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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.

Table 3
Experimental conditions for CPOX experiments

Reaction conditions	
O/C ratio	1.2
GHSV (scc g_{cat}^{-1} h^{-1})	50,000
Bed temperature (°C)	900
Catalyst bed (mg)	480
Pressure (MPa)	0.23

was performed for 1 h to establish baseline activity and selectivity of the catalyst. Next, the feed was switched to 1000 ppmw DBT in TD for 2 h. Finally, the feed was switched back to TD only for 2 h to examine activity recovery. Experimental conditions for the CPOX studies are shown below in Table 3.

After each experiment, carbon deposition was measured by temperature programmed oxidation (TPO). The catalyst was ramped from 200 to 900 °C by 1 °C/min under 5% O_2/N_2, and the CO_2 produced was continuously monitored by a Thermo Onix mass spectrometer (Model no. Prima δb, a 200 a.m.u. scanning magnetic sector).

2.2.3. *Product gas analysis*

The gases (H_2, O_2, N_2, CO, CO_2, and CH_4) were analyzed continuously using the mass spectrometer (Thermo Onix). Larger hydrocarbon products (C_2+) were analyzed using an HP5890 gas chromatograph equipped with a flame ionization detector. Six GC samples were taken over the course of a 5 h experiment: the first at steady state, then one per hour as the experiment progressed. Carbon balances for all experiments were 100 ± 10%.

The yield of each dry gas product, i.e. H_2, CO, CO_2, and CH_4 was calculated by the following equation:

$$\text{Yield of A}\,(\%) = \frac{\text{moles of A produced} \times 100}{N \times \text{moles of TD fed to the reactor}} \tag{1}$$

where N is the number of moles of H_2 per mole of hydrocarbon for H_2 yields and is the number of moles of carbon in the hydrocarbon fuel for yields of carbon containing products.

Hydrocarbon (HC) yields were determined using the following equation:

$$\text{HC yield}\,(\%) = \frac{\text{moles of HC produced} \times 100 \times i}{N \times \text{moles of TD fed to the reactor}} \tag{2}$$

where i is the number of moles of carbon per mole of hydrocarbon in the product (i.e. i would be 2 for ethane) and N is the number of moles of carbon in the hydrocarbon fuel.

A carbon balance was determined by the following equation:

$$\text{Carbon balance}\,(\%) = \frac{\left(\text{CO} + \text{CO}_2 + \sum_i^{i=1-6} i\text{C}_i\text{H}_r\right) \times 100}{N \times \text{moles of TD fed to the reactor}} \tag{3}$$

where i is the number of moles of carbon per mole of hydrocarbon in the product (i.e. i would be 2 for ethane), N is the number of moles of carbon in the hydrocarbon fuel and r is the number of hydrogen atoms contained in the hydrocarbon product.

2.2.4. *Equilibrium calculations*

Equilibrium values were determined by a Gibbs free energy minimization calculation using HSC chemistry software [36]. The calculations were made assuming a mixture of 2 mol% TD, 18 mol% O_2, and 80 mol% N_2 (O/C = 1.2), 0.23 MPa, and 900 °C.

Table 4
Equilibrium and blank reactor product yields, and carbon balance for the CPOX of TD at O/C = 1.2, 0.23 MPa, and 900 °C [1]

	Equilibrium[a]	Quartz sand (blank)[b]
H_2 yield (%)	90	17
CO yield (%)	92	42
CO_2 yield (%)	8.5	17
CH_4 yield (%)	0.1	8
Olefin and benzene yield (%)	0.0	23
Carbon balance (%)	N/A	90
Carbon formation ($g_{carbon}/g_{catalyst}$)	0	0.4

[a] Calculated by a Gibb's free energy minimization using HSC Chemistry Thermodynamic software [36].

[b] Measured at the end of the 5-h run.

3. Results and discussion

3.1. *CPOX of n-tetradecane only—blank reactor*

As reported earlier [1], the blank reactor results showed that TD conversion was complete within the accuracy of the measurements, with a significant selectivity to olefins and benzene (23%) and lower hydrocarbons such as methane (~10%). The distribution of measured products is compared to equilibrium values in Table 4 [1].

