

# Temperature-Programmed Reduction Studies of Platinum Supported on Gadolinia- or Zirconia-Ceria

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## Introduction

Platinum supported on ceria and doped-ceria oxides are being investigated as catalysts for the water-gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ ), which is used in many fuel cell fuel processors for reducing the concentration of CO in the fuel gas exiting the reformer [1-5]. Compared to commercial Cu/Zn and Fe/Cr oxide shift catalysts, these ceria-based Pt catalysts exhibit higher reaction rates, are less prone to deactivate during startup/shutdown cycles, and are not pyrophoric under reaction conditions typical of those employed in fuel cell fuel processors. The cost of these ceria-based Pt catalysts compared to the commercial Cu/Zn and Fe/Cr catalysts is an issue.

Research is focussing on understanding the reaction mechanism by which these ceria-based Pt catalysts operate to optimize the Pt utilization. Two different reactions mechanisms, one termed the “redox mechanism” [1] and the other termed the “formate mechanism” [4], have been proposed. In the “redox mechanism,” CO adsorbed on the surface of Pt particles is oxidized to  $\text{CO}_2$  by ceria at the Pt-ceria interface, resulting in the formation of an oxygen vacancy on the ceria surface. The oxygen vacancy is then replenished with oxygen from water generating  $\text{H}_2$ . During the reaction, Ce undergoes a change in oxidation state from Ce(IV) to Ce(III) and then back to Ce(IV), hence the name “redox mechanism.” In the “formate mechanism,” CO reacts with hydroxyl groups on the surface of reduced ceria to generate surface formates, which then react with water, decomposing to yield  $\text{CO}_2$  and  $\text{H}_2$ . Both mechanisms require that Pt be present as Pt(0). In the redox mechanism, Pt(0) is required for the adsorption of CO. In the formate mechanism, Pt(0) is required to promote the reduction of ceria via “hydrogen spillover” from the metal to the support [6]. Both mechanisms require a strong interaction between the Pt and ceria support. To enhance its chemical and physical properties, ceria is often doped with oxides such as gadolinia or zirconia [7]. Doping ceria with trivalent gadolinium increases the number of oxygen vacancies which could favor the formation of surface hydroxyl groups. Doping ceria with tetravalent zirconium increases the oxygen release rate which could facilitate oxygen transfer at the Pt-support interface. The objective of this study was to investigate the effect of the ceria dopant on the reducibility of Pt.

## Methods and Materials

Two different ceria dopants were investigated, gadolinia and zirconia. 3 wt% Pt supported on gadolinium-doped ceria,  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ , (Pt-CGO) and 3 wt% Pt supported on a zirconia-doped ceria,  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_{2.0}$ , (Pt-CZO), were prepared by using the incipient wetness process.  $\text{H}_2\text{PtCl}_6$  was used as the Pt precursor for both formulations. After impregnation of Pt, the samples were dried in air at 120°C overnight and then calcined

in air at 500°C for 2-h. The composition for gadolinium-doped ceria,  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ , was chosen because it has a relatively high concentration of oxygen vacancies while maintaining the ceria fluorite structure. The composition for zirconium-doped ceria,  $\text{Ce}_{0.80}\text{Zr}_{0.20}\text{O}_{2.0}$ , was chosen to be have the same molar ratio of ceria-to-dopant as CGO.

Temperature-programmed reduction (TPR) of samples of Pt-CGO and Pt-CZO were conducted at a heating rate of 2°C/min with a 4%  $\text{H}_2$ /balance He mixture flowing at 50 mL/min using a flow cell designed for use on the beamline at Sector 10, MR-CAT. The flow cell used a sample holder that allowed four different catalyst samples to be studied simultaneously. Two samples of each formulation were studied: a sample of the catalyst as prepared and a sample of the catalyst after a reduction/reoxidation process. The reduction/reoxidation process involved first reducing the catalyst by heating it under a flowing mixture of 4%  $\text{H}_2$ /He from room temperature to 500°C at a rate of 5°C/min and holding for 1-h at 500°C, then purging with  $\text{N}_2$  while maintaining the temperature at 500°C, and finally heating it under flowing air for 1-h at 500°C before cooling to room temperature in air. The reduction/reoxidation process was conducted in a microreactor system prior to loading the sample into the flow cell. The purpose of the reduction/reoxidation process was to simulate a startup/shutdown cycle. X-ray absorption spectra were collected at the Pt  $L_{III}$  edge in the transmission mode every 90 seconds. The X-ray absorption near edge structure (XANES) spectra were analyzed using factor analysis to determine the oxidation states of Pt and the relative abundance of the various Pt oxidation states. The extended fine structure (EXAFS) was analyzed to determine the Pt coordination number (CN).

