A feasibility study of niobium-containing materials for oxygen storage in three way catalytic converters

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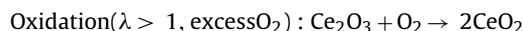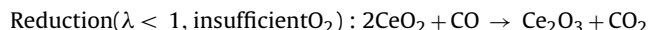
ARTICLE INFO

ABSTRACT

Materials containing Ce–Zr–Y and doped with between 0 and 15% niobium were analyzed for their oxygen storage capacity as potential materials for use in the three-way catalyst (TWC). An optimum amount of niobium was identified (7.5 cat mol%) that led to significantly higher oxygen storage capacity than the baseline niobium-free sample ($Zr_{0.70}Ce_{0.22}Y_{0.08}O_x$) at temperatures within the typical operating range of the TWC. The niobium-containing material also had higher rates and extents of reduction and oxidation than the baseline material during redox cycling tests performed at 500 °C. In addition to niobium as a potential dopant, Ce–Zr–Y formulations containing either Nd or Pr were also analyzed and the order of performance was found to be: Nb > Nd > Pr. Characterization of all niobium-containing materials indicated that niobium integrated into the Ce–Zr–Y oxide phase. In the future, the niobium-containing materials will be compared to state-of-the-art OSC materials in redox cycling environments more typical of the TWC.

1. Introduction

The purpose of the three-way catalyst (TWC) in gasoline vehicles is to achieve high conversion of carbon monoxide, unburned hydrocarbons and NO_x pollutants produced in the internal combustion engine. Their high conversion is ensured by maintaining a narrow air/fuel ratio (near $\lambda = 1$, stoichiometric) in the exhaust using an oxygen storage component (OSC) in the catalyst coupled with an electronic feedback control system. OSC materials have facile redox properties and thus can readily supply oxygen when the reaction is operating fuel rich ($\lambda < 1$) and remove oxygen when the reaction is operating fuel lean ($\lambda > 1$). For example, the reactions below demonstrate how ceria can contribute to oxygen storage in the TWC:

$$Reduction(\lambda < 1, insufficient O_2) : 2CeO_2 + CO \rightarrow Ce_2O_3 + CO_2$$

$$Oxidation(\lambda > 1, excess O_2) : Ce_2O_3 + O_2 \rightarrow 2CeO_2$$

Pure ceria, with facile CeO_2/Ce_2O_3 redox capacity, was the primary oxygen storage component in the TWC until it was found that CeO_2–ZrO_2 solid solutions had better performance [1–3]. Since

then, CeO_2–ZrO_2 solid solutions, frequently containing additional dopants such as Y, have been commercialized for use in the TWC.

Dopants to either pure ceria or ceria–zirconia solutions have been investigated to determine whether they can increase the total oxygen storage capacity, increase the reduction and oxidation rates, or improve the thermal stability of the OSC. The most effective dopants have typically been trivalent rare earth cations, such as La [4–9], Y [4–7,9–11], Pr [6,9,12–14], Ga [4], or Nd [4,6,9,12,14]. Studies have also investigated alkali-earth metals such as Ca [15,16], Mg [16], Sr [19–21], and Ba [21], transition metals such as Mn [17,18], Fe [22], and Co [22,14], or other elements including Sm [5], Bi [14], and Al [23]. The use of niobium in ceria–zirconia oxides was suggested in a 2003 patent by Delphi [15], which showed a promising impact of niobium on the OSC, but the use of niobium has not been further reported for this application.

Within the last few years the family of rare earths, including cerium, experienced a rapid increase in price upsetting the markets and initiating a search for methods to reduce their concentrations in the OSC. Similar to many of the effective rare earth dopants, niobium has a small ionic radius and is similar in size to zirconia. However, niobium pentoxide has thermodynamically poor redox properties in the operating range of the OSC (300–600 °C). Despite this, the Delphi's patent reports that niobium can enhance the oxygen storage capacity of Ce-containing materials [15]. Thus, the goal of this feasibility study is to determine whether niobium can enhance the oxygen storage capacity of the Ce-containing OSC, which could allow a decrease in the amount of cerium and other

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rare earth elements that are present. It is understood that testing in a TWC exhaust would be a required step in advancing this new material for real applications.

2. Experimental

2.1. Catalyst preparation

To determine the impact of niobium on common OSC formulations, oxides containing a constant ratio of Ce, Zr, and Y with increasing amounts of Nb were synthesized and assessed for their oxygen storage capacity. To prepare the materials, a water solution of the precursors, $Ce(NO_3)_3$, $ZrO(NO_3)_2$, $Y(NO_3)_3$, and ammonium niobate (V) oxalate ($C_6H_4NNbO_{12}$), was added by buret to vigorously stirred 0.2 M solution of ammonium hydroxide. Following precipitation, samples were filtered, triple washed, dried, and calcined (for 2 h in air at 550 °C). Samples were aged at 800, 900, or 1000 °C for 2 h in air. Niobium pentoxide (Nb_2O_5), used as a baseline, and the ammonium niobate (V) oxalate, used as a precursor, were graciously provided by CBMM (Compendio Brasileiro de Metalurgia e Mineracao).

