

Partial Oxidation (POX) Reforming of Gasoline for Fuel-Cell Powered Vehicles Applications

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Abstract—As a part of the development of a gasoline processor for integration with a proton-exchanged membrane (PEM) fuel cell, we carried out the POX reforming reaction of *iso*-octane, toluene and gasoline over a commercial methane reforming catalyst, and investigated the reaction conditions required to prevent the formation of carbon and the effect of fuel constituents and sulfur impurities in gasoline. The H₂ and CO compositions increased with increasing reaction temperature, while those of CO₂ and CH₄ decreased. It is desirable to maintain an O/C molar ratio of more than 0.6 and an H₂O/C molar ratio of 1.5 to 2.0 for vehicle applications. It has been found that carbon formation in the POX reforming of *iso*-octane occurs below 620 °C, whereas in the case of toluene it occurs below 640 °C. POX reforming of gasoline constituents led to the conclusion that hydrogen production is directly related to the constituents of fuels and the operating conditions. It was also found that the coke formation on the surface of catalysts is promoted by sulfur impurities in fuels. For the integration of a fuel processor with PEM fuel cell, studies are needed on the development of new high-performance transition metal-based catalysts with sulfur- and coke-resistance and the desulfurization of fuels before applying the POX reformer based on gasoline feed.

Key words: Gasoline POX Reforming, Methane Reforming Catalyst, PEM Fuel Cell, HTS, LTS

INTRODUCTION

Proton-exchanged membrane (PEM) fuel cells operating with H₂ from hydrocarbon steam reforming or partial oxidation are being accepted as the most appropriate power source for future-generation vehicles. The successful development of a fuel-cell powered vehicle is dependent on the development of a fuel processor [Chalk et al., 1998; Moon et al., 2000]. Hydrogen is the ideal fuel for a PEM fuel cell because it simplifies the system integration [Borroni-Bird, 1995]. However, since no hydrogen fuel supply infrastructure currently exists, fuel supply for fuel cell vehicles is directed at developing on-board fuels such as methanol and gasoline. Regarding the reforming process to generate hydrogen-rich gas on-board a vehicle, methanol yields the highest vehicle efficiencies among all the available liquid fuels [Borroni-Bird, 1995; Raman, 1999; Doctor and Lamn, 1999]. However, the lower efficiency of gasoline in comparison with methanol can be compensated by the much higher energy density of gasoline compared to methanol and also by the well developed infrastructure for gasoline [Borroni-Bird, 1995; Raman, 1999]. Therefore, gasoline is recommended as the best candidate fuel for the fuel-cell powered vehicle.

Major process technologies for reforming hydrocarbons and alcohols into hydrogen, carbon monoxide and carbon dioxide are catalytic steam reforming, partial oxidation (POX) and partial oxidation reforming (or autothermal reforming) [DOE, 1994; Sun and Lee, 1995]. Steam reforming reaction of hydrocarbon usually takes place at around 700 °C, which seems to guarantee the highest reforming efficiencies. But the drawback is that this reaction is endo-

thermic and therefore the reactor needs to be heated by combustion of the fuel itself. To date, no sulfur-tolerant steam-reforming catalyst has been found, resulting in the need for a very efficient and large unit for removing the sulfur from the fuel [DOE, 1994]. POX and POX reforming systems promise to have a much better dynamic than a steam reforming system since they do not require external heating and can be heated internally quickly by exothermic reaction of fuel. The sulfur tolerance for POX reforming system is also better than that of steam reforming. Considering the favorable factors required for the on-board generation of H₂ in a fuel cell vehicle, the POX reforming process attracts much attention primarily because of the low energy requirement due to the opposite contribution of the exothermic hydrocarbon oxidation and endothermic steam reforming, and also to the high space velocity compared to the POX process [Flynn et al., 1999]. In previous works [Moon et al., 2000, 2001], the authors studied the development of a gasoline fuel processor including POX reforming over an ICI-naphta reforming catalyst, high temperature water gas shift (HTS) reaction over Fe₃O₄-Cr₂O₃ catalyst and low temperature shift (LTS) reaction over Cu/ZnO/Al₂O₃ catalyst. We have pointed out the various experimental features of the gasoline processor as well as the goals to be achieved in the near future.

In this paper, as a part of the development of a gasoline fuel processor system for integration with a PEM fuel cell, we carried out the POX reforming reaction of *iso*-octane, toluene and gasoline over a commercial methane reforming (Haldor-Topsoe, HT) catalyst to explore its possibility for commercial purposes. In particular, this work focuses on the POX reforming conditions to minimize the energy needed by external heating, to maximize the production of hydrogen at low temperature, and to prevent the formation of carbon and the deactivation of catalyst by sulfur-containing impurities

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contained in gasoline.

