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RESEARCH NOTE

CO Oxidation below Room Temperature over Ir/TiO_2 Catalyst Prepared by Deposition Precipitation Method

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Iridium was supported on TiO_2 and other metal oxides by the deposition precipitation method and was examined for the oxidation of CO and of H_2. Iridium supported on TiO_2 was active at temperatures below room temperature for CO oxidation and was much more active than Ir/SnO_2, Ir/Al_2O_3, and Ir/Fe_2O_3. TEM observations showed that Ir was spread over the TiO_2 surface as a thin layer, 2 nm thick, the structure of which was completely different from those of other noble metal catalysts. © 2002 Elsevier Science (USA)

Key Words: **iridium catalyst; CO oxidation; hydrogen oxidation; deposition precipitation; support effect.**

1. INTRODUCTION

Catalytic CO oxidation has lately drawn considerable attention due to the growing applications in air purification, pollution control in automobiles, and incinerator exhaust gases. In addition to many different metal oxide catalysts, a wide variety of precious metal catalysts has been studied for low-temperature CO oxidation. Among them, it is noteworthy that Au nanoparticles deposited on oxide supports, such as Al_2O_3, SiO_2, TiO_2, MnOx, Fe_2O_3, and NiO, are very active for CO oxidation at room temperature (1–8). Although Pd/SnO_2 and Pt/SnO_2 were known to be active for the low-temperature oxidation of CO, they often required complicated pretreatments and relatively long induction periods (9–11). Recently, a Pd/CeO_2–TiO_2 catalyst was also reported to exhibit high catalytic activity for CO oxidation at low temperature (12).

Although Ir is situated among the same 5f orbital metals as Pt and Au, it has been investigated as a catalyst only for limited reactions: $deNO_x$ for automobile exhaust gases (13), hydrazine decomposition for rocket thrusters (14), and the hydrogenation of unsaturated hydrocarbons (15). Probably, this is because Ir resources are rare and expensive. For CO oxidation, Ir metal surfaces studied by IR, RIAS, and LEED have been reported (16, 17) and a comparison of supported iridium catalysts with other different noble metal catalysts was reported (18). The conventional Ir catalysts were all prepared by impregnation methods and were assumed to have Ir particles that weakly interacted with the support.

In this paper, supported Ir catalysts were prepared by the deposition precipitation method, abbreviated DP, to obtain stronger interactions of Ir metal particles with the supports and were studied for the oxidation of CO and H_2 at low temperatures, below 473 K.

2. EXPERIMENTALS

The metal oxides used as a support were Al_2O_3 (a reference sample from the Catalysis Society of Japan, JRC-ALO-7; specific surface area, 180 m^2/g), TiO_2 (Degussa, P-25, 60 m^2/g), SnO_2 (Kanto Chemical Co., Ltd., 50 m^2/g), and α-Fe_2O_3 (50 m^2/g), prepared by calcination in air at 627 K of the precipitates obtained from an aqueous solution of iron(III) nitrate by neutralizing with sodium carbonate. As an Ir precursor, reagent grade $IrCl_4$ (Kishida Chemicals) was used.

Iridium catalysts were prepared by the DP method using the following procedures. The metal oxide support (2 g) is dispersed in 2000 ml of an aqueous solution of $IrCl_4$ (0.5 mmol/L), the pH of which was adjusted to 7 using an aqueous solution of 0.1 N NaOH, unless otherwise stated. The content of Ir in the starting solution was 1.8 wt% with respect to the weight of the support. The dispersion was aged at room temperature for 1 h and was washed with distilled water several times. The solid material was vacuum dried at 0.4 Pa for 12 h and calcined in air at 673 K for 4 h. Actual Ir loadings in the calcined samples were determined by induced coupled plasma (ICP) analysis. For comparison, the impregnation method (IMP) was also used. TEM observations were performed with a JEOL JEM-3000F electron microscope at an accelerating voltage of 300 keV. XPS

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analyses were carried out with a Shimadzu ESCA-KM using Mg $K\alpha$ radiation for excitation.