Yields of H_2 and CO are significantly less than equilibrium for the blank reactor, while yields of CO_2 and methane are greater. Including yields of C_2–C_6 compounds, the carbon balance is roughly 90% over the course of the 5-h run. These products (C_2–C_6) were found to be primarily ethylene and propylene, which is consistent with the literature [37,38]. Although H_2O was not measured, a mass balance on H and O atoms shows a ratio of 2.4 ± 1.0, suggesting that steam is produced in substantial concentrations. At these conditions, carbon formation was not predicted by the equilibrium calculations; however it did form on the surface of the quartz, about 0.4 g_{carbon}/g_{cat} as measured after the 5 h run.

3.2. *CPOX of n-tetradecane + 1000 ppmw dibenzothiophene*

3.2.1. *0.5 wt% Rh/γ-Al_2O_3*

Figs. 1 and 2 show the effect of 1000 ppmw sulfur on the product yields for the 0.5 wt% Rh/γ-Al_2O_3 catalyst. There is an immediate and significant loss of H_2 and CO yields when the sulfur is added, with a corresponding increase in CO_2, CH_4, and unsaturates yields (unsaturates refers to olefins + aromatics). This suggests a loss of the reforming activity associated with the Rh active metal sites [14,39,40]. Deactivation by DBT may be attributed to the electron-dense Rh-metal clusters forming strong bonds to the lone pair electrons on the sulfur molecules [14]. As metal sites are occupied by sulfur, an increase in homogeneous reactions occurs in the system. Additionally, the DBT molecules also have two phenyl rings that can adsorb strongly to active metal sites. It is likely that these rings also contribute to the deactivation of the Rh-sites along with the sulfur. After 2-h in the presence of 1000 ppmw DBT, the H_2 and CO yields are 26 and 32%, respectively, which approaches the yields produced in the blank reactor, 17 and 42%, respectively, after 5-h on stream (Table 4).

Although both CO and H_2 yields decrease continuously in the presence of DBT, the H_2 yield decreases more rapidly with time on stream than the CO yield. The reasons for this are not entirely clear, but it might be speculated that the sites responsible for the steam reforming in the downstream portion of the catalyst bed may be deactivated. Steam is not measured continuously in these experiments, but a mass balance on the H and O atoms shows an H/O ratio of 2.1 ± 1.2 during the 2 h when DBT is present. This suggests that in the presence of sulfur, significant concentrations of

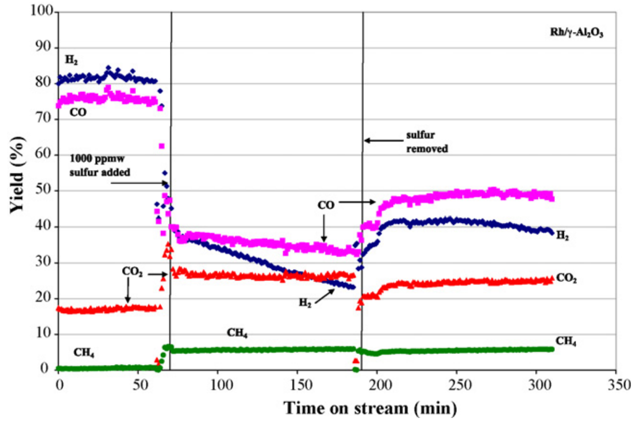

Fig. 1. Step response plot for 0.5 wt% Rh/γ-Al_2O_3 after the addition of 1000 ppmw DBT at an O/C = 1.2, 0.23 MPa, 900 °C and 50,000 scc/$g_{catalyst}$/h. H_2 (◆), CO (■), CO_2 (▲), and CH_4 (●).

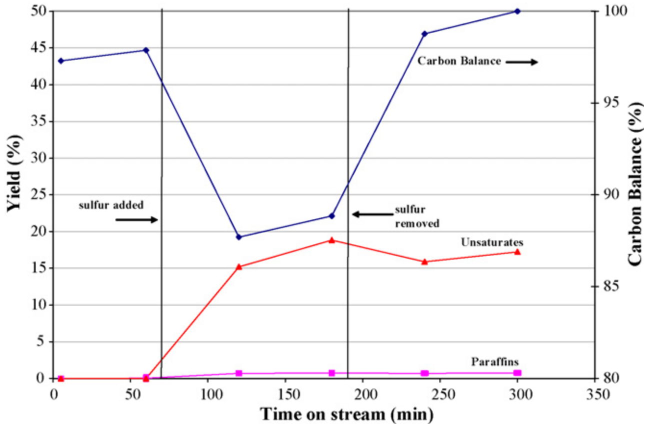

Fig. 2. Paraffins, unsaturates yields, and carbon balance for 0.5 wt% Rh/γ-Al_2O_3 during the 1000 ppmw DBT/TD experiment at an O/C = 1.2, 0.23 MPa, 900 °C and 50,000 scc/$g_{catalyst}$/h. Carbon balance (◆), unsaturates (▲), and paraffins (■).