EXPERIMENTAL

1. Chemicals

The *iso*-octane as a fuel source was supplied from J. T. Baker. Toluene was obtained from Jensei Chemical Co. *iso*-octane containing 100 ppm of sulfur was prepared by a mixing of the *iso*-octane and thiophene (99%+, Acros organics). Gasoline containing 300 ppm of sulfur was supplied from LG Caltex (Korea). Hydrogen (Deokyang Gas., 99.999%), air (Deokyang Gas., 99.999%) and nitrogen (Deokyang Gas., 99.999%) were used in the reaction and pretreatment of the catalysts. Argon (Deokyang Gas., 99.999%) was used as a carrier gas for GC.

2. Catalysts

The commercial methane-reforming catalyst (HP-R-67-7H) was supplied from Haldor Topsoe Inc. The catalyst, which was provided in the form of a cylinder with seven holes, consists of nickel oxide (NiO), silica (SiO₂) and magnesium aluminate (MgAl₂O₄). The catalyst in the form of powder with a mesh of 120/230 was used after crushing in this work.

3. Gasoline POX Reforming System

The schematic diagram of the gasoline POX reforming apparatus is shown in Fig. 1. It consists of four sections: feed supply section, preheater, POX reforming reactor and GC analysis section. The gases were delivered by mass flow controllers, and H₂O and liquid fuels were fed by liquid delivery pumps (Young Lin Co., model M930). The preheater and the POX reforming reactor were made of an Inconel 600 tube (0.095 m I.D. and 0.20 m length). The reaction temperature was controlled by a PID temperature controller and was monitored by a separate thermocouple in the catalyst bed. This arrangement was capable of ensuring an accuracy of ±1 °C for the catalyst bed temperature. The unreacted H₂O was removed

by an ice trap and then gas effluent was analyzed by GC.

4. Activity Measurements

The HT catalyst of 0.15-1 g was charged in the Inconel reactor and pretreated for 1 h at 700 °C under a hydrogen flow of 60 cc/min. All runs were conducted in the temperature range of 500-770 °C, space velocity of 4,000-50,000 h⁻¹ and feed molar ratios of H₂O/C=0.5-3.0 and O/C (O_{air}/C_{fuel})=0.5-2.0 at an atmospheric pressure. The vaporized fuel and water were mixed with oxygen and then passed over the heated catalyst zone. We have also performed the stability measurement of the reforming catalyst to check carbon deposition and sulfur tolerance. The gas effluent was analyzed on-line by a gas chromatograph (HP-5890 Series II) equipped with a TCD and a Carbosphere 80/100, 10'×1/8" SS column. Each component in the product stream was identified by a GC/MS (HP5890/5971) with an HP-1 capillary column (0.0002 m O.D. and 50 m length).

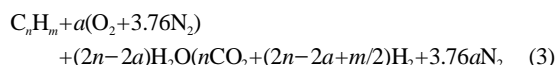
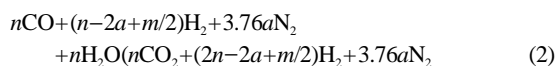
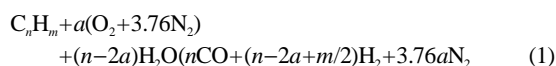
5. Catalyst Characterization

BET surface area and total pore volume of catalysts before and after the POX reforming reaction of *iso*-octane (C_s<5 ppm) and sulfur-containing *iso*-octane (C_s=100 ppm) were determined from N₂ adsorption isotherm measured at liquid nitrogen temperature with a sorption analyzer (Quantachrome Co., Autosorb-1C). Active metal surface area of catalysts was calculated by CO chemisorption at 400 °C using a sorption analyzer. The contents of carbon and sulfur before and after the reaction were analyzed by elemental inorganic analyzer [Leco Co., CS-344]. Structure of the catalysts before and after the reaction was analyzed by an XRD analyzer [Shimadzu Co., XRD-6000].

RESULTS AND DISCUSSION

1. Estimation of Reaction Heat for POX Reforming of *iso*-octane

The major reactions taking place during the POX reforming reaction of gasoline are given by the following stoichiometric reforming reaction: POX reforming reaction (1) and water gas shift reaction (2).



The first reaction is POX reforming reaction (1), the second one is the mildly exothermic water gas shift reaction (2), and the third one is an overall POX reforming reaction (3), where *a* is a molar ratio of oxygen/fuel. The heat of reaction for the gross-reaction depends on the molar ratio of oxygen/fuel, the molar ratio of H₂O/fuel and the reaction temperature. The heat of reaction for the POX reforming reaction of *iso*-octane is calculated by the Gibbs free energy minimization method [Smith and Missen, 1991]. The effect of O/C molar ratio on the heat of reaction in the POX reforming reaction of *iso*-octane is presented in Fig. 2. There is a gradual change from endothermic at sufficiently low O/C molar ratios to exothermic at high O/C molar ratios. The heat of reaction for the POX re-

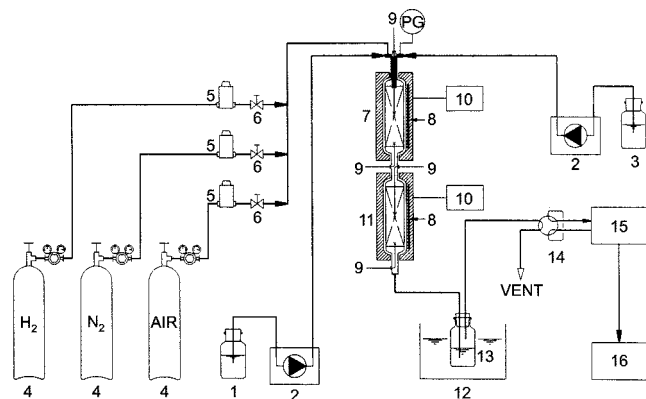


Fig. 1. A schematic diagram of gasoline POX reforming reaction system.

