

Catalytic Partial Oxidation of Diesel Fuel: Effect of Alkaline Earth Metal Dopant at the A-site of a Rh-Substituted Pyrochlore

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Introduction

The catalytic partial oxidation (CPOX) of diesel fuel can be used to provide a continuous source of synthesis gas ($H_2 + CO$) to solid oxide fuel cells. However, polynuclear aromatics and sulfur compounds present in these fuels can cause catalyst deactivation. Recently, it has been found that the substitution of Sr into the A-site of a Rh-substituted lanthanum zirconate pyrochlore ($La_2Rh_{0.11}Zr_{1.89}O_{7-y}$ -LRZ) limits the mechanism for deactivation of sites responsible for H_2 and CO compared to a non-Sr substituted LRZ pyrochlore and Rh/ γ - Al_2O_3 [1]. However, total effects of Sr on catalytic activity are not completely understood yet. Nor is it yet understood whether Sr is the optimal alkaline earth metal (AEM) to be doped into the A-site of the LRZ. The size of the dopant can induce structural distortions of the lattice as well as relaxations/expansions of lattice oxygen bonds which could presumably affect catalytic activity. The purpose of this study is to evaluate the effect of AEM substitution into the A-site of $La_{2-y}X_yRh_{0.05}Zr_{1.95}O_{7-y}$ (where X= Mg, Ca, Sr, or Ba) on the CPOX of n-tetradecane in the presence of polyaromatics and sulfur.

Materials and Methods

The pyrochlore catalysts were prepared using a variation of the Pechini method [2]. The experiments were run in a fixed bed reactor with an O/C = 1.2, GHSV = 50,000 h^{-1} , 900 °C, and 2 atm. n-tetradecane (TD), 1-methylnaphthalene (MN) and dibenzothiophene (DBT) were used as model diesel fuel compounds. Experimental procedure for reforming study was as follows: CPOX of TD was for 1 h, then 5 wt-% MN and 50 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 temperature programmed oxidation (TPO).

Results and Discussion

Figure 1 shows the H_2 yield during the experiments in which MN and DBT were added. The LRZ is continuously deactivated immediately by the sulfur and aromatic compounds because the sulfur and aromatic compounds adsorb strongly to its surface. The presence of any AEM is able to stabilize the H_2 yields compared to the unsubstituted LRZ (Fig. 1). There is no obvious relationship between basicity or size of dopant and activity has been observed, as the Mg catalyst produces the lowest yields while Ca catalyst produces the highest of the A-site substituted pyrochlores. Yields of the Sr- and Ba-substituted catalysts are roughly the same. Improved oxygen-ion conductivity by the AEM substitution is likely created by the oxygen vacancies in the 48f oxygen position and the presence of oxygen atoms in the 8b

position, which are normally vacant in an ordered pyrochlore [3]. LRZ and LMRZ catalysts are unable to fully recover activity after removal of MN and DBT from the feed, while LCRZ, LSRZ, and LBRZ all return to initial levels.

TPO results presented in **Table 1** show that LRZ has the highest amount of carbon deposition. From the TPO profile (not shown) this catalyst has more carbon deposited on Rh metal and oxide surface than the other catalysts, as judged by the TPO temperature peaks. Comparing TPO data from AEM substituted catalysts shows that LSRZ not only has least amount of carbon formed, but also the most reactive carbon (i.e. the carbon is oxidized at a lower temperature). Assuming oxygen-ion conductivity can be directly related to carbon formation-Sr has highest conductivity relative to the other AEMs.

Significance

Substitution of Mg, Ca, Sr, or Ba into A-site of pyrochlore improves oxygen-ion conductivity and makes the material less susceptible to deactivation by aromatics and sulfur. Of these, Sr has highest conductivity- at least measured by carbon formation.

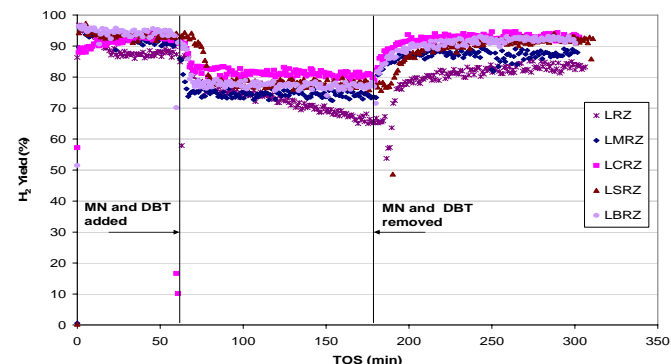


Figure 1. H_2 yield step response plot after the addition of 5-wt% MN and 50 ppmw DBT. LRZ (*), LMRZ (♦), LCRZ (◆), LSRZ (▲), LBRZ (●).

Table 1. Carbon formed after 5-wt% MN and 50 ppmw DBT/TD at 900°C and 50,000 h^{-1} .

	LRZ	LMRZ	LCRZ	LSRZ	LBRZ
Carbon Formed (g_{carbon}/g_{cat})	0.37	0.22	0.16	0.11	0.17

References

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