Selective catalytic oxidation: a new catalytic approach to the desulfurization of natural gas and liquid petroleum gas for fuel cell reformer applications

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Abstract

In both natural gas and liquid petroleum gas (LPG), sulfur degrades the performance of the catalysts used in fuel reformers and fuel cells. In order to improve system performance, the sulfur must be removed to concentrations of less than 200 ppbv (in many applications to less than 20 ppbv) before the fuel reforming operation.

Engelhard Corporation presents a unique approach to the desulfurization of natural gas and LPG. This new method catalytically converts the organic and inorganic sulfur species to sulfur oxides. The sulfur oxides are then adsorbed on a high capacity adsorbent.

The sulfur compounds in the fuel are converted to sulfur oxides by combining the fuel with a small amount of air. The mixture is then heated from 250 to 270 °C, and contacted with a monolith supported sulfur tolerant catalyst at atmospheric pressure.

When Engelhard Corporation demonstrated this catalytic approach in the laboratory, the result showed sulfur breakthrough to be less than 10 ppbv in the case of natural gas, and less than 150 ppbv for LPG. We used a simulated natural gas and LPG mixture, doped with a 50–170 ppmv sulfur compound containing equal concentrations of COS, ethylmercaptan, dimethylsulfide, methylethylsulfide and tetrahydrothiophene. There is no need for recycled H_2 as in the case for hydrodesulfurization.
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Keywords: Reformer; Natural gas; LPG; Sulfur; Desulfurization

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells promise to be an efficient and clean alternative to fuel combustion for primary power generation for use in stationary and mobile source applications. PEMs are more fuel-efficient than the internal combustion engine. Consequently, PEM fuel cells generate lower levels of CO_2, and produce virtually no CO, hydrocarbon or NO_x emissions.

PEM fuel cells operate on the basic principle of conversion of chemical energy into electrical energy. This avoids the greater thermodynamic limitations of traditional combustion energy generation cycles. Hydrogen gas is electrochemically oxidized to hydrogen ions at the anode, which pass through a proton conductive membrane to the cathode. There, they combine with electrochemically reduced oxygen (from the air) to produce H_2O.

Hydrogen gas is produced for the fuel cell stack from hydrocarbon fuels [1]. Catalytic reforming is the process by which the hydrocarbon fuel is converted to syngas (e.g. CO and H_2). The CO is further reacted with steam over a water-gas-shift catalyst to generate CO_2 and more hydrogen. The small amount of CO remaining can poison the PEM fuel cell anode, and so, it is oxidized to CO_2 using highly selective preferential oxidation (PrOx), further purifying the hydrogen.

Sulfur compounds occur naturally in hydrocarbon fuels, and they are also added as odorants. However, sulfur compounds deactivate the base metal water-gas-shift catalyst and the PrOx catalyst in the reformer stack, and the anode electrode of the fuel cell. Consequently, it is necessary to desulfurize the hydrocarbon feed to the lowest possible sulfur concentrations, preferably below 200 ppbv. There are two basic approaches for fuel desulfurization:

1. Passive adsorption
2. Catalytic transformation, followed by adsorption

The passive adsorption approach uses zeolites, metal impregnated carbons, and aluminas to remove the organic and inorganic sulfur compounds at ambient pressure and temperature [2]. Its simplicity is attractive since it requires little up front capital investment in the reformer design. How-

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ever, sulfur adsorption capacities are low, typically less than 2 g S/100 g adsorbent for NG and less than 1 g S/100 g for LPG. This requires large adsorption inventories and frequent change-outs. Also, since they accumulate heavier hydrocarbons, the spent adsorbents are hazardous and require special handling.

The catalytic-adsorption approach is attractive because of the lower maintenance costs and size. This is due to its greater sulfur adsorption capacities. However, it does require higher up-front capital investment to accommodate the required reagent addition and heating of the fuel.

The catalytic-adsorption approach most often used is hydrodesulfurization (HDS). This is where hydrogen added to the fuel reacts with the sulfur compounds to form H_2S. The process uses a HDS catalyst, typically $Ni-Mo/Al_2O_3$ or $Co-Mo/Al_2O_3$, followed by H_2S adsorption on zinc oxide at a temperature of 300–400 °C. For HDS of liquid fuels, hydrogen (H_2) partial pressures of 1000 to 2000 kPa and temperatures of 300–400 °C are required.

Because the sulfur compounds in natural gas and LPG are non-aromatic and of low molecular weight, HDS can be performed at lower H_2 partial pressures, 1 to 10 kPa, and temperatures of 200–400 °C depending on the catalyst and the sulfur speciation [3]. Zinc oxide adsorption capacities for H_2S in industrial applications are reported to be high, typically 15–20 g S/100 g adsorbent [4]. This is higher than passive adsorbents, thus lowering inventories of adsorbent and decreasing adsorbent replacement frequency. HDS requires adding hydrogen, which is recycled from one of the post-reformer points in the process. An additional drawback is the nature of the catalysts themselves. HDS catalysts require activation using a $H_2S–H_2$ mixture, and they contain priority pollutant metals (e.g. Ni, Co, and Mo) that require special handling and disposal.

