Determining the Oxygen Storage Capacity (OSC) of Ceria Materials by Oxygen Adsorption Isotherms

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Introduction

Ceria and zirconia metal oxides have considerable redox activity, making them valuable in several catalytic applications such as conversion of vehicle exhaust [1], production of CO and H_2 for fuel by solar energy [2], and deoxygenation of bio-oil pyrolysis products [3]. Surface reaction results in the formation of oxygen vacancies. Typical techniques for quantifying oxygen storage capacity (OSC) of ceria materials include dynamic oxygen pulses [4], CO pulses[4], CO temperature-programmed reduction (TPR) [5], or H_2 reduction [4]. The focus of this work is to look at the advantages and utility of oxygen adsorption isotherms to determine OSC—corresponding with oxygen vacancies in the ceria materials.

Materials and Methods

All catalysts were prepared by coprecipitation using cerium nitrate hexahydrate and zirconyl nitrate hydrate, dissolved in deionized water. The coprecipitation was modified by adding the precursor solution to an ammonium hydroxide solution while stirring continuously. The precipitate was filtered, rinsed with deionized water, and dried in an oven overnight at 100 °C. The catalysts were calcined at 500 °C for 4 hours in air with a ramp rate of 5°C/min.

A commercially available volumetric adsorption instrument (Micromeritics 3FLEX, chemisorption option) was used for the isotherms.

Results and Discussion

Oxygen storage capacity at three reduction temperatures is given in **Table 1** for each catalyst. Oxygen pulse experiments were used along with oxygen isotherms to validate the results. The repeatability and reproducibility were within 3%. The results indicate the addition of zirconia can at least double the OSC at temperatures between 200°C - 450 °C, while no measurable reducibility was measured for pure zirconia in the same temperature range.

Table 1. Oxygen uptake (mmol O_2 per gram) for different ceria-zirconia mixed oxides after reduction at different temperatures.

Ce composition (%)	450°C	300°C	200°C
100	0.138	0.040	--
60	0.390	0.072	--
46	0.328	0.046	--
0	--	--	--

The oxygen storage capacity (OSC) can be determined directly from the oxygen isotherm, as shown in **Figure 1**. The shape of these isotherms allows for confidence in the experimental results. Isotherms should monotonically increase with increasing pressure, and deviations can indicate gas contamination. Repeat experiments at different analysis temperatures (eg 50°C or 100°C) can also be used to validate results, as the irreversible oxygen uptake seems to be independent of analysis temperatures above 50°C (only a function of the reduction temperature). Also, the quality of the system and measurement can be determined based on pressure stability. By using pressure transducers that read in the range of 10^{-6} torr, the sensitivity of the measurement is approximately 0.1 μmole O_2 (0.002 cm^3 STP) below 1.5 torr.

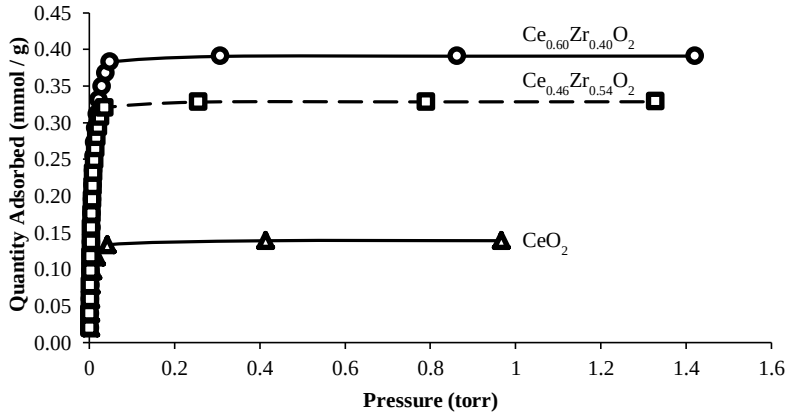

Figure 1. O_2 isotherm at 450°C, after isothermal reduction and purging at the same temperature, for different ceria-zirconia mixed oxides. 60% Ce (●), 46% Ce (■), and CeO_2 (▲).

Significance

Oxygen adsorption isotherms are an effective solution to determining the oxygen storage capacity (OSC) of ceria materials using commercially available instruments and agree well with typical dynamic chemisorption techniques.

References

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