

## In Situ Characterization of Ethanol Reforming Catalysts (Rh-Pd/CeO<sub>2</sub>) Using Time-Resolved X-Ray Diffraction

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### Introduction

The hydrogen production by the ethanol steam-reforming reaction has received considerable attention for its importance in fuel cell technologies and has been investigated over a series of metal supported catalysts [1, 2]. One particularly interesting system is that of Rh-containing CeO<sub>2</sub> catalyst because the presence of Rh atoms is reported to be crucial for forming the intermediates needed for the carbon-carbon bond dissociation [3]. In this work, we present a study of series in-situ time-resolved XRD measurements of the ethanol steam-reforming reaction over CeO<sub>2</sub>, Rh/CeO<sub>2</sub>, Pd/CeO<sub>2</sub> and Rh-Pd/CeO<sub>2</sub>.

### Materials and Methods

CeO<sub>2</sub>, Rh/CeO<sub>2</sub>, Pd/CeO<sub>2</sub> and Rh-Pd/CeO<sub>2</sub> samples are obtained from the University of Auckland, New Zealand. CeO<sub>2</sub> was prepared by precipitating white crystalline cerous nitrate solution using ammonia. The resulting slurry was washed and dried, and then calcined at 773 for 4 h in air. The Pd and/or Rh promoters were deposited by wet impregnation using stock solutions of Pd and/or Rh metals in 1 M of HCl. The catalysts were dried at 373 K and then calcined at 673 K for 4 h [2].

The time-resolved diffraction data were collected on beam line X7B of the National Synchrotron Light Source (NSLS). The samples were loaded into a glass capillary that was attached to a flow system [4]. A small resistance heater was wrapped around the capillary, and the temperature was monitored with a 1.0 mm chromel-alumel thermocouple near the sample. The composition of the gas leaving the capillary could be determined by means of gas chromatography or mass spectrometry. A MAR345 detector was used to record full X-ray patterns, and the powder rings were first integrated with the FIT2D code [5]. The XRD data were further analyzed using the GSAS (general structure analysis system) program [6].

The catalytic activities for the ethanol steam-reforming over the catalysts were monitored using a quadrupole mass spectrometer. A mixture of ethanol-water vapor was introduced into the gas stream by passing pure He through a bubbler containing ethanol-water (ethanol:H<sub>2</sub>O = 8:1). The total flow gas flow rate was maintained at 10 cc/min.

### Results and Discussion

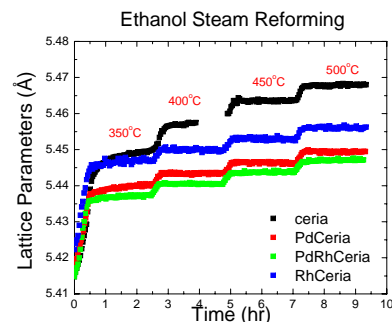
Prior to the ethanol steam-reforming reactions, the samples were first oxidized in 5% O<sub>2</sub> and then reduced in 5% H<sub>2</sub> at a temperature up to 500°C. Only a linear thermal expansion in the lattice parameters was observed for each of the catalyst during oxidation. However, the lattice expansions were significantly different when the samples were reduced in H<sub>2</sub>. For pure ceria, the slope of the lattice expansion increased slightly at high temperature due to the reduction of ceria. For 1wt%Rh/CeO<sub>2</sub>, there was a rapid increase in the lattice parameters at the temperature below 100°C. It is interesting to note that for 1wt%Pd/CeO<sub>2</sub>, there was an abrupt shift in the lattice parameters during reduction at a temperature of 160°C. These imply that Cl<sup>-</sup> species are present in the samples and both rapid expansions in the lattice parameters are due to

the formation of the CeOCl phase [7, 8]. For 1wt%Rh-1wt%Pd/CeO<sub>2</sub>, the lattice expansion was similar to that of 1wt%Pd/CeO<sub>2</sub> at high temperature.

For the ethanol steam-reforming reaction, 1wt%Rh-1wt%Pd/CeO<sub>2</sub> showed the highest catalytic activity, while pure ceria showed the least. The corresponding lattice expansion clearly showed that the pure ceria sample was much more reduced compared to the 1wt%Rh-Pd/CeO<sub>2</sub> under the same reaction condition (Figure 1). The redox properties of ceria have been extensively studied [9] and it is known that oxygen transfer between ceria and precious metal is important for the water-gas-shift reaction [10]. The fact that the extent of the reduction for 1wt%Rh-Pd/CeO<sub>2</sub> was low suggested the redox properties of ceria might play a role during the ethanol steam-reforming reaction.

### Significance

Under reaction conditions catalysts can undergo chemical transformations that drastically modified their characteristics during operation with respect to that obtained during the synthesis of the materials. Thus, it is critical to know the active phases to optimize the performance of the Rh-containing CeO<sub>2</sub> catalysts. The catalysts will be further investigated by EXAFS studies.



**Figure 1.** The lattice parameters for CeO<sub>2</sub>, 1wt%Rh/CeO<sub>2</sub>, 1wt%Pd/CeO<sub>2</sub> and 1wt%Rh-1wt%Pd/CeO<sub>2</sub> as a function of temperature under the ethanol steam-reforming condition.

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