Engelhard has developed a new catalytic-adsorption fuel desulfurization technology that does not require hydrogen recycle and whose by-products are non-hazardous. This technology combines the fuel with a sub-stoichiometric amount of oxygen (from air) and uses a sulfur tolerant monolith catalyst to oxidize selectively the sulfur compounds to sulfur oxides (SO_2 and SO_3, referred to collectively as SO_x). The SO_x species are then adsorbed downstream by an inexpensive high capacity particulate adsorbent. Sulfur slip from natural gas is below 10 ppbv. For liquid petroleum gas at maximum allowable sulfur levels (120 ppmw or 165 ppmv), the sulfur slip is less than 160 ppbv. The new process is called selective catalytic oxidation (SCO).

2. Experiment conditions

The selective sulfur oxidation catalyst is supported on a 62 cells-per-cm^2 monolith. The monolithic catalyst is then placed in a 2.54 cm quartz tube that is heated in a clam-shell furnace. Catalyst inlet and outlet temperatures are measured using thermocouples mounted 0.16 cm from the cat-

alyst faces. The gas mixtures are prepared using mass flow controllers. Total gas flow rates are 0.5–2 l/min.

For natural gas desulfurization experiments, methane is combined with CO_2, hexane, and the sulfur compound mixture, to obtain a reagent gas that is 2% (v/v) CO_2, 2000 ppmv hexane and 50 ppmv sulfur. For the LPG desulfurization experiments, the gas mixture is formulated to contain propane with 5% propylene, 1.7% hexane, and 60–180 ppmw total sulfur (parts per million on a weight basis with respect to the total hydrocarbon content of the mixture).

The sulfur compound mixture is equal concentrations of COS, ethylmercaptan (EM), dimethylsulfide (DMS), methylethylsulfide (MES, when it is present in the mixture) and tetrahydrothiophene (tHt). In our experience, the sulfur concentrations in the formulation are a worst case scenario, while the species represent extremes in lability (COS and EM) and stability (DMS, MES and tHt). Air is added to these mixtures to obtain oxygen to carbon ratios from 0.02 to 0.05. Sulfur species analysis is performed with a GC using a sulfur specific detector.

The catalyst is cycled through a sequence of space velocities, inlet temperatures, inlet sulfur concentrations, and oxygen-to-carbon ratios. Each condition is maintained for 30 min before sampling the exit gas stream and advancing to the next condition. The SO_x trap used in the catalyst experiments consists of 0.16 to 0.32 cm diameter spheres operated at a space velocity of 360/h. For the catalyst performance mapping experiments, the trap is used to protect the downstream reactor system from SO_x contamination.

The SO_x trap capacity was measured on a second reactor under steady-state conditions. The SO_x was generated using the SCO catalyst with a gas matrix containing 100 ppmv total sulfur (equal concentrations EM, DMS and tHt) in methane at an O_2/C ratio of 0.025 and at 275 °C. Complete conversion of the organo-S to SO_x is obtained under these conditions with a trap temperature between 200 °C and 350 °C. When measuring trap capacity, the trap pellets are ground and coated on a 62 cells-per-cm^2 monolith. The monolith is operated at 1200/h monolith space velocity. We obtain 10% relative agreement between the measurements for the monolith-supported trap and with the trap as pellets. The reactor outlet is bubbled through an aqueous solution containing a small amount of base and an acid–base indicator. SO_x breakthrough is indicated by the change in the indicator color.

A 3-kW pilot plant unit, equipped with a micro-GC, is used to measure major component concentrations, including methane, propane, propylene, O_2, CO_2, CO, and H_2. Propylene make over the catalyst is determined using chemically pure-grade propane as the feed on the pilot plant unit.

3. Results

A block diagram for the new SCO process is shown in Fig. 1. Air is added to the fuel at the appropriate O_2/C ratio,
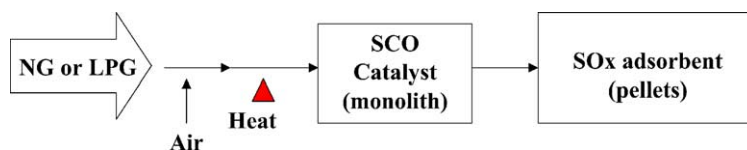
Fig. 1. Process flow diagram for selective catalytic oxidation (SCO). The fuel is mixed with air ($O_2/C = 0.02$ for NG, $O_2/C = 0.03$ for LPG), and heated from 250 to 275 °C. The SCO catalyst converts the sulfur in the fuel to SO_x that is then adsorbed by the SO_x adsorbent.

and the mixture is heated. The catalyst oxidizes the sulfur species to SO_x, which is then removed from the gas stream by the SO_x adsorbent. The oxygen not used in the oxidation of the sulfur compounds produces CO_2 and H_2O from the oxidation of the hydrocarbon fuel. The process has a small fuel penalty that can be partially recovered as heat from the fuel oxidation.

