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Automotive Polymer Electrolyte Fuel Cell Systems**

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Introduction

Polymer electrolyte fuel cell (PEFC) systems are a leading candidate for replacing the internal combustion engine in light duty vehicles. One method of generating the hydrogen necessary for the PEFC is reforming a liquid fuel, such as methanol or gasoline, via partial oxidation, steam reforming, or autothermal reforming (a combination of partial oxidation and steam reforming). The H₂-rich reformat can contain as much as 10% carbon monoxide. Carbon monoxide has been shown to poison the platinum-based anode catalyst at concentrations as low as 10 ppm,¹ necessitating removal of CO to this level before passing the reformat to the fuel cell stack.

The water-gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, is used to convert the bulk of the reformat CO to CO₂. Industrially, the WGS reaction is conducted over two catalysts, which operate in different temperature regimes. One catalyst is a FeCr mixed oxide, which operates at 350–450°C and is termed the high-temperature shift (HTS) catalyst. The second catalyst is a CuZn mixed oxide, which operates at 200–250°C and is termed the low-temperature shift (LTS) catalyst. Although these two catalysts are used industrially in the production of H₂ for ammonia synthesis, they have major drawbacks that make them unsuitable for transportation applications. Both the LTS and the HTS catalysts must first be “activated” before being used. For example, the copper in the copper oxide/zinc oxide LTS catalyst must first be reduced to elemental copper *in situ* before it becomes active for the WGS reaction. This reduction reaction is exothermic and must be carried out under well-controlled conditions using a dilute hydrogen stream (1 vol% H₂) to prevent high catalyst temperatures, which can result in sintering (agglomeration) of the copper particles and loss of active surface area for the WGS reaction. Also, once the catalyst has been activated by reduction, it must be protected from exposure to ambient air to prevent re-oxidation of the copper. The activated catalyst must also be protected from the condensation of liquids, for example, during start-up or transient operation. For these reasons, a more thermally rugged catalyst is needed which has sufficient activity to operate at the low temperatures that are thermodynamically necessary to achieve low CO concentrations.

No single metal, with the exception of copper, has high activity for both the dissociation of H₂O and oxidation of CO, two important elementary reaction steps for the WGS reaction.² Therefore, we are investigating bi-functional catalysts where one component of the catalyst promotes the adsorption and oxidation of CO and the other component dissociates the H₂O. The metals platinum, ruthenium, palladium, and cobalt were chosen as the CO-adsorbing component of the catalyst because they have moderate CO adsorption energies and are less prone to sintering than copper (i.e., higher melting points). The water-dissociating component was chosen to be a material that is readily oxidized and reduced at the oxygen partial pressures and temperatures encountered in the water-gas shift reactor ($p_{\text{O}_2} < 10^{-30}$, 180-400°C). This ready oxidation-reduction can form labile oxygen adatoms to oxidize co-adsorbed CO and release hydrogen. One such material is ceria doped with species that enhance the formation of oxygen ion vacancies. Dopant cations were chosen that promote the formation of oxygen vacancies in the ceria lattice by virtue of their lower valence state (i.e., trivalent cations) or their ability to cause strain in the ceria lattice (e.g., cations with smaller ionic radii). To test our hypothesis we chose gadolinium, samarium, yttrium, and praseodymium as the trivalent dopants and zirconia as a strain-causing dopant.

Experimental

The ceria and doped cerias tested as water-dissociating catalyst components are listed in Table 1. The ceria powders were either made by the glycine-nitrate process (Ceria, CZY, CZG, CZP) or purchased from Nextech (CSO) or Praxair (CGO). To briefly summarize the glycine-nitrate method, nitrates of cerium and the ceria dopants are dissolved in water and combined with glycine. This mixture is heated to evaporate the water and rapidly oxidize the nitrates. The resulting powder is calcined in air at 800°C for 2 h yielding a homogeneously doped ceria powder with a surface area of 30–60 m²/g. The active metals palladium and cobalt were dispersed on the doped-ceria powders by incipient wetness of a solution of the metal nitrates. Platinum was dispersed from a solution of hexachloroplatinate or platinum tetraamine. Ruthenium was dispersed from a solution of ruthenium nitrosyl nitrate. Typical loadings for palladium, cobalt, and ruthenium were 1 wt%. Platinum loadings ranged from 0.14 wt% to 1 wt%. The catalysts were dried at 80–120°C in air, and then activated by heating in either air or 4% H₂ (in helium) to convert the metal complex to elemental metal particles.

