

# Catalytic autothermal reforming of diesel fuel for hydrogen generation in fuel cells

## I. Activity tests and sulfur poisoning

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### Abstract

Polymer electrolyte membrane (PEM) fuel cells require hydrogen as the fuel source for generating power. Hydrogen can be produced in a fuel processor by the catalytic reforming of hydrocarbons. The objective of this paper is to present an analysis of the autothermal reforming (ATR) of synthetic diesel fuel in an adiabatic reactor using a Pt/ceria catalyst. ATR combines endothermic steam reforming and exothermic partial oxidation reactions in a single unit. This simple system provides higher efficiency and higher energy density than other conventional processes. The product composition as a function of the operating variables and the temperature and concentration profile inside the reactor were studied. Hydrogen was generated under adiabatic conditions by heating the feed mixture and ATR reactor to only 400 °C in contrast to higher temperatures reported in the literature. The stability of the catalyst and its response to the presence of S poison was also investigated. © 2005 Elsevier B.V. All rights reserved.

*Keywords:* Hydrogen; Autothermal reforming; Fuel processing; Sulfur poisoning; Diesel reforming; Fuel cells

### 1. Introduction

Polymer electrolyte membrane (PEM) fuel cells show considerable promise for vehicular and auxiliary power applications. The fuel cell is an efficient and environmentally friendly power generation system compared to conventional combustion engines [1]. Hydrogen, the fuel for fuel cells, can be stored in suitable storage devices or produced on-board by the catalytic reforming process. Hence, there is great interest in converting current hydrocarbon (HC)-based transportation fuels such as gasoline and diesel into hydrogen. Freightliner Inc. has successfully demonstrated on-board steam reforming of methanol for auxiliary power applications in trucks in 2003 [2]. Ballard makes fuel cells which have been used ex-

perimentally by several car makers, and were most convincingly demonstrated recently by Daimler's NECAR II, based on a Mercedes V-class MPV. Now Daimler has NEBUS, a fuel-celled powered bus, in regular service around Stuttgart, Germany [3].

Although the term "reformer" is often used for the whole system, the production of hydrogen actually occurs in three processes: (1) hydrogen is produced by autothermal reforming (ATR) [4–6] of a hydrocarbon ( $\text{fuel} + \text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{CO}_x + \text{H}_2$ ) where without water it is partial oxidation (POX) and without oxygen it is steam reforming (SR); (2) the water-gas shift reaction (WGS) ( $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ ) eliminates most of the CO, producing more hydrogen; (3) and any remaining CO is reduced to parts per million levels by selective, catalytic oxidation, usually referred to as preferential oxidation (PROX).

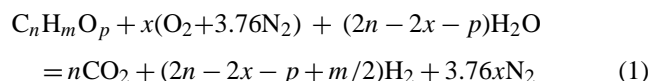
Steam reforming has the highest efficiency for hydrogen production. However, SR is an endothermic reaction and so an external source of heat is needed. Exothermic partial oxidation needs external cooling. The ideal fuel processor should

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combine the advantages of both to avoid complicated heat exchange.

Hydrogen production using autothermal reforming, which is a combination of SR and POX reactions, has recently attracted considerable attention due to its higher energy efficiency than other processes and also as a low investment process using a simple system design [6–11]. The ATR is a stand-alone process in which the entire hydrocarbon conversion is carried out in one reactor. The ATR process is generally defined by an idealized equation written as [7]:



where  $x$  is the oxygen-to-fuel molar ratio and at a value of zero, the equation reduces to the endothermic steam reforming; at  $x = n - p/2$ , Eq. (1) is the combustion reaction. Catalytic partial oxidation in the ATR process provides the heat required to drive the steam reforming reaction. ATR is potentially far more efficient than SR or POX processes alone and is capable of reforming higher hydrocarbons, which provide higher energy density. At autothermal operation there is no net energy input or energy output [8]. The ATR's equilibrium temperature and the reformed gas composition are dependent on the feed ratio (HC/H<sub>2</sub>O/air) [9,10]. Higher H<sub>2</sub>O/HC ratios reduce the CO yield with a lower equilibrium temperature [11].

Various fuels have been investigated for H<sub>2</sub> generation by reforming technologies for fuel cell systems. Suitable fuels involved gaseous HCs such as methane and propane [12] and liquid HCs such as alcohols [13], gasoline [14], and #2 diesel [15].

For heavy fuels such as JP-8 or kerosene, autothermal reforming conditions were achieved by using a reformer including a POX zone and a separate SR zone. The operating conditions were maintained such that oxygen (air) was preheated to 450 °C, and the temperature of POX chamber and SR chamber maintained at 1375 and 925 °C respectively [16]. In autothermal reforming of the diesel fuel, thermodynamic equilibrium can be achieved at the following operating conditions: a H<sub>2</sub>O/C ratio of 1.25, an O<sub>2</sub>/C ratio of 1 at an operating temperature of 700 °C [15]. While these fuels are rich in hydrogen, they also contain sulfur compounds as well as coke precursors. Unfortunately, the typical metal reforming catalysts are prone to deactivation by coking, as well as sulfur poisoning [17–19]. Whereas coking can be controlled with excess steam (and/or oxygen injection), the high sulfur levels in these fuels will require sulfur removal upstream of the reformer [20], if conventional reforming catalysts are employed.