3.1. Natural gas desulfurization

For the simulated natural gas mixture, air is added at O_2/C ratios of 0.02–0.03. No sulfur breakthrough (<5 ppbv) is observed at catalyst space velocities from 5000/h to 20 000/h, and total sulfur concentrations up to 50 ppmv. Slight breakthrough is observed at 40 000/h and 50 ppmv inlet sulfur (Fig. 2). Thus, for natural gas, the system can accommodate turn-down ratios of a factor of 8 without sulfur breakthrough.

3.2. LPG Desulfurization

Liquid petroleum gas (LPG) is more difficult to desulfurize because of the higher sulfur concentrations in the fuel. We mapped the catalyst performance as a function of inlet temperature, oxygen-to-carbon ratio, and space velocity.

The SCO technology has a broad temperature and space velocity operating window.

Fig. 3 shows a clear trend to lower S breakthrough as the temperature decreases and the O_2/C ratio approaches 0.03 from both higher and lower values. Lowest sulfur breakthrough is obtained with an inlet T of 250–270 °C, and O_2/C ratio of 0.03 (Fig. 4).

Fig. 5 shows the effect of inlet sulfur concentration on the outlet breakthrough concentration. In the operating window of O_2/C ratio of 0.03 and 250–260 °C, the reaction is approximately first order in sulfur concentration: the breakthrough concentration increases proportionately with inlet concentration, maintaining a constant conversion. At 275 °C inlet T, breakthrough rises at a more rapid rate with inlet concentration.

The catalyst performance is optimal at space velocities below 6000/h and inlet temperatures between 250 and 260 °C (Fig. 6). The total sulfur slip under these conditions is less than 0.160 ppmv.

Using the SCO technology, sulfur breakthrough, at maximum inlet sulfur concentrations of 120 ppmw (100 ppmv), is less than 0.160 ppmv under conditions for optimum catalyst performance. Speciation of the sulfur slip as a function of time-on-stream is shown in Fig. 7. Both COS and ethylmer-
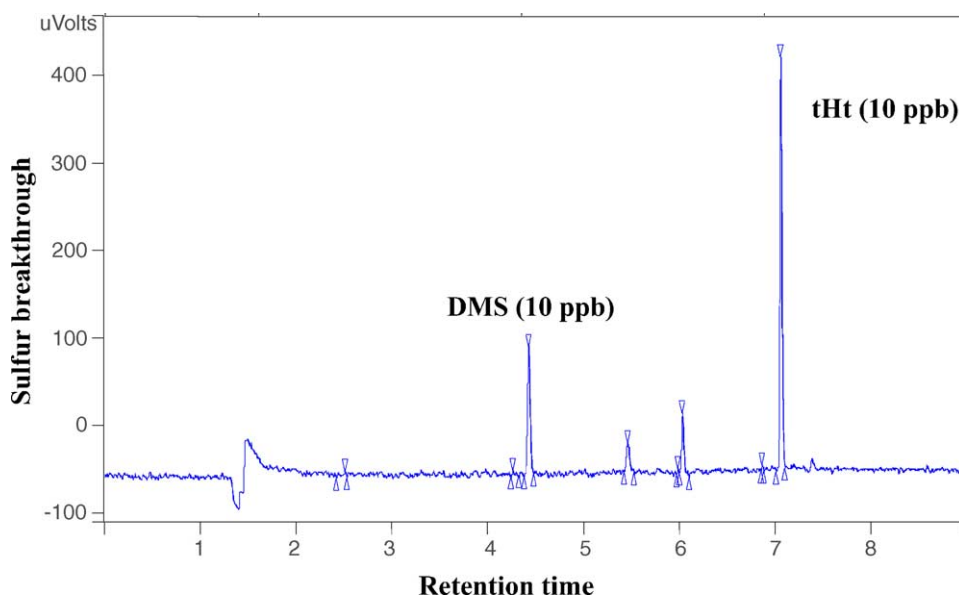

