

Autothermal Reforming Catalysts For Use In Fuel Processors For Automotive And Stationary H₂ Production

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Introduction

Reforming (i.e., partial oxidation, steam reforming, or autothermal reforming (ATR)) of infrastructure fuels, such as natural gas, liquefied petroleum gas, gasoline, or diesel, is one approach being investigated for distributed H₂ production for use with fuel cell systems being developed for automotive and stationary applications. One area of interest is reforming gasoline either on-board the vehicle or at the service station ("fore court" concept) to produce H₂ for automotive applications. One of the major challenges with reforming gasoline is the presence of sulfur, a known catalyst poison. Although the concentration of sulfur in gasoline in the U.S. is decreasing, to an average of 30 ppm beginning in 2006, the concentration is still high enough to negatively impact catalyst performance. Most new catalysts being developed for reforming gasoline are based on precious metals. Although precious metals are regarded as being more sulfur tolerant than commercial Ni steam reforming catalysts, they are susceptible to sulfur poisoning at this concentration. Since sulfur adsorption on to the active metal surface is the primary cause of catalyst poisoning, one must have an understanding of how the reaction parameters (e.g. temperature, steam-to-carbon ratio, fuel-to-air, etc.) influences the sulfur poisoning of the catalysts. The objective of this work is to investigate how the reaction temperature and the steam-to-carbon ratio affect the sulfur poisoning of Rh-based ATR catalyst.

Experimental

Catalyst samples containing 2 wt% Rh on lanthanum-stabilized alumina (Rh/La-Al₂O₃) were prepared using the incipient wetness technique. Samples of the catalyst (0.6 g, sieved to -20/+40 mesh) were tested in a microreactor system for ATR reforming of a sulfur-free (< 450 ppb S) gasoline or a sulfur-containing gasoline (34 ppm S), both obtained from Chevron-Phillips. The microreactor system consisted of a 0.5-in OD SS tube heated by a temperature-programmed furnace, which was maintained at a temperature of 700°C or 800°C. The gasoline feed rate was 0.15 mL/min and the air feed rate was 415 mL/min (STP), equivalent to an oxygen-to-carbon (O₂:C) ratio of 0.45. Three different water feed rates were investigated, 0.28, 0.36, and 0.43 mL/min, equivalent to steam-to-carbon (H₂O:C) ratios of 2, 2.5, and 3, respectively. Based on the feed rates, the gas hourly space-velocities (GHSV) ranged from 50,000-62,000 h⁻¹. The temperature profile in the catalyst bed was measured using an Omega K-type multiprobe thermocouple with the probes separated by 0.25 in. Samples of the product gas were analyzed for H₂, CO, CO₂, and C₁-C₈ hydrocarbons using a gas chromatograph (Hewlett Packard Model 6890 customized by Wasson) equipped with a mass spectrometer. Samples of the catalyst tested before and after ATR were characterized using CO chemisorption to estimate the Rh dispersion and extended X-ray absorption fine structure (EXAFS) analysis to determine the Rh coordination number. The X-ray experiments were conducted at the Advanced Photon Source at Argonne.

Results

Reactor studies

The Rh/La-Al₂O₃ catalyst samples were tested for ATR of sulfur-free and sulfur-containing gasolines at 700°C and 800°C. For ATR of sulfur-free gasoline, stable yields of H₂

were observed over a period of 75 h at 700°C and 66 h at 800°C as shown in Figure 1. The carbon selectivity to CO_x (CO + CO₂) exceeded 97% at 700°C and 99% at 800°C. Methane was the major hydrocarbon product at both temperatures. At 700°C, the yield of non-C₁ hydrocarbons (ethene, propene, butane, pentene, hexane, isooctane, benzene, and toluene) slowly increased from ~250 ppm to ~440 ppm over 75 h (Figure 1). At 800°C, the yield of non-C₁ hydrocarbons slowly decreased from ~70 ppm to ~10 ppm over 66 h (Figure 1).