ATR approach has been successfully applied to methane reforming at somewhat lower temperatures (800 °C) [21,22] but serious coking problems were observed when applied to the autothermal reforming of propane [23]. A group at Argonne National Laboratory has been utilizing autothermal reforming for higher hydrocarbon fuels for a number of years,

utilizing a noble metal catalyst [24,25]. Springman et al. [26] compared steam reforming with the autothermal reforming of *iso*-octane, hexane, toluene and gasoline over a proprietary rhodium catalyst at 800 °C, 5 bar, and steam/carbon ratios as high as 4. They reported that steam reforming resulted in heavy coke formations, particularly when the steam/carbon ratio dropped below about 1.8. However, under autothermal conditions (H<sub>2</sub>O/C = 1.5–2.4,  $T = 600$ – $800$  °C,  $P = 2$ – $5$  bar), coke formation was not observed. Palm et al. [27] also used noble metal catalysts to study the autothermal reforming of simulated diesel fuels at 545 °C and reported steady conversions of 96% for 20 h on stream. However, when 10–30 ppm of benzothiophene was added to the fuel, the conversion dropped dramatically. Sulfur is a severe poison for catalysts in fuel processors for fuel cells [28]. It is well known that very low levels of sulfur can deactivate various catalyst systems severely, by rearrangement of the surface structure upon adsorption of sulfur species [29,30]. Several studies have been devoted to the poisoning effect of sulfur in other catalytic applications, e.g. the effect of sulfur on Ni-based steam reforming catalysts has been reviewed by Rostrup-Nielsen [31] and the effect on three-way catalysts have been described by Gandhi and Shelef [32]. Sulfur exists in different chemical states depending on the reaction conditions. For the oxidative conditions applicable to catalytic combustion, sulfur species usually reacts to form sulfur dioxide or trioxide and sulfate species.

Catalyst formulations for ATR fuel processors depend on the fuel choice and operating temperature. For methanol, Cu-based formulations can be used [33]. For higher hydrocarbons the catalyst typically comprises of metals such as Pt, Rh, Ru and Ni deposited or incorporated into carefully engineered oxide supports such as ceria-containing oxides [34–39].

Considerable work was done on heavy hydrocarbons, however, there have not been any studies related to synthetic diesel fuel and JP8 and the performance of adiabatic reactors for autothermal reforming. In this paper, we discuss the results of a systematic study: (1) the effect of operating parameters on the product distribution and conversion efficiency of hydrocarbon mixtures in autothermal reforming (ATR); (2) the performance and stability of a 1% Pt/ceria catalyst; (3) the effect of sulfur poison on the catalytic activity. Synthetic diesel was chosen because of its high energy density and negligible sulfur content compared to other hydrocarbons and JP8.

## 2. Experimental

### 2.1. Reactor system

All the experiments were performed in a 3/8 in. adiabatic fixed-bed tubular (quartz) reactor. Liquid feed consisting of water and diesel was vaporized and mixed along with air in a preheater containing a silicon carbide bed to enhance mixing. Calibrated HPLC pumps and unit mass flow controllers were

used to control the flow rates. The gaseous mixture from the preheater was maintained at a temperature of 400 °C. The reactor with the catalyst bed was well insulated to achieve adiabatic reaction conditions. Thermocouples were placed to read the temperature profile inside the reactor tube. The hot product gas leaving the reactor was cooled down in a heat exchanger/condenser system to separate water and liquid hydrocarbons from the product gas. The dry product gas from the condenser was analyzed using a SRI gas chromatograph to monitor H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub> concentrations. Pressures above 2 psig were not encountered. In each test, 2 g of fresh non-diluted catalyst (pellets with an average size of 2 mm) was supported on a layer of quartz wool. The catalyst was prepared by impregnation and nitrate salts were used as precursors for Pt and Ceria to make up a final composition of 1% Pt on Ceria support. The fresh catalyst had a BET surface area of 68 m<sup>2</sup> g<sup>-1</sup>.

The experiments reported in this document were performed under the following conditions: steam/C ratio = 1–3, O<sub>2</sub>/C ratio = 0.5–2, preheater/reactor temperature = 400 °C, gas hourly space velocity (GHSV) = 17 000 h<sup>-1</sup>. Oxygen was never observed in the effluent during any of the experiments at any of the temperatures tested. Condensate from the reactor was considered to be unconverted/reformulated hydrocarbon.