Fig. 2. Gas chromatogram of SCO–SO_x adsorber outlet for simulated natural gas desulfurization. Sulfur is completely removed from natural gas. Sulfur breakthrough is observed only at high space velocity and high sulfur inlet concentration. The inlet gas is 50 ppmv total sulfur, 12.5 ppmv each sulfur species (COS, ethylmercaptan (EM), dimethylsulfide (DMS), tetrahydrothiophene (tHt)). Air at $O_2/C = 0.02$, 1.5% CO_2, 1000 ppmv hexane, balance methane.
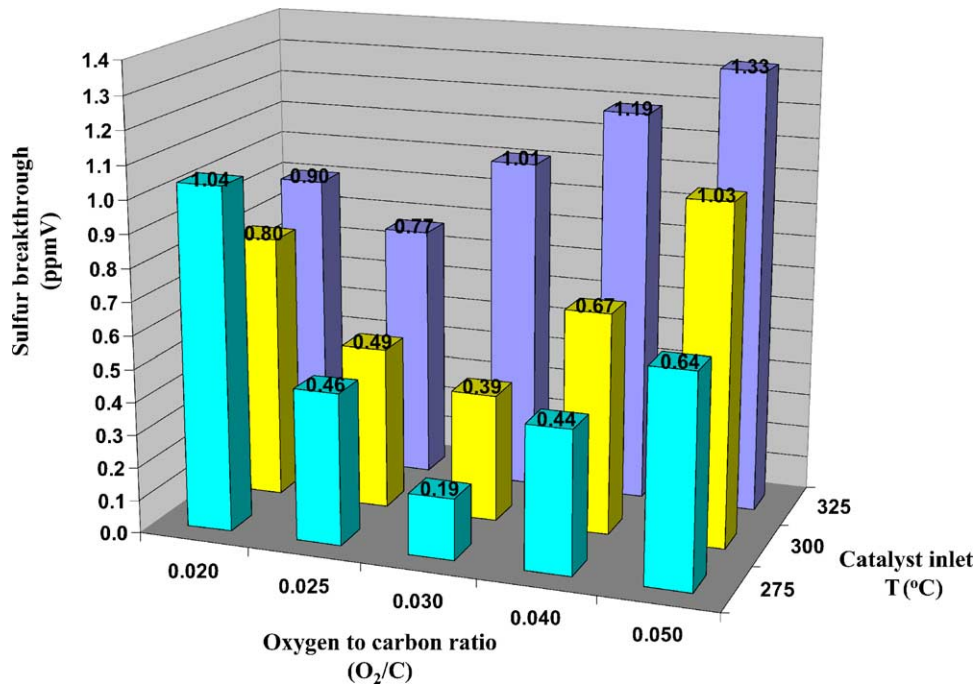
Fig. 3. Total sulfur slip from a simulated LPG mixture containing propane with 5% propylene, 1.7% hexane, and 120 ppmw total sulfur (equal concentrations of COS, ethylmercaptan, dimethylsulfide, tetrahydrothiophene). Air added to the O_2/C ratio shown. 5625/h space velocity. Lower S breakthrough is obtained at lower inlet temperature and an optimum O_2/C ratio of 0.03.

captan are completely converted. The breakthrough species are dimethylsulfide, methylethylsulfide, and thiophene (from tHt). The catalyst performance stabilizes after 120 h and is constant thereafter to 480 h.

We can control the oxygen-to-carbon ratio by monitoring the catalyst outlet temperature (Fig. 8). Outlet temperature increases with oxygen-to-carbon ratio from 0.02 to 0.04, with the outlet temperature at 0.04 and 0.05 nearly
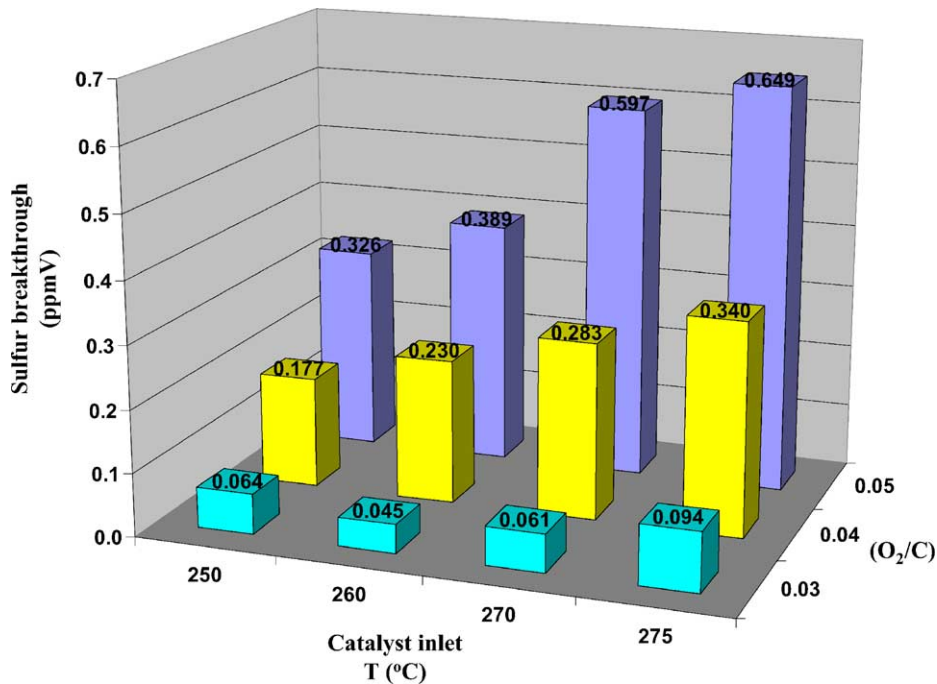

