XANES Study of the Reducibility of Pt Supported on Gadolinium-doped CeO$_2$

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Introduction

The water-gas shift (WGS) reaction (CO + H$_2$O $\leftrightarrow$ CO$_2$ + H$_2$) is an industrially important reaction used in the production of H$_2$. Recently, there has been an increased interest in the WGS reaction as a method for reducing the CO concentration in reformate, the term for the H$_2$-rich gas produced by reforming hydrocarbon fuels, in many fuel processors being developed for use with polymer electrolyte fuel cell (PEFC) systems. Because CO poisons the Pt anode catalysts in PEFCs, the CO level in reformate must be reduced to <100 ppm. The industrial low temperature (160-270°C) shift catalyst, CuZn oxide, and the high temperature (300-450°C) shift catalyst, FeCr oxide, have certain drawbacks, such as loss of activity resulting from thermal excursions and pyrophoric in the reduced state, which preclude their use in fuel processors for use with fuel cell systems.

Much of the interest in development of new WGS catalysts specifically tailored for use in fuel cell systems has focused on precious metals, primarily Pt, dispersed on ceria and doped cerias [1-4]. To achieve the goal of developing a Pt-ceria WGS catalyst with an activity similar to that of CuZn oxide in the temperature range of 200-300°C requires an understanding of how these catalysts function. The predominant view is that the WGS reaction occurs by a bifunctional redox mechanism where (1) CO is adsorbed on the Pt, (2) the absorbed CO is oxidized to CO$_2$ by oxygen from the ceria, which results in the reduction of the Ce^{4+} to Ce^{3+}, and (3) ceria is reoxidized by the dissociation adsorption of H$_2$O, which generates H$_2$, to complete the cycle [1]. Two critical issues are the temperatures at which Pt is reduced to Pt^0 and Ce^{4+} is reduced to Ce^{3+}.

Methods and Materials

The catalyst, 0.5 wt% Pt supported on gadolinium-doped ceria, Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$, (Pt-CGO) was prepared by an incipient wetness process. Temperature-programmed reduction (TPR) of Pt-CGO was conducted at a heating rate of 5°C/min with a 4% H$_2$/balance He mixture flowing at 50 mL/min using a flow cell designed for use on the beamline at sector 10, MR-CAT. The x-ray energy was scanned over the Pt-K and Ce-L$_{III}$ edges, and the x-ray fine structure (XAFS) portion of the spectrum at a rate of 1 scan every 2 minutes. The x-ray absorption spectra were collected in the fluorescence mode. TPR was conducted on two different samples from the same batch with the Pt spectra being collected from the first sample and the Ce spectra being collected from the second sample. For comparison, the TPR experiment was conducted in a more traditional manner, where changes in the H$_2$ concentration in the gas phase are measured, using an Altamira AMI-1 chemisorption unit equipped with a thermal conductivity detector (TCD).

Results

Fully oxidized Pt (Pt^{4+}) is present on the as-prepared Pt-CGO catalyst as shown in Figure 1. The reduction of Pt from Pt^{4+} to Pt^{+2} begins at ~130°C with 50% of the Pt being reduced to Pt^{+2} at 192°C, which correlates well with the temperatures at which the onset of the first peak (~130°C) and peak maximum (~190°C) are observed in the TCD signal using the Altamira AMI-1. The reduction of Pt^{+2} to Pt^0 begins at ~250°C and is completed at ~370°C. Again, there is good correlation between the XANES results and the temperature at which the peak maximum (330∞C) is observed for the second peak in the TCD signal using the Altamira AMI-1.

As shown in Figure 2, a two step reduction in the Ce is observed. The first reduction step begins at ~270°C and accounts for about 20-25% of the Ce being reduced from Ce^{4+} to Ce^{3+}. The temperature range at which this first reduction step occurs correlates well the the temperatures at which the reduction of Pt^{2+} to Pt^0 occurs. The second reduction step begins at ~450°C and
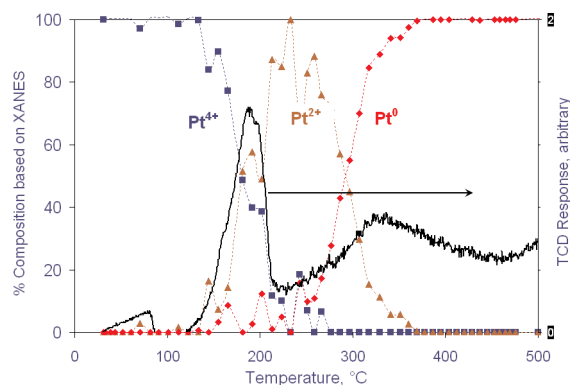

FIG. 1. Comparison of the % composition of Pt^{4+}/Pt^{+2}/Pt^0 oxidation states as determined by XANES with the TCD signal using an Altamira AMI-1 for the TPR reduction of Pt-CGO.
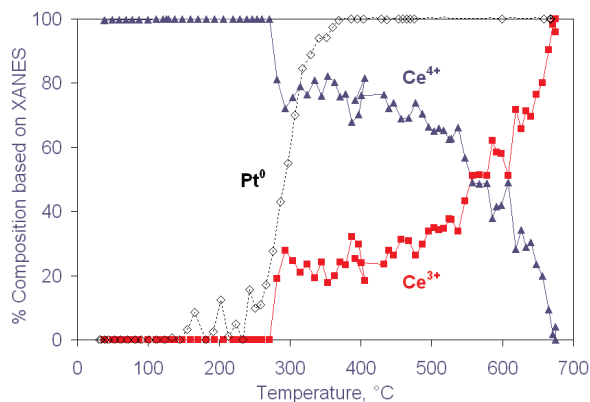
FIG. 2. *Comparison of the % composition of Ce³⁺/Ce⁴⁺ oxidation states with that of Pt⁰ as determined by XANES for the TPR reduction of Pt-CGO.*

is completed at ~650°C, with essential 100% of the Ce in the trivalent oxidation state.

Discussion

TPR studies of CeO_2 show a two-step reduction process with the first reduction, which occurs at ~500°C, involving the reduction of Ce^{4+} in the surface layer, and the second reduction, which occurs at 800°C, involving the reduction of Ce^{4+} in the bulk [5]. A two-step reduction process is also observed with CeO_2 doped with cations, such as Gd^{3+} or Zr^{4+}; however, the addition of the dopant can lower the temperature at which the reduction of Ce^{4+} occurs. The dispersion of a few weight percent of noble metals, such as Pt, Pd, or Rh, on CeO_2, has been shown to promote the reduction of the surface layer of Ce^{4+}, by a process referred to as "hydrogen spillover." In this process, H_2 is dissociatively absorbed on the noble metal generating atomic H•, which then "spills over" onto the CeO_2 with the formation of OH species, which causes the Ce to exist as a trivalent cation.

Although the reduction of Pt^{4+} begins at ~130°C for Pt-CGO, the reduction of the Ce^{4+} occurs only after oxidized Pt is reduced to Pt^0, which begins to occur at 270°C. This suggests that Pt^0 is necessary for "hydrogen spillover" to occur. Reduction of Ce in the bulk begins at ~450°C and appears to be completed at ~650°C. The presence of noble metals is believed to have little, if any, influence on the reducibility of Ce in the bulk [6]. Reduction of Ce in the bulk is not expected to participate in the shift reaction because it occurs at higher temperatures than the temperature range at which the WGS reaction is conducted in the fuel processor (200-450°C).

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