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NOTE

Selective Oxidation of CO in Hydrogen over Gold Supported on Manganese Oxides

Polymer electrolyte fuel cells (PEFC), as used in electric vehicles, operate at relatively low temperatures between 350 and 400 K (1). When hydrogen-rich fuel is produced from methanol, by the steam reforming and water gas shift reaction processes, the Pt anodes at these low temperatures are often poisoned by incomplete combustion products such as CO, reducing the overall fuel cell performance. Under normal running conditions the product hydrogen stream contains 25 vol% CO_2, a few vol% H_2O, and about 0.5–1 vol% CO. Thus, in order to obtain optimum performance the total concentration of CO in the gas stream should be reduced if possible to below 100 ppm.

Of the techniques available for removing CO, selective catalytic oxidation with molecular oxygen is the simplest and most cost effective. Oxidation of CO can be achieved over several catalyst systems; Oh and Sinkevitch have reported that Ru/Al_2O_3 and Rh/Al_2O_3 are active and selective for CO oxidation in H_2 diluted with N_2 at 403 K (2). Watanabe and his co-workers have also shown that at higher temperatures Pt/A-type zeolite exhibits good selectivity to CO oxidation in H_2 (3). However, since supported gold catalysts are, in contrast to Pt-group metal catalysts, intrinsically more active for CO oxidation than for H_2 oxidation (4), and since the catalytic activity of Au is enhanced by moisture (5) and almost insensitive to CO_2 (6), it has been decided to explore the use of supported gold catalysts in PEFCs.

To develop PEFCs for general use it is necessary to make catalysts that are able to operate at low temperature, that work in the presence of CO_2 and H_2O, and which have the ability to selectively remove CO from reformed gas by oxidizing CO to CO_2, while at the same time being inactive for the oxidation of H_2. Through the screening of support materials which give the largest difference in catalytic activity between the oxidation of CO and H_2 (4, 7, 8), we found Au/MnOx to be one of the best candidates for the removal of CO from hydrogen-rich fuel gases. Gold supported on manganese oxides has also been investigated by Hoflund and co-workers for CO oxidation reaction in an inert gas background (9) and by Iwasawa and his co-workers for the preparation method by use of an organo gold complex in the liquid phase (10, 11). Because supported gold catalysts prefer oxidizing pretreatments (12), our major concern has been whether Au/MnOx is stable in H_2.

Gold supported on Mn oxides was prepared by coprecipitation of an aqueous solution of $HAuCl_4$ and $Mn(NO_3)_2$ with an aqueous solution of Li_2CO_3 (13). The coprecipitates were washed several times until the pH of the supernatant reached a steady value and then filtered and dried overnight under vacuum, before finally calcining in air at 573 K.

Catalytic activity measurements were carried out in a micro fixed-bed reactor, with 0.20 g of catalyst sieved to 70 and 120 mesh (particle size 212–125 μm). The feed gas for the oxidation in air was 1.0 vol% H_2, or CO balanced with air to 1 atm. The feed gas composition for the oxidation of CO in hydrogen was 1.0 vol% CO, 1.0 vol% O_2, and H_2 balance. The flow rate was 33 ml/min (space velocity: $10^4\ h^{-1} \cdot$ ml/g-cat.). The concentration of CO in the effluent gas was analyzed by a gas chromatograph with a molecular sieve 13X column. The minimum detection level of CO was ca. 10 ppm.

The crystalline structure of Mn oxide support and the mean particle diameter of Au were analyzed by means of a Rigaku X-ray powder diffractometer (RU-200) with Ni-filtered Cu$K\alpha$ radiation. Crystallite sizes of Au were estimated from peak half-widths by using Scherrer's equation with corrections for instrumental line broadening.

Figure 1 shows that CO oxidation over Au/MnOx catalysts reaches 100% conversion at temperatures below 273 K, while H_2 oxidation takes place only at temperatures above 273 K. The temperature difference depends on Au content and is larger at an atomic ratio of $Au/Mn = 1/50$ than at $Au/Mn = 1/19$. The rates of CO oxidation at 243 K normalized to the total amount of gold are 4.2×10^{-3} and $6.5 \times 10^{-4}\ s^{-1}$ for $Au/Mn = 1/50$ and 1/19, respectively, while the normalized rates of H_2 oxidation at 423 K are 9.3×10^{-4} and $1.8 \times 10^{-3}\ s^{-1}$, respectively. The fact that the catalyst with $Au/Mn = 1/50$ exhibits a higher catalytic activity for CO oxidation may be explained by the fact that the turnover frequency based on the number of surface gold atoms exponentially increases with a decrease in particle diameter (8). Thus because the particle size in the Au/MnOx catalyst with 1/50 loading can be assumed from our experiences to be smaller than that with 1/19 (experimental confirmation

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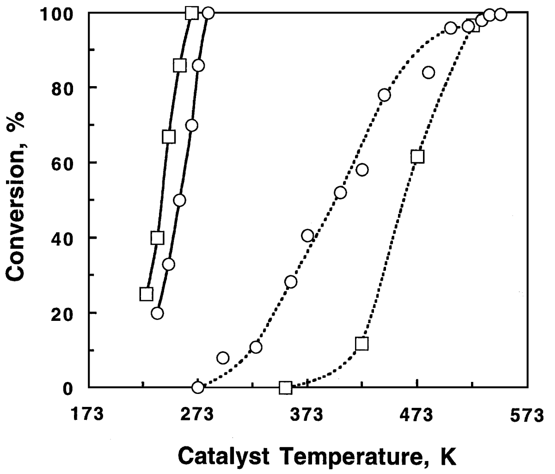

FIG. 1. Oxidation of CO and of H_2 in air over Au/MnOx catalysts. Au/MnOx catalysts were prepared by calcination in air at 573 K. □, Au/Mn = 1/50; ○, Au/Mn = 1/19; solid lines, oxidation of 1 vol% CO in air; dotted lines, oxidation of 1 vol% H_2 in air; space velocity, $10^4\ h^{-1} \cdot$ ml/g-cat.

was difficult because of the dark contrast in TEM), the overall activity increases.

