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Reducibility of catalyzed cerium–praseodymium mixed oxides

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Cerium–praseodymium mixed oxides covering a wide range of cerium/praseodymium ratios were synthesized, loaded with 2 wt% palladium, and characterized by X-ray diffraction and temperature-programmed reduction. Both the degree and average temperature of reduction of the catalyzed mixed oxides were found to increase with increasing praseodymium concentration. Quantitative results indicate that these materials may be useful, in conjunction with hydrocarbon traps, for treating automotive cold-start emissions.

KEY WORDS: ceria; praseodymia; hydrocarbon trap; TWC; OSC; TPR.

1. Introduction

Cerium oxide has been an important ingredient in automotive exhaust-gas catalysts since the introduction of the three-way catalyst (TWC) in the early 1980s [1]. Regarded primarily as a source of oxygen storage capacity (OSC), cerium oxide was at first simply incorporated as pure ceria, but now it usually appears in the form of a mixed oxide containing zirconium as well as possibly one or more additional rare-earth elements. Motivated by the dramatic improvement in TWC performance and durability made possible by the development of these mixed oxides, which began in the early 1990s, research continues into new oxygen storage materials aimed at specific applications, such as the reduction of cold-start emissions. Along this line, the present study considers the effect of praseodymium concentration on the reducibility of catalyzed cerium–praseodymium mixed oxides for possible use with hydrocarbon (HC) traps.

Work on cerium–praseodymium mixed oxides at Ford Research Laboratory was initially performed by Logan and Shelef, who prepared materials spanning the whole composition range and showed that oxygen, in amounts exceeding that from pure ceria, is available by both thermal desorption and temperature-programmed reduction with hydrogen [2]. Addition of platinum or palladium as a catalyst was found to lower the reduction temperature, but catalyzed reduction was only examined in the case of one mixed oxide composition, $Ce_{0.45}Pr_{0.55}O_y$, which exhibited the lowest average temperature of reduction. Shigapov *et al.* [3] later performed OSC measurements on a series of Pd-catalyzed mixed oxides, based on the same composition but prepared in high-surface-area form, demonstrating the ability of ceria–praseodymia to provide high levels of oxygen (200–1000 μmol O per gram oxide) at low temperatures (100–350 °C).

The addition of materials that can supply high levels of oxygen at low temperatures to the TWC should, in principle, help reduce cold-start emissions since initial engine start-up involves a brief period of fuel-rich operation (needed for starting and cold-engine combustion stability) that creates an engine-out gas containing too little oxygen to react with all of the reductants (unburned HC as well as H_2 and CO) present. Properly timed release of oxygen from the TWC would thus be expected to accelerate catalyst light-off. In practice, several parameters, such as spark timing, exert considerable influence over this complex, dynamical process, and it is challenging to adjust all of them so as to achieve optimal emissions results while ensuring stable combustion and smooth engine operation.

However, even if there is enough oxygen to react with all of the reductants present during the initial fuel-rich period of operation, some HC will pass through the TWC before light-off occurs. Materials that can adsorb HC initially and then release it after catalyst light-off, forming the basis for HC traps, may be added to the TWC, but their efficacy usually hinges on additional hardware or complex engine control to supply extra oxygen during HC release. Instead, the addition of an oxygen storage material like ceria–praseodymia to the combination of HC trap and TWC could provide the oxygen needed to react with the HC released if the release processes are synchronized. In this study, we find that reduction temperature, as well as amount of oxygen available from catalyzed cerium–praseodymium mixed oxides, can be varied over the typical temperature range of HC release by changing the cerium-to-praseodymium ratio.

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2. Experimental details

Cerium–praseodymium mixed oxides with the compositions $Ce_{0.9}Pr_{0.1}O_y$, $Ce_{0.8}Pr_{0.2}O_y$, $Ce_{0.7}Pr_{0.3}O_y$, $Ce_{0.5}Pr_{0.5}O_y$, and $Ce_{0.3}Pr_{0.7}O_y$ were synthesized and then catalyzed with 2 wt% Pd by wet impregnation at W. R. Grace & Co. – Conn. Mixed oxide surface areas ranged from 67 to 21 m^2/g (from highest to lowest cerium concentration). Additional samples of catalyzed $Ce_{0.5}Pr_{0.5}O_y$ were also prepared by incorporation of the Pd precursor during synthesis of the mixed oxide, but the loading in these samples was lower, only 0.2 wt% Pd.

