Co–Pt Bimetallic Catalysts for the Selective Oxidation of Carbon Monoxide in Hydrogen-Containing Mixtures

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Abstract—The performance of a Co–Pt powder and of Co–Pt catalysts supported on γ -Al₂O₃ and on the graphite-like carbon material Sibunit in selective CO oxidation in hydrogen-containing mixtures is considered. Fine particles of metal–metal solid solutions and intermetallides were obtained by the decomposition of a Co- and Pt-containing double complex salt in a hydrogen atmosphere at ~400°C. As compared to their Pt and Co monometallic counterparts, the bimetallic catalysts are more active and allow the CO concentration in hydrogen-containing mixtures to be reduced from 1 to 10⁻³ vol %. This effect is likely due to the formation of bimetallic particles of a Co–Pt solid solution on the support surface.

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In recent years, the design and commercialization of power plants based on proton exchange membrane fuel cells (PEMFCs) have attracted keen interest from researchers all over the world. This interest stems from the already demonstrated and recognized advantages of fuel cells over conventional power sources. These advantages include high chemical-to-electric energy conversion efficiency, noiseless operation, and modularity. Due to their modularity, PEMFCs can readily be combined into stacks to vary the electric power within the given technology. The fuel in a PEMFC is hydrogen, and the oxidizer is atmospheric oxygen. The only atmospheric emission resulting from the operation of a PEMFC is water vapor, so PEMFCs meet the most stringent environmental regulations. Although PEM-FCs are still rather expensive, many countries consider them to be promising for improving power supply systems in a variety of applications ranging from mobile phones and vehicles to dwellings.

However, there are difficulties preventing PEMFCs from gaining widespread use. These include the absence of a developed hydrogen infrastructure and the challenging problem of safe hydrogen storage. In view of this, researchers' attention is now focused on developing a fuel processor capable of producing the necessary amount of a hydrogen-containing gas from hydrocarbons (natural gas, gasoline, methanol, ethanol, etc.) just at the PEMFC operation site. It is this problem that has recently occupied the foreground of research in the field of fuel cells, as is indicated by the large number of relevant publications [1–3].

Hydrogen production in a fuel processor involves several steps. Initially, the hydrocarbon stock is converted into a hydrogen-containing mixture by steam, air, or autothermal reforming followed by the steam conversion of the resulting carbon monoxide. The mixture usually consists of H₂, CO₂, CH₄, N₂, H₂O, and ~0.5–2 vol % CO. However, this mixture cannot be fed into a PEMFC because CO concentrations above 0.001–0.01 vol % (10–100 ppm) poison the fuel cell electrode [1–3]. For this reason, the second step is CO reduction to 10 ppm by fine purification of the hydrogen-containing gas. The most promising purification method is catalytic CO oxidation in the presence of H₂.

This purification technique involves two simultaneous catalytic reactions, namely, CO oxidation and H_2 oxidation. Therefore, an efficient catalyst must be both highly active and selective toward CO oxidation in the presence of H_2 .

Numerous supported metal catalysts have been suggested for CO oxidation in the presence of H₂, including active and selective Pt- and Ru-containing catalysts supported on γ -Al₂O₃ and carbon materials [4–12]. Nevertheless, it is vital to enhance the activity of these catalysts and to reduce their noble metal content. A way of solving this problem is by employing bimetallic catalysts and metal catalysts promoted with metal oxides.

Igarashi et al. [13] suggested the bimetallic catalyst Pt–Ru/mordenite. This catalyst was found to be more active than Pt/mordenite or Ru/mordenite. It was assumed that Pt–Ru alloy particles form on the support surface during synthesis. The fact that the bimetallic catalyst Pt–Ru/mordenite is more active than the Pt and Ru monometallic catalysts is explained in terms of the following "bifunctional mechanism": the CO molecules, adsorbed on Pt, are oxidized by the nearest oxy-