Figure 2 shows, however, that even in H_2 streams CO can be selectively oxidized over the Au/MnOx catalyst with 1/50 Au/Mn loading. The conversions of CO are over 95% at temperatures of 323 to 353 K. At this temperature range the catalytic activity is stable for 2 days and importantly is observed to improve with time on stream. The conversion of CO in H_2 at 289 K however tends to go down to 50% with time on stream although it reaches 100% in air (see Fig. 1). The conversion of CO in H_2 at 393 K is ca. 85%, implying that at a higher temperature O_2 is competitively consumed by H_2.

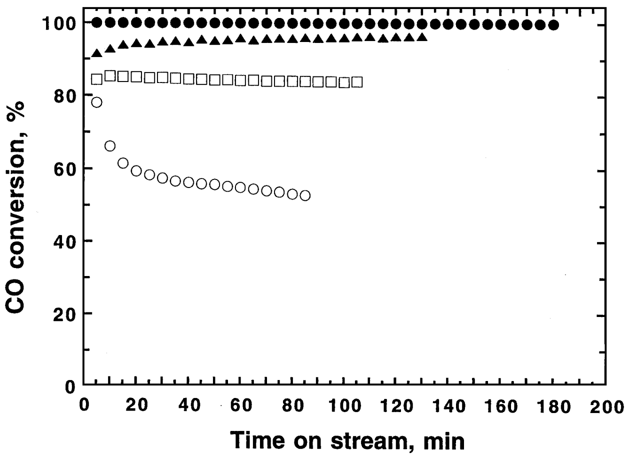

FIG. 2. Time-on-stream change of CO conversion over Au/MnOx (Au/Mn = 1/50) at different temperatures in a feed stream containing 1.0 vol% CO and 1.0 vol% O_2 in an H_2 background. The catalyst was prepared by calcination in air at 573 K. Catalyst temperature: ○, 289 K; ●, 323 K; ▲, 353 K; □, 393 K. Space velocity, $10^4\ h^{-1} \cdot$ ml/g-cat.

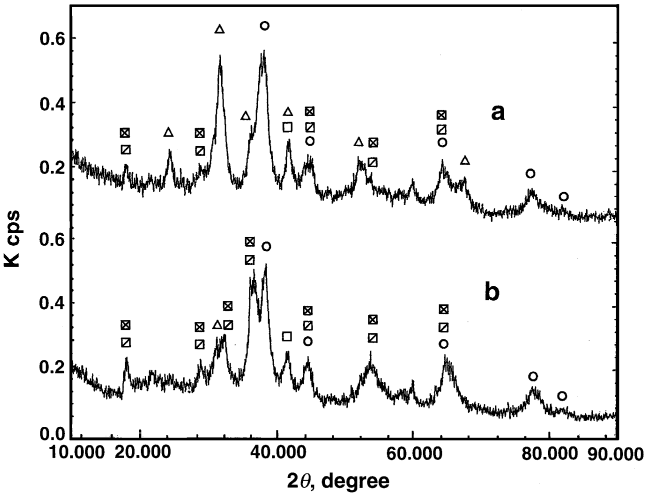

FIG. 3. XRD patterns for the Au/Mn (1/50) coprecipitate calcined at 573 K before and after reaction. (a) Fresh sample before catalytic activity measurements; (b) after catalytic activity measurements at 393 K. ○, Au; △, $MnCO_3$; □, MnO; ⧄, Mn_3O_4; ⊠, Mn_2O_3.

The morphology of the Au–Mn coprecipitate calcined in air appears neither simple nor homogeneous in TEM, which is very different from that of Au–Fe coprecipitates (4). In TEM photographs one can observe densely packed Mn compounds which gave very dark contrast in TEM and loosely coagulated Mn compounds which were composed of primary particles of about 10–100 nm in diameter. The latter part contained much more Au than the former part.

Figure 3 shows X-ray diffraction patterns for the Au/Mn (1/50) coprecipitate before and after catalytic reaction. The sample calcined in air at 573 K consists mainly of metallic gold particles and $MnCO_3$. After catalytic activity measurements for CO oxidation in H_2 for 1 day, even though the catalyst temperature was raised only to 393 K, decomposition of $MnCO_3$ occurred to form crystalline manganese oxides, MnO, Mn_3O_4, and Mn_2O_3. This was accompanied by a sintering of the gold particles to give a mean particle diameter of 2.8 nm.

The transformation of $MnCO_3$ during reaction into Mn oxides, which may act as a more effective support for Au, can explain why the catalytic activities are stable and often increase gradually with time on stream. The reversible transformation between the three manganese oxides, MnO, Mn_3O_4, and Mn_2O_3, depends on the O_2 concentration and temperature, which may perhaps explain why Au on Mn oxides is stable in H_2 atmospheres.

In comparison with the Pt/A-zeolite catalysts (3) which are active at temperatures above 470 K under similar reaction conditions, the Au/MnOx catalyst is able to operate at temperatures below 400 K in the downstream when connected directly to the PEFCs. The gold catalyst has also been found to be resistive to both CO_2 and H_2O contained in the feed stream with a wide range of concentrations. It seems to offer numerous advantages over Pt-based catalysts in that the CO conversion is larger, readily exceeding 95%, and that the selectivity for hydrogen conversion is smaller than that for CO.

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