Fig. 4. Effect of catalyst inlet temperature and O_2/C ratio on total sulfur slip. LPG mixture containing propane with 5% propylene, 1.7% hexane, and 120 ppmw total sulfur (equal concentrations of COS, ethylmercaptan, dimethylsulfide, tetrahydrothiophene). Air added to the O_2/C ratio shown. 5625/h space velocity. Lower S breakthrough is obtained at inlet temperature less than 275 °C and an optimum O_2/C ratio of 0.03.
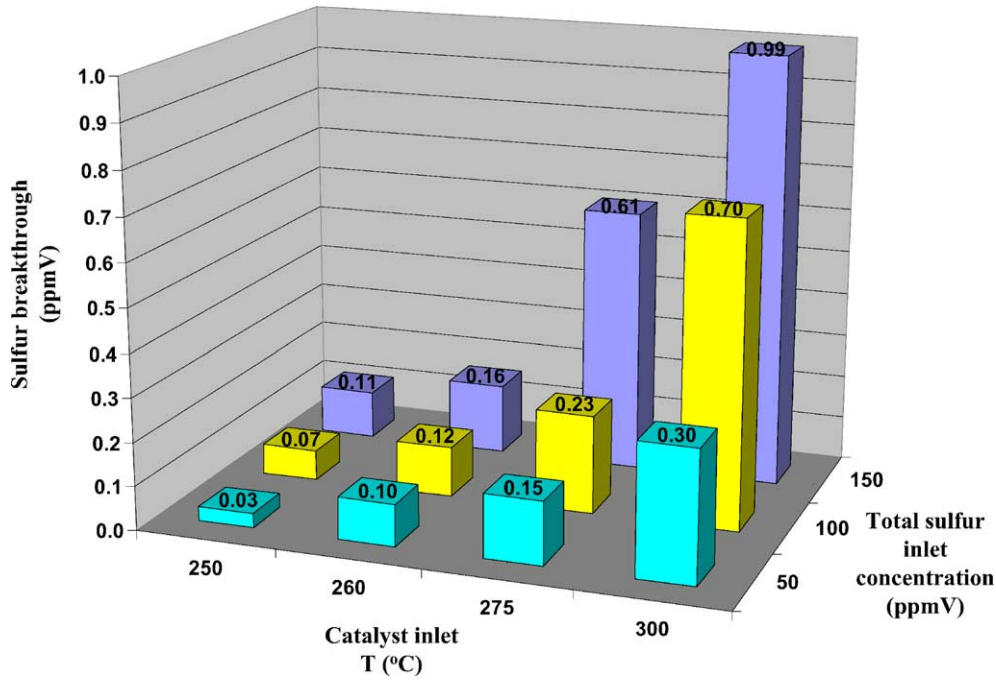
Fig. 5. Effect of inlet sulfur concentrationon the total sulfur slip from a simulated LPG mixture containing propane with 5% propylene, 1.7% hexane, and 60 ppmw (50 ppmv), 120 ppmw (100 ppmv), 180 ppmw, (150 ppmv) total sulfur (equal concentrations of COS, ethylmercaptan, dimethylsulfide, methylethylsulfide, tetrahydrothiophene).$O_2/C = 0.03$. 5625/h space velocity. Sulfur conversion is constant with inlet concentration at $T < 275\,^\circ\mathrm{C}$.
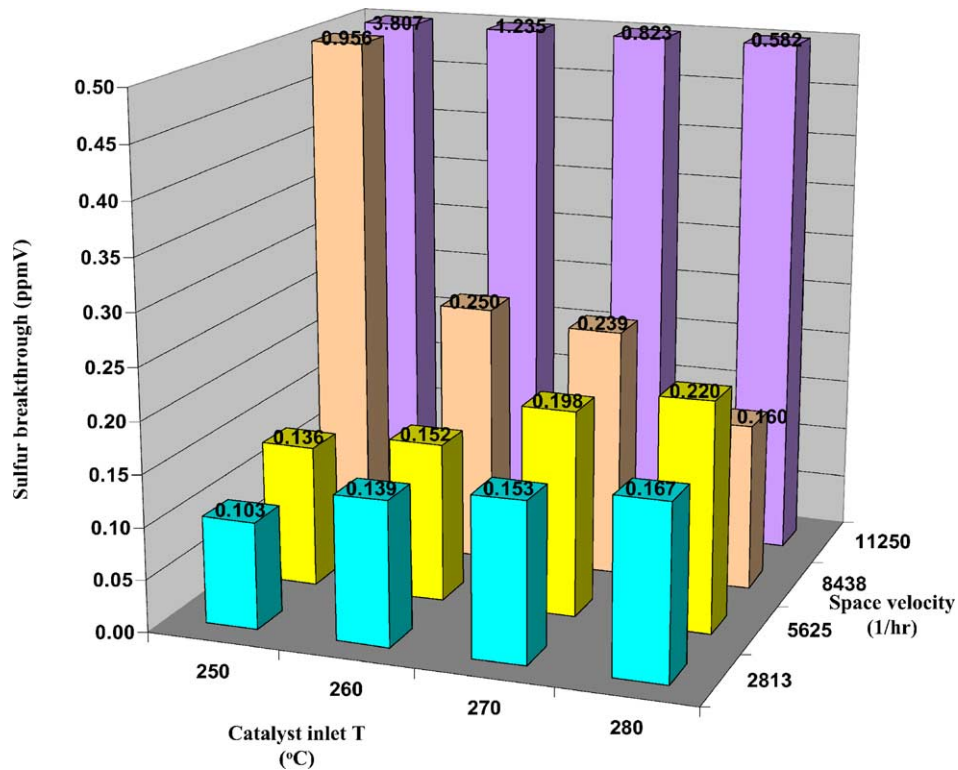