steam, likely formed by oxidation of the fuel at or near the inlet of the bed [41–43] is not further reacted (via steam reforming reactions) in the downstream portion of the bed.

When the sulfur is removed, the activity does not return to pre-sulfur levels, indicating irreversible poisoning of the active sites, at least over the time scale of these experiments. Three times more carbon is formed in the presence of sulfur than in the directly comparable experiment of the CPOX of TD only (0.27 g_{carbon}/g_{cat} versus 0.90 g_{carbon}/g_{cat}) [1]. TPO results (not shown) indicate that this carbon can be assigned to the Rh metal surface and Rh-support interface [1]. This suggests that the presence of sulfur appears to poison the activity of the catalyst through carbon formation on the active sites, rather than by poisoning the metal itself.

3.2.2. Lanthanum zirconate (LZ)

The effects of sulfur on the CPOX activity and conversion of LZ are shown in Figs. 3 and 4. Note that the initial (pre-sulfur) yields of H_2 and CO are somewhat less for the LZ than the 0.5 wt% Rh/γ-Al_2O_3, which can be attributed to the lack of the noble metal in the catalyst. Similar to the 0.5 wt% Rh/γ-Al_2O_3, after the introduction of DBT, there is an immediate and significant drop in yields of H_2 and CO to levels essentially the same as those reached by the 0.5 wt% Rh/γ-Al_2O_3 after 2 h in the presence of sulfur (compare Figs. 1 and 3). In conjunction with this activity loss, there is a corresponding increase in CO_2, CH_4, and unsaturates yields.

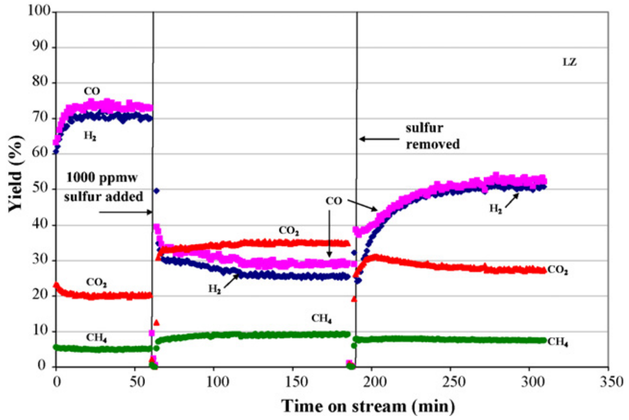

Fig. 3. Step response plot for LZ after the addition of 1000 ppmw DBT at an O/C = 1.2, 0.23 MPa, 900 °C and 50,000 scc/$g_{catalyst}$/h. H_2 (◆), CO (■), CO_2 (▲), and CH_4 (●).

Unlike the 0.5 wt% Rh/γ-Al_2O_3, the H_2 and CO yields for LZ approach those of the blank reactor immediately after sulfur is introduced. However, the H_2/CO ratio in the presence of DBT (0.88/1) is only slightly different than during the initial 1 h CPOX of TD (0.96/1), suggesting that sulfur may as a kinetic inhibitor on the LZ. Similar to the 0.5 wt% Rh/γ-Al_2O_3, the sulfur likely adsorbs to the active sites on the LZ surface responsible for synthesis gas production, thus decreasing the reforming rate and selectivity of the catalyst (as shown by the increase in unsaturates, CH_4 and CO_2 in the presence of sulfur; Figs. 3 and 4). Since there is no continuous decrease in H_2 yield in the presence of DBT, it appears that the sulfur may have a weaker interaction with the LZ surface because it is unable to form a stable sulfide and irreversibly poison the active sites as it did to the 0.5 wt% Rh/γ-Al_2O_3. However, once the sulfur is removed, the pre-sulfur activity is not restored, so there is at least some irreversible deactivation.

