Model $Pt/Ce_xPr_{1-x}O_2$ (x = 1 or 0.9) NOx storage-reduction catalysts

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Introduction

In catalytic applications, ceria is frequently doped with rare earth elements in order to modify its electronic and/or structural properties. In the case that trivalent cations are incorporated into the CeO_2 lattice, anion vacancies are created by a charge-compensating effect, resulting in an increase in oxygen-storage capacity (OSC). If the dopant has variable oxidation state, as is the case with praseodymium, the resulting vacancies are extremely mobile. This strongly influences the redox properties of the ceria by increasing both total and kinetic oxygen storage [1]. In view of the foregoing, we reasoned that the addition of praseodymium to ceria should be beneficial for NOx storage-reduction applications. Indeed, a study by Rohart and co-workers [2] found that doping 8 wt% Pr into a Ce-Zr mixed oxide resulted in a significant increase in the efficiency of NOx storage (for samples loaded with 1 wt% Pt), particularly at lower temperatures (200-350 ºC). This increase was found to correlate with improved activity for NO oxidation over this temperature range. However, despite this promising result, there do not appear to have been any other reports concerning the properties of Ce-Pr mixed oxides in NOx storage-reduction (NSR). Therefore, in this study we studied model $Pt/Ce_{0.9}Pr_{0.1}O_2$ NSR catalysts prepared via several different routes and, for comparison purposes, their Pt/CeO_2 analogs.

Materials and Methods

Pt/CeO_2-M and $Pt/Ce_{0.9}Pr_{0.1}O_2$-M catalysts were prepared, where M indicates the synthesis method of the ceria-based support: N (nitrate calcination), C (activated carbon template) and U (homogeneous precipitation with urea). $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa-Aesar, 99.99%) and $Pr(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich, 99.9%) were used as precursors. Platinum was loaded on the resulting CeO_2 and $Ce_{0.9}Pr_{0.1}O_2$ powder supports by incipient wetness impregnation using aqueous $Pt(NH_3)_4(NO_3)_2$ in the appropriate concentration to obtain a metal loading of 1 wt.%. The impregnated supports were placed in a muffle furnace held at 250 ºC (flash calcination); once introduced, the temperature was raised to 500 ºC and held there for 30 min. Catalyst characterization and evaluation was performed using previously report methods [3].

Results and Discussion

Model $Pt/Ce_{0.9}Pr_{0.1}O_2$ NSR catalysts were prepared via three different routes, as were their Pt/CeO_2 analogs. Raman data (not shown) indicated the presence of lattice vacancies in the $Ce_{0.9}Pr_{0.1}O_2$ supports, arising from replacement of Ce with Pr in the lattice. Moreover, for the Pr-containing samples, H_2-TPR profiles contained high temperature bulk reduction peaks which were less pronounced compared with their Pt/CeO_2 analogs, indicating that the presence of praseodymium enhances oxygen mobility due to the creation of lattice defects.

When tested under lean-rich cycling conditions at 200 ºC, 300 ºC and 400 ºC, the cycle-averaged NOx conversion of each $Pt/Ce_{0.9}Pr_{0.1}O_2$ sample was in each case substantially higher than that of its Pt/CeO_2 analog, amounting to a difference of >10% in the absolute NOx conversion in some cases. As shown in Table 1, the trends for catalyst NOx storage efficiency (NSE), defined as the amount of NOx stored in the lean phase divided by the amount of NOx fed, mirror those for the NOx conversion. Indeed, it is apparent that lean phase NSE is the main determinant of the cycle-averaged NOx conversion; this follows from the fact that rich phase NOx release from the catalysts (i.e., the amount of NOx liberated without reduction) is relatively minor. In the absence of significant differences in surface area and platinum dispersion between the $Pt/Ce_{0.9}Pr_{0.1}O_2$ samples and their Pt/CeO_2 analogs, the improved NSE of the Pr-promoted samples can be attributed to their higher oxygen mobility and greater reducibilty. This should both favor the adsorption of NO as nitrites and the oxidation of nitrites into more thermally stable nitrate, resulting in superior lean phase NSE.

Table 1. NOx conversion, storage and release at 200 ºC under lean-rich cycling conditions.*

Catalyst	NOx conv. (%)	NOx storage eff. (%)	Rich phase NOx release (%)
Pt/CeO_2-N	69.1	72.5	4.7
Pt/CeO_2-C	49.7	52.6	5.5
Pt/CeO_2-U	54.5	57.6	5.4
$Pt/Ce_{0.9}Pr_{0.1}O_2$-N	74.2	76.8	3.4
$Pt/Ce_{0.9}Pr_{0.1}O_2$-C	53.1	56.4	5.9
$Pt/Ce_{0.9}Pr_{0.1}O_2$-U	65.7	70.1	6.3

* Conditions: 120 s lean (300 ppm NO, 5% O_2, 5% CO_2, 5% H_2O, bal. He), 10 s rich (1.34% H_2, 4% CO, 5% CO_2, 5% H_2O, bal. He), GHSV = 30,000 h^{-1}.

As shown in Table 1, $Pt/Ce_{0.9}Pr_{0.1}O_2$-N, prepared by the nitrate calcination method, displays superior performance with respect to the materials prepared by the urea and carbon-templating routes. According to H_2 chemisorption, the Pt dispersion in $Pt/Ce_{0.9}Pr_{0.1}O_2$-N (and Pt/CeO_2-N) is higher than for the samples prepared by the other routes, while H_2-TPR results indicate that it undergoes surface reduction at slightly lower temperatures. This is indicative of a strong interaction between Pt and the $Ce_{0.9}Pr_{0.1}O_2$-N support, resulting in higher oxygen mobility and comparatively better reducibility – and hence, NSE – than the other $Pt/Ce_{0.9}Pr_{0.1}O_2$ samples.

Significance

These results suggest that ceria-based mixed oxides incorporating Pr are promising materials for NOx storage-reduction catalysts, particularly for low temperature applications.

References

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