Samples were calcined in a muffle furnace at 600 °C for 12 h and then subjected to 12 h of a redox treatment at 1050 °C. X-ray diffraction (XRD) patterns were obtained with a Scintag X2 diffractometer using CuK_α radiation. Temperature-programmed reduction (TPR) measurements were performed with a Micromeritics AutoChem II 2920 system. Prior to each TPR run, the sample ($\sim$100 mg) was pre-treated by raising its temperature to 500 °C under a flow of 10% O_2 in He. The sample was then cooled to room temperature under the flow of 10% O_2 in He, flushed with Ar as it further cooled to −50 °C, and finally its temperature was ramped to 500 °C under a flow of 9% H_2 in Ar at a rate of 10 °C/min. Detailed descriptions of the TPR measurement process and redox treatment method are available elsewhere [4].

3. Results

The XRD pattern from 2 wt% $Pd/Ce_{0.5}Pr_{0.5}O_y$, calcined at 600 °C, is shown in figure 1(a) (offset by 3000 cps). This pattern is typical of all the mixed oxide compositions, which are indistinguishable by XRD at this stage because of the breadth of the peaks. After the redox treatment at 1050 °C, the peaks are sharper, as shown in figure 1(b), and a composition-dependent shift in peak position, consistent with formation of solid solutions of CeO_2 and PrO_2, is apparent through detailed examination of the patterns from 87 to 90 °C, as shown in figure 2. (Splitting of the peaks at large angle in figures 1(b) and 2 is due to a doublet in the CuK_α radiation. Patterns in figure 2 are offset by multiples of 500 cps.) A second phase, resembling Pr_6O_{11}, is evident in the Pr-rich sample. These results are consistent with previous findings [5–7].

The TPR curves (reflecting H_2 consumption as a function of temperature) from samples calcined at 600 °C are shown in figure 3 (offset by multiples of 0.15), and corresponding curves from samples subjected to the redox treatment at 1050 °C are shown in figure 4 (offset by multiples of 0.05). Quantitative results obtained by integration of such curves are presented in table 1.

An XRD pattern obtained from the 1050 °C/redox-treated 2 wt% $Pd/Ce_{0.5}Pr_{0.5}O_y$ sample, reduced at 350 °C in 1% H_2, is shown in figure 5(a) (offset by 2000 cps). The shift in position of the main peaks to lower

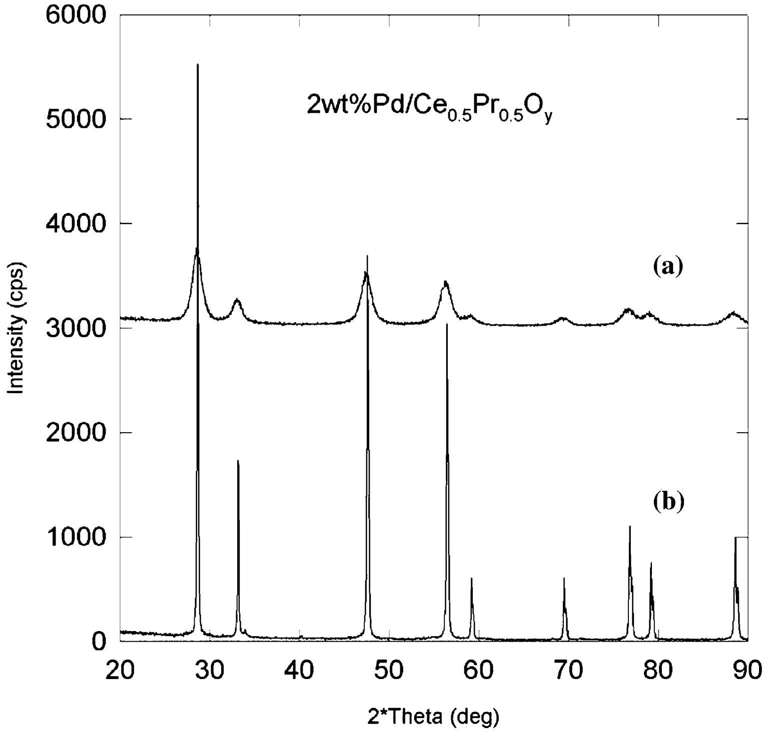

Figure 1. XRD patterns from samples of 2 wt% $Pd/Ce_{0.5}Pr_{0.5}O_y$ (a) calcined at 600 °C and (b) after the redox treatment at 1050 °C.