Properties of the catalysts

Catalyst	Before the reaction		After the reaction	
	$S_{\rm BET},{\rm m^2/g}$	$V_{\rm por},{\rm cm^3/g}$	$S_{\rm BET},{\rm m^2/g}$	$V_{\rm por},{\rm cm^3/g}$
2 wt % (Co–Pt)/C; Co/Pt = 1	300	0.3	300	0.3
2 wt % (Co–Pt)/ γ -Al ₂ O ₃ ; Co/Pt = 1	150	0.5	150	0.5
Co–Pt (powder); Co/Pt = 1	1	-	1	-
Pt/γ-Al ₂ O ₃	150	0.5	150	0.5
Co/γ-Al ₂ O ₃	150	0.5	150	0.5

gen atoms, which are mainly adsorbed on Ru. A number of studies have been devoted to Pt/γ -Al₂O₃ and Pt/mordenite catalysts promoted with iron oxide [14– 17]. This promoter enhances the activity and selectivity of the platinum catalysts. This effect arises from the strong interaction between platinum and iron oxide [15]. Part of the platinum surface in these catalysts is covered with iron oxide. This causes a decrease in the energy of the bonding between Pt and the adsorbed CO molecules, thereby favoring CO oxidation to CO₂ by oxygen of the iron oxide. The reduced iron oxide is then reoxidized by oxygen from the gas phase.

Earlier, we suggested highly active, Al_2O_3 -supported, Co–Pt bimetallic catalysts [18]. The activity of these catalysts in CO oxidation in the presence of hydrogen is higher than the activity of the Al_2O_3 -supported Co and Pt catalysts. This finding was confirmed by a later study [19]. A Co–Pt/TiO₂ catalyst [20] was also reported. Again, its activity in CO oxidation in the presence of hydrogen was found to be higher than the activity of the corresponding monometallic catalysts Co/TiO₂ and Pt/TiO₂. Based on indirect data, it was assumed that the higher activity of the Co–Pt catalysts as compared to the Pt and Co monometallic catalysts is due to the formation of a Co–Pt bimetallic phase [19, 20].

Here, we report the properties of a Co–Pt powder and of Co–Pt catalysts supported on γ -Al₂O₃ and on the graphite-like carbon material Sibunit [21] in the selective oxidation of carbon monoxide in hydrogen-containing gas mixtures. The powder and supported catalysts were prepared by the decomposition of a double Co–Pt complex salt in a hydrogen atmosphere at moderate temperatures (~400°C), a procedure allowing fine particles of metal–metal solid solutions and intermetallides to be obtained [22].

EXPERIMENTAL

The Co–Pt powder was obtained by the decomposition of the double complex salt $[Co(NH_3)_5NO_2][Pt(NO_2)_4] \cdot 1.5H_2O$ in a hydrogen atmosphere at 400°C. This salt, which is poorly soluble in water, was synthesized by mixing aqueous solutions of $[Co(NH_3)_5NO_2]Cl_2$ and $K_2[Pt(NO_2)_4]$. It will be demonstrated below that the Pt–Co powder thus obtained con-

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sists largely of a solid solution with a face-centered lattice and its composition is $Co_{0.5}Pt_{0.5}$. The possibility of the formation of Pt–Co bimetallic particles was proved in another work [23].

The supports in (Co–Pt)/C and (Co–Pt)/ γ -Al₂O₃ were, respectively, Sibunit (graphite-like carbon) and (Co–Pt)/ γ -Al₂O₃ as spherical granules ~1 mm in diameter. Sibunitt had $S_{\text{BET}} = 300 \text{ m}^2/\text{g}$ and a pore volume of 0.3 cm³/g, and γ -Al₂O₃ had $S_{\text{BET}} = 150 \text{ m}^2/\text{g}$ and a pore volume of 0.5 cm³/g.

