



Catalytic performance and characterization of Al₂O₃-supported Pt–Co catalyst coatings for preferential CO oxidation in a micro-reactor

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ABSTRACT

Platinum–cobalt (Pt–Co) catalyst coatings are studied for preferential oxidation of carbon monoxide (PROX) in hydrogen-rich gas streams. Experimental results show a role for cobalt in improving catalytic activity. The most active catalyst coating can decrease carbon monoxide concentrations from 1% to a value of less than 10 ppm for GHSV values ranging from 40,000 to 120,000 ml g⁻¹ h⁻¹. This catalyst coating can work at a wide window of operation in terms of temperature. Transmission electron microscopy, selected-area electron diffraction, and diffuse reflectance infrared Fourier transform spectroscopy show that the addition of Co forms Pt₃Co intermetallic compounds and slightly increases the average particle size. *In situ* laser Raman spectroscopy reveals the co-existence of Co metal and its oxides on the catalyst surface, due to gradual oxidation of Co by gas phase oxygen within the initial stage of the PROX reaction. The promotional effect of Co during PROX is confirmed and ascribed to this Pt₃Co intermetallic compound and the synergetic effect of Co⁰ and Co^{ox}. The high accessibility of the reactant to Pt₃Co species appears favorable and crucial for PROX.

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1. Introduction

As CO is very harmful to the Pt-based electrocatalysts in proton exchange membrane fuel cells (PEMFC), CO concentrations in the feed stream to the anode must be decreased to a fairly low level [1,2]. The CO tolerance (target 2005) is 10 ppm in steady state and 100 ppm in transient, for a durability of 20,000 h, that will be reduced (target 2011) to 1 ppm in steady state and 25 ppm in transient, for a durability of 40,000 h [3]. There are several methods for removal of CO from a H₂-rich stream, including cryogenic separation, pressure swing adsorption, selective diffusion, preferential oxidation of carbon monoxide (PROX), and CO methanation. Among these methods, the selective diffusion, PROX and the selective CO methanation have been considered to be promising [4].

The PROX reaction requires an active, selective, and stable catalyst. A number of supported noble metals, including Pt [5], palladium (Pd) [6], ruthenium (Ru) [7], gold (Au) [8], rhodium (Rh) [9], and iridium (Ir) [10], are now being widely studied for this purpose by various investigators. The interest in PROX catalysts has concentrated on supported Pt-based catalysts due to their high activity, selectivity, and stability. Different promoters, such as Co [11], iron (Fe) [12], cerium (Ce) [13], lanthanum (La) [13], niobium

(Nb) [14], and alkali metals [15] have been tested for their ability to increase catalytic activity to PROX. Among these promoters, Co is the most common additive in Pt-based catalysts as it shows good performance with PROX. Jain et al. [16] reported that Co- and Fe-promoted Pt/Al₂O₃ catalysts were more active and selective than manganese (Mn)-, tin (Sn)-, copper (Cu)-, nickel (Ni)-, and chromium (Cr)-promoted Pt/Al₂O₃ catalysts. Suh et al. [17] found similar advantages to Co-promoted Pt/Al₂O₃ catalysts compared with Ni- and Mn-promoted Pt/Al₂O₃ catalysts. A Pt–Co bimetallic catalyst supported on yttria-stabilized zirconia was also reported by Ko et al. [18] to carry out a high CO conversion at 380–423 K.

At the present time, PROX reactors usually have a fixed-bed composition. However, compared with fixed-bed reactors, straight-channel monolith reactors with thin-film catalyst coatings are known to enhance the diffusion of reactants toward active sites and they show low heat capacity, thus providing rapid response to changes in the operating conditions [19]. Microchannel reactors with catalyst coatings have negligible external and internal mass transport limitations, as well as enhanced heat transport characteristics. Consequently, these reactors show advantages such as rapid heating and cooling, suppression of hot spots, fast response rates, and easy integration with miniaturized devices [20]. On account of these characteristics, intrinsic safety and easy scale up micro-structured reactors seem to be ideally suited for this reaction when coupled to PEMFC systems in low to medium power output applications [21–23].

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For monolith and microchannel reactors, an active catalyst coating is crucial. Despite the potential advantages of these reactors, only a few papers on catalyst coatings for PROX can currently be found, including those of Pt/Al₂O₃ [20], Rh-K/Al₂O₃ [24], Pt-MIX (1% Pt on 50% 3A zeolite and 50% Al₂O₃) [25], Cu/CeO_{2-x} [26] and Pt-Fe/mordenite [27]. However, for most of these catalyst coatings, an outlet CO concentration of less than 10 ppm was always obtained at high temperatures (>460 K), or with the use of a large number of precious metals in the catalyst coatings preparation. Hence, the challenge of designing and preparing a catalyst coating with high activity and economy to PROX still remains.

A Pt-Co catalyst coating is expected to show excellent performance for PROX, since Pt-Co based catalysts in the form of powder or pellets are generally superior to other Pt-based catalysts in performance. However, there are few reports on the use of this type of catalyst coating. To the best of our knowledge, only Kim et al. [28] have developed a Pt-Co catalyst coating. Their coating could reduce CO concentrations to less than 50 ppm, but they were unable to achieve the 10 ppm target level, even at the high O₂/CO ratio of 2.5. In addition, the Pt loading was always over 1 wt% for the reported catalyst coating. Clearly more efforts are needed to produce an active Pt-Co catalyst coating at low temperatures that has a low Pt loading.