The synthetic diesel fuel and JP8 fuel were supplied by South West Research Institute (SWRI) and were not treated further. In case of a complex multi-component (>100) fuel like diesel, it is difficult to obtain a complete chemical breakdown. Conversely, from the elemental analysis (C: 83.92 wt.%, H: 14.66 wt.%, O: 1.42 wt.%) of the synthetic diesel, the average chemical composition of the experimental fuel was calculated. The carbon material balance from preliminary experiments showed about 14% loss, which can be attributed to unconverted hydrocarbon condensate, coke deposition on the catalytic surface and/or analytical error. An efficient method to evaluate the fuel processor's performance is to calculate the hydrogen yield, by calculating the ratio of hydrogen in the product to the hydrogen in the reactants (diesel + water).

Initial experiments under isothermal conditions at an operating temperature of 800 °C showed a large temperature gradient (~150 °C) across the catalytic bed and also along the length of the reactor and it is hard to understand reaction data when the temperature profile is as dramatic as in an ATR. However, even with a furnace around the reactor, the actual temperatures inside the reactor still changed a lot as the reaction went from exothermic to endothermic. Therefore, we elected to preheat the reactants to 400 °C and conduct the reaction in an insulated tube, achieving reasonable "adiabatic" conditions.

### 3. Results and discussion

The dependencies of product distribution on the reaction parameters: O<sub>2</sub>/C ratio, H<sub>2</sub>O/C ratio and space velocity were

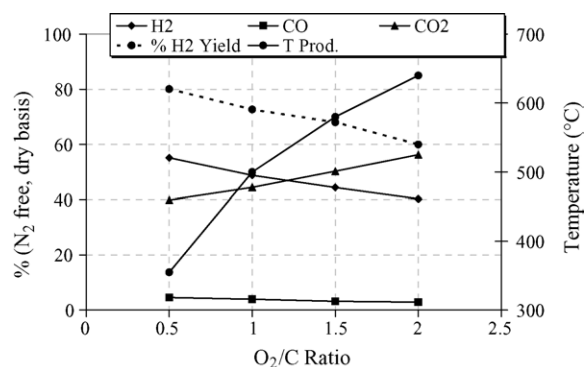


Fig. 1. Product distribution, hydrogen yield and products' temperature as a function of O<sub>2</sub>/C ratio during diesel ATR at H<sub>2</sub>O/C ratio of 2.5, reactor temperature of 400 °C and GHSV = 17 000 h<sup>-1</sup>.

investigated during the ATR reaction of synthetic diesel. Temperature and hydrogen concentration profiles inside the reactor were also studied. Long-term performance of the catalyst was investigated using two different fuels.

#### 3.1. Effect of operating conditions on hydrogen yield

The product distribution as a function of O<sub>2</sub>/C ratio for reforming the synthetic diesel at H<sub>2</sub>O/C = 2.5 is shown in Fig. 1. Also displayed are the hydrogen yield and the reaction temperature. Hydrogen concentration gradually decreased by increasing the O<sub>2</sub>/C ratio associated with a rise in the CO<sub>2</sub> concentration. Fifty-six percent hydrogen (dry and nitrogen free basis) was observed at an O<sub>2</sub>/C of 0.5 and it dropped to 40% at the O<sub>2</sub>/C of 2. The CO<sub>2</sub> concentration increased from 40 to 55% with an increase in the O<sub>2</sub>/C ratio from 0.5 to 2. The methane concentration (not shown) almost remained unaffected with O<sub>2</sub>/C variation whereas CO concentration decreased with increasing O<sub>2</sub>/C ratio. The overall trend shows that an O<sub>2</sub>/C ratio of 0.5 is effective for the reaction at the H<sub>2</sub>O/C of 2.5. The exit temperature increased from 360 to 640 °C and the hydrogen yield dropped from 80 to 60% with an increase in the oxygen feed.

Fig. 1 also illustrates the change in the reaction temperature measured at the outlet of the catalytic bed with a variation in the molar ratios of oxygen and diesel. The temperature increased from 360 to 640 °C as the O<sub>2</sub>/C ratio increased from 0.5 to 2 associated with a decrease in the H<sub>2</sub> and CO concentrations. The temperature rise is probably due to an increase in the H<sub>2</sub> and CO oxidation reactions with an increase in the O<sub>2</sub>/C ratio.

Fig. 2 shows the product distribution as a function of H<sub>2</sub>O/C ratio at a fixed O<sub>2</sub>/C ratio of 1. Hydrogen concentration at the reaction conditions of 400 °C and O<sub>2</sub>/C molar ratio of 1 increased from 47 to 52% as the H<sub>2</sub>O/C ratio increased from 1.5 to 3.0. The influence of steam ratio on CO concentration is apparent as its value decreased from 16% at the H<sub>2</sub>O/C of 1.5 to approximately 5% at the molar ratio of 3. In general, to avoid coke deposition, a high molar ratio of H<sub>2</sub>O/C is preferred for generating the gas mixture containing