The (Co–Pt)/C and (Co–Pt)/ γ -Al₂O₃ catalysts were prepared in several steps from aqueous solutions of the complexes $[Co(NH_3)_5NO_2]Cl_2$ and $K_2[Pt(NO_2)_4]$. The catalyst preparation procedure was discussed in an earlier publication [24]. The support was impregnated with a $K_2[Pt(NO_2)_4]$ solution by the incipient-wetness method and was then air-dried at 110°C. The resulting material was impregnated with a $[Co(NH_3)_5NO_2]Cl_2$ solution by the incipient-wetness method and was again air-dried at 110°C. These operations produce the double complex salt [Co(NH₃)₅NO₂][Pt(NO₂)₄] and KCl in the pores of the support. Next, the solids were reduced in a hydrogen atmosphere at 400°C for 2 h. The total metal content of a catalyst was 2 wt %, and the Pt/Co atomic ratio was close to unity. For KCl removal, the catalyst granules were brought into warm distilled water and, after 5–10 min, the supernatant solution was poured out. This procedure was repeated until the supernatant was free of chloride ions.

For comparison, we prepared the monometallic catalysts Pt/γ -Al₂O₃ and Co/γ -Al₂O₃ by impregnating γ -Al₂O₃ with [Co(NH₃)₅NO₂]Cl₂ and K₂[Pt(NO₂)₄] solutions by the incipient-wetness method. The metal content of these catalyst was 2 wt %.

The supported catalysts and the Co–Pt powder were characterized by a variety of physicochemical methods.

The specific surface area (S_{BET}) and the pore volume (V_{por}) of the supports and catalysts were derived from the complete 77-K nitrogen adsorption isotherms (ASAP-2400 instrument, Micrometrics, United States). These parameters of the catalysts were the same before and after the reaction (Table 1). Moreover, the S_{BET} and V_{por} values of the catalysts were equal to the S_{BET} and V_{por} values of their respective supports.

The X-ray powder diffraction patterns of the catalysts for phase analysis were recorded on a DRON– Seifert-RM4 diffractometer (CuK_{α} radiation, graphite monochromator in the reflected beam, amplitude-discrimination scintillation detector, $2\theta = 5^{\circ}-135^{\circ}$, scanning with 0.02° increments). The data obtained were compared to JCPDS standard data (electronic version PCPDFWIN) [25]. The diffraction data were processed using the PowderCel 2.4 program, which allowed the phase composition, unit-cell parameters, and the coherent-scattering domain size (*D*) to be determined.

Kinetic measurements for CO oxidation in hydrogen-containing gas mixtures were detailed in an earlier paper [9]. The reaction was carried out at atmospheric pressure in a flow quartz reactor. The reactor was a Ushaped tube with a length of 40 cm, an inner diameter of 8 mm, and a wall thickness of ~1 mm and had a thermocouple well with an outer diameter of 3 mm at its central axis. A weighed portion of the catalyst (granule diameter, ≤ 1 mm) or the Co-Pt powder mixed with powdered quartz (particle size, ~1 mm) was charged into the reactor. The total height of the catalyst bed was 12 cm. The reactor inlet and outlet were fitted with a filter to prevent the small catalyst particles entrained by the flowing gas from entering the gas inlet and outlet capillary piping. The reaction temperature was measured with a chromel-alumel thermocouple placed in the center of the catalyst bed. The catalyst was given no pretreatment before the experiment.

The reactant and product concentrations at the reactor inlet and outlet were identified using a Kristall-2000 chromatograph (Russia) equipped with a thermal-conductivity detector, a flame-ionization detector, and a methanizer accessory using a nickel catalyst (NKM-4 brand). The combination of the methanizer and the flame-ionization detector allowed any hydrocarbon present in the gas mixture along with CO and CO₂ to be quantified with high sensitivity. The gas mixture being analyzed was separated in a column packed with the molecular sieve NaX (for the thermal-conductivity detector) or with Porapak Q (for the flame-ionization detector). The sensitivity of this method makes possible measurement of CO, CH₄, and CO₂ concentrations down to ~10⁻⁴ vol % and O_2 concentrations down to 10^{-3} vol %. The oxidation of carbon monoxide in hydrogen-containing mixtures was characterized in terms of CO conversion (X_{CO}), O₂ conversion (X_{O_2}), and selectivity (S), which were calculated using the equations