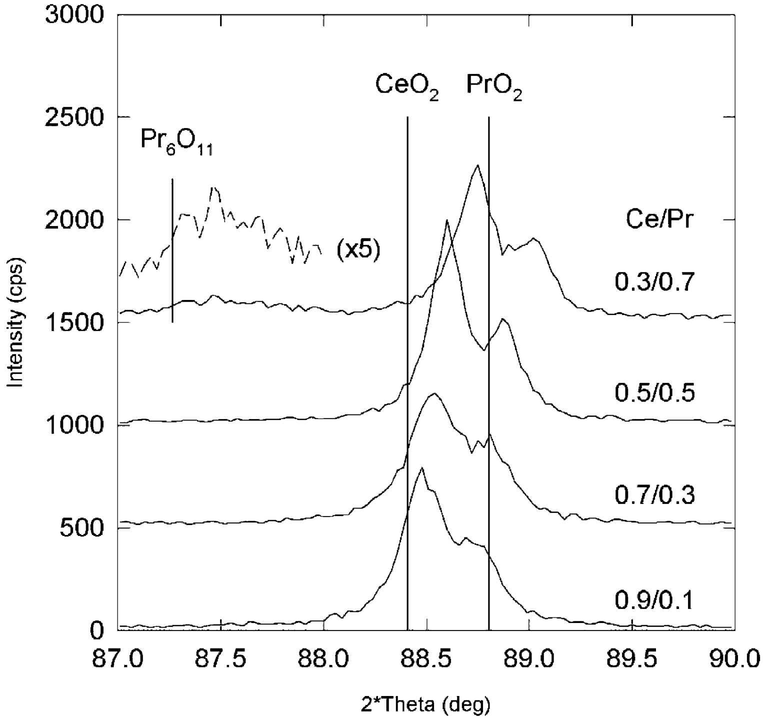

Figure 2. XRD patterns from 2 wt% Pd/$Ce_{1-x}Pr_xO_y$ samples after the redox treatment at 1050 °C.

angle, compared with the pattern in figure 5(b) from the unreduced sample (reproduced from figure 1(b)), reflects the removal of oxygen from the mixed-oxide lattice. The increase in lattice constant, from 0.539 to 0.550 nm, corresponds closely to that expected for the transformation of $Ce_{0.5}Pr_{0.5}O_2$ to $Ce_{0.5}Pr_{0.5}O_{1.75}$, in which primarily Pr undergoes a change in valence, from nearly 4 to 3 [6]. Small new peaks, some of which are marked with asterisks in figure 5(a), arise from the pseudofluorite-type structure, characteristic of cubic rare-earth sequioxides [5,6]. The strongest peak from metallic palladium is also marked in figure 5(a). In contrast,

