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Catalytic partial oxidation of *n*-tetradecane using Rh and Sr substituted pyrochlores: Effects of sulfur

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ABSTRACT

The presence of high levels of organosulfur compounds hinders the catalytic partial oxidation (CPOX) of logistic fuels into a H_2-rich gas stream for fuel cells. These species poison traditional supported metal catalysts because the sulfur adsorbs strongly to electron dense metal clusters and promotes the formation of carbon on the surface. To minimize deactivation by sulfur, two substituted lanthanum zirconate (LZ) pyrochlores ($La_2Zr_2O_7$), identified in a previous study [D.J. Haynes, D.A. Berry, D. Shekhawat, J.J. Spivey, Catal. Today 136 (2008) 206], were investigated: (a) La–Rh–Zr (LRZ) and La–Sr–Rh–Zr (LSRZ). Using unsubstituted lanthanum zirconate and a conventional 0.5 wt% Rh/γ-Al_2O_3 as comparisons, these four catalysts were exposed to a feed containing 1000 ppmw dibenzothiophene (DBT) in *n*-tetradecane (TD). DBT rapidly deactivated both the 0.5 wt% Rh/γ-Al_2O_3 and LZ. The LRZ catalyst experienced a gradual deactivation, suggesting that Rh substitution into the pyrochlore structure, by itself, cannot completely eliminate deactivation by sulfur. However, the additional substitution of Sr stabilized yields of H_2 and CO in the presence of DBT at levels only slightly below those observed without sulfur in the feed. After sulfur was removed from the feed, each catalyst was able to recover some activity. The recovery appears to be linked to carbon formed on active sites. The 0.5 wt% Rh/γ-Al_2O_3, LZ, and LRZ all had comparable amounts of carbon formed on the surface: 0.90, 0.80 and 0.86 g_{carbon}/g_{cat}, respectively. Of these three catalysts, only the LRZ was able to recover a significant portion of initial activity, suggesting that the carbon formed indiscriminately on the surface, and not solely on the active sites. LSRZ was able to regain almost its initial activity once sulfur was removed from the feed, and had the least amount of carbon on the surface (0.30 g_{carbon}/g_{cat}). It is hypothesized that oxygen-ion mobility, which results from Sr substitution, reduces carbon formation and the deactivation by sulfur.

1. Introduction

The transition to a hydrogen economy will require the reforming of hydrocarbons such as methane and logistic fuels (i.e. diesel and jet) using various catalysts [1–8]. Logistic fuels in particular offer a convenient and cost-effective source of hydrogen since the infrastructure needed to produce and distribute them is in place [9]. The conversion of these fuels into a hydrogen-rich synthesis gas by catalytic partial oxidation (CPOX) is an efficient and practical method to produce the feed stream required for solid oxide fuel cells (SOFC's), which can be used in transportation and remote/stationary applications [10–13]. However, the catalytic reforming of such fuels has proven difficult because they contain both aromatics, which are precursors to carbon formation, and organic sulfur, which is known to poison reforming catalysts [13–15].

Transportation fuels, also known as middle distillates, are complex blends of large molecular weight paraffins (C_{10}–C_{20}), naphthenes, and aromatics [16]. An approximate distribution of these components is shown in Table 1 [16]. The sulfur content for commercial diesel fuel is currently regulated in the U.S. to 15 ppm [17,18], but can be as high as 3000 ppm for military fuels [13,19].

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Table 1
General distribution of components found in middle distillate feedstocks; adapted from [16]

Component	Weight percent (%)
Saturated hydrocarbons (paraffins and naphthenes)	55–80
Monoaromatics	15–25
Diaromatics	5–15
Polyaromatics	0–5

Much progress has been made with commercial hydrotreating processes to reduce sulfur to the mandated levels [20–22]; however, some organosulfur compounds tend to be difficult to remove through the hydro-desulfurization process because of the spatial hindrance of the two phenyl groups [20,23]. Thus, in reforming these fuels, catalysts will inevitably be exposed at least some level of organosulfur compounds.

Although we are concerned here solely with sulfur poisoning, catalyst deactivation in the CPOX of these fuels occurs by both carbon formation and sulfur poisoning [13,14]. Aromatic compounds and sulfur bond strongly to the active metal sites on the surface. Among other properties that affect the rate of deactivation, Barbier et al. reported that the interaction between the active metal sites, and aromatics and sulfur is influenced by the ensemble size of the active metal [24–27]. They showed that larger supported metal clusters are more prone to carbon or sulfur adsorption than a well-dispersed metal [27].

These findings suggest that it may be advantageous to incorporate an active metal into the structure of a thermally stable material to decrease the ensemble size and therefore the rate of deactivation. In addition to minimizing the rate of deactivation by sulfur poisoning, it would be expected that such a catalyst would also have improved resistance to carbon deposition.