For ATR of sulfur-containing gasoline, the catalyst deactivated rapidly at 700°C with the H₂ yield decreasing by more than 80% over 75 h, as shown in Figure 2. At 800°C, the H₂ yield decreased by less than 20% over the same time period, with most of the loss in activity occurring during the first 5 h (Figure 2). After 75 h on stream, the carbon selectivity to CO_x was 62% at 700°C and 95% at 800°C. Methane was the major hydrocarbon product at both temperatures. Significantly more non-C₁ hydrocarbons were produced at 700°C than 800°C. At 700°C, the hydrocarbons with the highest concentrations were propene, butene, benzene, toluene and ethene (Figure 3). Other hydrocarbons included hexene, isooctane, propane, pentane, hexane, and pentene. At 800°C, the hydrocarbons with the highest concentrations were benzene, toluene, ethane, and ethene (Figure 4) with lesser amounts of propene and pentene. The concentration of benzene and toluene increased with time whereas the concentration of alkanes and alkenes stabilized after a few hours.

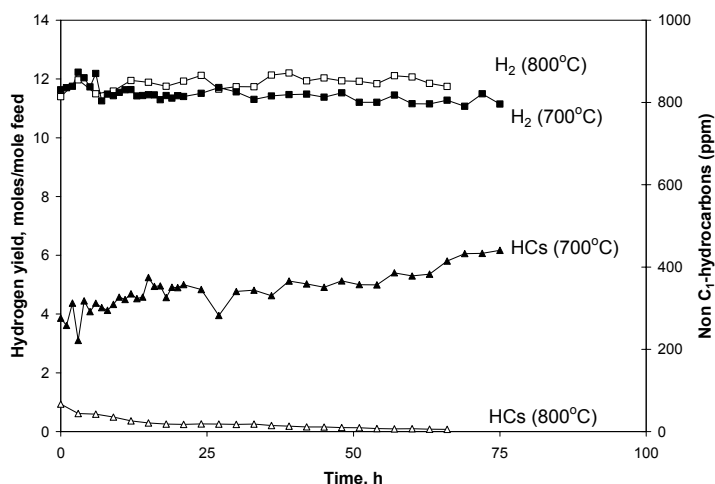


Figure 1. Comparison of the H₂ and non-C₁ hydrocarbon yields (HCs) for ATR of sulfur-free gasoline at furnace temperatures of 700°C and 800°C (O₂:C=0.45 and H₂O:C=2).

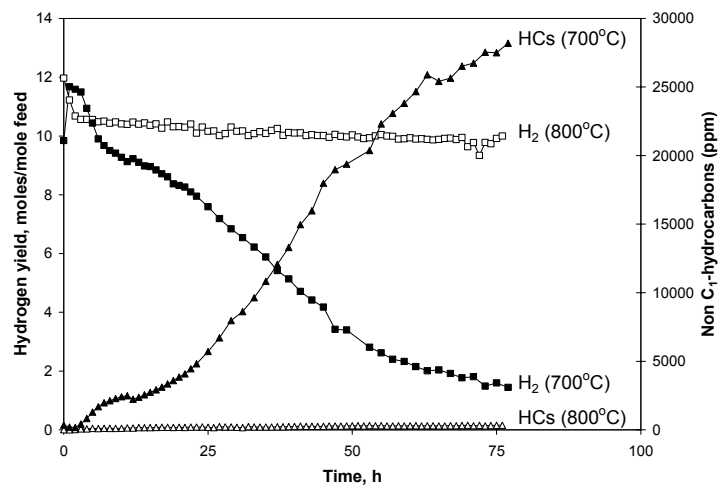


Figure 2. Comparison of the H₂ and non-C₁ hydrocarbon yields (HCs) for ATR of 34 ppm S gasoline at furnace temperatures of 700°C and 800°C (O₂:C=0.45 and H₂O:C=2).

