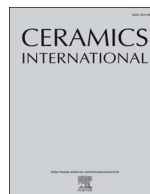




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## Characterization of calcination temperature on a Ni-substituted lanthanum-strontium-zirconate pyrochlore

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### ABSTRACT

A lanthanum strontium zirconate pyrochlore material was substituted with Ni, and the effect of calcination temperature on important catalytic properties was evaluated. The introduction of the Ni into the pyrochlore decreased the BET surface as compared to non-Ni containing materials due to enhanced sintering. The presence of Ni dispersed in the precursor material produced oxygen vacancies which improved solid state diffusion of the pyrochlore cations, and lowered the onset of crystallization by almost 100 °C compared to the baseline material without Ni. Furthermore, only a small amount of Ni was found to be soluble in the structure up to 1000 °C, at which point almost no Ni occupies lattice positions in the pyrochlore crystal structure. The Ni was found to exsolve to the surface and grain boundary regions of the pyrochlore and reside on the surface as NiO. Heating to temperatures greater than 800 °C also led to the formation of a La<sub>2</sub>ZrNiO<sub>6</sub> perovskite phase. Surface composition, as measured by XPS, showed a decrease in Ni concentration at the surface as the calcination temperature was increased. This was likely due to the formation of larger Ni particles with increasing temperature, as well as the migration of the Ni into the bulk through the formation of the La<sub>2</sub>ZrNiO<sub>6</sub> phase. Temperature programmed reduction results showed that increasing the calcination temperature resulted in particle growth of the NiO and a weaker interaction with the pyrochlore surface, which made the NiO more reducible at lower temperatures. Multiple reduction-oxidation TPR/TPO cycles showed that the results were not reproducible from cycle-to-cycle for the lowest calcination temperature material (700 °C) due to an amorphous La-Zr-O phase initially present. However, materials calcined at all other temperatures showed an almost identical TPR/TPR profiles after the second cycle.

### 1. Introduction

The shale gas revolution has created an abundance of cheap and readily available natural gas supplies in the United States. For the foreseeable future, steam reforming of methane will remain one of the primary large scale conversion routes of CH<sub>4</sub> until technologies enabling the direct conversion of CH<sub>4</sub> into chemicals (e.g. methane to aromatics) are commercially competitive. Although steam reforming is a mature technology, there are still critical issues from a catalytic standpoint that pose a challenge to the traditional catalysts.

Ni-based materials are the most widely used catalysts for methane reforming, owing to its favorable cost and activity [1]. However, carbon formation, as well as loss of active metal surface area through sintering remain difficult to overcome. In particular whisker based carbon is known to be especially problematic over Ni catalysts, and it can form in

the pores of the catalyst and lead to a physical breakdown of the catalytic material, as well as reactor plugging [2].

Addressing these issues requires a thermally stable material, as well as control of the active Ni metallic sites to minimize the irreversible adsorption of carbon. Furthermore, the formation of whisker carbon can be limited by ensuring that the Ni clusters remain small, because smaller particles have a higher saturation concentration for carbon in the Ni lattice, which then minimizes the driving force for carbon diffusion through the Ni crystal [3].

Mixed metal oxide materials like pyrochlores have demonstrated these attributes which are desirable for reforming catalysts. A pyrochlore has the general formula A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> and cubic crystalline structure [4], and is attractive as a catalyst due to the thermal stability, as exhibited in non-catalytic applications like thermal barrier coatings [5,6] as well as the ability to modify the catalytic activity of the material

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through the incorporation of a wide variety of different cations into the A- and B-sites [7,8]. The partial substitution of the B-site with a catalytically active metal may promote the formation of small, stable, and well-dispersed active sites at the surface, which are needed to minimize the irreversible formation of carbon [7]. Within limits, both the A and B sites can be modified using promoting metals which can serve two functions 1) create oxygen vacancies in the structure which should improve oxygen mobility- which provides localized oxygen from the structure to react with adsorbed carbon, which limits its accumulation [9,10] and 2) promote gasification of surface carbon, e.g. by increasing surface basicity [11,12].

Studies on pyrochlores have demonstrated their activity and selectivity as reforming catalysts [7,13–18]. A wide range of metals like Rh, Pt, Ru, and Ni have been incorporated into a lanthanum zirconate pyrochlore, and shown high conversions and selectivities to syngas for dry (CO<sub>2</sub>) reforming as well as catalytic partial oxidation (CPOX) reactions of different fuels like methane and diesel fuel [7,13–18]. In particular, it has been shown that the catalytic activity lanthanum zirconate pyrochlore substituted the Rh, Ru, or Ni can produce stable conversions and syngas selectivities during the CPOX of a surrogate diesel fuel containing 5 wt% 1-methylnaphthalene and 50 ppm sulfur [7,15,19].

Although the incorporation of different active reforming metals into the structure has been evaluated to improve the catalytic activity of the lanthanum zirconate pyrochlore, we are not aware of any systematic study to characterize the effect of calcination temperature on the properties of a Pechini derived Ni substituted lanthanum zirconate pyrochlore that is directly applicable for the steam reforming of methane. Studies by Bussi and coworkers [20,21] have shown a Ni-La-Zr pyrochlore solid solution for the steam reforming of glycerol and ethanol, produced via the co-precipitation of nitrates with oxalic acid, were highly stable reforming catalysts. These materials showed high selectivities to syngas and resistance to carbon formation at temperatures 500–650 °C. The heating temperature can influence important catalytic properties such as the incorporation of Ni, strength of interaction between the different components, as well as particle size of the Ni, among other properties. Here we report the effects calcination treatment at different temperatures during synthesis on the substitution and dispersion of the Ni within the structure, and the structural and physical changes that influence the coordination environment of the pyrochlore cations and their interaction with Ni. Specifically, the catalysts will be examined structurally, chemically, and compositionally, to determine how temperature affects important physical and chemical properties of Ni-based pyrochlores.

