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Hydrogen and CO Adsorption Property of Pd Particles on SnO_2 and Their Application to Electrode Catalysts

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Pt and Pd catalysts supported on SnO_2 were prepared by the impregnation method. Even at room temperature, the PdO particles in PdO/SnO_2 were easily reduced to metallic Pd and absorbed H_2 with the H_2/Pd weight ratio of 0.3 %. Adsorption of CO on PdO/SnO_2 and Pt/SnO_2 samples was significantly suppressed because of the interaction between the precious metals and SnO_2; the metal surface area was difficult to estimate by the CO pulse technique. The Pt/SnO_2-containing electrode can function as oxidation catalyst selective to H_2 in CO/H_2 mixture because it selectively adsorbed H_2.

Key words: Pt/SnO_2, PdO/SnO_2, CO adsorption, Support effect

1. INTRODUCTION

Recently much attention has been paid to effective hydrogen production, since hydrogen is used as fuel for polymer electrolyte fuel cells. When natural gas is reformed with steam to produce hydrogen, considerable amount of CO is also produced. The platinum anode of polymer electrolyte fuel cells is poisoned by CO adsorption in the reformed fuel. Therefore, CO must be removed by shift reaction and selective combustion reaction. However, this complicated system can reduce the efficiency of the fuel cell system. If functional materials, which selectively adsorb H_2, are produced, these can be used as electrode catalysts. It has previously been reported that high dispersion of PdO can be achieved by employing SnO_2 as a support [1-4]. In the present investigation, hydrogen and CO adsorption property of Pd and Pt particles on SnO_2 was investigated. The strong chemical interaction between the components has been confirmed. The electrochemical activity was examined.

2. EXPERIMENTAL

2.1 Catalyst preparation

Palladium and platinum catalysts were prepared by the impregnation method. The SnO_2 support (Wako Pure Chemical Industries, Ltd.) was impregnated with an aqueous solution of $Pt(NO_2)_2(NH_3)_2$ and $Pd(NO_2)_2(NH_3)_2$ (Tanaka Kikinzoku Kogyo K.K.). The mixture was kept on a steam bath at 80°C until the solution evaporated. The dried powders were calcined at 400°C for 40 min and reduced in 10% H_2 diluted with N_2.

For electrode catalyst, above-mentioned catalyst with a precious metal loading of 20wt.% was reduced in 10% H_2/N_2 stream for 30 min at 90 and 400°C. A sample without this reduction treatment was also used as an electrode catalyst. 10 mg of the catalyst powder was dispersed in 5-ml ethanol, and then, 25 μl of this mixture was dropped onto a glassy carbon electrode with a surface area of 0.07 cm^2 and dried. Accordingly, electrode catalyst loading on the glassy carbon electrode was 0.057 mg/cm^2. Subsequently, 25 μl of a mixture of 1wt.% Nafion (Aldrich) and

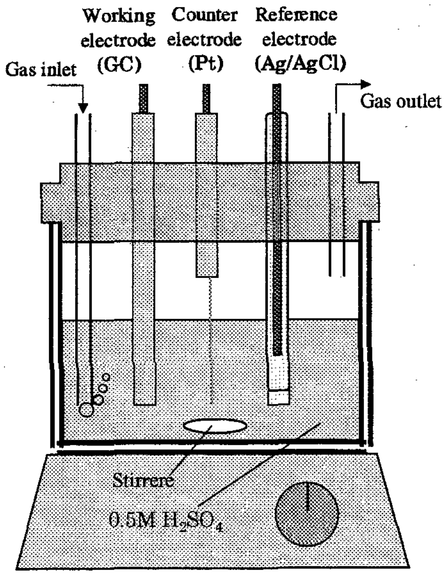

Fig. 1 Apparatus for electrochemical oxidation

carbon black (Vulcan XC-72, Cabot) with a carbon black content of 10 mg/ml was dropped to the electrode surface. After dried in ambient conditions, the electrode was used as a working electrode.

2.2. Characterization of the catalysts

The samples were characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), BET surface and IR spectra.

Temperature-programmed reduction was performed in a quartz tube reactor, and the amount of consumed hydrogen was measured by a TCD detector. A weighed amount (25 mg) of the sample after calcination was placed in the reactor, and the 5% H_2 – 95% Ar gaseous mixture was fed to the reactor at 25 ml/min. The temperature was raised to 800°C at a heating rate of 10°C/min. The amount of H_2 was detected by TCD. BET surface area was measured by N_2 adsorption at the liquid nitrogen temperature.