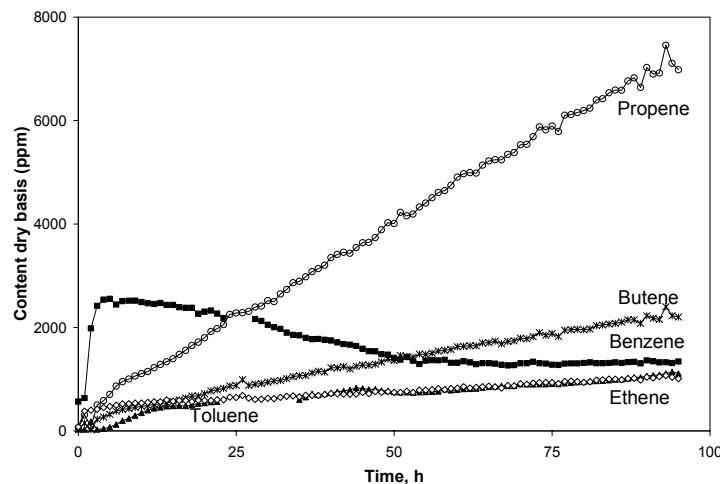


Figure 3. Yield of selected non-C₁ hydrocarbons for ATR of 34 ppm S gasoline at a furnace temperature of 700°C (O₂:C=0.45 and H₂O:C=2).

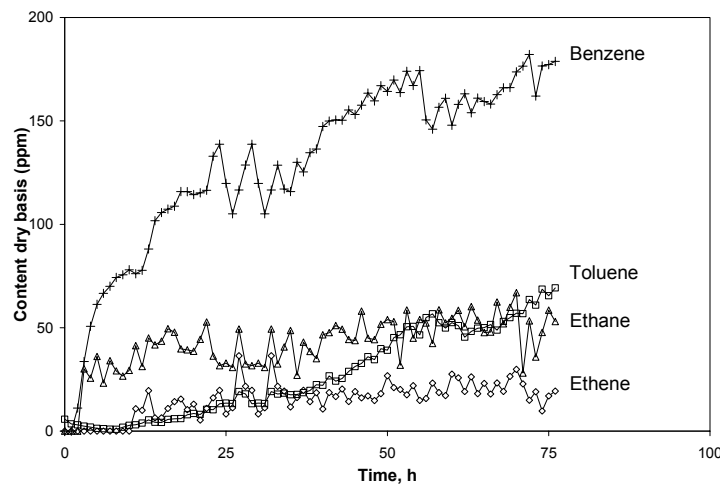


Figure 4. Yield of selected non-C₁ hydrocarbons for ATR of 34 ppm S gasoline at a furnace temperature of 800°C (O₂:C=0.45 and H₂O:C=2).

For ATR, the exothermic oxidation reactions proceed at a much faster rate than the endothermic steam reforming reactions. As a consequence, the temperature at the inlet of the catalyst bed is higher than the temperature at the exit of the bed [Ito et al., 1999]. For ATR of 34 ppm S gasoline at 700°C, both the inlet and exit temperatures initially decreased (Figure 5). After 5 h, however, the inlet temperature stabilized and remained constant for over 70 h, whereas, the exit temperature slowly increased from 665 to 710°C and the concentration of the non-C₁ hydrocarbons increased with time (Figure 2). Both of these observations suggest the loss of steam reforming activity. For ATR of sulfur-containing gasoline at 800°C, both the inlet and exit temperatures were relatively constant over 75 h, suggesting that the effect of sulfur on the catalyst was small (Figure 5). No changes were observed in the inlet and exit temperatures for ATR of sulfur-free gasoline at 700°C or 800°C (not shown).

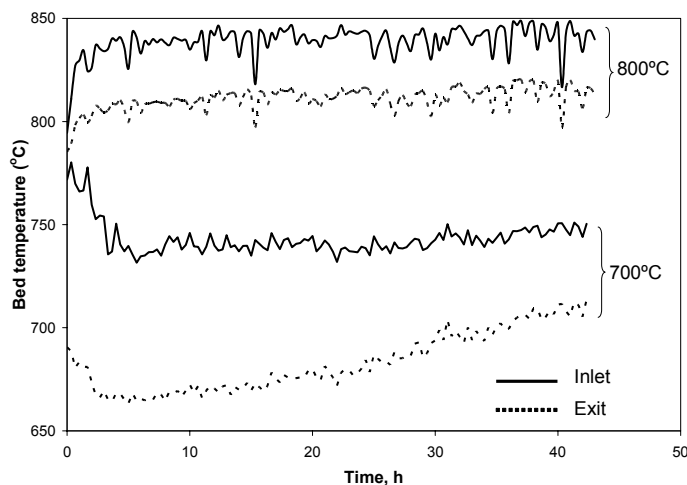


Figure 5. Inlet and exit catalyst bed temperatures during ATR of 34 ppm S gasoline at furnace temperatures of 700°C and 800°C.