A class of mixed metal oxides, called pyrochlores, can be modified by substituting multiple elements into the parent structure [28,29]. Pyrochlores are derivatives of the simple fluorite structure with the general formula $A_2B_2O_7$, in which the A and B cations are arranged in a cubic unit cell structure with an $Fd3m$ ($Z = 8$, $a = 1$ nm) space group [30,31]. With the proper valence state (+3 for A-site and +4 for B-site) and ionic radius ratio (r_A/r_B must be between 1.46 and 1.80), the A cation is generally a larger rare-earth metal which is coordinated to 8 oxygen anions; while the B cation is a smaller transition metal, and is coordinated to 6 oxygen anions [31,32].

Substituting for A or B cations alters the catalytic activity and resistance to deactivation in the CPOX of liquid fuels. It is generally believed that, with the proper selection, substitution of a lower valence cation into the A-site will result in improved oxygen-ion conductivity in the material at elevated temperatures [33], which limits carbon formation during reforming reactions such as CPOX [34,35]. Meanwhile, the partial substitution of the B-site cations with an active reforming metal can be used to improve the catalytic activity of the material.

In a previous study [1], a lanthanum zirconate ($La_2Zr_2O_7$) pyrochlore was substituted with Rh only, as well as Rh + Sr, to give $La_2Rh_yZr_{(2-y)}O_{7+\xi}$ (LRZ) and $La_{(2-x)}Sr_xRh_yZr_{(2-y)}O_{7+\xi}$ (LSRZ) catalysts, respectively. Each pyrochlore catalyst was characterized to determine whether the dopants, Rh and Sr, were substituted into the structure and then screened for activity in the CPOX of n-tetradecane (TD). Activity results were compared to a commercial Rh/γ-Al_2O_3 catalyst. H_2 pulse chemisorption and temperature programmed reduction results from the earlier work [1], indicated the Rh metal was effectively substituted into the pyrochlore structure and was reducible. The CPOX of TD demonstrated that the Rh substituted in the LRZ and LSRZ was able to produce high synthesis gas yields that were comparable to traditional supported Rh/γ-Al_2O_3 at the same conditions, and significantly improved catalytic activity compared to unsubstituted LZ.

Although the earlier work [1] has shown that the Rh-substituted pyrochlore is active for CPOX of TD only, the present study examines the effects of the addition of sulfur (dibenzothiophene, DBT) on the CPOX of TD. The objective of this paper is to determine the effects of substituting Rh and Sr into a $La_2Zr_2O_7$ pyrochlore for the CPOX activity and deactivation by sulfur poisoning. The catalysts examined are the same as the previous study [1]: $La_2Rh_{0.11}Zr_{1.89}O_{6.95}$ (LRZ) and $La_{1.50}Sr_{0.50}Rh_{0.10}Zr_{1.90}O_{6.70}$ (LSRZ). Product yields and selectivities (especially H_2 and CO) are compared to those produced over unsubstituted LZ and a conventional supported 0.5 wt% Rh/γ-Al_2O_3.

2. Experimental

2.1. Catalyst synthesis and characterization

The catalyst synthesis method and physical properties of the catalyst used in this study have been reported previously [1], and are summarized below in Table 2.

2.2. CPOX experiments

2.2.1. Reactor configuration

The configuration of the reactor unit used for the catalytic studies has been described in detail elsewhere [14]. Briefly, a fixed bed continuous flow reactor (Autoclave Engineers, Model no. BTRS Jr.) was used for catalyst testing. The liquid feed was vaporized in a temperature-controlled preheating furnace set at 375 °C. The catalyst bed was diluted with quartz sand at a weight ratio of 5/1 quartz-to-catalyst to minimize temperature gradients and avoid channeling. A split-tube furnace encapsulated the reactor tube, and provided temperature control. Bed temperature was monitored by an axially centered thermocouple.

2.2.2. CPOX studies

n-Tetradecane (TD) was chosen as a model paraffin component of diesel, while 1000 ppmw dibenzothiophene (DBT) was added as a representative organosulfur compound. A blank reactor run (CPOX of TD only, no DBT) using only quartz sand in the reactor tube was performed for 5 h to quantify the gas phase reactions. The CPOX experiments involved three steps. First, the CPOX of TD only

Table 2
Summary of characterization results from previous study [1]

	Rh/γ-Al_2O_3	LZ	LRZ	LSRZ
Synthesis method	Commercial (Alfa Aesar)	Pechini method		
Rh metal loading (wt%)	0.5	N/A	2.0	2.0
XRD (phase)	N/A[a]	Pyrochlore	Pyrochlore	Binary phase composite perovskite-pyrochlore. Defect $SrZrO_3$
Rh dispersion (by H_2 pulse chemisorption) (%)	73	N/A	2	5

[a] Did not perform XRD on this material.