- | | |
|-------------------------|---------------------------|
| 1. Water | 9. Thermocouple |
| 2. HPLC pump | 10. Temp. controller |
| 3. Fuel | 11. Reactor |
| 4. Cylinder | 12. Refrigerator |
| 5. Mass flow controller | 13. Water trap |
| 6. Needle valve | 14. 6-Port sampling valve |
| 7. Preheater | 15. Gas chromatograph |
| 8. Electric heater | 16. Personal computer |

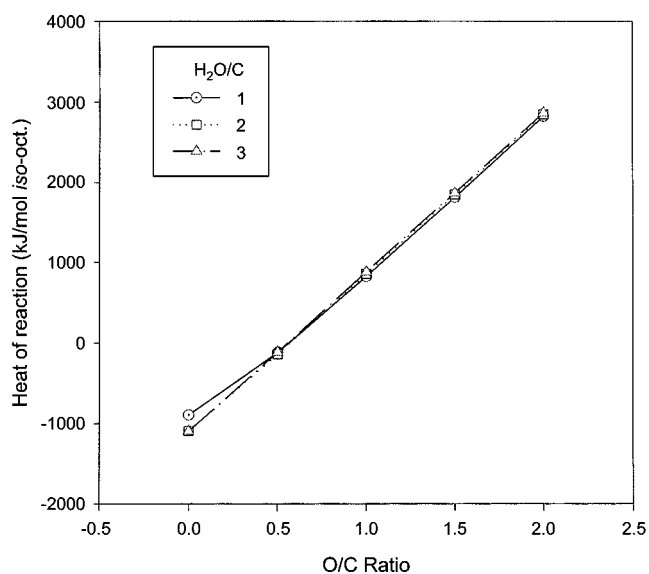


Fig. 2. The estimation of the heat of reaction in the POX reforming reaction of *iso*-octane.

forming reaction of *iso*-octane can be properly controlled by varying the O/C molar ratio and the H₂O/C. As shown in the figure, the overall reaction can be shifted to the exothermic region by maintaining the O/C molar ratio of higher than 0.6. The advantage of tuning the reaction energy by properly varying the O/C molar ratio makes POX reforming superior to steam reforming. Hence, considering a low energy requirement, an O/C molar ratio of 0.6 is favorable for the POX reforming reaction of *iso*-octane.

2. Estimation for Reactor Temperature Required to Prevent the Formation of Carbon

Generally, the reforming of hydrocarbons always has potential to form carbon. If the reactor is not properly designed or operated,

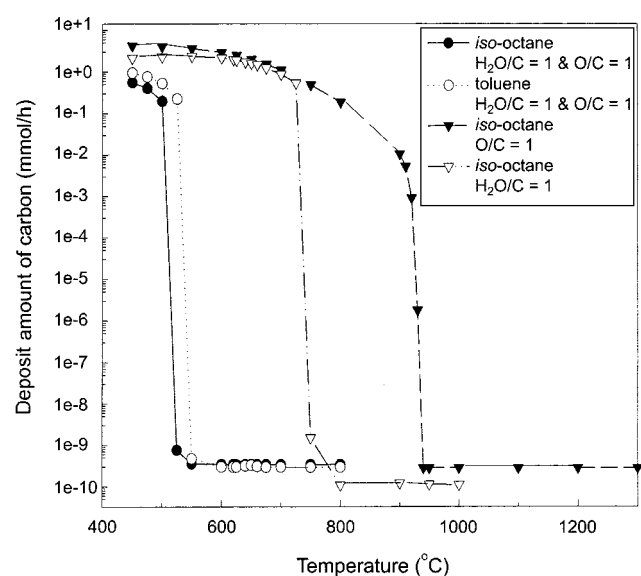


Fig. 3. The amount of carbon deposited as a function of temperature for the POX reforming reactions of *iso*-octane or toluene, assuming thermodynamic equilibrium.

coking is inclined to occur. Reactor temperature required to prevent the formation of carbon during the reforming process of *iso*-octane and toluene was estimated by PRO-II simulation program, assuming thermodynamic equilibrium. [Smith, 1991; PRO-II reference manual, 1994]. The amount of carbon formed as a function of temperature for four reforming reactions is presented in Fig. 3. If the feed consists of *iso*-octane (1 gmol/h) and air at O/C=1, the coke of more than 1.E-9 μ mol/h would form in the partial oxidation of *iso*-octane at temperature up to 950 °C. If the feed consists of *iso*-octane (1 gmol/h) and H₂O at H₂O/C=1, coke of more than 1.E-9 μ mol/h would form in the steam reforming of *iso*-octane at the temperature up to 800 °C. If water is added at the molar ratio of H₂O/C=1 while maintaining the O/C ratio=1, reactor temperature in the POX reforming of *iso*-octane can be lowered to 560 °C before carbon formation occurs. If the POX reforming of toluene (1 gmol/h) is carried out at the same feed condition, coking can be avoided at temperature above 600 °C. It was found that the reactor temperature showing the carbon formation in the POX reforming of *iso*-octane is lower than the temperature in that of toluene.

