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\textsubscript{0.45}Pr\textsubscript{0.55}O\textsubscript{y}, which exhibited the lowest average temperature of reduction. Shigapov \textit{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 \textmu mol 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\textsubscript{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 Cu$K_x$ radiation. Temperature-programmed reduction (TPR) measurements were performed with a Micromeritics AutoChem II 2920 system. Prior to each TPR run, the sample (~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 Cu$K_x$ radiation. Patterns in figure 2 are offset by multiples of 500 cps.) A second phase, resembling Pr$_6$O$_{11}$, 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