Fig. 6. Total sulfur slip dependence on space velocity and inlet temperature. Simulated LPG mixture containing propane with 5% propylene, 1.7% hexane, and 120 ppmw (100 ppmv) total sulfur (equal concentrations of COS, ethylmercaptan, dimethylsulfide, tetrahydrothiophene).$O_2/C = 0.03$. Space velocity and inlet temperature as shown. Lower S breakthrough is obtained at inlet temperature less than $270\,^\circ\mathrm{C}$ and SV < 6000/h.
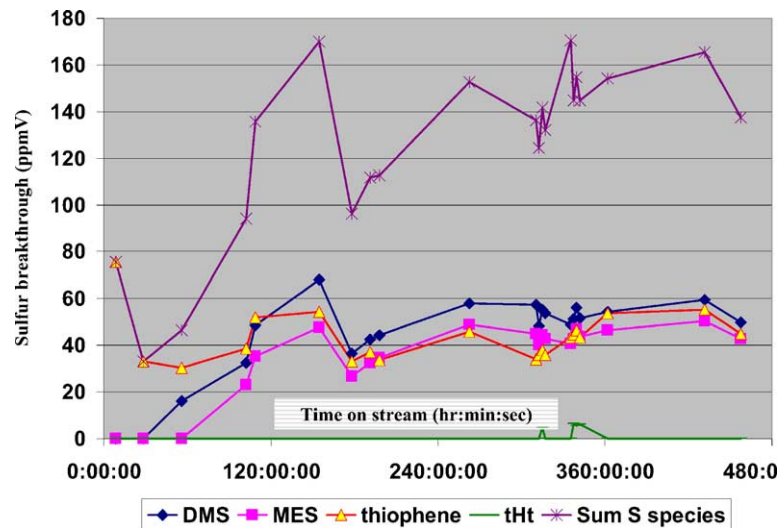
Fig. 7. Speciation of the sulfur slip. Simulated LPG mixture containing propane with 5% propylene, 1.7% hexane, and 120 ppmw (100 ppmv) total sulfur (equal concentrations of COS, ethylmercaptan, dimethylsulfide, tetrahydrothiophene). Inlet $T = 260\,°C$. $O_2/C = 0.03$. SV = 5625/h.
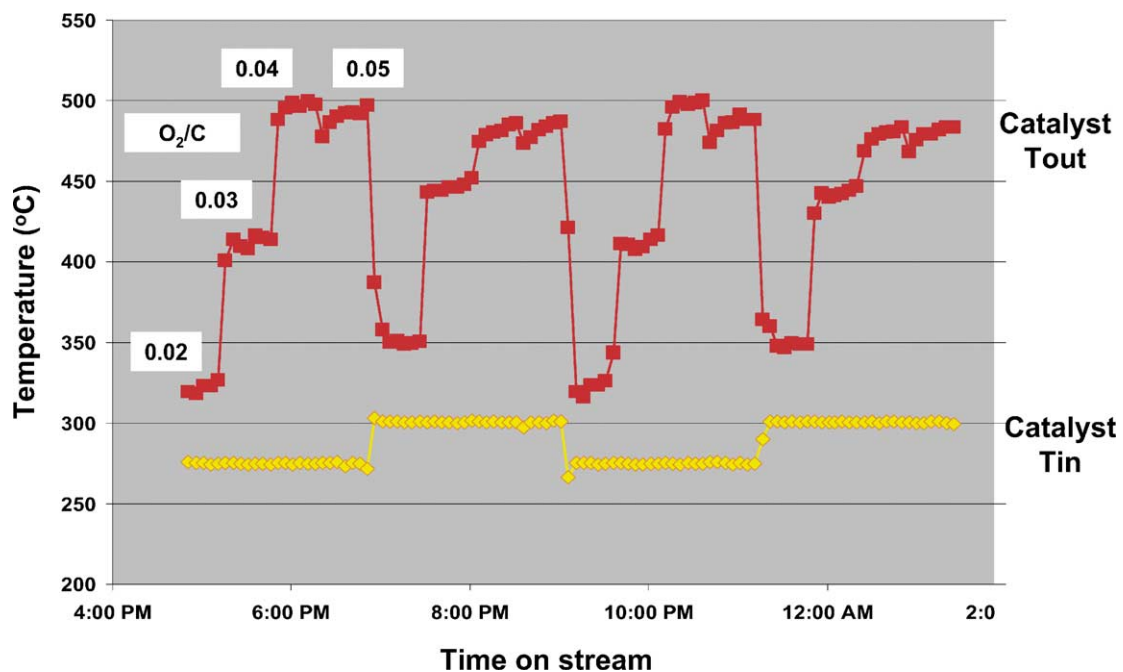