## Results

Pt(IV) is initially the principle oxidation state of Pt on all samples of Pt-CGO and Pt-CZO as shown Figs. 1 and 2. The data was best fit assuming that the Pt(IV) is a mixture of  $\text{PtO}_2$  and Pt oxychlorides.

For the as prepared sample of Pt-CGO, the reduction of Pt(IV) to Pt(II) begins at ~90°C. Pt(II) is relatively unstable under these reaction conditions and is easily reduced to Pt(0) at temperatures above ~125°C. The relative abundance of Pt(0) is 0.8 at 200°C and >0.95 at 300°C. The reduction/reoxidation process causes the Pt to be more easily reduced than it is on the as prepared sample. For the reduced/reoxidized sample of Pt-CGO, the reduction of Pt(IV) to Pt(II) begins at ~50°C. As with the as prepared sample, Pt(II) is relatively unstable and is easily reduced to Pt(0) at a temperature of ~60°C. The relative abundance of Pt(0) is 0.6 at 100°C and >0.9 at 200°C.

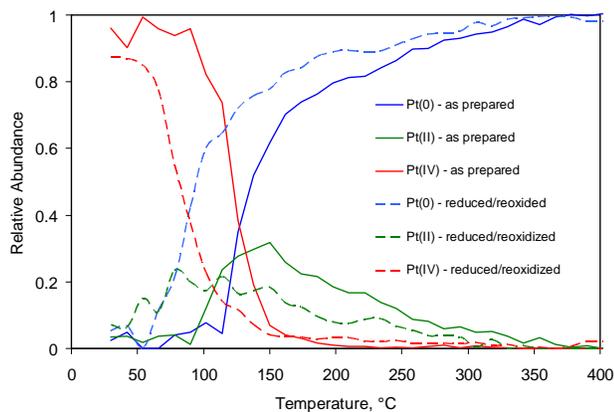


Figure 1. The relative abundance of Pt oxidation states as a function of temperature for TPR of 3 wt% Pt-CGO as prepared and after the reduction/reoxidation process.

Pt(IV) is more stable on Pt-CZO than on Pt-CGO. Although the data suggests that Pt(IV) begins to reduce to Pt(II) at a lower temperature on Pt-CZO (~50 °C) than Pt-CGO (~90 °C), significant reduction of Pt(IV) to Pt(II) is observed at a higher temperature on Pt-CZO (~175°C) than Pt-CGO (~125°C). As with Pt-CGO, Pt(II) is relatively unstable, especially above 175°C, and is easily reduced to Pt(0). For example, the relative abundance of Pt(0) is <0.1 at 150°C, 0.4 at 200 and 0.75 at 210°C. Unlike Pt-CGO, there is evidence for some oxidized Pt, primarily Pt(II), at 400°C, although the relative abundance is relatively low, <0.1. As was observed with Pt-CGO, Pt is more easily reduced on the sample after the reduction/reoxidation process than it is on the as prepared samples; however, the effect of the reduction/reoxidation process on lowering the reduction temperature for Pt-CZO is less than on Pt-CGO.

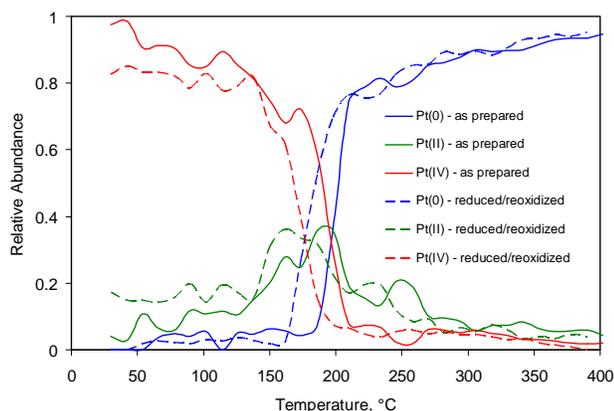


Figure 2. The relative abundance of Pt oxidation states as a function of temperature for TPR of 1 wt% Pt-CZO as prepared and after the reduction/reoxidation process.