Assuming that the adsorption of sulfur by Rh is reversible, the fraction of the Rh surface covered by sulfur (and hence blocking active sites on the catalyst) will depend on a number of factors including the temperature and the concentration of sulfur-containing species in the gas-phase. A study was conducted to see if the loss in activity attributed to sulfur poisoning could be restored by switching the feed from sulfur-free gasoline to sulfur-containing gasoline and then back to sulfur-free gasoline. At 700°C, only 50% of the H₂ yield observed during the first sulfur-free cycle was recovered when the feed was switched from sulfur-containing to sulfur-free gasoline (Figure 6). At 800°C, nearly 100% of the H₂ yield observed during the first sulfur-free cycle was recovered within 1 h when the feed was switched from 34 ppm S to sulfur-free gasoline (Figure 6). Because significantly more carbon (coke) was present on the catalyst after ATR at 700°C compared to catalyst tested at 800°C (Table 1), it is possible that 700°C was not high enough temperature to gasify the carbon after switching back to the sulfur-free gasoline.

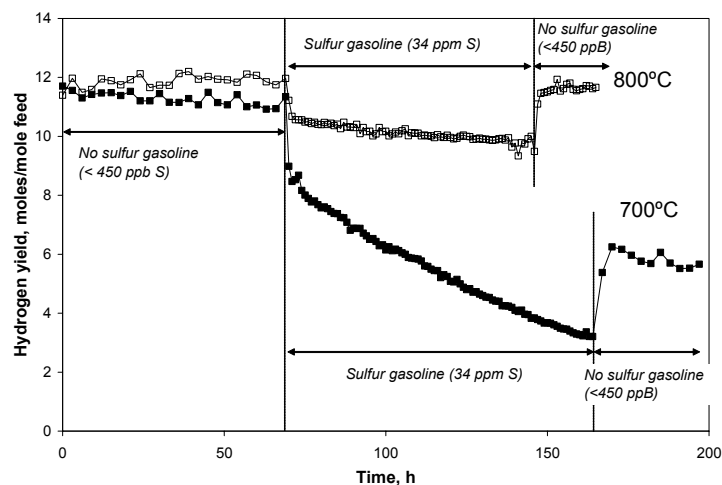


Figure 6. Comparison of the effect of cycling between 34 ppm S and sulfur-free gasolines on the H₂ yields at furnace temperatures of 700°C and 800°C (O₂:C=0.45 and H₂O:C=2).

The effect of the H₂O:C ratio on the extent of sulfur poisoning at 700°C was investigated. The loss of catalytic activity, in terms of the yield of H₂, decreased as the H₂O:C ratio was increased from 2.0 to 3.0 (Figure 7). At a H₂O:C ratio of 3.0, the H₂ yield decreased rapidly from 12 to 10.5 moles of H₂ per mole of gasoline when the feed was switched from sulfur-free to 34 ppm S gasoline but then remained essentially constant for over 75 h. At H₂O:C ratios of 2.0 and 2.5, a continuous decrease in H₂ yield was observed after the fuel was switched from sulfur-free to sulfur-containing gasoline. Higher concentrations of olefins, such as ethene, propene and butene, and aromatic compounds, such as benzene and toluene, were observed at H₂O:C ratios of 2.0 and 2.5 than at 3.0. The hydrocarbon yields increased with time at H₂O:C ratios of 2.0 and 2.5 but remained relatively stable at a H₂O:C ratio of 3.0 after switching to the sulfur-containing gasoline.