3. POX Reforming of *iso*-octane

Based on the results of estimation of the heat of reaction for the POX reforming of *iso*-octane, the effect of reaction parameters such as O/C molar ratio, H₂O/C molar ratio, reaction temperature and space velocity on the product distribution were investigated.

The effect of O/C molar ratio on the product distribution in the POX reforming reaction of *iso*-octane at the reaction condition of 700 °C, space velocity=8,770 h⁻¹ and molar ratio of H₂O/C=3 is presented in Fig. 4. Conversions were all above 99.9%. Hydrogen concentration decreased with increasing the O/C molar ratio. The CO and CH₄ concentrations decreased with increasing the O/C molar ratio, whereas the CO₂ concentration increased. When the O/C molar ratio increased from 1.0 to 1.5, H₂ concentration showed a gradual decrease. A probable reason for these phenomena is that the produced hydrogen can be oxidized by oxygen contained in air. There-

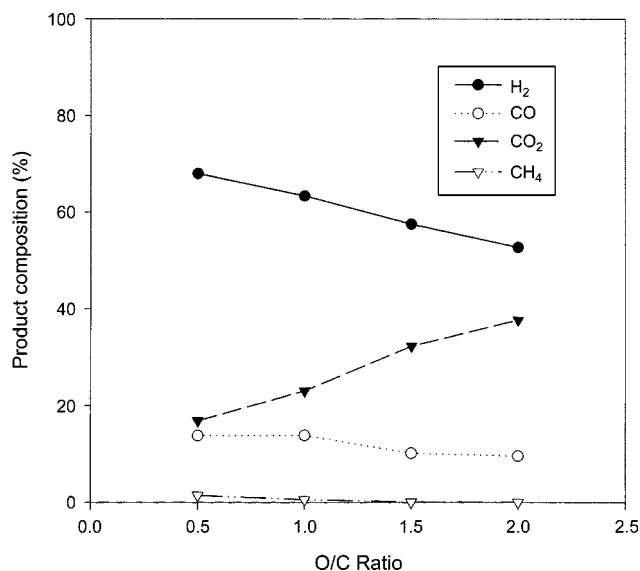


Fig. 4. The effect of O/C molar ratio on the product distribution in the POX reforming reaction of *iso*-octane at the reaction conditions of reaction temperature=700 °C, space velocity=8,770 h⁻¹ and H₂O/C molar ratio=3.

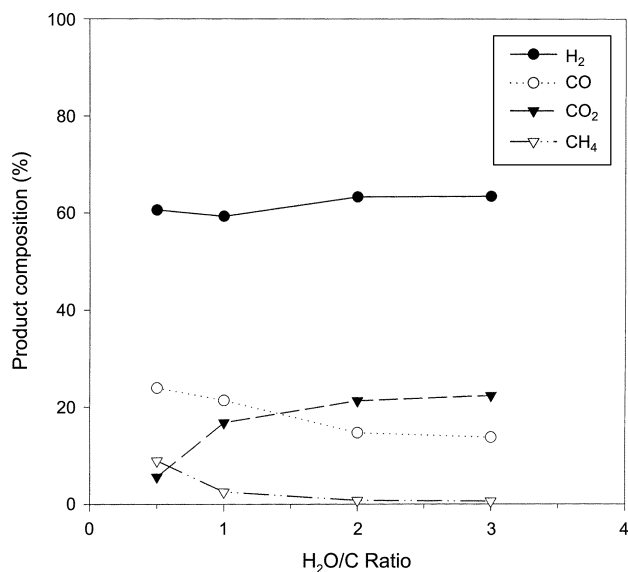


Fig. 5. The effect of H₂O/C molar ratio on the product distribution in the POX reforming reaction of *iso*-octane at the reaction conditions of reaction temperature=700 °C, space velocity=8,770 h⁻¹ and O/C molar ratio=1.

fore, an increase in the O/C molar ratio of more than 1 results in decreasing performance of fuel processor. Whereas, in the case of O/C molar ratio of less than 0.6, the POX reforming reaction of *iso*-octane is endothermic (Fig. 2). It was identified that an O/C molar ratio between 0.6 and 1.0 is desirable to maximize the production of hydrogen and to minimize energy heated by combustion of the fuel itself.

