

The Effect of Steam Oxidation on the Activity of Ceria-Praseodymia Mixed Catalysts in the Water-Gas-Shift Reaction

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Introduction

Ceria and ceria-supported metals have been widely studied as catalysts for the water-gas-shift (WGS) reaction [1, 2], playing an important role in promoting the oxidation of CO in applications such as emission-control. According to the proposed reaction mechanism [3], CO adsorbs to the precious-metal sites and reacts with ceria's oxygen to form CO₂, followed by desorption and ceria reoxidation by steam.

Praseodymia (Pr₆O₁₁), a neighboring lanthanide oxide with similar properties as ceria, was hypothesized to show comparable performance under WGS conditions. Praseodymium has multiple stable oxidation states similar to cerium and the oxide is known to release its loosely-bound oxygen at lower temperatures than ceria. Despite these advantages, praseodymia and ceria-praseodymia oxides demonstrated poor WGS performance, likely due to their inability to undergo oxidation by H₂O.

Materials and Methods

The support oxides of pure ceria and praseodymia were initially prepared by thermal decomposition of respective nitrates, while the Ce_{0.5}Pr_{0.5}O_{2-x} support was prepared using the citric acid method [4]. A palladium promoter was deposited on all of the supports using wet impregnation. WGS reaction rates to determine catalytic activity were studied under differential reaction conditions (<10% conv.) and were found by GC analysis of the reactants and products. The oxidation states of catalysts exposed to various conditions were determined using flow titration [5], monitoring oxygen consumption from air flow (21% O₂, 79% N₂) by a mass spectrometer. Thermodynamic redox properties of the catalysts cited in the analysis were determined in a previous study [6] using the coulometric titration method.

Results and Discussion

Pd-promoted PrO_x, 35 m²/g, and Ce_{0.5}Pr_{0.5}O_{2-x}, 42 m²/g, both exhibited an order of magnitude decrease in WGS performance compared to ceria, 67 m²/g, at differential reaction conditions. Both praseodymium-based catalysts had initially performed as well as the ceria catalyst, but were gradually "deactivated" over time (~1 h) until steady state conversion was reached. The slow decrease in performance suggested a disruption in the WGS mechanism, in that the catalysts were not being reoxidized by steam. Reduction of the oxides by H₂ and subsequent exposure to steam (Fig. 1) demonstrates that significantly more reoxidation occurs with ceria than either of the praseodymium-based catalysts. Oxidation states of catalysts exposed to WGS conditions were determined to be comparable to those reoxidized by steam.

Examining the redox properties of both PrO_x and Ce_{0.5}Pr_{0.5}O_{2-x} at significant WGS conversions (i.e. 10 to 100%, corresponding to 19:1 to 1:1 H₂/H₂O mixtures at equilibrium, or an equivalent oxygen fugacity, log(P(O₂)), range of -24 to -20) determined by coulometric titration, reveals that both catalysts are nearly deficient of atomic oxygen available for removal [6]. The equilibrium data also illustrates that ceria is almost entirely oxidized in this fugacity range and would suggest that ceria, unlike the praseodymium-based catalysts, could be further reduced and subsequently oxidized by steam.

Significance

A potential approach to finding enhanced catalysts for various oxidation-reduction reactions suggests focusing on selecting catalysts which have significant oxygen reduction potentials at the reaction conditions. Catalysts that fail to exhibit this potential are expected to remain in a reduced or a near-reduced state during the course of a reaction.

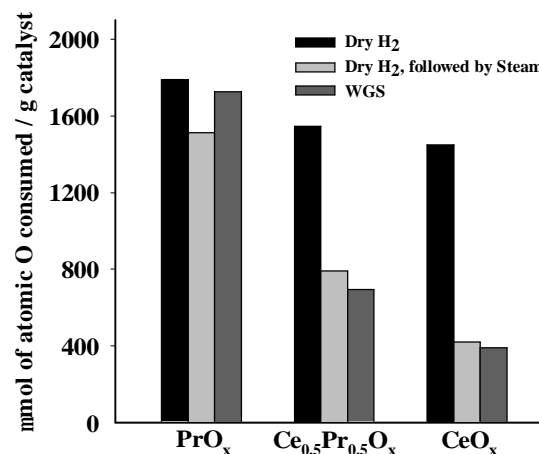


Figure 1. Atomic oxygen consumption by 1 wt.% Pd promoted oxide catalysts following reduction by pure H₂ gas, subsequent partial oxidation by 76 torr H₂O in He gas, and water-gas shift (WGS) conditions as determined by flow titration at 873 K.

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