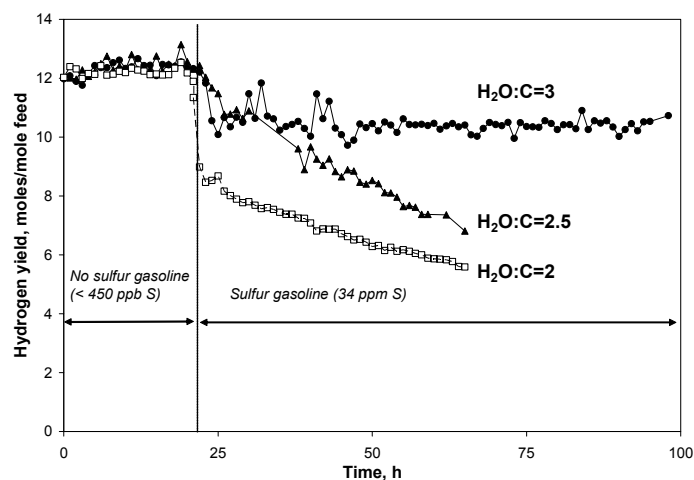


Figure 7. Effect of H₂O:C ratio on H₂ yield for ATR of 34 ppm S gasoline at a furnace temperature of 700°C (O₂:C=0.45).

Catalyst Characterization Studies

CO chemisorption was used to estimate the Rh dispersion on various catalyst samples before and after ATR (Table 1). For the post-ATR samples, the Rh dispersion was measured before and after treating the samples with a mixture of 4% O₂/He at 300°C for 30

min. The purpose of the O₂ treatment was to gasify any carbon that may have formed on the catalyst surface during the ATR tests and would inhibit CO uptake by Rh. Various samples were also analyzed using EXAFS to determine the Rh coordination number (CN), which is also an indication of the dispersion of Rh (Table 1).

Prior to ATR, the Rh was well-dispersed, with a dispersion of 55% based on CO chemisorption and a CN of 6.5 obtained from EXAFS. After ATR of sulfur-free gasoline, the Rh dispersions were 24% and 14% (both after O₂ treatment) and the CNs were 9.2 and 8.5 on the samples tested at 700°C and 800°C, respectively. The O₂ treatment had little effect on the Rh dispersion for these two samples, consistent with the elemental analysis which showed these samples to be relatively free of carbon and sulfur (Table 1). After ATR of 34 ppm S gasoline, the Rh dispersions were 14% and 13% (both after O₂ treatment) and the CNs were 10.0 and 8.2 on the samples tested at 700°C and 800°C, respectively. The O₂ treatment resulted in the Rh dispersion increasing from 4 to 14% on the sample tested at 700°C and from 6 to 13% on the sample tested at 800°C. The apparent increase in the Rh dispersion could be attributed to the removal of sulfur during the treatment process. Sulfur adsorbed on Rh can block the uptake of CO, leading to an underestimation of the Rh dispersion. For a Rh dispersion of 10%, the amount of sulfur required for full coverage (assuming a stoichiometry of 1:1) is estimated to be 0.06 wt%, consistent with the amount of sulfur on the two samples tested with sulfur-containing gasoline (Table 1). The CN decreased from 10.0 to 7.4 when the sample tested at 700°C was heated in air at 700°C for 2 h suggesting that the Rh became redispersed. There was essentially no difference in the CN when the sample tested at 800°C was heated in air at 700°C for 2 h. Although there is a discrepancy in the extent of Rh sintering between the two experimental techniques, the experimental error for the EXAFS analysis is rather large.

Table 1. Rh dispersion (%) as measured by CO chemisorption, Rh coordination number (CN) based on EXAFS analysis, and the wt% of C and S as determined by elemental analysis. (All ATR samples tested at a H₂O:C=2 unless otherwise noted.)