The effect of H₂O/C molar ratio on the product distribution in the POX reforming reaction of *iso*-octane at the reaction condition of 700 °C, space velocity=8,770 h⁻¹ and molar ratio of O/C=1 is shown in Fig. 5. Hydrogen concentration slightly increased as the H₂O/C molar ratio increased from 0.5 to 3.0. The influence of H₂O/C molar ratio on the CO concentration is much more evident as its value decreased from 25% at the H₂O/C molar ratio of 0.5 to nearly 15% at the molar ratio of 3.0. The CH₄ concentration also decreased with increasing H₂O/C molar ratio. If there is no coke deposition, a high H₂O/C value is preferred for generating the fuel gas mixture containing the high concentration of hydrogen and the low concentrations of CO as well as CH₄. It is desirable that the H₂O/C molar ratio is around 1.5-2.0 for the POX reforming of *iso*-octane. But, considering the amount of water required in the water gas shift (HTS and LTS) reactors of POX reforming system, high molar ratio of H₂O/C=2-3 may be more desirable in a gasoline fuel processor for fuel cell-powered vehicle applications.

The effect of reaction temperature on the product distribution in the steam reforming and the POX reforming of *iso*-octane is presented in Fig. 6. The steam reforming of *iso*-octane was carried out at the temperature range of 650 to 780 °C, space velocity of 8,770 h⁻¹ and feed molar ratio of H₂O/C=3. Hydrogen concentration in the temperature range of 650 to 770 °C was unaffected by temperature. However, CO concentration increased with a rise in temperature, and the CO₂ and CH₄ concentrations decreased with increasing temperature. It was found that the maximum hydrogen concentration based on dry gas was more than 70% for steam reforming of

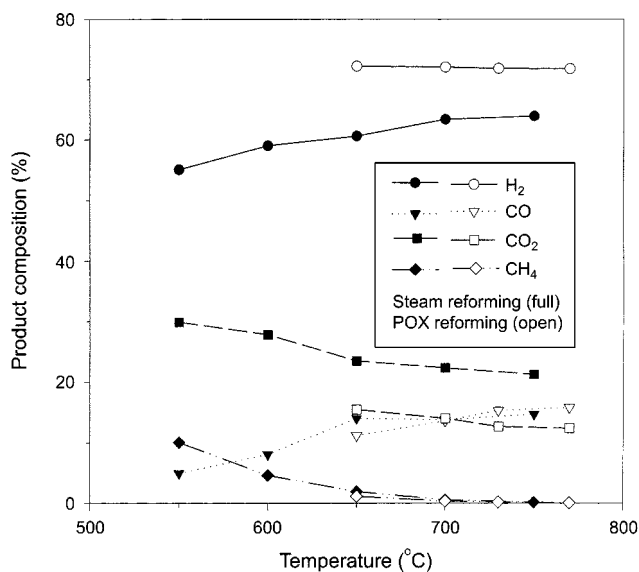


Fig. 6. The comparison of the product distribution for the steam reforming and the POX reforming of *iso*-octane at the reaction conditions of space velocity=8,770 h⁻¹, O/C molar ratio=1 and H₂O/C molar ratio=3.

iso-octane. It was also found that carbon deposition over the catalyst was severely brought out in the temperature range of 500 to 620 °C. The POX reforming of *iso*-octane was carried out at the reaction condition of space velocity of 8,770 h⁻¹, feed molar ratios of O/C=1 and H₂O/C=2. Hydrogen concentration increased slightly with increasing temperature. However, the CO concentration drastically increased until 650 °C with a rise in temperature and thereafter slightly increased up to 750 °C. The CO₂ and CH₄ concentrations decreased with increasing temperature. Catalyst at a low temperature below 600 °C was especially more susceptible for deactivation by the coke deposition. Thus, hydrogen enrichment in the

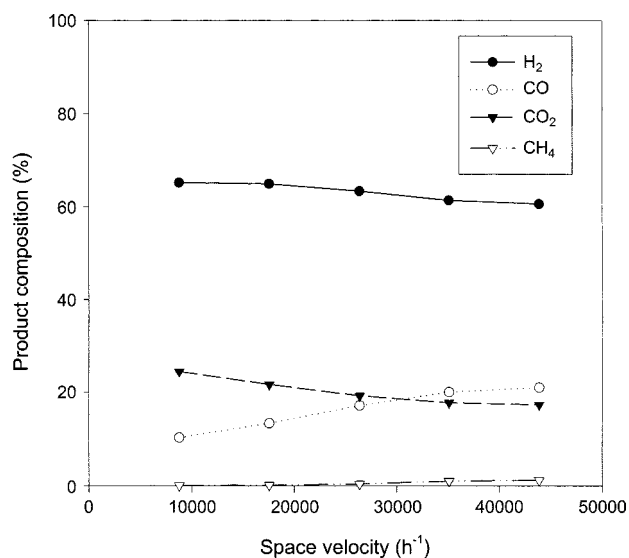


Fig. 7. The effect of space velocity variations for the POX reforming of *iso*-octane at the reaction conditions of reaction temperature=700 °C, H₂O/C molar ratio=3 and O/C molar ratio=1.

effluent mixture is possible by operating the POX reactor at high reaction temperatures; however, at sufficiently high temperatures there occurs an adverse effect due to drastic increase in the CO concentration. Hence, a reaction temperature of 700 °C was found to be ideal for the POX reforming of *iso*-octane. Even though steam reforming gives maximum hydrogen concentration more than POX and POX reforming [DOE, 1994], it is an endothermic process where the heat of reaction is provided by the external combustion of fuel. Therefore, it is an undesirable process as a primary fuel processor for automotive applications.

