selectivity.

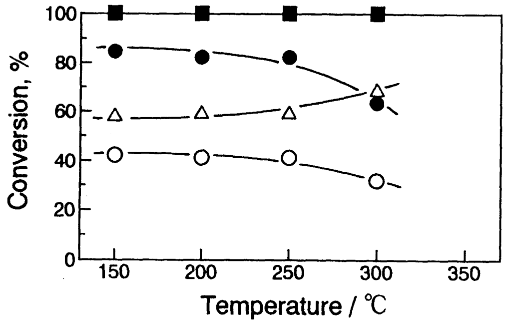

Figure 3. Effects of the reaction temperature on the gross O_2 conversion (■) and the CO conversion (●) or on the fractions of O_2 consumption for the oxidation of CO (○) and H_2 (△), respectively, over Pt/Al_2O_3 in mixed gases (1% CO + 1% O_2 + H_2) under the same W/F as that of Figure 2.

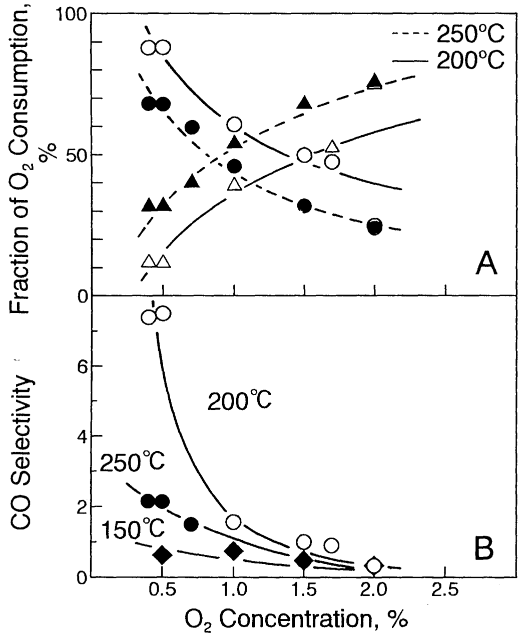

Figure 4. Effects of O_2 concentration in mixed gases (1% CO + H_2) on the fractions of O_2 consumption for the oxidation of CO(○,●) and H_2(△,▲), shown in (A), and the effects on the selectivities for the oxidation of CO to CO_2, shown in (B), over Pt/AZE(○,●) or over Pt/Al_2O_3(◆) under the same W/F as that of Figure 2.

In conclusion, the newly proposed Pt/AZE catalyst showed exceptionally high selectivity for the oxidative elimination of CO from the 1% mixed gas with large excess H_2; 10 times larger than the selectivity of Pt/Al_2O_3 under similar conversion levels. The potential of CO rejection to very low levels have been demonstrated for Pt/AZE.

References

1 S. Gottesfeld and J. Pafford, J. Electrochem. Soc., **135**, 2651 (1988); S. Gottesfeld, U.S. Patent 4910099 (1990).
2 J. G. E. Cohn, U.S. Patent 3216783 (1965).
3 J. C. Bonacci, U.S. Patent 4238468 (1980).
4 N. E. Vanderborgh, C. A. Spirio, and J. R. Huff, Extended Abstracts of the International Seminar on Fuel Cell Technology and Applications, The Hague, The Netherlands, Oct. 1987, p. 253.
5 N. V. Vanderborgh, J. Guante, R. E. Dean, and R. D. Sutton, Abstracts of the Fuel Cell Seminar, long Beach CA., Oct. 1988, p. 52.
6 S. H. Oh and R. M. Sinkevitch, J. Catalysis, **142**, 254 (1993).