2.3. Electrochemical experiment

Anodic voltammetry experiments were carried out in 0.5M H_2SO_4 with usual three-electrode arrangement in a electrochemical cell as shown in Fig. 1 using Solartron 1287 electrochemical interface. A platinum rod with an outer diameter of 6.0 mm and Ag/AgCl (NaCl saturated) were used as counter and reference electrodes, respectively. The reference electrode has a potential of E = +0.212 V versus the reversible hydrogen electrode (RHE) and all potentials were referred to the RHE, unless otherwise noted. Before anodic voltammetry measurements, nitrogen purging was done by bubbling nitrogen for 15 min to remove oxygen dissolved in 0.5M H_2SO_4. In the case of CO-stripping voltammograms, after CO was supplied to the electrochemical cell for 1 hour, bulk CO was removed by bubbling nitrogen through it for 15 min. The CO-stripping voltammograms were measured between −0.2 and 1.2 V (vs. Ag/AgCl) with a scan rate of 20 mV/s at room temperature. Voltammograms of H_2 electrooxidation was measured by feeding H_2 as bubble at 5 ml/min to the working electrode in the range of −0.2 and 1.2 V (vs. Ag/AgCl) with a scan rate of 2 mV/s at room temperature.

3. RESULTS AND DISCUSSION

3.1 Characterization of PdO/SnO_2 prepared by the impregnation method

The BET surface area of SnO_2 was 4.0 m^2/g, but the BET surface area of PdO/SnO_2 and Pt/SnO_2 increased with an increase in precious metal loading. The surfaces area of precious metal can be roughly estimated by subtracting the surface area of SnO_2 (SnO_2 weight x 4.0 m^2/g) on the assumption that precious particles were dispersed on SnO_2. The precious metal particle diameter can be estimated by 6V/S to be *ca.* 10 and 4 nm for PdO and Pt, respectively, as listed in Table 1.

Temperature-programmed reduction of PdO/SnO_2 was carried out as shown in Fig. 2. Reduction of SnO_2 was observed at around 780°C. The reduction of SnO_2 initiated at slightly lower temperature and the peak was broadened with an increase in PdO content. This may be caused by hydrogen that was supplied from reduced Pd particles and facilitated reduction of SnO_2. While the PdO particles on ZrO_2 started to be reduced at around 80°C, as indicated by the positive peak, a negative peak due to hydrogen desorption was observed for PdO/SnO_2 at 60°C. A part of the palladium in PdO/SnO_2 may have been easily reduced to Pd/SnO_2 even at room

Table 1 . Physical properties of PdO/SnO_2 and Pt/SnO_2

Catalyst	BET surface area (m^2/g)	The amount of CO adsorbed[a] (μmol/g)	Particle diameter of PdO or Pt (nm)	H_2/Pd weight ratio (%)
1.1 wt% PdO/SnO_2	4.9	n.a.	8.0	-
5.7 wt% PdO/SnO_2	7.6	n.a.	10.3	0.29
11 wt% PdO/SnO_2	11	28	11.1	0.32
22 wt% PdO/SnO_2	18	33	10.6	0.35
5 wt% Pt/SnO_2	9.0	n.a	3.3	
10 wt% Pt/SnO_2	13.4	n.a	3.2	
20 wt% Pt/SnO_2	20.8	n.a	3.4	
40 wt% Pt/SnO_2	21.6	86	6.0	
50 wt% Pt/SnO_2	16.6	100.	9.9	-

a) The amount of CO adsorbed was measured after reduction at 350°C;
n.a. means no adsorption was observed.

temperature after the switch of the atmosphere into hydrogen at 25°C; then hydrogen was stored in metallic Pd particles as hydride. The observed desorption can be ascribed to the decomposition of hydride partially formed in the sample.

As shown in Table 1, Pd/SnO_2 adsorbed very little CO. These phenomena had been interpreted as the formation of Pd-Sn alloy of surface of Pd particles [5] or as the strong interaction between dispersed Pd and SnO_2[6]. Therefore, it is concluded that the metallic Pd on SnO_2 hardly adsorbs CO when they are in a strong interacting state. Although the amount of H_2 desorbed from the catalyst increased, the H_2/Pd weight ratio was essentially identical to 0.30%. This indicates that H_2 is stored on only a part of the Pd particles.