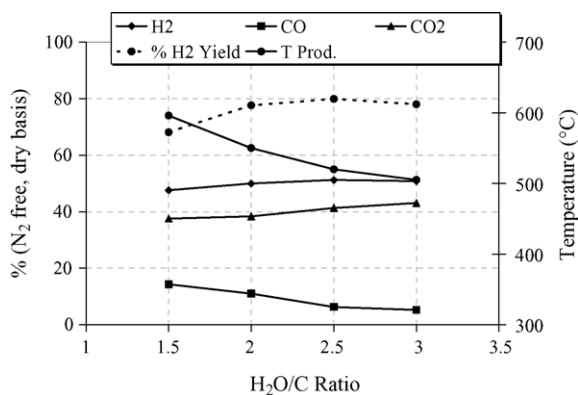


Fig. 2. Product distribution, hydrogen yield and products' temperature vs. H<sub>2</sub>O/C ratio during diesel ATR at an O<sub>2</sub>/C ratio of 1, reactor temperature of 400 °C and GHSV = 17 000 h<sup>-1</sup>.

a high concentration of hydrogen and low concentrations of both CO and CH<sub>4</sub>.

In view of the above observations, higher hydrogen yield during ATR seems possible by operating the reactor at a H<sub>2</sub>O/C ratio of 2.5 and an O<sub>2</sub>/C ratio of 0.5, these conditions however occur at extreme ends of the measured variables. Similar trends were observed for gasoline feed in the ATR reactions [40].

Product distribution for the synthetic diesel ATR over a 1% Pt/ceria catalyst at H<sub>2</sub>O/C = 2.5 and O<sub>2</sub>/C = 0.5 is shown as a function of gas hourly space velocity in Fig. 3. There is a little change in the product distribution as the GHSV increased from 9000 to 17 000 h<sup>-1</sup> and the hydrogen yield increased by 3%. The slight increase in yield is probably a result of increased mass transport across the bed at elevated space velocities. At high space velocities (>18 000 h<sup>-1</sup>), a decrease in the H<sub>2</sub> concentration associated with an increase in the CO concentration was observed. This could be due to increased breakthrough of heavier cracking products or a change in the selectivity of the catalyst towards water-gas shift reaction leading to higher CO and lower H<sub>2</sub> concentrations (Fig. 3). In light of these observations, the remaining experiments were carried out at a GHSV of 17 000 h<sup>-1</sup>.

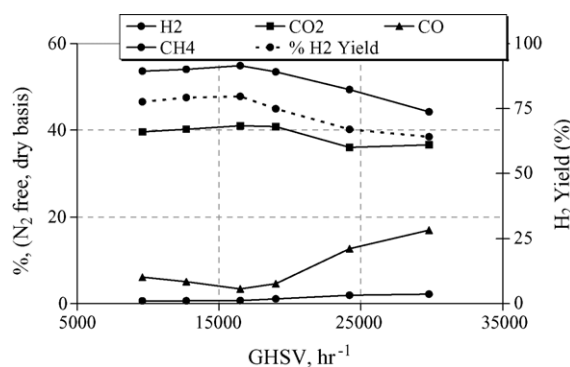


Fig. 3. Product distribution and hydrogen yield as a function of space velocity (GHSV) at H<sub>2</sub>O/O<sub>2</sub>/C ratio of 2.5/0.5/1 and reactor temperature of 400 °C.

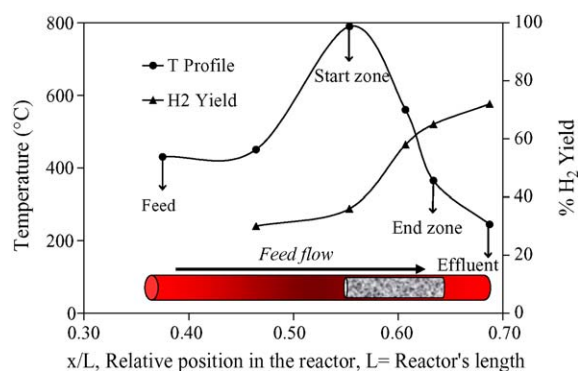


Fig. 4. Temperature profile and hydrogen yield as a function of relative position inside the adiabatic autothermal reforming reactor.

### 3.2. Temperature profile and the autothermal reaction

The temperature profile inside the adiabatic reactor is shown in Fig. 4. The measured temperature increased rapidly as the feed stream at 400 °C approach the surface of the catalytic bed and then gradually decreased from 800 to 365 °C down the catalytic bed (Fig. 4). These observations indicate that the exothermic oxidation reactions occur at the front of the catalytic bed followed by the endothermic steam reforming reactions that result in a temperature drop along the bed. Further decrease in temperature of the products down the reactor (non-insulated portion) since the leading edge of the T profile can precede the actual catalyst bed because of thermal diffusion as illustrated by Son et al. [41]. Furthermore, measured molar hydrogen concentration increased 50% down the catalytic bed, which may be due to the increased steam reforming (endothermic) activity. However, it is possible that the observed profiles of concentration and temperature may not reflect the actual conditions since these experiments were conducted using catalyst particles of significant size which result in lower heat and mass transport. The size for catalyst pellets was chosen based on initial experiments aimed at finding the optimal size to avoid pressure drop across the bed (for the conditions listed in the above section).