$$X_{\rm CO} = \frac{[\rm CO]_0 - [\rm CO]_{out}}{[\rm CO]_0} \times 100\%,$$
$$X_{\rm O_2} = \frac{[\rm O_2]_0 - [\rm O_2]_{out}}{[\rm O_2]_0} \times 100\%,$$

$$S = \frac{1}{2} \frac{[CO]_0 - [CO]_{out}}{[O_2]_0 - [O_2]_{out}} \times 100\%,$$

where $[CO]_0$ and $[O_2]_0$ are the inlet CO and O_2 concentrations and $[CO]_{out}$ and $[O_2]_{out}$ are the outlet CO and O_2 concentrations.

RESULTS AND DISCUSSION

The oxidation of CO in hydrogen-containing mixtures was initially studied for the Co–Pt powder. Figure 1 shows the temperature dependences of the outlet CO concentration, O_2 conversion, and selectivity for this system.

For the initial oxygen concentration 1.5 vol %, the outlet CO concentration is 300 ppm at 100–110°C, the O_2 conversion is 100%, and *S* is about 30%. Raising the O_2 concentration in the reaction mixture to 2.5 vol % makes it possible to reduce [CO]_{out} to <10 ppm at 100–110°C. In this case, the oxygen conversion is again complete, but the selectivity is decreased to ~20%. Thus, the Co–Pt powder is an active catalyst for selective CO oxidation in hydrogen-containing mixtures.

The phase composition of the Co-Pt powder before and after the selective oxidation of CO in the presence of H₂ was determined by X-ray diffraction. The diffraction patterns for this powder and for some Co-Pt solid solutions and intermetallides are presented in Fig. 2. The strongest reflections from the Co-Pt powder before the reaction (diffraction pattern 1) are broad and are assigned to the fcc lattice of the solid solution with a unit-cell parameter of a = 3.771(2) Å. This unit-cell parameter implies that the mean volume per atom of the solid solution is $V_{\text{mean}} = 13.41 \text{ Å}^3$. This value coincides closely with the half-sum of the atomic volumes of cobalt and platinum ($V_{Co} = 11.02 \text{ Å}^3$, $V_{Pt} = 15.09 \text{ Å}^3$). Therefore, the main phase of the Co-Pt powder is the $Co_{0.5}Pt_{0.5}$ solid solution. The coherent-scattering domain size of this phase derived from diffraction profiles is 50–70 Å.

Along with the strong reflections from the $Co_{0.5}Pt_{0.5}$ phase, weak superstructure peaks are present in the diffraction pattern of the Co–Pt powder before the reaction. These peaks occur in nearly the same positions as the reflections from the CoPt intermetallide (tetragonal lattice with a = 3.803 Å and c = 3.701 Å, according to JCPDS file no. 43-1358) [25]. However, their low intensity and the absence of tetragonal splitting suggest only that the solid solution is incompletely ordered. Note that the main reflections are asymmetric and broadened on their small-angle side. This is explained by the fact that the Co–Pt powder before the reaction contains a small amount of a solid solution with a higher platinum content.

The profiles and intensities of all reflections from the Co–Pt powder after the reaction (diffraction pattern 2) are nearly the same as the reflection profiles and intensities observed before the reaction. Note only that the



Fig. 1. Temperature dependences of (a) the outlet CO concentration, (b) O_2 conversion, and (c) selectivity for CO oxidation in the presence of H₂ on the Co–Pt powder catalyst. Feed composition (vol %): CO, (*1*) 1.5 and (*2*) 2.5; O_2 , 65; H₂, 10; H₂O, 20; CO₂ and He, the balance. GHSV = 8000 h⁻¹.

set of weak reflections is better pronounced in this diffraction pattern. These reflections arise from an fcc solid solution with a = 3.898(5) Å, whose composition is, accordingly, Co_{0.1}Pt_{0.9}. The amount of this solid solution in the powder is no larger than 5 wt %.