FITR spectra of CO adsorbed on reduced catalysts were observed as shown in Fig. 3. For 1.1 wt% PdO/Al_2O_3, the IR spectrum can be attributed to the bands from CO species adsorbed physically and chemically on Pd particles. As indicated in the spectra (a) for Pd/Al_2O_3 and (c) for Pd/SnO_2, the bands at 2120 cm^{-1} and 2180 cm^{-1} can be attributed to the physisorbed CO, whereas that at 2080 cm^{-1} for (a) can be attributed to the linear CO species, and those at around 1850 cm^{-1} to the bridged CO species. The bands for physisorbed CO disappeared on purging with He. On the other hand, the band intensities for CO chemisorbed at 2080 and 1850 cm^{-1} did not change by purging CO with He for 5 min, as shown in the spectrum (b). However, in the spectrum (c) for 1.1 wt% PdO/SnO_2, only physically adsorbed CO was observed in CO-containing atmosphere. Therefore, no peaks were observed after purging with He, as shown in the spectrum (d).

The XRD pattern of Pt/SnO_2 is shown in Fig. 4. The sharp SnO_2 lines were predominant for the samples (a) after calcinations in air at 400°C. After reduction at 90°C, a broad peak assigned to Pt was observed at around 40°. Although peak separation was difficult, the crystallite size of Pt is small; this order corresponded to that of the diameter of Pt particles (3.4 nm) estimated from the increase in BET surface area (b). However, if it was reduced at 400°C, $PtSn_2$ and $PtSn_4$ compounds was observed.

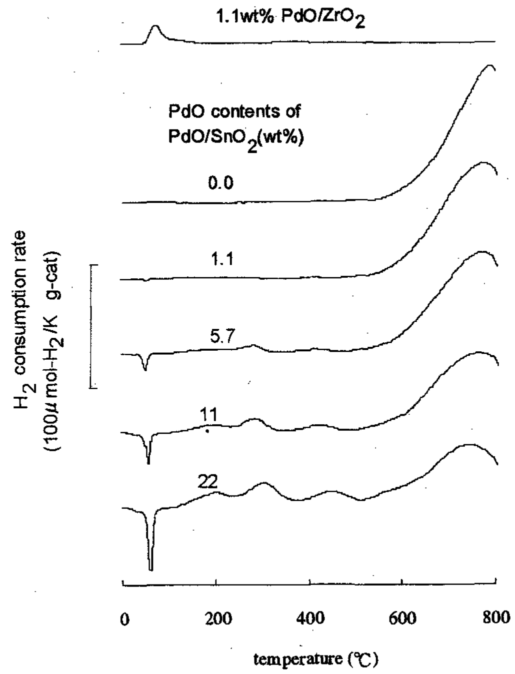

Fig. 2. Temperature-programmed reduction of PdO/SnO_2 with various Pd loadings:
Feed gas: 5.0% H_2- 95% Ar; heating rate: 5.0°C/min.

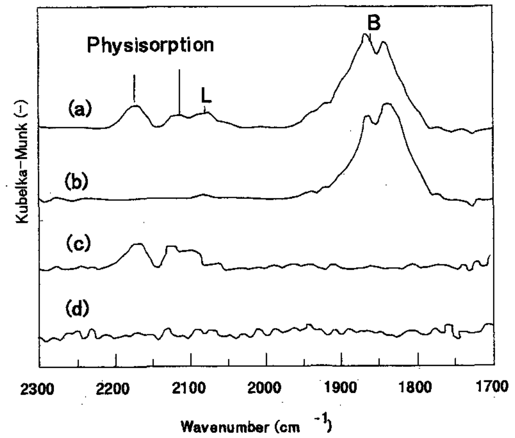

Fig. 3. FTIR spectra of CO adsorbed on Pd particles of the samples prepared by reduction of supported PdO catalysts: (a), CO adsorbed at 1.0 kPa on reduced 1.1 wt % PdO/Al_2O_3; (b), after flushing with He for 5 min; (c), CO adsorbed at 1.0 kPa on reduced 1.1 wt % PdO/SnO_2; (d), (c) after flushing with He for 5 min.