The EXAFS region of the spectra of all four samples was analyzed to determine the Pt-Pt CN. Based on the coordination number, an average particle size was estimated. Subnanometer particles were observed on all samples, with the coordination number and average particle size being slightly smaller on the

Table 1. Pt-Pt coordination number (CN) and average particle size for Pt-CGO and Pt-CZO samples.

Sample	Coordination Number (CN)	Particle Size (nm) [10]
Pt-CGO – as prepared	4.5 +/- 0.8	0.53 +/- 0.05
Pt-CGO – reduced/reoxidized	4.5 +/- 0.8	0.53 +/- 0.05
Pt-CZO – as prepared	3.2 +/- 0.8	0.45 +/- 0.05
Pt-CZO – reduced/reoxidized	3.2 +/- 0.8	0.45 +/- 0.05

Pt-CZO sample than the Pt-CGO sample as shown in Table 1. The reduction/reoxidation process did not effect the Pt-Pt coordination number or particle size.

## Discussion

Microreactor kinetic studies were conducted on Pt-CGO and Pt-CZO samples at various Pt loadings ranging from 1 to 5 wt% as well as for Ce:Zr ratios, ranging from 0-100% Ce, in addition to the ratio used in this study [5,7]. The kinetic studies showed high CO conversion rates at  $\geq 250^\circ\text{C}$  for both Pt-CGO and Pt-CZO, well above the temperature required for the reduction of oxidized Pt to Pt(0), and consistent with both the redox and formate reaction mechanisms. The kinetic studies also showed that was essentially no difference in the activity of Pt-CGO and Pt-CZO when compared on a per gram of Pt basis [8].

The TPR studies suggest Pt is more difficult to reduce on Pt-CZO than Pt-CGO which could be attributed to the better ability of CZO to release oxygen than CGO and thus better stabilize the oxidized Pt. However, the reducibility of Pt is known to depend on the Pt particle size with smaller particles being more difficult to reduce than larger Pt particles. As shown in Fig. 3, 3.0 wt% Pt-CGO reduces at a much lower temperature than 0.5 wt% Pt-CGO. The TPR for 0.5 wt% Pt-CGO was previously reported [9]. Although the Pt-Pt coordination number, and hence the average particle size, was not determined for the 0.5 wt% Pt-CGO sample, it is expected that smaller diameter Pt particles are present on 0.5 wt% Pt-CGO than on 3 wt% Pt-CGO. However, the estimated Pt particle sizes for the 3 wt% Pt-CGO and 3 wt% Pt-CZO are not that drastically different, 0.53 nm and 0.40 nm, and do not completely account for the differences in the reducibility of Pt on the two samples. The observation that the Pt was more easily reduced on both the CZO and CGO samples after the reduction/reoxidation process is attributed to the fact the Pt was not completely reoxidized to Pt(IV) during the reoxidation step.

Further studies are necessary to determine why oxidized Pt appears to be more stable on CZO than on CGO. However, it has little or no effect on the water-gas shift reaction rate since Pt is reduced Pt(0) on both CZO and CGO at temperatures well that at which appreciable water-gas shift activity is observed,

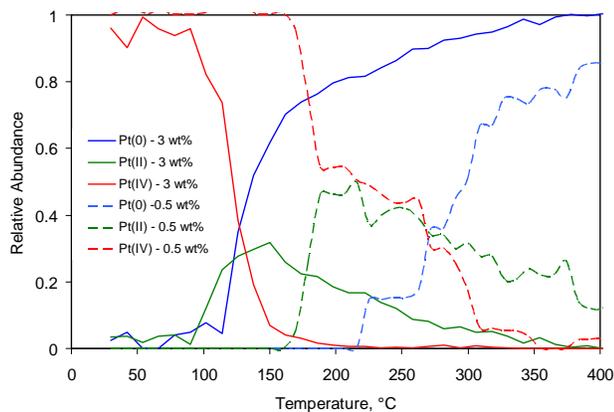


Figure 3. Comparison of the relative abundance of Pt oxidation states as a function of temperature for TPR for 0.5 and 3 wt% Pt-CGO.

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