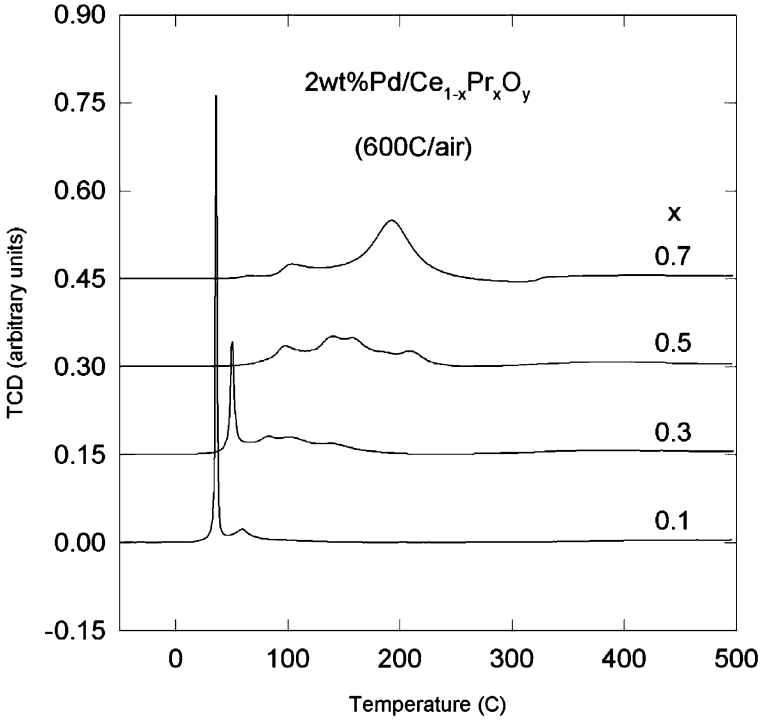

Figure 3. TPR curves from 2 wt% Pd/$Ce_{1-x}Pr_xO_y$ samples calcined at 600 °C.

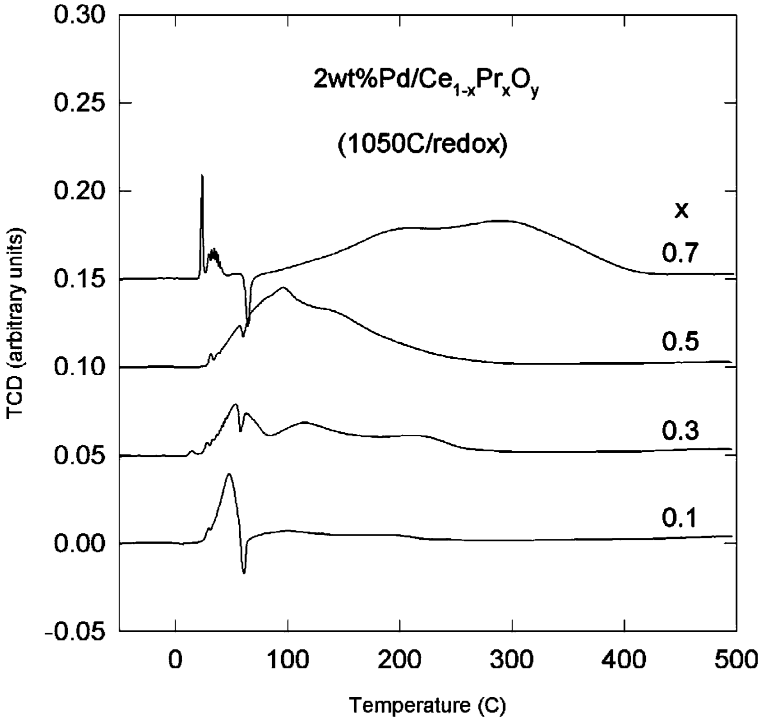

Figure 4. TPR curves from 2 wt% Pd/$Ce_{1-x}Pr_xO_y$ samples after the redox treatment at 1050 °C.

most of the palladium in the unreduced sample exists as palladium oxide. Taking 1449 μmol-H_2/g for the reduction of $Ce_{0.5}Pr_{0.5}O_2$ to $Ce_{0.5}Pr_{0.5}O_{1.75}$ together with 188 μmol-H_2/g for the reduction of PdO yields a total of 1637 μmol-H_2/g, which is close to the value listed in table 1 for this sample.

4. Discussion

Previous studies have shown that cerium–praseodymium mixed oxides undergo reduction between 400 and 600 °C [2,7]. The present work shows that addition of 2 wt% Pd catalyzes the reduction at temperatures below this range, with an average temperature of reduction that tends to increase as praseodymium concentration increases. Based on the result obtained from the sample made by incorporation of the Pd precursor (not presented), which contained only 0.2 wt% Pd, the catalytic effect of the noble metal also depends on metal loading. In the case of the 0.2 wt% Pd sample, reduction occurred between about 200 and 400 °C (versus 50 and 250 °C for 2 wt% Pd). A similar result was obtained previously for the somewhat smaller loading of 0.13 wt% Pd on $Ce_{0.45}Pr_{0.55}O_y$ [2].