The presence of sulfur results in carbon formation on the LZ (0.80 g_{carbon}/g_{cat}) that is roughly equal to that on the 0.5 wt% Rh/γ-Al_2O_3 (0.90 g_{carbon}/g_{cat}), and is qualitatively similar as, measured by the position and size of the TPO curve (not shown). Compared to the results of a 5-h run with TD alone [1], the presence of sulfur increases total carbon deposition from 0.30 to 0.80 g_{carbon}/g_{cat} on the LZ.

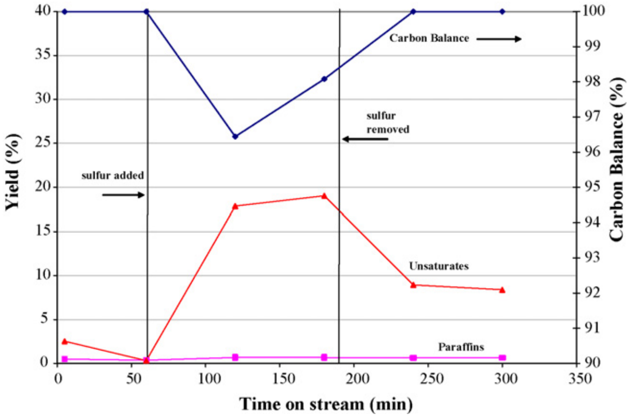

Fig. 4. Paraffins, unsaturates yields, and conversion for LZ during the 1000 ppmw DBT/TD experiment at an O/C = 1.2, 0.23 MPa, 900 °C and 50,000 scc/$g_{catalyst}$/h. Carbon balance (◆), unsaturates (▲), and paraffins (■).

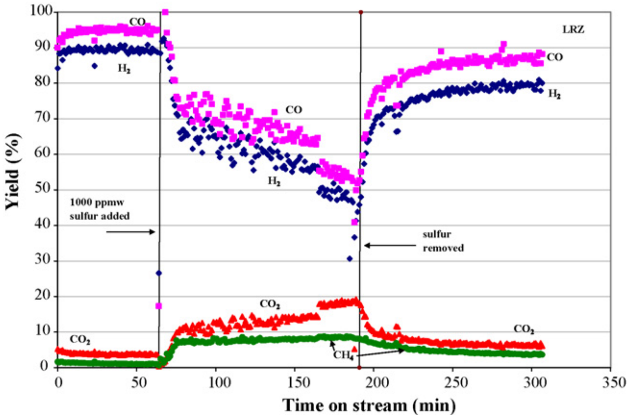

Fig. 5. Step response plot for LRZ after the addition of 1000 ppmw DBT at an O/C = 1.2, 0.23 MPa, 900 °C and 50,000 scc/$g_{catalyst}$/h. H_2 (◆), CO (■), CO_2 (▲), and CH_4 (●).

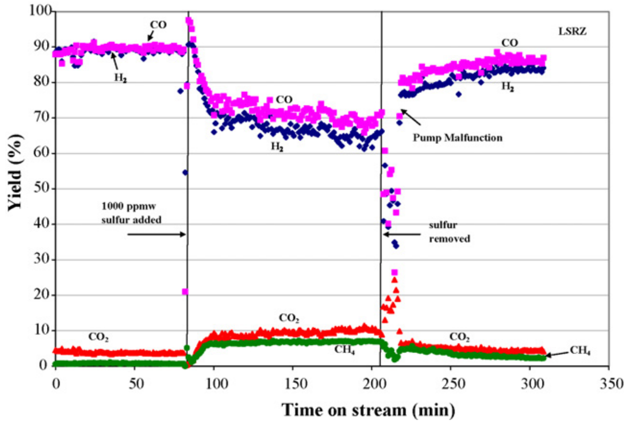

Fig. 7. Step response plot for LSRZ after the addition of 1000 ppmw DBT at an O/C = 1.2, 0.23 MPa, 900 °C and 50,000 scc/$g_{catalyst}$/h. H_2 (◆), CO (■), CO_2 (▲), and CH_4 (●).

3.2.3. *Lanthanum–rhodium–zirconate (LRZ)*

The substitution of Rh into the LZ catalyst results in significant improvement in the pre-sulfur yields of H_2 and CO, but there is still significant deactivation due to the addition of sulfur (Figs. 5 and 6).