The powder catalyst sample (100 mg) was placed on a ceramic wool plug in a quartz tube with an inner diameter of 6 mm. Before measurement of the catalytic activity, the catalyst sample was pretreated in a stream of 20 vol% H_2 in Ar at SV $= 20000\ h^{-1}$ ml/g-cat and at 523 K for 1 h in a fixed-bed flow reactor. The activity measurements for the oxidation of CO and of H_2 were carried out by passing the reactant gas (1 vol% CO or H_2 in air) at a flow rate of 33 ml/min (SV $= 20000\ h^{-1}$ ml/g-cat). The reactant and effluent gases were analyzed by a gas chromatograph (Shimadzu GC-8A) with a thermal conductivity detector (TCD) and with a column of molecular sieves 13X (5 m) at 333 K.

3. RESULTS AND DISCUSSION

Temperatures for 50% conversion ($T_{1/2}$) in H_2 oxidation over Ir/Al_2O_3 and Ir/Fe_2O_3 catalysts pretreated by hydrogen reduction are 363 and 455 K, respectively. On the other hand, $T_{1/2}$ in CO oxidation over Ir/Al_2O_3 and Ir/Fe_2O_3 catalysts pretreated by hydrogen reduction are 430 and 479 K, respectively. Over Ir/Al_2O_3 and Ir/Fe_2O_3 catalysts, H_2 oxidation proceeds at lower temperatures than CO oxidation. This feature is similar to those of other typical noble metal catalysts. The catalytic activity of Ir/SnO_2 was slightly higher for CO oxidation than for H_2 oxidation, as $T_{1/2}$ in H_2 and CO oxidation are 421 and 458 K. Moreover, it should be noted that CO oxidation over the Ir/TiO_2 catalyst takes place at temperatures even below room temperature and at much lower temperature than H_2 oxidation ($T_{1/2} = 420$ K). This feature is the same as that of highly dispersed Au catalysts (1–7).

The pH of the aqueous solution of $IrCl_4$ was assumed to influence the interaction of Ir with the support (19); therefore, the pH of aqueous $IrCl_4$ solution was adjusted using NaOH to a fixed point, ranging from 3 to 10. Figure 1 shows the time-on-stream changes of the conversion of CO over the Ir/TiO_2 catalysts prepared by DP under different pH conditions. Although gradual deactivation was observed, the complete oxidation of CO over Ir/TiO_2 prepared by DP at pH 7 took place at least for 1 h at 300 K. In contrast, Ir/TiO_2 prepared by IMP showed a rapid deactivation of the initial activity at 300 K. In comparison with the Ir/TiO_2 prepared by DP at pH 7, those prepared at pH 3, 5, and 10 showed the rapid deactivation of the initial catalytic activity and that prepared at pH 8 showed the full CO conversion after more than 3 h. The Ir/TiO_2 catalyst prepared at pH 8 was pretreated in an air stream instead of a hydrogen-containing stream at 523 K for 30 min; it was not active for CO oxidation at room temperature, which was clearly different from the high catalytic activity of Ir/TiO_2 pretreated in a hydrogen stream. This difference indicates that the Ir metal phase produced by hydrogen reduction pretreatment is active for CO oxidation at low temperatures, whereas the oxidized phase of iridium metal is much less active. Therefore, the deactivation during the time-on-stream in the room temperature reaction seemed to occur due to the reoxidation of the active metal phase of the catalysts.