Table 1
H_2 consumption (μmol-H_2/g-sample) by 2 wt% Pd/$Ce_{1-x}Pr_xO_y$ between −50 and 500 °C

Treatment	x					
	0.0[a]	0.1	0.2	0.3	0.5	0.7
600 °C/air	551	1032	1299	1369	1670	1900
1050 °C/redox	99	661	896	1129	1699	2058

[a] Reference sample made from typical high-surface-area (of order 100 m^2/g) ceria.

Considerable structure, entirely reproducible from sample to sample, is apparent in the curves of figures 3 and 4. An interpretation of this structure is beyond the scope of this study, but a few general observations can be made. First, as might be expected, the TPR curve from the sample with the lowest praseodymium concentration in figure 3 looks similar to that from 2 wt% Pd on CeO_2, reported previously [4]. In that case, a single feature attributed to the simultaneous reduction of PdO and “surface” CeO_2 appears at low temperature, between 0 and about 50 °C. The reduction of PdO is thought to facilitate the reduction of “surface” CeO_2, which otherwise would occur at higher temperature, between 350 and 550 °C. The coupling that exists between these two components does not significantly alter the character of PdO, however. In contrast, a distinct feature clearly identifiable with reduction of PdO is absent for $x > 0.3$ in figure 3. This suggests that a strong interaction between the palladium oxide and the cerium–praseodymium mixed oxide exists. Indeed, mixed oxides involving palladium oxide and several rare-earth sesquioxides, including praseodymia, are well known.

Further, the 1050 °C redox treatment appears to have a relatively modest effect on the interaction between the palladium oxide and the cerium–praseodymium mixed oxide. Although particles of PdO and

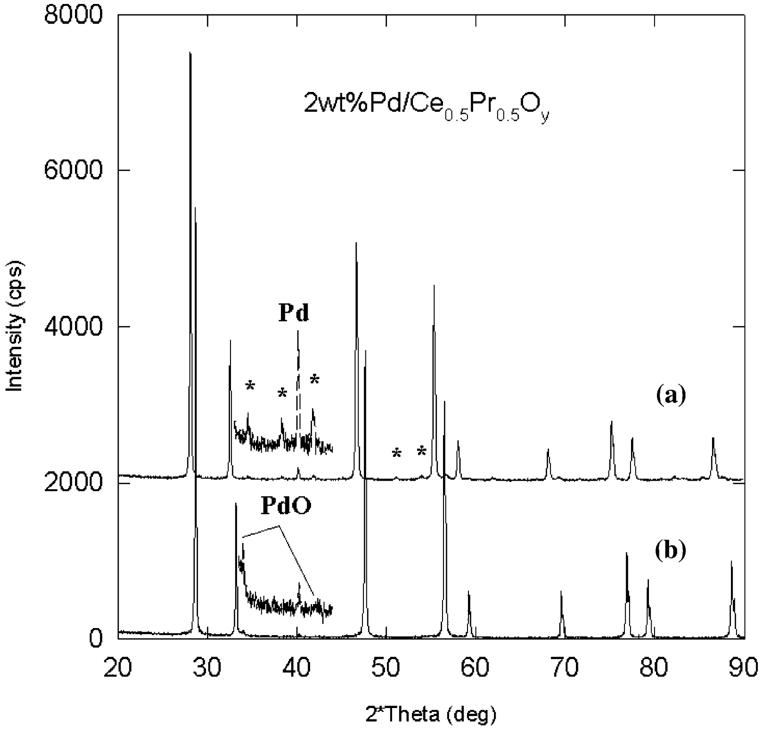

Figure 5. XRD patterns from samples of 2 wt% Pd/$Ce_{0.5}Pr_{0.5}O_y$ after the redox treatment at 1050 °C. Pattern (a) was obtained following an additional treatment, 350 °C in 1% H_2, and (b) is the same as figure 1(b). Regions from 33 to 44 are expanded by a factor of 10. Asterisks mark some of the peaks from the pseudofluorite-type structure, characteristic of cubic rare-earth sequioxides.