The continuous decline in H_2 and CO yields in the presence of sulfur suggests deactivation rather than kinetic inhibition, at least over the time scale of this experiment. One noticeable difference between the LRZ, LZ, and 0.5 wt% Rh/γ-Al_2O_3 catalysts is the much more complete recovery of initial activity for the LRZ when the sulfur is removed (see Figs. 5 and 6). The Rh atoms in the LRZ are incorporated into the pyrochlore structure [1], as opposed to simply supported by the pyrochlore. This eliminates the possibility that the Rh atoms will sinter, and apparently provides some resistance to irreversible deactivation by DBT.

As with the other catalysts (0.5 wt% Rh/γ-Al_2O_3 and LZ), the presence of sulfur significantly increases the formation of carbon versus a directly comparable 5-h run without sulfur for the LRZ—from 0.32 to 0.86 g_{carbon}/g_{cat} [1]. The TPO results (not shown) show that the reactivity of the carbon in both cases is essentially the same—there is simply more carbon deposited on the LRZ in the presence of sulfur than for a directly comparable 5-h run with TD only.

This amount of carbon on the LRZ after the sulfur run is essentially the same as the 0.5 wt% Rh/γ-Al_2O_3 catalyst in terms of total amount (0.86 g_{carbon}/g_{cat} versus 0.90 g_{carbon}/g_{cat}) and reactivity (as measured by TPO, results not shown). However, this carbon does not adversely affect the recovery of activity on the LRZ as severely as for the 0.5 wt% Rh/γ-Al_2O_3, suggesting that the deactivation observed on the LRZ in the presence of sulfur is not due solely to carbon deposition, but could be attributed to readily reversible sulfur poisoning.

3.2.4. *Lanthanum–strontium–rhodium–zirconate (LSRZ)*

The addition of strontium to the pyrochlore significantly improves its resistance to deactivation by sulfur. As shown in Figs. 7 and 8, there is the expected decrease in H_2 and CO yields when sulfur is introduced, but the decline in activity over the 2 h period of time when sulfur is present is far less rapid than for the LRZ. The activity recovers to near-initial levels once the sulfur is removed.

Strontium stabilizes the activity in the presence of sulfur, with the H_2 and CO yields reaching near steady-state values after roughly 1 h after the addition of sulfur. This drop in synthesis gas yields to near stationary levels suggests that sulfur kinetically inhibits the reforming reaction. The substitution of Sr^{2+} for La^{3+} may create oxygen vacancies in the pyrochlore lattice, permitting the oxygen anions in the structure to become mobile at the high reaction temperatures [35]. Improved oxygen ion conductivity assists the overall reforming reactions through the movement of bulk lattice oxygen to active sites at the surface in which sulfur and carbon readily adsorb. Then redox reactions between the localized

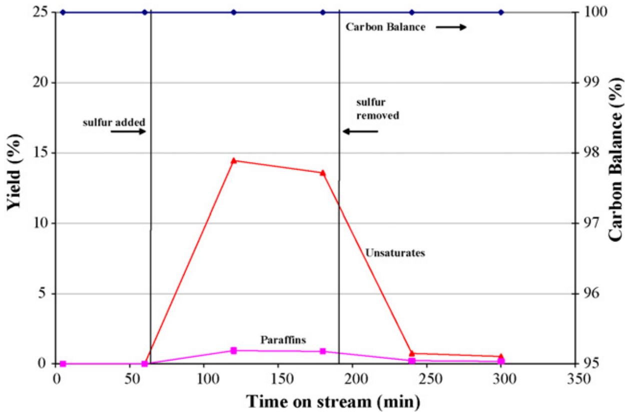

Fig. 6. Paraffins, unsaturates yields and conversion for LRZ during the 1000 ppmw DBT/TD experiment at an O/C = 1.2, 0.23 MPa, 900 °C and 50,000 scc/$g_{catalyst}$/h. Carbon balance (◆), unsaturates (▲), and paraffins (■).