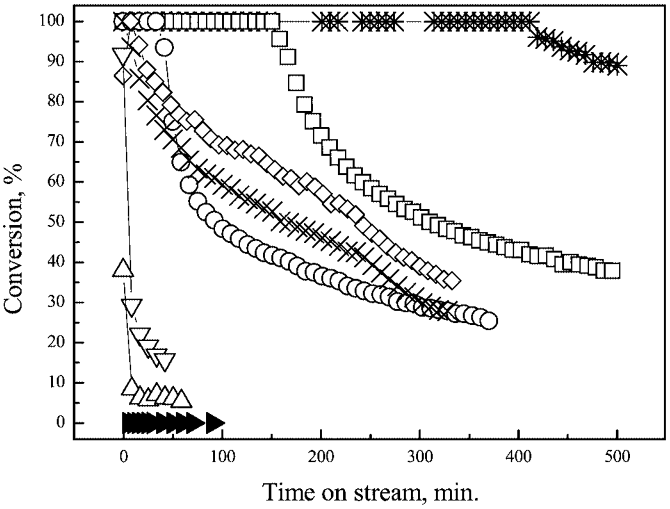

FIG. 1. Conversion of CO at 300 K as a function of the reaction time in CO oxidation over Ir/TiO_2 catalyst prepared by the IMP and DP methods under different pH conditions and the in the stream of humidified reactant gas. △, pH 3 (6 ppm H_2O, H_2 reduction); ▽, pH 5 (6 ppm H_2O, H_2 reduction); ○, pH 7 (6 ppm H_2O, H_2 reduction); □, pH 8 (6 ppm H_2O, H_2 reduction); ◇, pH 10 (6 ppm H_2O, H_2 reduction); ✳, pH 8 (6000 ppm H_2O, H_2 reduction); ×, IMP (6 ppm H_2O, H_2 reduction); and ►, pH 8 (6 ppm H_2O, air calcination).

From ICP analyses of the Ir/TiO_2 catalysts prepared at pH 3, 5, 7, 8, and 10, the actual Ir loadings were 0.57, 0.64, 1.14, 1.48, and 0.85 wt%, respectively, showing that the Ir loading was maximum at pH 8. The interaction between Ir^{4+} and the TiO_2 surface increases above the point of zero charge (P.Z.C.) of TiO_2 (about 7) because its surface is negatively charged. The solubility of iridium hydroxide decreases with an increase in pH of the starting solution. These two reasons can account for the maximum Ir loading at pH 8.

The TEM images of the Ir/TiO_2 prepared by DP at pH 8 are shown in Figs. 2a–2b. The deposited Ir was found to spread over the TiO_2 surface as a thin layer of Ir or IrO_2 about 2 nm thick. From Fig. 2a-1, it was found that the Ir layer was heterogeneously deposited onto the select TiO_2 particles. From EELS measurements for the Ir-rich and Ir-poor parts of this sample, it was also found that Ir thin layer was mainly deposited onto the rutile TiO_2 particles (results not shown). This structure was completely different from those of other noble metal catalysts, where the noble metals were deposited on the supports as fine particles. Comparing the Ir phase lattice constant calculated