Pd are clearly present in the 2 wt% Pd/$Ce_{0.5}Pr_{0.5}O_y$ sample before and after, respectively, the TPR runs, and negative peaks that likely arise from palladium hydride decomposition appear at about 70 °C in all the curves in figure 4, only the $x = 0.7$ curve exhibits a well-resolved feature resembling reduction of PdO. In

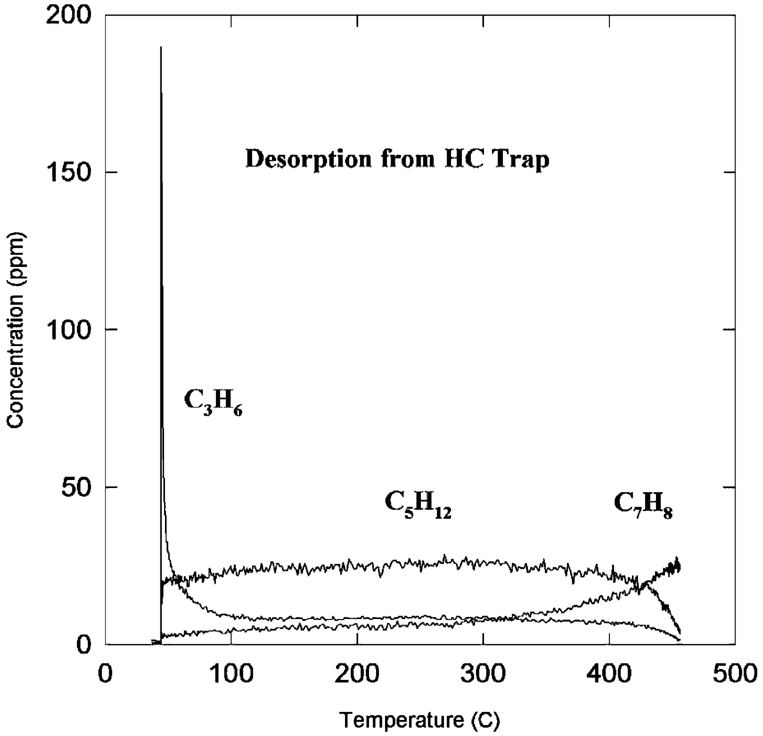

Figure 6. Thermal desorption of pre-adsorbed hydrocarbon species from a commercially feasible HC trap.

addition, the average temperature of reduction tends to increase with increasing praseodymium concentration in figure 4 in about the same way as in figure 3.

As shown in table 1, much more hydrogen is consumed by cerium–praseodymium mixed oxide at temperatures relevant to automotive catalysis than by pure cerium oxide. Since oxygen for this reaction comes from the bulk of the mixed oxide, its availability is not greatly affected by loss of surface area or sintering. Unlike cerium–zirconium mixed oxide, where bulk reduction is associated with a change in the valence state of Ce, the bulk reduction of cerium–praseodymium mixed oxide is thought to involve primarily Pr, and thus the amount of oxygen that is available tends to increase with increasing praseodymium concentration.

The possibility of utilizing catalyzed cerium–praseodymium mixed oxides in HC traps can be roughly gauged by comparing the average temperature of reduction and amount of oxygen available with typical HC desorption data, as shown in figure 6. This particular data was obtained from a laboratory simulation of engine start-up, involving exposure of approximately 7 cm^3 of a commercially feasible monolithic HC trap to a flowing stream (2 L/s) of N_2 containing a blend of hydrocarbons (0.84 vol% propylene, 0.34 vol% isopentane, and 0.23 vol% toluene) and 10 vol% H_2O vapor for 60 s; the hydrocarbon portion was then replaced with N_2, and the sample was heated (at approximately 1 °C/s) while concentrations of the three hydrocarbon species exiting the sample were monitored with a chemical ionization mass spectrometer [8]. Although each hydrocarbon has its own distinct desorption profile, the different temperature ranges can be well matched with the reduction profiles of particular catalyzed cerium–praseodymium mixed oxide compositions. Further, the amount of oxygen available from a reasonable loading of catalyzed mixed oxide (of order 0.1 g on each cm^3 of monolithic trap) is theoretically more than enough to fully oxidize all of the HC released.

5. Conclusions

This study has shown that both the degree and average temperature of reduction of palladium-catalyzed cerium–praseodymium mixed oxides can be "tuned" by varying the cerium/praseodymium ratio. This capability could prove useful in engineering a possible solution to the cold-start automotive emissions problem based on combining an oxygen storage material with an HC trap.

Acknowledgements

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