



Preparation, characterization and application of K-PtCo/Al₂O₃ catalyst coatings for preferential CO oxidation



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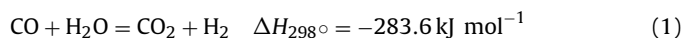
ABSTRACT

K-PtCo/Al₂O₃ catalyst coatings were studied concerning preferential oxidation of carbon monoxide (PROX) in hydrogen-rich gas streams. It has been found that the addition of potassium can enhance the catalytic activities at temperatures below 413 K, thus can widen the window of operation in terms of reaction temperatures. The most active catalyst coating of 1.5K-Pt₂Co (Pt 1 wt.%, Co 2 wt.%, and K/Co molar ratio of 1.5) can reduce carbon monoxide concentrations from initial 1% to less than 10 ppm at a high GHSV of 120,000 ml g⁻¹ h⁻¹ in a temperature range 393–433 K. The structure of catalyst coatings has been thoroughly characterized using multi-techniques, such as high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR), *in situ* laser Raman spectroscopy and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS). The addition of K has evidenced to promote the formation of Pt₃Co and increase the particle size as identified by TEM and XPS. Pt₃Co plays an important role in PROX. For PtCo/Al₂O₃ catalyst coatings, a redox equilibrium for Co during PROX was found. In contrast, with the addition of K, this redox equilibrium disappeared, probably because of the increased amount of Pt₃Co phase in the catalyst surface region.

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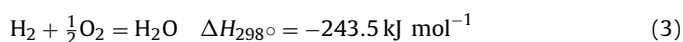
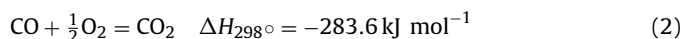
1. Introduction

Proton exchange membrane fuel cells (PEMFC) and phosphoric acid fuel cells (PAFC) have been studied extensively in recent years, showing considerable promise for both stationary and automotive power supply. These fuel cells typically use the electrochemical reaction between hydrogen, as the fuel, and air or oxygen, as the oxidant. The hydrogen fuel produced by reforming of organic molecules such as alcohols [1] generally contains low levels of CO as an impurity. For PEMFC, ultralow levels of CO in hydrogen fuel (commonly below 10 ppm) are mandatory in order to prevent the poisoning of the Pt-based PEMFC's catalysts [2]. The water-gas shift reaction (Eq. (1))



is considered as the first cleaning step, which can only reduce the CO contents to 0.5–1% CO [3]. Further reducing CO to 10 ppm is still a challenge for fuel cell application. Several methods have been

developed for the removal of CO from H₂-rich streams in the last decades, including cryogenic separation, pressure swing adsorption, selective diffusion, CO selective methanation (CO-SMET) [4], and preferential oxidation of CO (PROX) (Eq. (2), avoiding oxidation of hydrogen as shown in Eq. (3)).



In general, in order to reduce the loss of energy efficiency, the consumption of H₂ should be avoided when removing CO. Comparatively, among the listed methods of CO removal, CO-SMET and PROX are effective and feasible methods for the development of practical applications [5,6].

The development of catalysts with higher activity and selectivity is always the most important technique for the PROX reaction. Supported noble metals, such as Pt [7], Pd [8], Ru [9], Au [10], Rh [11], and Sn [12], have been evaluated. Pt-based bimetallic catalysts prepared by adding other metals, such as Co [13], Nb [14], Ce [15], Au [16], and Sn [17], have found to be promising candidates.

The PROX reaction is usually carried out in a fixed-bed reactor, which has a number of inherent problems, such as hot and cold spots as well as a poor response to transients. Comparatively,

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straight-channel monolith reactors with thin-film catalyst coatings have proved to enhance the diffusion of reactants toward the active sites and they show low heat capacity, which provides rapid responses to changes in the operating conditions of fuel cells [18]. Micro-channel reactors with catalyst coatings show negligible external and internal mass transport limitations as well as enhanced heat transport characteristics. So, these reactors have advantages, such as rapid heating and cooling, suppression of hot spots, fast response rates, and easy integration with miniaturized devices [19]. Likely, with the concerns of intrinsic safety and scale up, micro-structure reactors are ideally suited for PROX when coupled with PEMFC systems in low- to medium-power output applications [20,21].

The properties of the catalyst coatings are crucial to monolith and micro-channel reactors. However, studies about the catalyst coatings for PROX is limited [22–27]. As far as most of the reported catalyst coatings are concerned, an outlet CO concentration of less than 10 ppm was obtained at high temperatures (>460 K) for PROX. Therefore, deep insight into catalyst coatings for PROX is highly desired.

One of our previous studies has reported that a Pt-Co/Al₂O₃ catalyst coating was active for PROX by decreasing CO concentration to less than 10 ppm in a simulated reformat gas containing H₂O and CO₂, which was attributed to the formation of Pt₃Co inter-metallic compounds [28]. In addition, the promotional effects of alkali metals on Pt-based powdered catalysts have been studied for this reaction. Masatoshi et al. [29] reported that a K-Pt/Al₂O₃ powdered catalyst was very active in the PROX reaction because the potassium weakened the interaction between CO and Pt by changing the adsorption sites. Kwak et al. [30] found that the addition of sodium to powdered Pt-Co/Al₂O₃ catalysts could promote the formation of Pt-Co bimetallic phases and improve the catalytic performance. To our best knowledge, few works were reported for the Pt-Co catalyst coatings promoted by alkali metals for PROX; in particular, the structure of active sites for Pt-Co catalysts upon the addition of alkali metals and corresponding catalytic mechanisms are still unclear.