Fig. 8. Catalyst outlet temperature as a function of O_2/C ratio and catalyst inlet temperature. The clear differentiation of outlet T at the recommended O_2/C ratio is a control parameter for the O_2/C ratio. Simulated LPG mixture containing propane with 5% propylene, 1.7% hexane, and 120 ppmw (100 ppmv) total sulfur (equal concentrations of COS, ethylmercaptan, dimethylsulfide, methylethylsulfide, tetrahydrothiophene. 11000/h space velocity.

identical. This might be due to an increase in steam reforming activity (an endothermic reaction) with increasing O_2/C ratio.

Changes in inlet sulfur concentration have little effect on the catalyst outlet temperature once the catalyst reaches its light-off temperature. However, the sulfur concentration does impact the light-off and consequently, the outlet temperature at inlet temperatures below $250\,°C$ (Fig. 9). Light-off is not observed at $200\,°C$ inlet, and occurs only at lower inlet sulfur concentrations below $250\,°C$. Low sulfur breakthrough is observed only when the outlet temperature is above $350\,°C$, indicating complete light-off.

4. Discussion

The selectivity of the SCO catalyst is apparent from its ability to utilize available oxygen to oxidize low concentrations of sulfur compounds to SO_x in the presence of high concentrations of hydrocarbon. Equilibrium calcula-
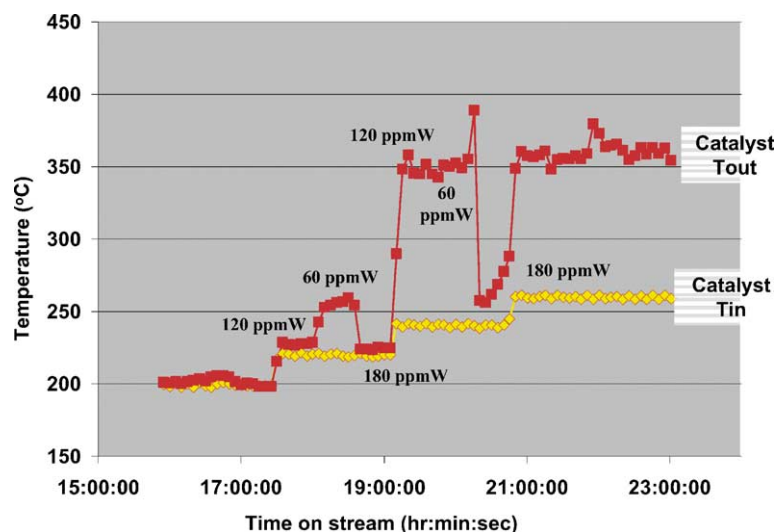
Fig. 9. Impact of fuel sulfur concentration on the light-off of the SCO catalyst. Catalyst light-off, as indicated by the increase in outlet temperature, occurs above 250 °C at higher inlet sulfur concentrations. Simulated LPG mixture containing propane with 5% propylene, 1.7% hexane, and 60 ppmw (50 ppmv), 120 ppmw (100 ppmv), 180 ppmw, (150 ppmv) total sulfur (equal concentrations of COS, ethylmercaptan, dimethylsulfide, methylethylsulfide, tetrahydrothiophene).$O_2/C = 0.03$. 5625/h space velocity.

tions predict the formation of H_2S and thiophene from the sulfur species, and consumption of the oxygen to oxidize the hydrocarbon to CO_2, CO, and H_2. Experimentally, we observe that the catalyst selectively oxidizes the sulfur to SO_x, and that no CO or H_2 are formed from partial oxidation of the hydrocarbon. The sulfur compound thiophene is formed from dehydrogenation of tetrahydrothiophene, but at much lower concentrations than that predicted from the equilibrium calculations.