Fig. 7 shows the effect of space velocity variations for the POX reforming of *iso*-octane at a reaction temperature of 700 °C and molar ratios of $H_2O/C=3$ and $O/C=1$. Hydrogen concentration remained fairly stable in the space velocity range of 8,000 h^{-1} to 18,000 h^{-1} and then decreased slightly in the range of 18,000 h^{-1} to 45,000 h^{-1} . The influence of space velocity on the CO concentration is much more evident as its value increased from 10% at the space velocity of 8,000 h^{-1} to nearly 20% at the space velocity of 45,000 h^{-1} . These phenomena may be interpreted as that the water gas shift reaction was restricted by increasing the space velocity. The CO_2 concentration decreased with increasing the space velocity, whereas the CH_4 concentration increased.

4. POX Reforming of *iso*-octane and Toluene

To investigate the effect of aromatic hydrocarbon as fuel, a POX reforming of toluene was carried out at the reaction condition of space velocity of 4,390 h^{-1} and feed molar ratios of $H_2O/C=1$ and $O/C=1$. The product distribution for the POX reforming of toluene is similar to that of *iso*-octane under the tested reaction conditions. Hydrogen concentration increased with increasing reaction temperature. It was found that the maximum hydrogen concentration is less than 55% in the POX reforming of toluene (Fig. 8). The CO concentration increased from 25% to 29% with increasing reaction temperature from 650 °C to 770 °C, whereas the CO_2 and CH_4 concentrations decreased with increasing reaction temperature. Fig. 8 shows the comparison of the product composition and coke forma-

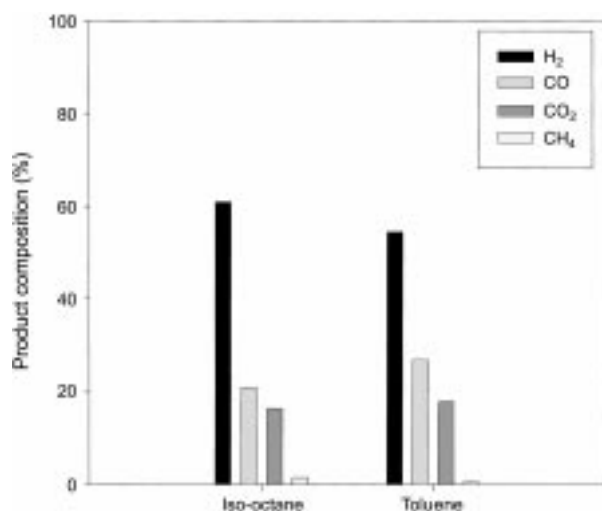
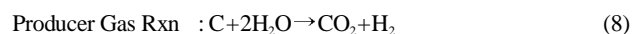
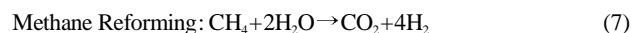
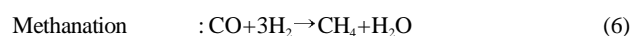
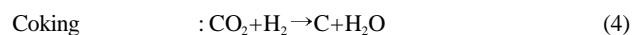


Fig. 8. The comparison of the product composition and coke deposition temperature for the POX reforming reactions of *iso*-octane and toluene, respectively. reaction temperature =700 °C, O/C molar ratio=1, H_2O/C molar ratio=1 and space velocities=8,770 h^{-1} .

tion temperature for the POX reforming reactions of *iso*-octane and toluene. A reaction temperature of 700 °C, molar ratios of $O/C=1$ and $H_2O/C=1$ and space velocities of 8,770 h^{-1} for *iso*-octane and 4,390 h^{-1} for toluene were used. It was found that the hydrogen concentration for the POX reforming of toluene is lower than that of *iso*-octane even though the space velocity of toluene is half of that of *iso*-octane. It was also identified that carbon formation temperature in the POX reforming of toluene is higher than that of *iso*-octane, as per Fig. 3. In short, compared to *iso*-octane, the POX reforming reaction of toluene occurs at higher reaction temperature. It was found that carbon deposition in the POX reforming of *iso*-octane occurs below 620 °C, whereas in the POX reforming of toluene it occurs below 640 °C. It was also found that carbon deposition over the catalyst was severely brought out in the temperature range of 500 to 640 °C.