## 2. Materials and methods

### 2.1. Catalyst synthesis method

Pyrochlore catalysts were synthesized by a variation of the Pechini method [22]. Stoichiometric amounts of dissolved metal nitrates were combined with an aqueous citric acid (CA) solution at a ratio of 1.2:1 CA to total metal ions. The solution was stirred and heated to 70 °C, at which point ethylene glycol (EG) was added (EG:CA molar ratio = 1). After EG addition, the solution was left stirring at 70 °C to drive off water until a clear viscous gel remained. The gel-containing beaker was placed in a heating mantle pre-heated to 70 °C. The temperature of the mantle was increased to 130 °C to promote the polyesterification reaction between the citric acid and ethylene glycol. Once the reaction was complete, the precursor material was dried over night at 130 °C, and then crushed and calcined at 700 °C, 800 °C, 900 °C, or 1000 °C for 8 h.

### 2.2. Material characterization

#### 2.2.1. Compositional analysis and surface area measurements

Compositional analysis of the pyrochlore samples was determined using a Perkin Elmer 300D Nexion ICP-MS. 25 mg of sample was placed

into a Teflon lined microwave vessel to which a mixture 2:1 of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> was added by pipette. Surface area measurements were performed using a Micromeritics ASAP 2020 instrument. BET measurements were conducted using nitrogen adsorption at 77 K. A 5 point, low surface area measurement was used as the samples were anticipated to have surface areas < 15 m<sup>2</sup>/g. The range of P/P<sub>0</sub> ratio (where P is the partial vapor pressure of the adsorbate gas in equilibrium with the surface at 77 K, and P<sub>0</sub> is the saturated pressure of the adsorbate gas) used for these experiments was 0.07–0.2.

#### 2.2.2. Thermogravimetric and digital thermal analysis

A TA Instruments SDT Q600 unit was used for simultaneous DTA-TGA analysis of the precursor powers, which were heated by 5 °C/min from ambient to 1000 °C for 30 min 50 sccm air purge was flown over the sample and blank reference crucible. An online mass spectrometer was used to record concentrations of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub>.

#### 2.2.3. X-Ray characterizations

Phase analysis of powder samples was examined using a PANalytical X'pert Pro X-Ray diffraction system, model number PW 3040 Pro. The device consisted of a ceramic diffraction X-ray tube containing Cu K $\alpha$  radiation at a wave length of K $\alpha$  1.54184 Å. Power requirements during operation were 45 kV and 40 mA. Jade v9.6 Materials Data Inc. was used for phase identification and pattern analysis, as well as for peak fitting, and crystallite size determination. The Scherrer equation was used for crystallite size determination. High Score Plus was used to determine the relative degree of crystallinity. For this calculation, 0.15 g of sample was scanned over 20–80° 2 $\theta$  range at 0.026°/s rate and 120 s step time. A bending factor of 5, and granularity of 21 was used for background determination. The background for the most crystalline material, 1000 °C calcination temperature, was assumed to be the base line (i.e. denominator for the % crystallinity calculation) with a crystallinity of 100%. A constant background intensity for the obtained scan of this material using the defined background parameters was found to be 758.5 counts. The scans for the 700–900 °C materials each produced a background intensity, which when normalized to the 785.5 counts gives the crystallinity % relative to the most crystalline material.

In-situ XRD was performed to evaluate the change in crystal structure of the Pechini derived material during heating under conditions similar to those used for calcination. The sample was placed in an 8 mm alumina sample holder in an Anton Parr HTK 1200 N high temperature oven chamber. A TCU-1000N control unit, with a Eurotherm 2604 controller was used to control temperature, which was measured by a thermocouple set below the sample holder. Prior to the experiment, the Pechini material was heated to 400 °C for 4 h to remove carbon. Instruments settings were similar to those described earlier, as were the scan parameters – 0.026°/s scan rate and a 120 s step time. The heating profile was similar to calcination used for powder preparation. A 5 °C/min ramp rate was used to heat from ambient to 600 °C where the first scan was performed. The material was then heated incrementally by 5 °C/min to 700–1000 °C, with 6 isothermal scans performed at each temperature.

XANES studies of Ni substituted pyrochlore were taken at the Double Crystal Monochromator (DCM) beamline at the Center for Advanced Microstructures and Devices (CAMD), at Louisiana State University. The operating energy of CAMD is 1.3 GeV, with a typical ring current between 50 and 150 mA. The measurements were performed at the High-Energy X-Ray Absorption Spectroscopy Beamline on an 11-pole, 7.5 T multi-pole wiggler. The edge was calibrated to 8333 eV, with a Ni foil. A NiO standard (99.9% metals basis, Sigma-Aldrich) was used in this study. X-Ray absorption spectra were collected for the Ni K-edge in fluorescence mode from –200 eV below the edge to 14 keV above the edge relative to the Ni K-edge energy. The steps were 5 eV from –200 eV to –30 eV, 0.3 eV from –30 eV to 30 eV around the edge, and k = 0.05 up to k = 14. Fluorescence spectra were obtained with an 80 mm<sup>2</sup> Ketek silicon drift detector by

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