Table 1. Doped ceria compositions tested and BET surface areas before metal addition

Symbol	Composition	BET Surface Area (m²/g)
Ceria (undoped)	CeO ₂	27.9
CGO	Ce _{0.8} Gd _{0.2} O _{1.9}	36.0
CSO	Ce _{0.85} Sm _{0.15} O _{1.925}	93.4
CZY	Ce _{0.8} Zr _{0.1} Y _{0.1} O _{1.95}	42.2
CZG	Ce _{0.8} Zr _{0.172} Gd _{0.025} O _{1.99}	59.9
CZP	Ce _{0.8} Zr _{0.172} Pr _{0.025} O _{1.99}	52.0

The platinum-on-doped-ceria catalyst was supported on high-surface-area, >200 m²/g, γ-alumina extrudates. Several methods and materials were tested for this deposition. Two platinum precursors were used: hexachloroplatinic acid and platinum tetraamine nitrate. The doped ceria and the platinum were either deposited simultaneously or sequentially using the incipient wetness technique. For the simultaneous deposition, the alumina extrudates were imbued with a solution of cerium nitrate, dopant

nitrate, and platinum tetraamine nitrate, dried at 80°C, then flash-fired in air at 600°C. This process was repeated until the desired weight loading of Pt/doped-ceria was achieved. For the sequential deposition, the alumina extrudates were first imbibed with the solution of cerium nitrate and dopant nitrate, dried at 80°C, then flash-fired at 600°C in air. This was repeated until the desired weight loading of doped-ceria was achieved (50 wt%). The doped ceria/alumina substrate was then imbued with a platinum tetraamine nitrate solution and dried at 80°C. The resulting catalyst was then either directly heated to 230°C in 4% H₂ (in helium) just before to water-gas shift testing, or flash-fired at 600°C in before the treatment with 4% H₂.

The WGS activity measurements were carried out with two simulated reformat feeds, one with a low CO concentration (1.02% dry) and the other with a high CO concentration (10% dry). For the low CO feed stream, the composition was 0.46% CO, 8.55% CO₂, 21.6% H₂, 55% H₂O, and bal. N₂ (Dry Basis: 1.02% CO, 19.1% CO₂, 48.2% H₂, and bal. N₂). The high CO reactant stream composition was 6.86% CO, 9.12% CO₂, 29.29% H₂, 31.43% H₂O, 1.36% CH₄, and bal. N₂ (Dry Basis: 10% CO, 13.3% CO₂, 42.72% H₂, 1.98% CH₄, and bal. N₂). All activity results shown below are for the low CO concentration reformat. A small amount of catalyst (0.1–0.3 g) was ground with a mortar and pestle and mixed with alumina powder to achieve a total sample weight of approximately 1 g. Before testing, the catalysts were reduced at 230°C for 1–2 h with 4% H₂ (in helium). To eliminate the effect of mass transfer on the measurements and to get the kinetically-limited activity, the reactor was operated in a differential mode (CO conversions <10%). The flow rate of the simulated reformat was varied to achieve carbon monoxide conversions of less than 10% in general and less than 2% for the majority of the tests. The outlet CO concentration was determined with either Horiba (0–2 vol%) or ZRH (0–15 vol%) infrared gas analyzers. The outlet CO₂ concentration was determined using the ZRH analyzer. Outlet compositions were also analyzed with an HP 5890 gas chromatograph fitted with two J&W Scientific columns: (1) GS-MolSieve with Ar as the carrier gas for analysis of H₂, CH₄, and CO and (2) GS-Q with He as the carrier gas for analysis of CO₂. The specific surface area of the entire catalyst was determined using nitrogen adsorption BET analysis on a Micromeritics ASAP 2010.

Results and Discussion

The highest WGS activities were observed with platinum as the active metal. The catalysts with ruthenium and cobalt as the active metal exhibited methanation activity at the higher test temperatures (>350°C). The platinum catalysts were active for the WGS reaction over the entire 180–400°C range, did not require activation by *in situ* reduction, and did not lose their activity upon exposure to air at 21–550°C. Given the high activity of the platinum catalysts relative to the other metals studied, a detailed study of the effect of ceria-dopant and preparation method was undertaken with platinum as the active metal.

The dopants did, indeed, significantly improve the WGS activity of the ceria catalyst; the zirconia- and praseodymium-doped catalyst (CZP) showed the greatest improvement, with twice the activity of the undoped ceria catalyst (see Fig. 1). It can be concluded that the dopant effect is not merely a surface area effect by comparing the BET surface areas given in Table 1 and the WGS activities shown in Fig.1 (e.g., CZP has the highest WGS activity while CSO the highest surface area).