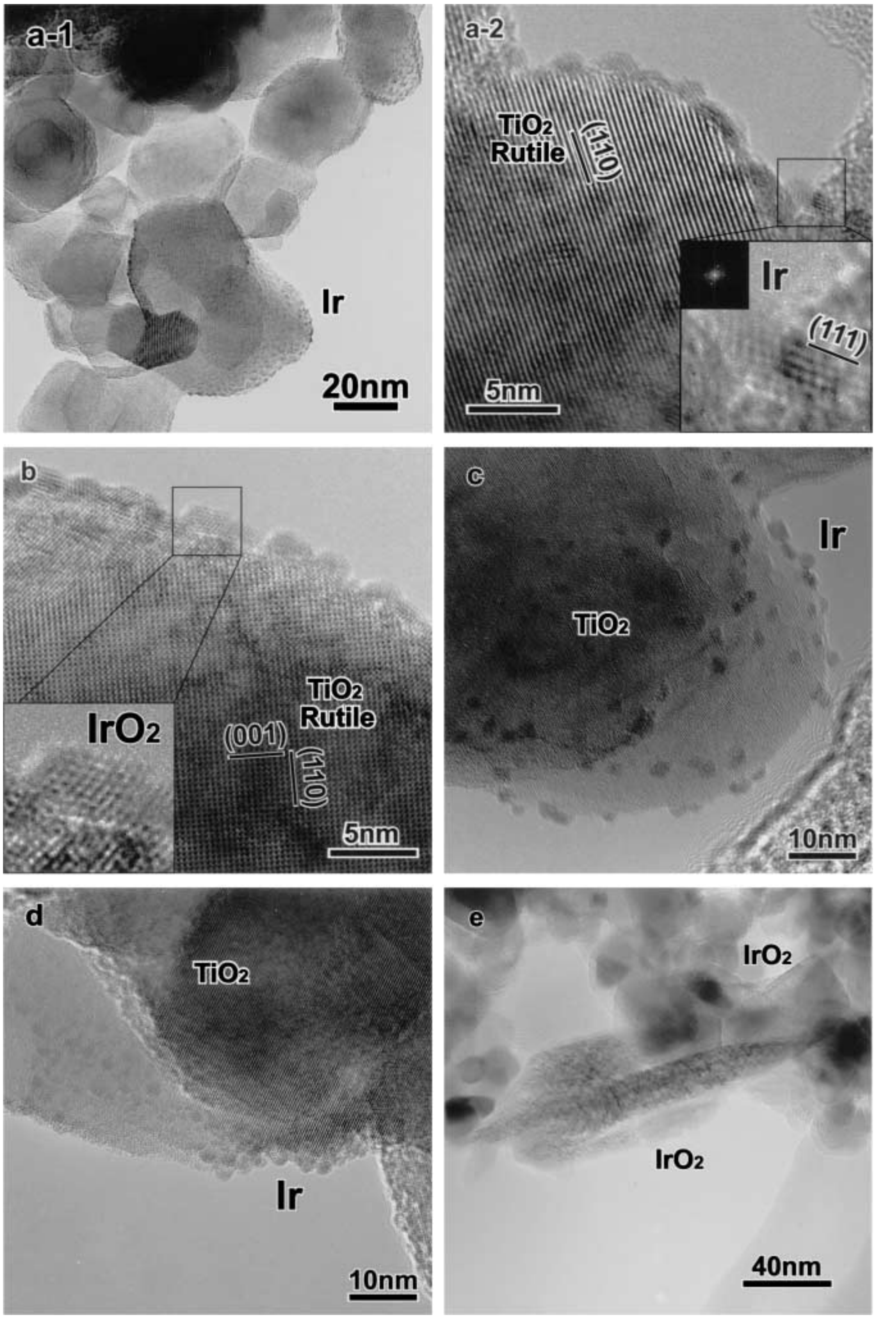

FIG. 2. TEM images of the Ir/TiO_2 catalysts prepared by the DP method followed by pretreatment at 523 K: (a-1) prepared at pH 8 and calcined in the hydrogen stream (low magnification); (a-2) prepared at pH 8 and calcined in air (high magnification); (b) prepared at pH 8 and calcined in the hydrogen stream (high magnification); (c) prepared at pH 3 and calcined in air (low magnification); and (d) prepared at pH 5 and calcined in air (low magnification). (e) Ir/TiO_2 prepared by IMP and calcined in air (low magnification).

from the TEM images, the metal phase of Ir was found to be produced by the hydrogen reduction pretreatment, while the iridium oxide was formed by calcination in air. Moreover, it was found that the Ir thin layer was epitaxially deposited onto the TiO_2 support surface. TEM images of Ir/TiO_2 prepared by DP at pH 3 and 5 are also shown in Fig. 3. The TEM image of Ir/TiO_2 prepared by DP at pH 3 showed that the isolated small Ir particles were deposited on the support, while that of Ir/TiO_2 prepared by DP at pH 5 showed the nonsmooth Ir layer and the aggregates of the Ir clusters. This is good evidence that the amount of loading and the structure of the Ir could be controlled by changing the pH of the precursor solution in the DP method. Additionally, it was also found that the dispersion

