

Low-Temperature Hydrocarbon/CO Oxidation Catalysis supporting HCCI Emissions

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Introduction

Homogeneous charge compression ignition (HCCI) strategies have uniquely & effectively shown the ability to decrease engine emission levels of both PM (soot) & NO_x [1]. HCCI combustion is initiated in several locations at a time; this makes the fuel/air mixture burn nearly simultaneous. The resulting lower combustion temperatures result in lower NO_x and soot production. However, there are trade-offs between low NO_x emissions and the products of incomplete combustion (CO and unburned hydrocarbons). For enabling the HCCI application, oxidation catalysts will need to be employed for CO and hydrocarbon oxidation, and must be effective at temperatures lower than conventional oxidation catalysts [1]. Research is underway developing catalyst materials for achieving CO and hydrocarbon oxidation at temperatures below typical light-off for existing oxidation catalysts. For oxidation environments, transition metals (e.g. Pr, Tb) have been incorporated into CeO₂ systems as it is believed that they enhance the low-temperature redox capacity of the system, improving its low-temperature oxidation capacity [2, 3].

Materials and Methods

Ce_xPr_{1-x}O₂ supports were prepared by thermal decomposition of the respective Ce(NO₃)₂•6H₂O and Pr(NO₃)₂•6H₂O solutions. Pd/Ce_xPr_{1-x}O₂ catalysts were prepared by incipient wetness technique, employing Pd(NH₃)₄(NO₃)₂ solution. All activity measurements were performed with 100 mg catalyst powder with an 80 – 100 mesh size, with a total flow rate of 200 SCCM, 400 SCCM, and 800 SCCM. The gas composition interrogated was 10% oxygen, 8% CO₂, 7% H₂O, 2500 ppm CO, 250 ppm C₃H₆, 250 ppm C₃H₈, and 500 ppm CH₄ (2000 ppm C₁).

Results and Discussion

A series of catalysts have been interrogated employing Pr in various levels blended into a Pd/CeO₂ system. Figure 1 shows the results of activity measurements on CO, C₃H₆, C₃H₈, and CH₄, for 0 – 100% Pr blended into the CeO₂ system. Results identified an optimum loading of 10 – 20% Pr in the CeO₂ support.

Characterization efforts have been performed in an attempt to elicit structure-activity relationships within the Ce_xPr_{1-x}O₂ system, including BET measurements, pore size distribution measurements, TPR/TPO analysis, XRD analysis, and H₂ chemisorption measurements. BET measurements showed minimal loss of surface area with increased Pr through 20% (Ce_{0.8}Pr_{0.2}O₂), at which point additional Pr (>20%) resulted in significant loss of surface area. Similarly, pore size distribution results showed that through 20% Pr loading, larger pores arose, subtly shifting the pore distribution maxima towards larger pores asymmetrically, whereas >20% Pr significantly decreased the maxima, with drastic broadening of the peak towards larger pores asymmetrically. H₂ chemisorption measurements showed

increased synergy of the Pd with the support at 10 – 20% Pr loading, resulting in >100% measured dispersion, the actual dispersion masked by hydrogen spill-over [4]. TPO studies demonstrate the ability to more readily oxidize the Pd metal as Pr is blended into the CeO₂ system, through 20% Pr (Ce_{0.8}Pr_{0.2}O₂). XRD analyses showed that Pr blends into the CeO₂ system as PrO₂, however in its natural state void of CeO₂, Pr will form Pr₆O₁₁ (PrO_{1.83}). Similarly, the crystal cell structure shows slight swelling of the cell parameter at 10 – 20% Pr, which is lost at >20% Pr loading.

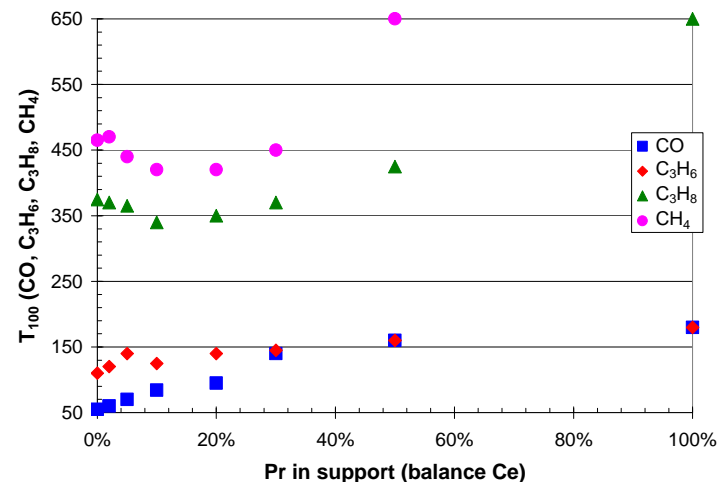


Figure 1. Activity measurements of Pr blended into a Pd/CeO₂ system employing 100 mg catalyst at a flow rate of 400 SCCM.

It is believed that blending in of Pr into the CeO₂ system brings about a larger reservoir of available oxygen, and increased synergy with the Pd metal phase, resulting in an improved (i.e. lower active temperature) redox capacity of the system. However, due to the nature of the Pr phase, it is believed that the additional Pr also brings about a swelling and weakening of the support phase to the point of collapse with >20% Pr loading.

References

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