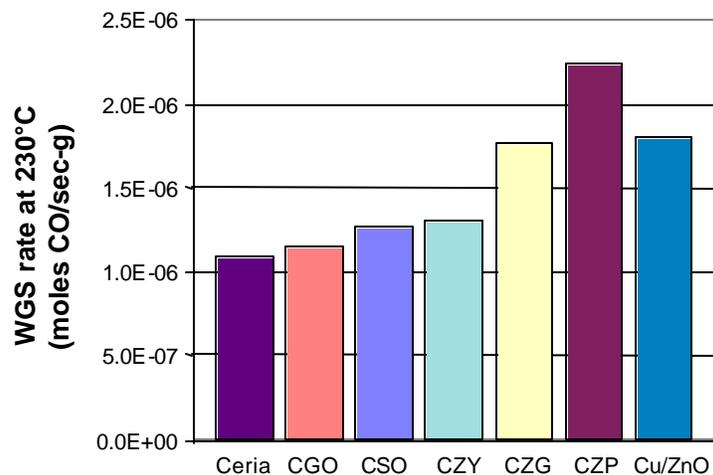


Figure 1. WGS reaction rates at 230°C for 1 wt% Pt/doped ceria catalyst powders. Cu/ZnO is Süd-Chemie Inc.’s C18-7. The reactant gas was “Low CO” reformat (see experimental section).

We found that supporting the platinum/CGO catalyst on high-surface-area γ -alumina extrudates nearly doubled the WGS activity of the catalyst (see Fig. 2). We also found that the specific platinum precursor used and the pre-activation procedure followed can dramatically affect the activity of the catalyst. The highest activity was seen when the catalyst was prepared using platinum tetraamine nitrate as the platinum precursor, and the catalyst was calcined at 600°C prior to reduction in the WGS reactor. The procedure for coating doped ceria and platinum on the γ -alumina also has an effect on the catalyst activity. The highest activity was obtained by first coating the γ -alumina extrudates with doped ceria, and then coating the doped ceria/ γ -alumina with platinum (sequential deposition) rather than by coating the γ -alumina simultaneously with a mixture of doped ceria and platinum (see Fig. 3).

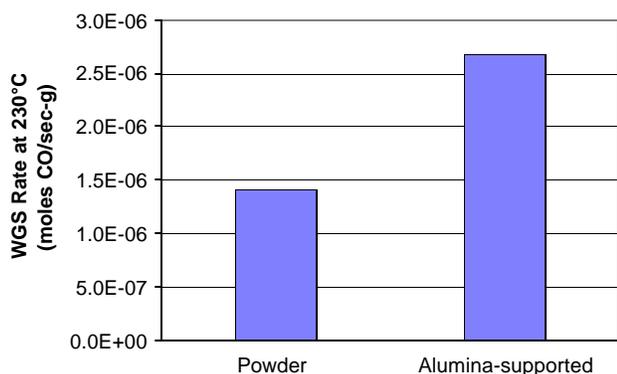


Figure 2. The effect of supporting the 1 wt% Pt/Ce_{0.8}Gd_{0.2}O_{1.9} catalyst on γ -alumina extrudates. “High CO” reformat.

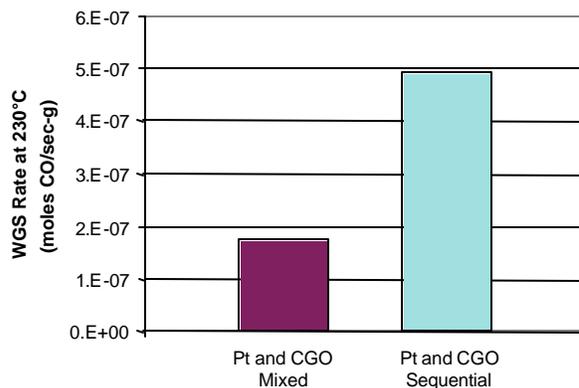


Figure 3. The effect of the coating procedure on the WGS activity of the 0.14 wt% Pt/Ce_{0.8}Gd_{0.2}O_{1.9} (CGO)/ γ -alumina catalyst. “Low CO” reformat.

Conclusion

The platinum/doped ceria/ γ -alumina catalyst presented here has WGS activity that is comparable to commercial Cu/ZnO catalysts. However, unlike the commercial FeCr and Cu/ZnO catalysts, this catalyst does not have to be activated by *in situ* reduction, does not lose its activity upon exposure to air at 21–550°C, and is active over a wide temperature range (180–400°C) so that it can be used effectively as both the HTS and the LTS catalyst. These properties of the platinum/doped ceria catalysts make them suitable for use in fuel processors for transportation applications. However, the high cost of precious metals, even at loadings as low as the 0.14 wt% achieved in this work, may prohibit the use of these catalysts in light duty vehicles. Our research is now focused on replacing the platinum in these catalysts with less costly metals without sacrificing catalyst activity or durability.

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