The above data suggest that the Co–Pt powder, which consists largely of an fcc solid solution, is an active catalyst for selective CO oxidation in the pres-

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Fig. 2. (1, 2) X-ray diffraction patterns from the Co–Pt powder (1) before and (2) after CO oxidation in the hydrogencontaining mixture. (3–5) Theoretical diffraction patterns for (3) the $Co_{0.5}Pt_{0.5}$ solid solution, (4) the $Co_{0.1}Pt_{0.9}$ solid solution, and (5) the CoPt intermetallide.

ence of H_2 . Since the Co–Pt powder and the supported Co–Pt catalysts were prepared in similar ways, we believe that particles of the Co–Pt solid solution form on the support surface, as in the case of the powder.

Figure 3 illustrates the catalytic properties of the supported bimetallic ((Co–Pt)/ γ -Al₂O₃ and (Co–Pt)/C) and monometallic (Pt/ γ -Al₂O₃ and Co/ γ -Al₂O₃) catalysts in CO oxidation in the presence of hydrogen.

Clearly, the activity of the Co/ γ -Al₂O₃ catalyst is low. Even at a higher reaction temperature of 230°C, the CO concentration decreased only from 1 to 0.73 vol % and the O₂ conversion was as low as ~20%. The Pt/ γ -Al₂O₃, (Co–Pt)/C, and (Co–Pt)/ γ -Al₂O₃ catalysts are substantially more active. The temperature dependences of [CO]_{out}, X_{O_2} , and S_{CO} for these catalysts are similar and are only shifted relative to one another along the temperature axis. The highest activity is shown by the bimetallic catalysts (Co–Pt)/C and (Co–Pt)/ γ -Al₂O₃; the lowest activity, by the monometallic catalyst Pt/ γ -Al₂O₃. The Co–Pt catalysts reduce the CO concentration in the mixture to a lower level than the monometallic catalysts (Co–Pt)/C and (Co–Pt)/ γ -Al₂O₃. With the bimetallic catalysts (Co–Pt)/C and (Co–Pt)/ γ -Al₂O₃.



Fig. 3. Temperature dependences of (a) the outlet CO concentration, (b) O₂ conversion, and (c) selectivity for CO oxidation in the presence of H₂ on the catalysts (*1*) 2 wt % (Co–Pt)/C, (*2*) 2 wt % (Co–Pt)/ γ -Al₂O₃, (*3*) 2 wt % Pt/ γ -Al₂O₃, and (*4*) 2 wt % Co/ γ -Al₂O₃. Feed composition (vol %): CO, 1; O₂, 1.5; H₂, 65; H₂O, 10; CO₂ 20; and He, the balance. GHSV = 8000 h⁻¹.

10 ppm in the hydrogen-containing mixture is achieved at rather low temperatures of 110–130 and 125–150°C, respectively. At these temperatures, the O₂ conversion is complete and selectivity is ~30%. With Pt/ γ -Al₂O₃, this low CO level is not usually achieved, the outlet CO concentration being 80–150 ppm. Again, the oxygen conversion is complete and selectivity is ~30%.

These results suggest that the supported Co–Pt catalysts are active and selective in CO oxidation in hydrogen-containing mixtures. It is important that the (Co–Pt)/C and (Co–Pt)/ γ -Al₂O₃ catalysts, as well as the Co–Pt powder, show stable performance under the reaction conditions. No decrease in activity was observed for these catalysts throughout a ~50-h-long experiment.

Unfortunately, the X-ray diffraction characterization of the (Co–Pt)/C and (Co–Pt)/ γ -Al₂O₃ catalysts did not allow us to identify any Co–Pt bimetallic phase. The integrated intensity of the reflections from the metals is low because of the low metal content (2 wt %) of the catalysts, and the small size of the metal particles causes reflection broadening, thus making the diffraction pattern difficult to interpret. At the same time, based on the data obtained for the Co–Pt powder and on the fact that the bimetallic catalysts (Co–Pt)/C and (Co–Pt)/ γ -Al₂O₃ are more active than the monometallic catalysts Co/ γ -Al₂O₃ and Pt/ γ -Al₂O₃, we believe that the active component in the supported Co–Pt catalyst is a Co–Pt solid solution.

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