	Rh dispersion (%)	CN	Carbon (wt%)	Sulfur (wt%)
As prepared	55	6.5±0.7	--	--
ATR no S @ 700°C	22(24 ^a)	9.2±0.8	0.16±0.03	0.034±0.010
ATR S @ 700°C	4(14 ^a)	10.0(7.4 ^b) ±1.0	44.60±2.23	0.070±0.020
ATR S @ 700°C (H ₂ O:C=3)	--	--	2.99±0.05	0.087±0.020
ATR no S @ 800°C	12(14 ^a)	8.5±0.8	0.59±0.02	0.051±0.010
ATR S @ 800°C	6(13 ^a)	8.2(8.5 ^b) ±0.8	0.34±0.02	0.030±0.010

^a Treated in 4% O₂/He at 300°C (30°C/min) prior to CO chemisorption measurement.

^b Treated in air at 700°C for 2 h after ATR with sulfur-containing gasoline.

Discussion

Based on thermodynamic analyses, the sulfur present as organo-sulfur compounds in the sulfur-containing gasoline is converted to H₂S during ATR. This H₂S is regarded as the primary sulfur poison for many catalysts, including Ni steam reforming catalysts [Rostrup-Nielsen, 1982]. Studies have suggested that H₂S adsorbs strongly and dissociatively on metal surfaces and that the adsorbed sulfur prevents or modifies further adsorption of reactant molecules [Bartholomew, 2001]. The extent of sulfur coverage of the metal depends on a

number of factors, including the temperature and concentration of H₂S in the gas-phase above the catalyst surface.

Our results are consistent with sulfur adsorption being the primary mechanism for sulfur poisoning of Rh/LaAl₂O₃. We observed a significant improvement in the performance when the reactor temperature was increased from 700 to 800°C, based on a comparison of the H₂ and non-C₁ hydrocarbon yields for ATR of 34 ppm S gasoline at 700 and 800°C. In addition, nearly 100% of the activity was recovered when switching from sulfur-containing gasoline to sulfur-free gasoline at 800°C. Increasing the reaction temperature has been shown to have a beneficial effect on the performance of Ni-based catalysts when steam reforming sulfur-containing fuels [Morita and Inoue, 1965; Koningen and Sjöström, 1998; Zheng et al. 2003].

Our studies suggest that sulfur poisoning has a greater impact on the steam reforming reactions than it does on the oxidation reactions. An increase in the exit temperature was observed with time when reforming 34 ppm S gasoline at 700°C, indicating that the endothermic steam reforming reactions were being inhibited; however, no increase in the inlet temperature was observed, suggesting that the exothermic oxidation reactions were less affected by sulfur. The yields of olefinic compounds, such as ethene, propene, and butene, and aromatic compounds, such as benzene and toluene, increased when the feed was switched from sulfur-free to sulfur-containing gasoline. Since O₂ was not present in the product stream when reforming either gasoline, it is suggested that the oxidation reactions were completed whether or not sulfur was present in the gasoline. Therefore, the increase in the hydrocarbon yields is attributed to a decrease in the steam reforming activity of the catalyst.

Our studies also show the beneficial effect of increasing the H₂O:C ratio on the performance of Rh/La-Al₂O₃ when reforming sulfur-containing gasoline, although the reasons are not fully understood. The regenerative effect of steam on sulfur-poisoned Ni catalysts has been reported in the literature [Morita and Inoue, 1965; Koningen and Sjöström, 1998]. During steam regeneration, it has been suggested that H₂O promotes the regeneration of sulfur-poisoned Ni catalysts by completely oxidizing the Ni [Rostrup-Nielsen, 1982]. Because our study was conducted under ATR conditions, we would not expect the Rh to be completely oxidized because of the high H₂ content in the gas phase.

Conclusions

The presence of ~30 ppm sulfur in gasoline poisoned the Rh/La-Al₂O₃ catalyst, with the effect of sulfur being more pronounced at 700°C than at 800°C. At 800°C, sulfur poisoning appeared to be reversible, with nearly 100% recovery of the catalyst performance when the feed was switched from sulfur-containing to sulfur-free gasoline. At 700°C, only 50% of the catalyst performance could be recovered when the feed was switched from the sulfur-containing to sulfur-free gasoline, which is attributed to excessive coking that occurred while reforming the 34 ppm S gasoline. Increasing the H₂O:C ratio from 2 to 3 led to a significant improvement in the performance of the catalyst at 700°C.

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