3.2 Anodic voltammetry

Results of CO-stripping voltammetry were shown in Fig. 5. In the case that adsorbed species exist, complete oxidation of the adsorbed species was accomplished in a single scan; no oxidation current was monitored during the second scan. When the as-calcined Pt/SnO_2 electrode catalyst, namely the catalyst without reduction treatment, was used (a), both H_2 oxidation and CO oxidation were observed. This indicates that Pt/SnO_2 adsorbs both CO and H_2. The peak potential of CO oxidation over Pt/SnO_2 electrode catalyst was 0.76 V, whereas that over commercial Pt/C (Johnson Matthey)

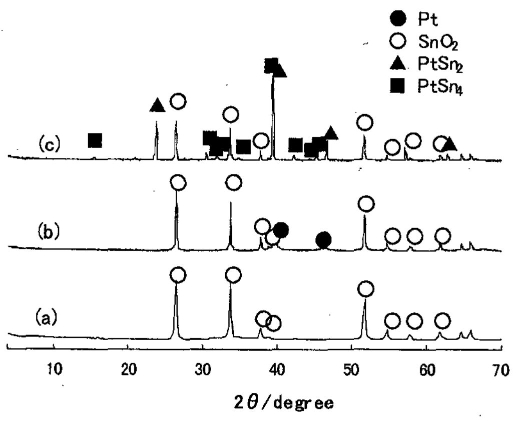

Fig. 4 XRD pattern for Pt/SnO_2
a) calcined at 400°C
b) calcined at 400°C and reduced at 90°C
c) calcined at 400°C and reduced at 400°C

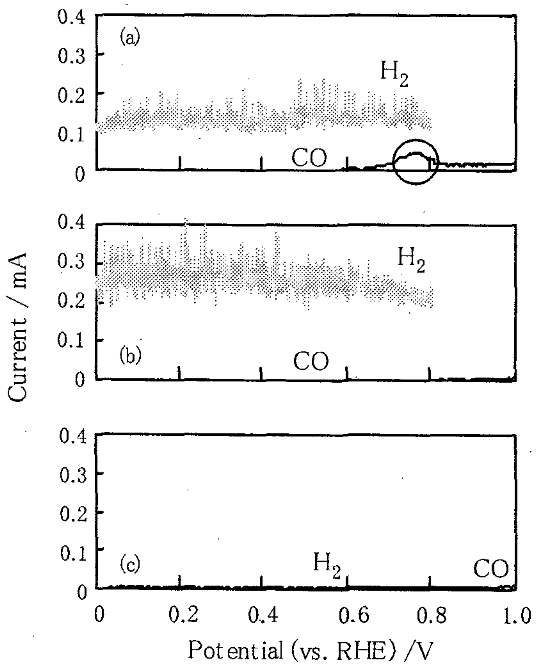

Fig. 5 Anodic voltammetry on Pt/SnO_2
a) calcined at 400°C
b) calcined at 400°C and reduced at 90°C
c) calcined at 400°C and reduced at 400°C

measured in the identical conditions was 0.82 V. In addition to the peak shift of CO electrooxidation to lower potential, the potential for the onset of CO electrooxidation over Pt/SnO_2 also shifted to lower value, when it is compared to that over Pt/C. These results suggest that CO is adsorbed onto Pt of the Pt/SnO_2 more weakly than to Pt of the Pt/C. When Pt/SnO_2 was reduced at 400°C after calcination in air (c), neither CO nor H_2 electrooxidation current was observed. This means that neither CO nor H_2 is adsorbed onto the catalyst after high temperature reduction treatment. As indicated by the XRD measurement shown in Fig. 4, intermetallic compounds were formed after the high temperature reduction treatment at 400°C, giving rise to no adsorption of CO or H_2. On the other hand, when Pt/SnO_2 was reduced at 90°C (b), no CO oxidation was observed, while H_2 oxidation was observed. This indicates that Pt/SnO_2 reduced at 90°C selectively adsorbed H_2, and did not adsorb CO. This electrode had electrochemical activity for electrooxidation of H_2. Therefore, this material can be applied to fuel cell as a CO-tolerant anode, because it adsorbed H_2 without adsorbing CO.

4. CONCLUSION

The physical property of PdO/SnO_2 was quite different from ordinarily supported PdO catalysts. The PdO and Pt particles were dispersed on SnO_2 even at high loading. A part of PdO particles were reduced to metallic particles even at room temperature. The Pd and Pt particles dissociatively adsorb H_2, while the reduced Pd/SnO_2 and Pt/SnO_2 species in strong chemical interaction adsorbs very little CO. However, high temperature reduction produced $PtSn_2$ and $PtSn_4$ or $PdSn_2$ and $PdSn_4$ compounds, resulting in no adsorption of CO or H_2.

5. ACKNOWLEDGEMENTS

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