To understand the reaction better and the response of the catalyst for the individual reactions, an experiment was conducted to find out the activity of the catalyst and the order of reactions inside the reactor. Fig. 5 shows the product distribution for different reactions. Three types of reactions: autothermal (ATR), steam reforming (SR) and partial oxidation (POX) were carried out for reforming synthetic diesel over the Pt catalyst. The POX reaction yielded lower H<sub>2</sub>, CO and higher CO<sub>2</sub> concentrations compared to ATR, whereas the SR reaction was not active at the conditions tested. These observations support the idea that the POX reaction aids the SR reaction resulting in higher hydrogen concentration due to active steam reforming reaction down the catalytic bed as observed in Fig. 4.

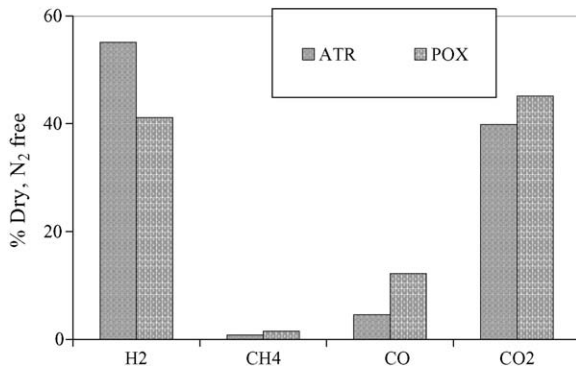


Fig. 5. Comparison of autothermal reforming, partial oxidation and steam reforming of diesel fuel over 1% Pt/ceria catalyst at H<sub>2</sub>O/C of 2.5 (SR) and O<sub>2</sub>/C of 0.5 (POX).

### 3.3. Catalytic stability

It is important for the autothermal reformer to perform well over long time periods with out any loss of activity or efficiency. Hence, the Pt catalyst was tested for its stability with time and the reactor was operated with feed entering at 400 °C. Fig. 6 shows the catalytic stability for the ATR reaction using the synthetic and JP8 diesel fuels. The synthetic diesel is virtually sulfur-free whereas the JP8 has ~1000 ppmw S. The synthetic diesel feed exhibits good stability over the time period investigated showing that coking is not an issue when reformed at these conditions. Hydrogen yield was stable at 79%, and so were the other major products without any sign of deactivation. But, JP8 fuel contains significant sulfur concentration and the catalyst is prone to poisoning which is evident in the figure.

Since the catalytic reforming activity of the synthetic diesel fuel was stable over the time period tested, the loss in activity while reforming the JP8 fuel may partially be attributed to the presence of sulfur in the fuel. As the subject of interest in this research is sulfur related poisoning of the ATR catalysts, further studies were carried out to identify the effect of organic sulfur and its surrogates on the catalytic activity with time.

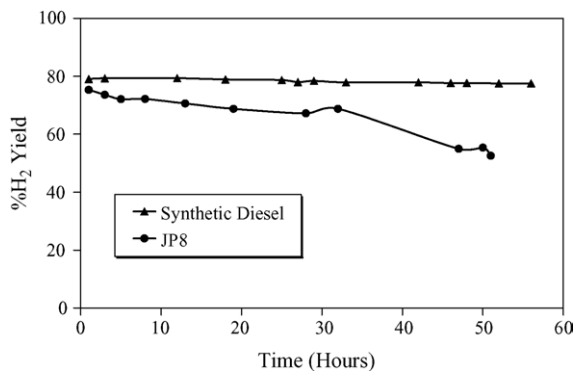


Fig. 6. Long-term activity of the 1% Pt/ceria catalyst for the autothermal reforming of synthetic diesel fuel ~10 ppm S and JP8 ~1000 ppm S at H<sub>2</sub>O/O<sub>2</sub>/C ratio of 2.5/0.5/1 and reactor temperature of 400 °C.

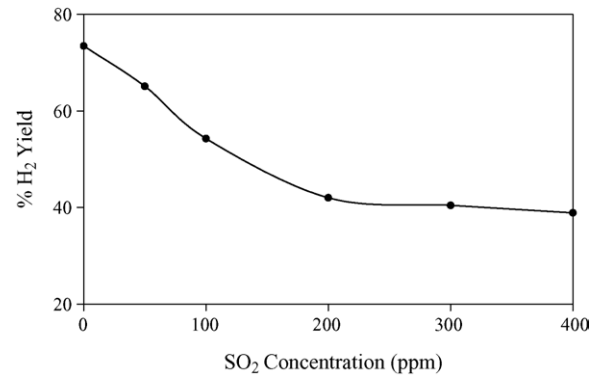


Fig. 7. Effect of SO<sub>2</sub> concentration on hydrogen yield during autothermal reforming of synthetic diesel fuel over the 1% Pt/ceria catalyst at H<sub>2</sub>O/O<sub>2</sub>/C ratio of 2.5/0.5/1, reactor temperature of 400 °C and GHSV = 17 000 h<sup>-1</sup>.