The most representative reaction model for the PROX reaction over bimetallic Pt-Co catalysts has been proposed as a dual site non-competitive adsorption mechanism [16]. According to this mechanism, the Co oxide provides active O₂ to the reaction and undergoes reoxidation by O₂ from the gas phase. Komatsu and Tamura [29] reported that a Pt₃Co intermetallic compound is the active species for PROX at low temperatures. The electron-deficient Pt atoms adsorb CO weakly compared with Pt metal, accelerating the adsorption of O₂ onto the intermetallic compound surface. The Co atoms in the compound also adsorb O₂. The active species and the corresponding catalytic mechanism of Pt-Co catalysts for PROX still require further study.

In the present paper, we investigate the preparation of an active Pt-Co catalyst coating in an annular micro-reactor by optimizing the catalyst composition for PROX in H₂-rich gas streams. The performances of the optimized catalyst coating at various operating conditions are also studied. To understand the role of the Co promoter in the catalyst, detailed structural studies were carried out using a combination of techniques including X-ray diffraction (XRD), transmission electron microscopy (TEM), *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), *in situ* Laser Raman Spectroscopy, and X-ray photoelectron spectroscopy (XPS). Our aim is to clarify the catalytic properties of Pt-Co catalyst coatings for the PROX reaction and to obtain an active catalyst coating with low Pt loading. The ultimate goal is to produce a low Pt catalyst that can reduce the CO concentration in H₂-rich gas streams to low ppm levels at low temperatures and high gas hourly space velocity (GHSV).

2. Experimental

2.1. Catalyst coating preparation

A diagram of the annular micro-reactor is shown in Fig. 1a. The reactor consists of an internal iron-chromium-aluminum (Fe-Cr-Al) alloy cylinder coaxially placed in an external stainless steel tube. Gases flow downward toward the annulus between the cylinder and the tube. The gap of the annulus was kept constant at 0.6 mm.

Before starting the coating procedure, all of the Fe-Cr-Al alloy cylinder supports were washed with acetone in an ultrasonic bath for 30 min to remove the superficial impurities, and then rinsed

with deionized water. The Fe-Cr-Al alloy cylinder supports were put into a sodium hydroxide (NaOH) solution for 10 min and rinsed with deionized water. Finally, the Fe-Cr-Al alloy cylinder supports were heated from room temperature to 1223 K at a heating rate of 5 K min⁻¹ for approximately 5 h, and then cooled to room temperature. Consequently, a thin alumina film was formed on the surface [30]. This Al₂O₃ film greatly improves the adherence of the catalyst layers onto the walls of the reactors.

The Pt-Co/Al₂O₃ coating catalysts were prepared according to the following procedure: A γ -Al₂O₃ powder prepared by our group with a surface area of 185 m² g⁻¹ was ball-milled for 24 h, and slowly added into a solution of nitric acid, chloroplatinic acid hexahydrate, and cobalt nitrate under stirring to prepare γ -Al₂O₃ slurry. After stirring for 2 h, the slurry was left to stand for 2 h. The Fe-Cr-Al alloy cylinder was dipped multiple times into the slurry until the desired loading of 3.1 mg cm⁻² was reached. After air-drying and subsequent calcination at 773 K for 1 h, a catalyst coating was formed. The adhesion between the catalyst coating and the FeCrAl alloy after the preoxidation treatment was very good. No detachment or uncovered areas were observed [31,32]. Catalyst coatings prepared by this impregnation method are hereafter denoted as COAT-(A)Pt(B)Co, where A is the Pt loading and B is the Co loading in wt%. It should be noted that the real Pt and Co loadings measured by ICP are very close to the theoretical amounts of the catalyst during the preparation process.

2.2. Activity test

The set-up to test for activity is shown in Fig. 1b. It includes a feed gas supply, static mixer unit, evaporator (pre-heater) unit, annular micro-reactor, and an online gas chromatography (GC) analyzer. Before entering the annular reactor, feed gases are mixed in the static mixer. The annular micro-reactor was placed in a self-made tubular furnace. The temperatures of the furnaces were controlled by proportional-integral-differential (PID)-temperature-controllers with E-type thermocouples inserted into the middles of the pre-heater as well as the annular micro-reactor. Two E-type thermocouples were placed at the inlet and outlet of the Fe-Cr-Al alloy cylinder support.

Prior to the reaction, each catalyst was pretreated by the addition of water at a flow rate of 0.5 ml min⁻¹ using a syringe pump, under H₂ flow, at 673 K for 2 h. This novel pretreatment technique of adding water to the catalyst can reduce the size of the metallic Pt particles [33,34]. After pretreatment, the temperature was gradually decreased for 4 h to the reaction temperature in a helium (He)-atmosphere. The flow was then switched from He to a feed stream containing 50% H₂, 0.5–1.5% O₂, 1% CO, 0–20% CO₂, 0–16% H₂O and He under atmospheric pressure. All gas compositions were controlled using Seven-Star mass flow controllers.

An online GC with a thermal conductivity detector (TCD) was used to measure the inlet and outlet O₂ concentrations, and a flame ionization detector (FID) was used for CO, methane (CH₄), and carbon dioxide (CO₂). A molecular sieve (5A) column was used for the separation of He, O₂, CH₄, and CO. A TDX column was used for CO₂. A converter was used after the column to convert CO or CO₂ to CH₄. As the minimum detection level of the FID detector is 1 ppm CH₄, the minimum detector level for CO and CO₂ is also 1 ppm. For all catalysts, no significant amount of CH₄ could be detected over the entire temperature region of 373–473 K. Good reproducible measurements on the catalytic activities were achieved.

Since the change in total gas volumetric flow rate during the reaction was relatively small, CO conversion, O₂ conversion, and CO₂ selectivity for the PROX process were calculated as follows:

$$\text{CO conversion (\%)} = \frac{M[\text{CO}]_{\text{in}} - M[\text{CO}]_{\text{out}}}{M[\text{CO}]_{\text{in}}} \approx \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100$$

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