Some of the side reactions that take place during the POX reforming of *iso*-octane are the coking reaction, methanation reaction and producer's gas reactions given by:



Coking is highly undesirable as it leads to clogging and deactivation of the catalyst and extreme care must be taken to prevent carbon formation. It was identified that coke formation is a function of fuel constituents, oxygen/fuel molar ratio, H_2O /fuel molar ratio and reaction temperature [Fig. 3 and Fig. 8]. To minimize the for-

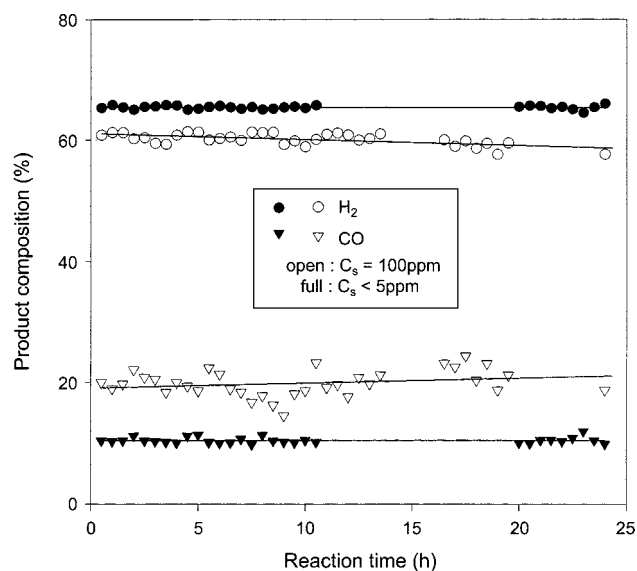


Fig. 9. The catalytic stability for the POX reforming of *iso*-octane containing less than 5 ppm of sulfur and *iso*-octane with 100 ppm of sulfur at the reaction conditions of reaction temperature=700 °C, H_2O/C molar ratio=3, O/C molar ratio=1 and time on stream=24 h.

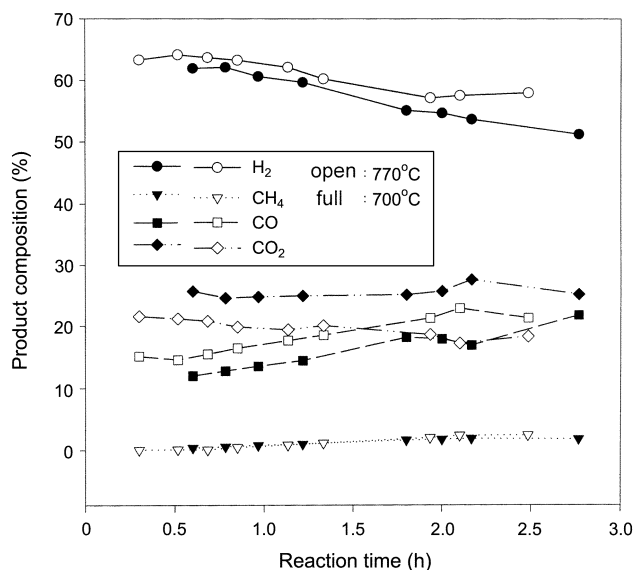


Fig. 10. The sulfur tolerance of the HT catalyst for the POX reforming of gasoline containing sulfur of 300 ppm at the reaction conditions of reaction temperatures=700 °C and 770 °C, space velocity=15,380 h⁻¹, H₂O/C molar ratio=3, O/C molar ratio=1 and time on stream=3 h.

mation of carbon at low temperature, detailed studies on the development of catalyst with coke-resistance and the benchmarked fuels are needed in the future.

5. Catalytic Stability Test for POX Reforming of *iso*-octane

Fig. 9 shows the catalytic stability for the POX reforming of *iso*-octane containing less than 5 ppm of sulfur and *iso*-octane with 100 ppm sulfur at the reaction conditions of 700 °C and molar ratios of H₂O/C=3 and O/C=1 over 24 h. Conversions were all above 99.9%. We could not find any change in the hydrogen production in POX reforming of *iso*-octane during the time period investigated. But the hydrogen production decreased in POX reforming of sulfur-containing fuels (C_s=100 ppm) (Fig. 10). The characteristic results of catalysts before and after the reaction are summarized in Table 1. BET surface area and active metal area of catalysts after the POX reforming reaction decreased 14% and 58%, respectively. Carbon contents deposited on catalysts after the POX reforming of *iso*-octane (C_s<5 ppm) and sulfur-containing *iso*-octane (C_s=100 ppm) were 7% and 24%, respectively. These results can be interpreted as that the coke deposition on the surface of catalyst was promoted by sulfur impurities in fuels.

Fig. 10 shows the results of the POX reforming of gasoline containing 300 ppm of sulfur at the reaction temperatures of 700 °C and

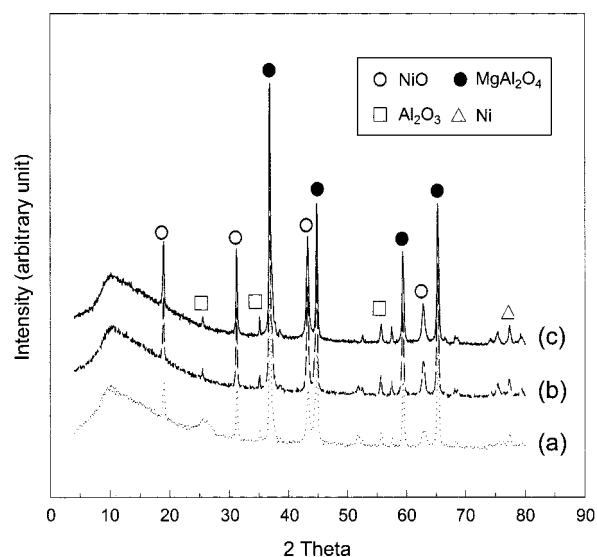


Fig. 11. XRD pattern of catalysts before and after the reaction.