Due to the high number of gas components in the feed gas mixture, it is very difficult to separate the influence of different gas components on the sulfur poisoning of catalysts. In order to better understand the complex phenomena in the catalytic autothermal reactions, the effect of different gas components should be known. Hence, sulfur poisoning was further investigated by injecting different surrogates for sulfur present in the hydrocarbon feed. It is well known that most of the sulfur contained in the hydrocarbon fuels converts to H<sub>2</sub>S at low temperatures (300–400 °C) in non-oxidizing atmosphere and to SO<sub>2</sub> at higher temperatures (>600 °C) in an oxidizing atmosphere [42]. The S-containing feed was hence prepared by the addition of small amounts of SO<sub>2</sub> or H<sub>2</sub>S to the synthetic diesel feed.

Fig. 7 shows the hydrogen yield when SO<sub>2</sub> was added in various proportions (0–400 ppm) to the feed gas mixture. The experiments were performed with the Pt catalyst at 400 °C (GHSV = 17 000 h<sup>-1</sup>) and quick measurements were taken at each concentration level. The expected inhibition effect on hydrogen generation of the S poison is quite clear. The hydrogen yield dropped drastically from 75 to 40% with an increase in the amount of poison up to 200 ppm of SO<sub>2</sub> and then stabilized for higher concentrations; this could be due to the saturation of the surface.

Similarly, Fig. 8 shows the effect of H<sub>2</sub>S poison (0–200 ppm) on the ability of the catalyst to extract hydrogen autothermally from the synthetic diesel fuel. These experiments were carried under the same conditions described above. A similar trend as observed with SO<sub>2</sub> poison was noticed which resulted in an activity loss. The amount of hydrogen generated dropped from 75 to 55% with an increase in H<sub>2</sub>S concentration up to 70 ppm and then stabilized for higher concentrations; again due to possible surface saturation. Hepolla and Simmell reported similar effects of H<sub>2</sub>S on Ni-based hot gas cleaning catalysts during steam and carbon dioxide reforming of hydrocarbons and it was concluded that the loss in activity occurs as a result of sulfide formation on active sites [43].

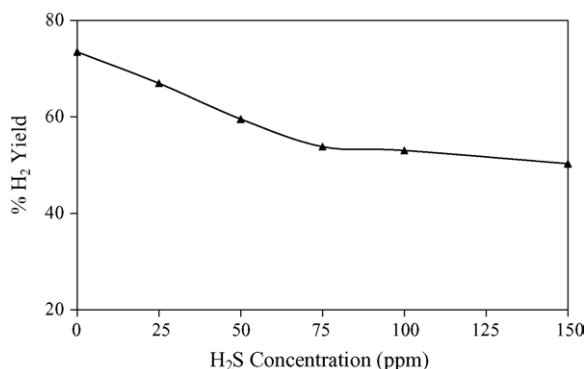


Fig. 8. Effect of H<sub>2</sub>S concentration on hydrogen yield during autothermal reforming of synthetic diesel fuel over the 1% Pt/Ceria catalyst at H<sub>2</sub>O/O<sub>2</sub>/C ratio of 2.5/0.5/1, reactor temperature of 400 °C and GHSV = 17 000 h<sup>-1</sup>.

Long-term experiments were conducted to find the effect of sulfur surrogates on the autothermal reforming activity of the Pt catalyst. In a string of experiments the reactions were started with pure feed and after stabilizing the reactions, the S-containing feed (H<sub>2</sub>S or SO<sub>2</sub>) was supplied. The feed was then switched back to the original mixture. This process was repeated twice as shown in Figs. 9 and 10. Each of these feed changes was made without suspending the reactions.

When the S-containing feeds were supplied to the reactor, the hydrogen yield dropped sharply and after a certain period of time, the decrease in concentration slowed and a stable H<sub>2</sub> yield was achieved. The poisoning seems to be partly reversible, because the H<sub>2</sub> yield increased sharply once the S contaminant in the feed was removed. Although the concentration increased to a certain extent, the original level was not achieved, this may be due to an irreversible adsorption of S on the catalytic surface; this phenomenon could be explained by the fact that the adsorbed sulfur was probably not totally removed from the catalyst by removing the source of sulfur poison from the feed gas stream, probably due to the formation of chemisorbed sulfur entities on the surface or in the bulk phase or due to a very slow sulfur desorption as a result of low catalyst bed temperature (450 °C).

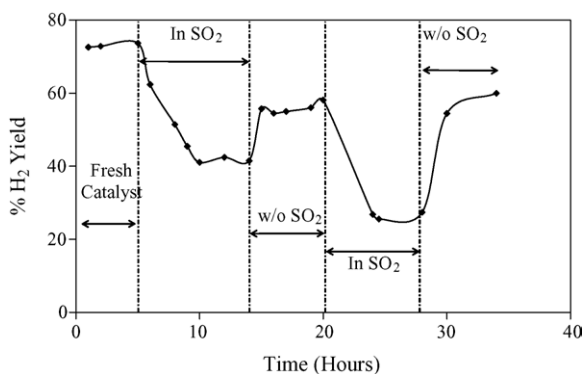


Fig. 9. H<sub>2</sub> yield as a function of time in presence of 200 ppm of SO<sub>2</sub> during autothermal reforming of synthetic diesel fuel over the 1% Pt/ceria catalyst at H<sub>2</sub>O/O<sub>2</sub>/C ratio of 2.5/0.5/1, reactor temperature = 400 °C and GHSV = 17 000 h<sup>-1</sup>.