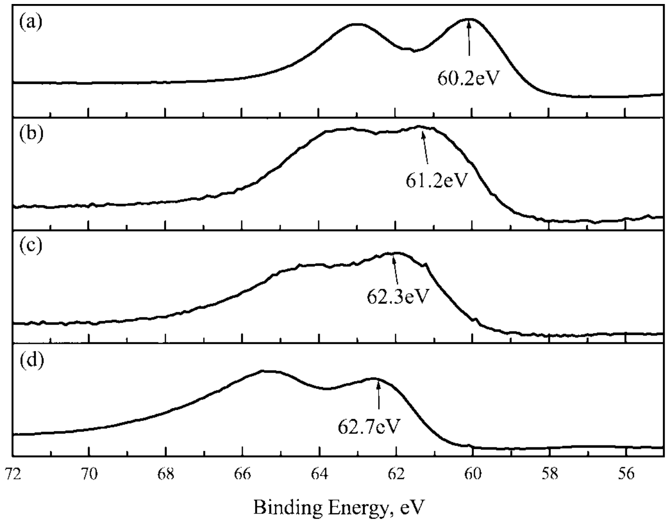

FIG. 3. Ir 4f spectra for (a) Ir metal, (b) Ir/TiO_2 prepreated by H_2, (c) Ir/TiO_2 calcined in air, and (d) IrO_2.

of Ir/TiO_2 prepared by IMP was much worse than that of Ir/TiO_2 prepared by DP, as both extremely large IrO_2 particles (about 50 nm) and small IrO_2 particles (less than 5 nm) existed.

For the Ir/TiO_2 prepared by DP at pH 8, XPS analysis was carried out. Figure 3 shows the Ir 4f spectra of (a) Ir metal, (b) Ir/TiO_2 pretreated by H_2, (c) Ir/TiO_2 calcined in air, and (d) IrO_2. It was found that the binding energy of the Ir 4f peak decreased on H_2 pretreatment in the case of Ir/TiO_2. This indicated that the deposited IrO_2 thin layer was reduced by H_2 reduction. This result is in good agreement with the TEM observation. However, the peak position of Ir 4f in Fig. 3b was slightly different from that in Fig. 3a. This suggested that the surface or Ir thin layer was metallic and the boundary of Ir thin layer was oxide. Therefore, it can be concluded that the deposited Ir thin layer has the strong heterojunction with the TiO_2 support.

To investigate the moisture effect on CO oxidation, the reactant gas containing moisture at about 6 ppm was humidified to a level of 6000 ppm. As shown in Fig. 1, the catalytic activity of Ir/TiO_2 prepared by DP at pH 8 increased with an increase in the moisture in the reactant gas. The Ir/TiO_2 catalyst could maintain 100% conversion of CO oxidation for 7 h in the presence of 6000 ppm moisture. This characteristic is advantageous for practical applications as a low-temperature environmental catalyst. The water-promoted oxidation of CO was also reported over Pd/SnO_2, Pt–Sn alloy, and Au/TiO_2 (20, 21). In the case of Pd/SnO_2, it was proposed that the role of the water vapor was to increase the spillover of activated CO molecules (20). On the other hand, a work of Schryer has emphasized the activation of oxygen molecules with water molecules at the Pt–Sn alloy (22). In the case of Ir/TiO_2, as the Ir was spread over the TiO_2 surface as a thin layer, water was adsorbed onto the exposed Ir surface as well as onto TiO_2. Therefore, the agreeable explanation was that the exposed Ir metal surface could resist the reoxidation by the water adsorption, as adsorbed water depressed the interaction between activated oxygen and the active Ir metal surface.

While the catalytic activity in CO oxidation over Ir/TiO_2 was much higher than those over Ir/SnO_2, Ir/Fe_2O_3, and Ir/Al_2O_3, the activity over Ir/TiO_2 was also greatly dependent on the preparation conditions. This suggested that the activity of CO oxidation was directly associated with the structure of the Ir metal phase deposited on the supports and the selection of the support. In other words, this feature might be related to its nano-level epitaxially deposited smooth layer structure on the TiO_2 support surface. From TEM observation and XPS analysis, it was found that this smooth Ir metal phase produced by H_2 pretreatment was the active site, and the surface of the Ir thin layer and the boundary of the Ir thin layer with the support were metal and oxide, respectively. Therefore, it can be assumed that this smooth Ir thin layer structure with a strong interaction between Ir thin layer and TiO_2 support provided the resisting catalytic activity for the CO oxidation. In conclusion, the Ir nano-layered structure was obtained in the Ir/TiO_2 catalyst prepared by the DP method at pH 8, and it can be assumed that this structure is a key to the resisting catalytic activity for CO oxidation at low temperature.

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