The selectivity to SO_x species decreases with increasing temperature as evidenced by the increase of organic sulfur species breakthrough as the inlet temperature rises (Fig. 3). For the LPG system, there is also a "sweet spot" with respect to oxygen-to-carbon ratio (Fig. 2). The sulfur breakthrough is a minimum at the optimal O_2/C ratio of 0.03. One can rationalize these results as the increase in the kinetics of the hydrocarbon partial oxidation reactions with increasing temperature. The temperature increase can be due to higher inlet T or from the greater exotherm at higher O_2/C ratio. The increase in sulfur breakthrough at lower O_2/C ratio is clearly from the selectivity decreasing with lower O_2 concentration.

A SCO catalyst start-up and shutdown protocol is required to ensure long catalyst life. We have observed catalyst deactivation under three conditions.

First, and most obvious, is the catalyst deactivation at high temperature. This occurs when the rich fuel–air mixture is purged from the reactor with air, or by adding the fuel–air mixture to air above the catalyst light-off temperature of 150 °C. The resulting exotherm can exceed 700 °C.

Second, the catalyst deactivation is also observed upon exposure of the catalyst to fuel without air being present. We have observed catalyst deactivation due to fuel exposure at the operating temperature of the catalyst (250–275 °C) and at ambient temperature.

And third, deactivation occurs when the catalyst is exposed to the fuel–air mixture at ambient temperature.

The deactivation mode in all cases appears to be precious metal sintering. This deactivation mode is curious for the ambient temperature cases, and is probably due to coke accumulation and burn off when the catalyst temperature is raised. We recommend that the system start up with air at ambient temperature, and that the fuel–air mixture be introduced when the catalyst has reached 100 °C. The system is shut down by cooling the catalyst in the fuel–air mixture until a temperature of 100 °C is reached, at which point air is used to displace the mixture.

Once the SCO catalyst has converted the sulfur compounds in the fuel to SO_x, the SO_x must be removed from the gas stream. This is accomplished with a SO_x trap. We have developed traps for both the SO_2 and SO_3 species formed by the sulfur compound oxidation. Placing a trap for SO_3, upstream of a trap for SO_2, maximizes the SO_x trap total capacity. Without the upstream trap, the SO_3 displaces the SO_2 from the downstream trap since SO_2 is more difficult to adsorb than SO_3. Using this trap combination, we are able to achieve trap capacities of 6.7 g S/100 g trap, within 97% of the stoichiometric trap capacity.

A comparison of the three desulfurization approaches (SCO, passive adsorption, and HDS) is shown in Table 1.

All three desulfurization approaches, (passive adsorption, HDS, and SCO) require the use of an expendable adsorbent. A higher adsorbent sulfur capacity will decrease the size of the sulfur removal module and/or increases the time between adsorbent change-outs. Both HDS and SCO have higher adsorbent capacity for the than the passive adsorbents. The adsorbent for HDS is ZnO, which has a reported capacity of 15–20 g S/100 g adsorbent. However, these extremely high ZnO capacities are under conditions of high

Table 1
Comparison of fuel desulfurization technologies

	Selective catalytic oxidation	Passive adsorption	Hydrodesulfurization (HDS)
NG relative adsorbent volume	2	7	1
LPG relative adsorbent volume	2	14	1
Species compatibility	For all sulfur species and fuel compositions	Separate inorganic, organic S adsorbers; sensitive to fuel composition	For all sulfur species and fuel compositions
Hazards	None	Spent adsorber is hazardous waste	Catalyst is toxic and requires special activation
Operating requirements	Air addition and elevated temperature (250–280 °C)	Ambient temperature and pressure	Hydrogen recycle and elevated T (300–400 °C)

total pressure (1000 kPa or greater), high H_2 partial pressure (100 kPa and higher), and/or high inlet concentrations of H_2S (>300 ppmv) [4]. It is unclear if these high capacities of ZnO will be obtained under fuel reformer type conditions.

Unlike HDS, the SCO system does not require hydrogen recycling. The SCO system does not require special handling because it contains no hazardous or priority pollutant components as does the HDS system (e.g. Ni, Co, Mo).

5. Conclusion

The desulfurization of hydrocarbon fuels is essential for the successful implementation of fuel cell technology where the H_2 is produced by catalytic reforming. Up until now, the fuel desulfurization operation required the use of relatively low capacity adsorbents or hydrogen recycle for hydrodesulfurization. The selective catalytic oxidation approach is an alternative to HDS and passive adsorption for the removal of sulfur from natural gas and LPG fuels for fuel reformer applications. This new desulfurization method is effective and environmental friendly.

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