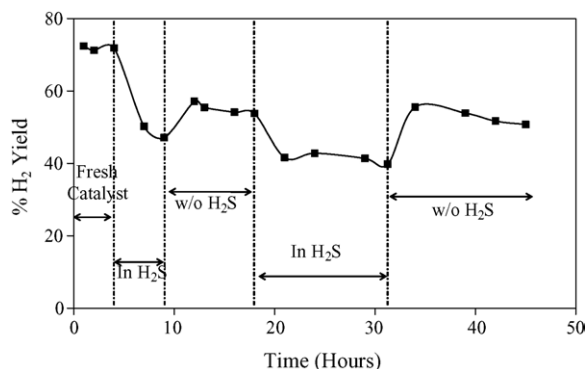


Fig. 10. H<sub>2</sub> yield as a function of time in presence of 150 ppm of H<sub>2</sub>S during autothermal reforming of synthetic diesel fuel over the 1% Pt/ceria catalyst at H<sub>2</sub>O/O<sub>2</sub>/C ratio of 2.5/0.5/1, reactor temperature = 400 °C and GHSV = 17 000 h<sup>-1</sup>.

Figs. 11 and 12 show the response of CO, CH<sub>4</sub> and CO<sub>2</sub> to the presence of 200 ppm of SO<sub>2</sub> poison in the feed stream. Similar results were obtained for these gases as noted for the hydrogen generation in Fig. 9. Methane and carbon monoxide concentrations increased with SO<sub>2</sub> addition. Removal of poison from the feed resulted in decreased concentrations, although the original values were never obtained. However, carbon dioxide concentration decreased with time, in agreement with the results obtained for CO production, which could

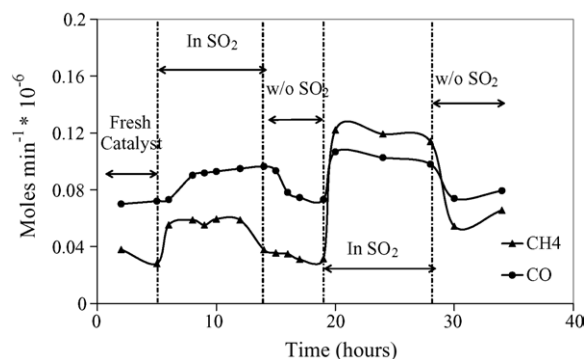


Fig. 11. Molar concentrations of CO and CH<sub>4</sub> as a function of time in presence of SO<sub>2</sub> poison (200 ppm) from the long-term studies described in Fig. 7.

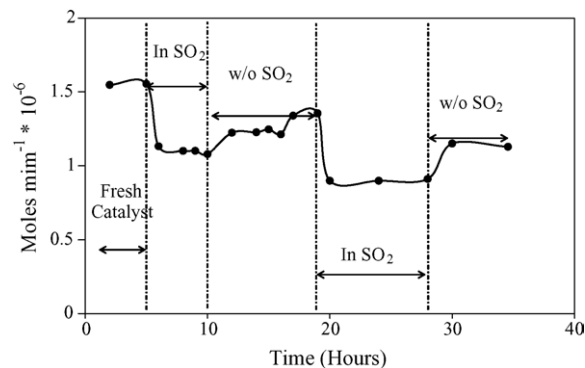


Fig. 12. CO<sub>2</sub> concentration with time in presence of SO<sub>2</sub> poison (200 ppm) from the long-term experiments discussed in Fig. 7.

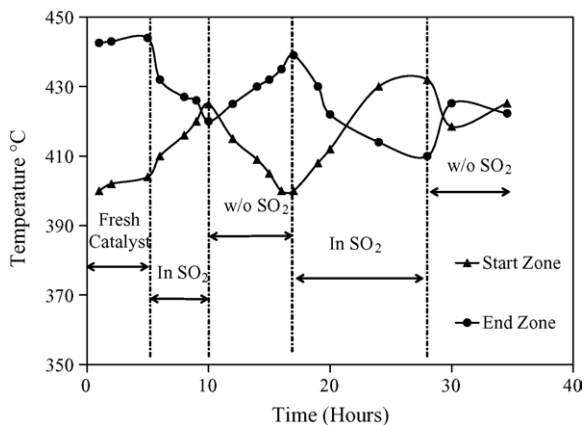


Fig. 13. Effect of S poison ( $\text{SO}_2$ : 200 ppm) on the catalytic bed temperature. Temperature read at the start and end of catalytic bed during the long-term experiments discussed in Fig. 7.

be possibly due to a decrease in the CO oxidation activity of the catalyst in presence of irreversibly adsorbed/chemisorbed sulfur species on the surface.