(a) fresh catalyst, (b) catalyst used for 24 h in POX reforming of *iso*-octane, (c) catalyst used for 24 h in POX reforming of *iso*-octane containing 100 ppm of sulfur.

770 °C, space velocity of 15,380 h⁻¹ and molar ratios of H₂O/C=3 and O/C=1 for 3 h. It was found that the HT catalyst was severely prone to be poisoned by sulfur contained in gasoline. It was also found that the catalyst deactivation by sulfur poisoning is more severe at 700 °C than at 770 °C. This leads to the conclusion that a high operating temperature of above 770 °C is desirable to minimize the deactivation of catalyst by sulfur poisoning in the POX reforming of fuels containing relatively higher amount of sulfur. The effluent gas mixture from the POX reactor gave progressively lesser concentrations of H₂ and CO and higher concentrations of CO₂ and CH₄ as a result of sulfur poisoning over the catalyst surface. Recently, the ANL research group [Kopasz, 2000] reported that the effect of sulfur impurities on the catalyst performance depends on the ingredients of catalyst. Sulfur appears to improve the hydrogen yield for Pt-containing ANL catalyst, but appears reversely to poison Ni-containing catalyst. Instances of sulfur acting as a promoter in catalytic reforming of *n*-heptane and oxidation reactions have been reported in the literature [Burch, 1999; Querini, 1996]. It was also reported that Pt pricing and loading are significant factors in the economics of fuel cell systems [DOE, 2000]. Platinum is approximately 20% of the total system cost at present Pt loadings and fuel cell performance. Therefore, the development of high performance catalysts based on transition metal is required to com-

Table 1. Characteristics of the catalysts before and after the POX reforming of *iso*-octane (C_s<5 ppm) and sulfur-containing *iso*-octane (C_s=100 ppm)

| Catalyst | BET surface area (m ² /g) | Total pore volume (cc/g) | Exposed metal area (m ² /g) | Deposit amount (wt %) | |
|---|--------------------------------------|--------------------------|--|-----------------------|--------|
| | | | | Carbon | Sulfur |
| Before the reforming* | 24.9 | 0.154 | 0.504 | 0.1 | 0.003 |
| Used in the POX reforming (C _s <5 ppm) | 21.9 | 0.170 | 0.219 | 7.0 | 0.004 |
| Used in the POX reforming (C _s =100 ppm) | 16.3 | 0.175 | 0.199 | 24.0 | 0.006 |

*Reaction conditions: reaction temperature=700 °C, feed molar ratios of H₂O/C=3 and O/C=1 and time on stream=24 h.

mercialize gasoline fuel processor.

X-ray diffraction (XRD) patterns of the catalysts before and after the reaction are presented in Fig. 11. We could not observe any major changes in the phase pattern of the catalysts after the POX reforming reaction of *iso*-octane and sulfur-containing *iso*-octane feeds. Although some graphitic carbon was deposited on the HT catalyst, the formation of metallic carbides such as nickel carbide and nickel-aluminum carbide was not formed during the gasoline reforming. This is evident from the identical nature of the XRD patterns of the fresh and used systems.

To integrate a fuel reformer with a PEM fuel cell, studies on the development of the new high-performance transition metal-based catalysts with sulfur- and coke-resistance and the fuel processor system consists of desulfurizer, POX reformer, HTS, LTS and a preferential partial oxidation reactor will be required for automotive applications.

CONCLUSIONS

As a part of the development of a gasoline reforming system for integration with the a PEM fuel cell, we investigated the POX reforming reaction of *iso*-octane, toluene and gasoline over a commercial methane reforming catalyst. It was found that carbon deposition in the POX reforming of *iso*-octane occurs below 620 °C, whereas in the case of toluene it occurs below 640 °C. These results reveal that the choice of the feed constituents and operation conditions in the POX reforming of gasoline as fuel is critical; a gasoline containing low concentration of aromatic constituents is always preferable under the autothermal reforming conditions. It was identified that the commercial HT catalyst was prone to be poisoned by sulfur contained in gasoline, but there is no coke deposition at 700 °C under the tested conditions. Due to a low energy requirement for the POX reforming, it is desirable to maintain an O/C molar ratio of more than 0.6 and an H₂O/C molar ratio of 1.5 to 2.0. It was found that the coke deposition on the surface of catalyst was inclined to be promoted by sulfur impurities in fuels. It was also found that an operating temperature above 770 °C is more desirable to minimize the deactivation of catalyst by sulfur poisoning in the POX reforming of gasoline. For integration fuel reformer with PEM fuel cell, studies on the development of the new high-performance catalysts with sulfur- and coke-resistance will be needed in the future.

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