As a baseline comparison to the niobium-containing samples, both a niobium-free sample containing Ce, Zr, and Y ($Nb0 = Zr_{0.70}Ce_{0.22}Y_{.08}O_x$) and a pure ceria–zirconia ($Zr_{0.76}Ce_{0.24}O_x$) were studied. All samples had the same Zr:Ce ratio as niobium-containing samples (3.25) and the preparation procedures were the same as those stated above excluding the addition of relevant precursors. The yttrium-containing baseline sample outperformed the pure ceria–zirconia sample for every condition studied and is therefore used as the primary baseline material throughout the paper. Additionally, to test the impact of preparation method, a niobium-impregnated sample was prepared using the incipient wetness method. For this sample the baseline niobium-free sample ($Nb0 = Zr_{0.70}Ce_{0.22}Y_{.08}O_x$) was calcined at 550 °C for 2 h in air and then impregnated with the niobium oxalate to obtain the same Nb:Ce:Zr:Y ratio as the Nb2 sample in Table 1 (7.5 cation wt% Nb). The sample was then re-calcined for 2 h in air at 550 °C and aged. Samples impregnated with precious metal were prepared using the incipient wetness method with the pre-calcined OSC materials (550 °C) and a non-alkali, non-chloride platinum precursor. Samples were impregnated to achieve a loading of 0.5 wt% Pt and were re-calcined (for 2 h in air at 550 °C) and aged.

2.2. Performance testing and characterization

A measurement related to the oxygen storage capacity of each material was assessed using thermal gravimetric analysis (TGA) using a Netzsch STA 449F3 unit. Temperature programmed reduction and oxidation (TPR/TPO) measurements were performed with a heating and cooling rate of 5 °C/min. Samples were dried in nitrogen at 150 °C for 1 h in the TGA prior to all measurements. For TPR segments, samples were heated in 100 mL/min of 2% H_2/N_2; for TPO segments, samples were exposed to the same heating rates in 120 mL/min of 1% O_2/N_2. In addition to TPR/TPO testing, isothermal redox cycling was performed at 500 °C. Ten cycles alternating between 60-min reducing segments (2% H_2/N_2) and 60-min oxidizing segments (1% O_2/N_2) were performed. Both the TPR/TPO tests and redox cycling tests were repeated on additional preparations of each formulation for reproducibility.

Materials were characterized using BET, XRD and Raman and niobium concentrations in selected samples were verified using XRF. Single-point BET surface area was collected using a Quantachrome ChemBET. Room temperature XRD was performed to provide insight into the structure of the samples and the solubility of niobium into the oxide solutions. Powder XRD patterns
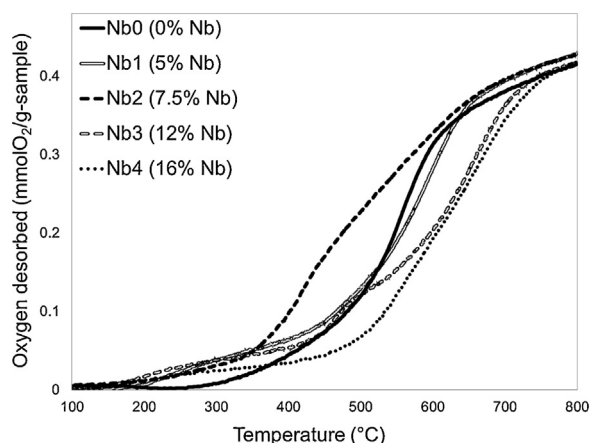

Fig. 1. Total oxygen desorbed by each material in Table 1 during TPR (5 °C/min in 100 mL/min of 2% H_2/N_2) after aging at 800 °C for 2 h in air.

were recorded with an X'Pert Pro PANalytical X-ray diffractometer using Cu-Kα radiation of wavelength 1.541 Å, a scanned angle range 10°–100° with step size of 0.01° and count time per step of 60 s. Raman spectra were collected using a LabRam Aramis microscope (Horiba) equipped with a 500-mW 532-nm laser as the excitation source. The beam was attenuated with a D1 filter. Spectra were collected using a 1200 grooves/mm diffraction grating and a 50× objective lens. XRF was completed on a Bruker S4 wavelength dispersive spectrometer to confirm the niobium concentrations in selected samples.

3. Results

3.1. Oxygen storage capacity of niobium-containing materials

The primary materials investigated were Ce–Zr–Y oxides with varying amounts of niobium. The composition of these materials, including their cerium and niobium concentrations (cation mole%), and their BET surface areas after aging for 2 h in air at 800, 900, or 1000 °C are given in Table 1. These aging temperatures represent the upper limit of temperatures expected in the automobile exhaust. Increasing niobium concentrations led to lower BET surface areas but all materials (including the niobium-free material) had significant losses in surface area after aging at 900 or 1000 °C.

A model test for oxygen storage capacity of each material was performed by measuring the oxygen released by the material during reduction cycles (as a weight loss) or by measuring the oxygen consumed by the material during oxidation cycles (as a weight gain). It should be mentioned that oxidation is relatively fast compared to the reduction so only the reduction will be used to assess the assumed oxygen storage capacity of the materials. The total oxygen released by the material during the first reduction cycle (measured as a weight loss and translated into mmol O_2/g sample) for each material is shown in Fig. 1. From this data, the total oxygen released by each material at 500, 400 and 300 °C is plotted as a function of niobium concentration in Fig. 2. The data in these figures represent the average of at least two separately prepared samples of each formulation. The maximum error in the reduction capacity (mmol O_2/g sample) at any given temperature never exceeded 8% for samples of the same formulation.

As shown in Figs. 1 and 2, all formulations containing niobium had higher oxygen storage capacity than the baseline Nb0 material ($Zr_{0.70}Ce_{0.22}Y_{0.08}O_x$) between 150 and 350 °C. In addition to the enhancement in reduction that was measured between 150 and 350 °C for all niobium-containing samples, the Nb2 sample ($Zr_{0.65}Ce_{0.20}Y_{0.075}Nb_{0.075}O_x$) exhibited enhanced reduction