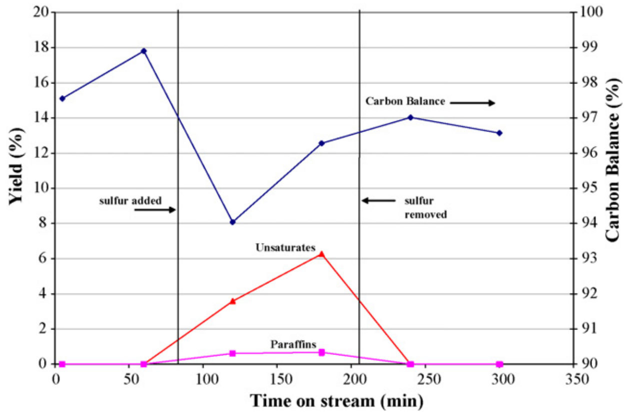

Fig. 8. Paraffins, unsaturates yields and conversion for LSRZ during the CPOX 1000 ppmw DBT/TD at an O/C = 1.2, 0.23 MPa, 900 °C and 50,000 scc/$g_{catalyst}$/h. Carbon balance (◆), unsaturates (▲), and paraffins (■).

Table 5
Amount of carbon formed on pyrochlore catalysts LZ, LRZ and LSRZ, as well as 0.5 wt% Rh/γ-Al_2O_3 at the end of 5 h sulfur experiment (CPOX of TD only for 1 h, 1000 ppmw DBT/TD for 2 h and TD only for 2 h) at O/C = 1.2, 0.23 MPa, 900 °C, and 50,000 scc/$g_{catalyst}$/h

Catalyst	Carbon deposition (g_{carbon}/g_{cat})[a]
Rh/γ-Al_2O_3	0.90
LZ	0.80
LRZ	0.86
LSRZ	0.30

[a] As measured by TPO.

oxygen that is partially coordinated at the lattice surface and the adsorbed sulfur, as well as carbon formed due to the presence of sulfur, limit the deactivation that was previously observed by LRZ, LZ, and the Rh/γ-Al_2O_3. Oxygen vacancies created by this process may be replenished by the incorporation of oxygen from steam or O_2 in the feed. This appears to be consistent with the observed decrease in carbon deposition for the LSRZ catalyst compared to the others reported here (Table 5).

Like the other catalysts studied, sulfur increases the amount of carbon deposition for the LSRZ compared to an identical run with no added sulfur (from 0.17 to 0.30 g_{carbon}/g_{cat}; see [1]). The carbon on the LSRZ is similar in reactivity (TPO results not shown), there is simply more carbon deposited when sulfur is present in the feed.

4. Conclusions

Effects of the addition of 1000 ppmw dibenzothiophene (DBT) to *n*-tetradecane (TD) resulted in a loss of activity for each catalyst. The 0.5 wt% Rh/γ-Al_2O_3 and unsubstituted lanthanum zirconate (LZ) suffered an instantaneous deactivation by the DBT. The substitution of Rh into the pyrochlore form, LRZ, produces a catalyst that was less susceptible to deactivation by the sulfur compared to 0.5 wt% Rh/γ-Al_2O_3. Rather than an immediate deactivation, the LRZ showed a gradual activity loss over the time DBT was present in the feed. It is unclear, at least over the time scale of the experiment, whether activity would have reached a steady level or continued to decline until the catalyst was completely deactivated. Further substitution with Sr into the pyrochlore structure stabilized the synthesis gas yields and reduces the effect of DBT to primarily that of kinetic inhibition.

After sulfur experiments, all catalysts showed more carbon formation compared to CPOX of TD-only in a previous study [1]. This carbon formation appears to be linked to the ability to recover activity after the sulfur is removed from the feed. Each catalyst was able to recover some activity once DBT was removed. The 0.5 wt% Rh/γ-Al_2O_3 showed the least amount of recovery because of the larger amounts of carbon on active metal. LZ recovered more activity than the 0.5 wt% Rh/γ-Al_2O_3, but yields were still significantly less than initial levels. LRZ showed similar amounts of carbon formation to LZ and the 0.5 wt% Rh/γ-Al_2O_3, but was able to regain most of its initial activity after the DBT was removed. This suggests that less carbon forms on the active sites (Rh metal). Sulfur addition caused less carbon deposition on the LSRZ than any of the other catalysts. Removal of the sulfur resulted in the recovery of almost initial activity levels, indicating the effects of sulfur were reversible. It is believed that the oxygen ion conductivity may have reduced the deactivation of catalyst by carbon deposition and by sulfur.

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