

## Catalytic Partial Oxidation of n-Tetradecane on Rh and Sr Substituted Pyrochlore Catalysts

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### Introduction

Catalyst deactivation by the high levels of sulfur and aromatics limits the catalytic partial oxidation (CPOX) of diesel fuel into a H<sub>2</sub>-rich stream for fuel cells. These species poison traditional supported metal catalysts because they adsorb strongly to electron dense metal clusters and promote the formation of carbon on the surface. The substitution of noble metals into a thermally stable pyrochlore structure (A<sub>2</sub>B<sub>2</sub>O<sub>7</sub>) may reduce cluster size and prevent deactivation by sulfur and aromatics [ 1 ]. Rhodium has been identified as a candidate CPOX catalyst because of its high selectivity to synthesis gas and resistance to carbon formation [ 2 ]. In the work presented here, Rh and Rh + Sr were substituted into a La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore structure to give La<sub>2</sub>Rh<sub>x</sub>Zr<sub>(2-y)</sub>O<sub>(7-z)</sub> (LRZ) and La<sub>(2-x)</sub>Sr<sub>x</sub>Rh<sub>y</sub>Zr<sub>(2-y)</sub>O<sub>(7-z)</sub> (LSRZ) catalysts, respectively. Their resistance to deactivation and carbon formation were examined by the CPOX of a mixture of model compounds to represent a diesel fuel. The results were compared to a commercial Rh/Al<sub>2</sub>O<sub>3</sub> catalyst.

### Materials and Methods

The pyrochlore catalysts were prepared using a variation of the Pechini method [ 3 ]. The experiments were run in a fixed bed continuous-flow reactor with an O/C = 1.2, a GHSV = 50,000 h<sup>-1</sup>, 900 °C, and 2 atm. n-tetradecane (TD), 1-methylnaphthalene (MN) and dibenzothiophene (DBT) were used as model diesel fuel compounds. CPOX of TD for 5 h was used to screen catalysts for activity and selectivity. In a separate experiment, CPOX of TD was carried out for 1 h, then 5 wt-% MN and 1000 ppmw DBT in TD was run for 2 h, then the feed was switched back to TD for 2 h to examine recovery. Carbon deposition was measured by a temperature programmed oxidation (TPO) using 5% O<sub>2</sub>/N<sub>2</sub> and a ramp rate of 1°C/min.

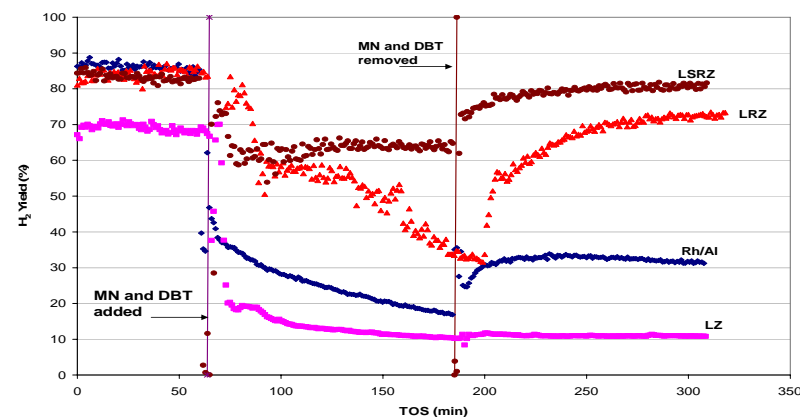
### Results and Discussion

H<sub>2</sub> yields after reforming TD for 5 h are given in **Table 1** for each catalyst. Rh/Al<sub>2</sub>O<sub>3</sub> is highly active for the CPOX of TD with minimal carbon formation. The Rh-only pyrochlore (LRZ) has activity similar to that of the Rh/Al<sub>2</sub>O<sub>3</sub>, and also has minimal carbon formation. Substitution of Sr with Rh increases the activity of the catalyst and reduces the amount of carbon formed. The observed performance increase may be due to increased lattice oxygen mobility that results from the formation of structural defects after substitution of Sr<sup>2+</sup> for La<sup>3+</sup> [ 4 ].

**Table 1.** H<sub>2</sub> yield and carbon formed after 5 hrs of reforming TD at 900°C and 50,000h<sup>-1</sup>.

|   | Blank | Equil | Rh/Al | LZ   | LRZ  | LSRZ |
|---|-------|-------|-------|------|------|------|
| H <sub>2</sub> Yield (%)                                | 17.0  | 85.0  | 82.0  | 75.0 | 80.0 | 85.0 |
| Carbon Formed (g <sub>carbon</sub> /g <sub>cat.</sub> ) | 0.4   | 0.0   | 0.27  | 0.29 | 0.32 | 0.17 |

**Figure 1** shows the H<sub>2</sub> yield during the experiments in which MN and DBT were added. After the feed is switched to the MN + DBT/TD mixture, the H<sub>2</sub> yields drop for each catalyst. LZ and Rh/Al<sub>2</sub>O<sub>3</sub> are deactivated immediately by the sulfur and aromatic compounds because the contaminants adsorb strongly to their surface. Upon removal of MN and DBT the two catalysts are unable to recover activity. Substitution of Rh into the structure modifies the properties of Rh metal and creates a surface that is less susceptible to deactivation by the DBT and MN. LSRZ recovers activity quickly, reaching pre-exposure H<sub>2</sub> yield within minutes, probably because the oxygen mobility prevents the accumulation of contaminants as well as carbon.



**Figure 1.** H<sub>2</sub> yield step response plot after the addition of 5-wt% MN and 1000 ppmw DBT. Rh/Al<sub>2</sub>O<sub>3</sub> (♦), LZ (■), LRZ (▲), LSRZ (●).

### Significance

Substitution of Rh and Sr into a pyrochlore has modified the properties of Rh such that it retains high activity, and is less susceptible to deactivation by aromatics and sulfur.

### References

- Barbier, J.; Marecot, P. *Journal of Catalysis* **1986**, *102*, 21.
- Hickman, D. A.; Haupfear, E. A.; Schmidt, L. D. *Catalysis Letters* **1993**, *17*, 223.
- Pechini, M. P. Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor United States, 1963.
- Liu, D.-J.; Krumpelt, M. *International Journal of Applied Ceramic Technology* **2005**, *2*, 301.