In this paper, we investigate the preparation of an active K-PtCo/Al₂O₃ catalyst coating, and the PROX reaction was carried out using an annular micro-reactor. The catalyst composition for PROX in H₂-rich gas streams was optimized. To understand the role of K, the origins of active sites were studied using a combination of techniques, including high-resolution transmission electron microscopy (HRTEM), *in situ* laser Raman spectroscopy (LRS), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR), and *in situ* diffuse-reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS). The aim of the present study was to examine the effect of K addition into the PtCo/Al₂O₃ catalyst coatings and to develop a substantive method to prepare an active catalyst coating with low Pt loading.

2. Experimental

2.1. Catalyst coating preparation

The catalyst coatings were prepared using an impregnation method [31]. Briefly, a γ -Al₂O₃ powder (home made) with a surface area of 248 m² g⁻¹ was ball-milled for 24 h and slowly added into a stirred solution of nitric acid, chloroplatinic acid hexahydrate, cobalt nitrate and potassium nitrate. The slurry was stirred for 2 h, left to stand for 2 h, and coated on a Fe-Cr-Al alloy cylinder. The catalyst coatings were air-dried and calcined at 773 K for 2 h. It should be noted that the Pt, Co and K loadings were identified with controlling the concentration of chloroplatinic acid hexahydrate, cobalt nitrate and potassium nitrate. Catalyst coatings prepared by

this impregnation method are hereafter denoted as (a) k-(b)Pt(c)Co, where *a* is the molar ratio of K to Pt. The *b* and *c* are the Pt and Co loadings in wt.%, respectively. The real metal loading of the samples is very close to the nominal value as measured by inductively coupled plasma (ICP).

2.2. Catalytic measurements

The activity measurements were carried out using an annular micro-reactor consisting of an internal cylinder coaxially placed in an external tube. The catalyst was deposited on the walls of the annular micro-reactor. The details of this set-up can be seen in a previous study [28]. Before the reaction, the catalyst was pre-treated with water at a flow rate of 0.25 ml min⁻¹ using a syringe pump under a H₂ flow at 673 K for 2 h. Then, the temperature was gradually decreased to a reaction temperature under a He flow. The feed gas contains 50% H₂, 20% CO₂, 1% O₂, 1% CO, 16% H₂O, 0.5% CH₄ and He as a balance gas.

The effluent of the reactor consisted of H₂, CO₂, CO, He, CH₄, and H₂O, which was removed from the exit gas by passing the stream through a cold trap. An online gas chromatography (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 to determine the concentration of CO, CH₄, and CO₂. A molecular sieve (5A) column was used to separate He, O₂, CH₄, and CO, and a TDX column was used to isolate CO₂. After the column, a converter was used to convert CO or CO₂ to CH₄. The minimum detection level for CO and CO₂ was 1 ppm. CO₂ selectivity is defined as the ratio of O₂ consumption for CO oxidation over the total O₂ consumption.

2.3. Catalyst characterization

N₂ adsorption-desorption measurements were performed using a Micrometrics Tristar 3000 apparatus. Prior to measurement, the samples were degassed under a vacuum at 573 K for 24 h. The specific surface area was determined using the multipoint Brunauer-Emmett-Teller (BET) method. The pore volume and pore size distribution were calculated according to the Barrett-Joyner-Halenda (BJH) method.

The TEM and HRTEM images were obtained at room temperature on a JEM 2100F (UHR), which was operated at an accelerating voltage of 200 kV. For qualitative analysis, selected-area electron diffraction (SAED) patterns were obtained from specimen areas using scanning transmission electron microscopy (STEM) images of approximately 100 nm. The samples were prepared by dipping a Cu-grid (made of an ultrathin pure carbon-support film with no formvar backing) into a sonicated dispersion of the sample in deionized water. The average particle size was estimated from a statistical result of 100 particles randomly selected in the TEM images.

The XPS measurements were performed using a Thermo ESCALAB 250 spectrometer. A monochromatic Al K α radiation source ($h\nu = 1486.6$ eV) was used at a spot size of 500 μ m. The analyzer was in constant resolution mode and used a pass energy of 20 eV. The full width at half maximum (FWHM) of the Ag 3d_{5/2} peak at 0.6 eV was determined using a clean silver specimen. The energy scale was internally calibrated by setting the Al 2p peak to 74.4 eV. Prior to curve fitting, X-ray satellites and inelastic backgrounds (Sherwood-type) were subtracted. A Gaussian of 80% and a Lorentzian peak of 20% were used for peak deconvolution.

In situ Raman spectra were obtained using a confocal Raman microscope (Renishaw inVia microscope). The Raman scattering of the samples in an *in situ* cell (Linkam, THMS600) were excited using an argon (Ar) ion laser (514 nm). The spectra were collected with a 1 cm⁻¹ spectral resolution (1800 lines/mm grating). The cell

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