$\text{SO}_2$  poisoning also affected the catalytic temperature. The response of catalytic bed temperature: front zone (reactants) and end zone (products) to  $\text{SO}_2$  poison is shown in Fig. 13. The reactants temperature decreased by  $25^\circ\text{C}$  while the products temperature increased by  $20^\circ\text{C}$ . This observation can be explained by the variation in products distribution during the actual reaction. A possible reason might be the containment of endothermic steam reforming reaction by sulfur poisoning resulting in a temperature increase in the end zone and hence a drop in the hydrogen concentration.

The presence of 150 ppm of  $\text{H}_2\text{S}$  poison in the feed stream resulted in similar results with respect to CO,  $\text{CH}_4$  and  $\text{CO}_2$  concentrations along with the change in catalytic bed temperature as observed over the  $\text{SO}_2$  poison.

An experiment was carried out to imitate the irreversible-adsorption phenomenon observed over the Pt catalyst in presence of sulfur surrogate. One percent of Pt/ceria catalyst was employed for this experiment involving autothermal reforming of JP8 fuel and synthetic diesel fuel that differ in sulfur content. The experiments were carried out under similar conditions as tested for the above set of experiments. The results from these experiments are presented in Fig. 14.

Initially, JP8 fuel consisting  $\sim 1000$  ppm of sulfur content was employed in to the ATR reactor resulting in a 15% drop in hydrogen concentration with time ( $\sim 10$  h). This loss in activity is due to the catalyst poisoning by sulfur contained in the fuel. When the feed was switched to synthetic diesel fuel consisting  $< 10$  ppm of sulfur content, the hydrogen yield increased and stabilized with time. As expected, the original level of conversion could not be achieved, which can be attributed to the irreversible sulfur poisoning of the catalytic surface.

It is possible that in presence of sulfur-laden fuels like JP8, continuous adsorption of sulfur species occur on the catalytic

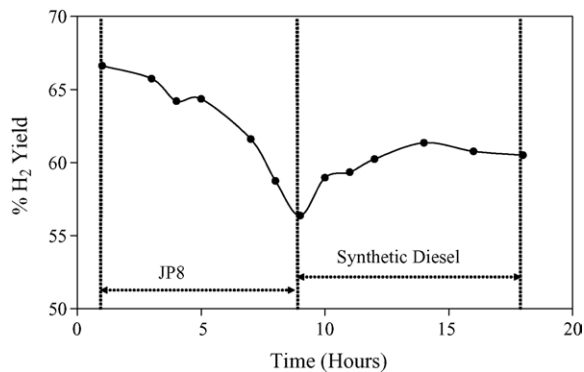


Fig. 14. Hydrogen yield as a function of time in presence of two different fuels that consist of different amounts of sulfur (synthetic diesel fuel and JP8).

surface resulting in an activity drop. It is well known that most of sulfide species are easily removed by chemical treatment (oxygen–hydrogen regeneration and/or by their interaction with reacting surface hydrocarbon intermediates) [44]. Formation of sulfate species by the oxidation of sulfur or sulfide is quite possible and it is known to resist chemical treatments [45]. This suggests an explanation for the difference between physical and chemical adsorption of sulfur species. It is possible that after the source of sulfur is removed, the hydrocarbon feed and hydrogen-rich environment at high temperatures removes the physically adsorbed sulfur entities resulting in partial revival of the activity leaving behind some of the permanently adsorbed sulfate species. This may be one of the reasons why the original activity was hard to restore.

The formation and location of these sulfate entities and the poisoning mechanism was investigated using surface characterization techniques and will be reported in part II of this paper.

#### 4. Conclusions

Autothermal reforming of synthetic diesel fuel is investigated for potential applications in auxiliary power units.

Experiments were carried out to study the effect of oxygen-to-carbon ratio, water-to-carbon ratio and space velocity on the performance of an autothermal reformer to produce hydrogen from synthetic diesel fuel over a 1% Pt/ceria catalyst. An  $\text{O}_2/\text{C}$  ratio of 0.5 and a  $\text{H}_2\text{O}/\text{C}$  ratio of 2.5 at a GHSV of  $17000\text{ h}^{-1}$  were found to be ideal for ATR of synthetic diesel fuel. In this work, it was found that diesel can be reformed (ATR) to produce hydrogen under adiabatic conditions by heating the feed mixture/ATR reactor to only  $400^\circ\text{C}$  in contrast to the previous studies that utilized a temperature above  $700^\circ\text{C}$  to achieve similar performance [14,15]. The temperature profile inside the reactor revealed that the exothermic reactions occur initially, which drive the endothermic reactions down the catalytic bed. Experiments have shown that steam reforming alone is not active under the conditions tested. The catalyst exhibited good stability

for the ATR of synthetic fuel but it is prone to poisoning by S-containing fuels. A reversible–irreversible adsorption of sulfur species was observed during the poisoning studies.

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