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Steam reforming of hydrocarbon fuels

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Abstract

InnovaTek has developed a proprietary catalyst formulation for the fuel processor that is being developed for use with polymer electrolyte membrane fuel cells. The catalyst has been tested for the steam reforming of various hydrocarbons such as natural gas, *iso*-octane, retail gasoline, and hexadecane. A 300 h continuous test has shown that the catalyst has very stable performance for steam reforming of *iso*-octane at 800 °C with a steam/C ratio of 3.6. The same catalyst was also tested for steam reforming hexadecane (a surrogate of diesel) for 73 h as well as natural gas for over 150 h continuously, without deactivation or carbon deposition. Sulfur tolerance of the catalyst was tested using *iso*-octane containing various concentrations of sulfur. There was no catalyst deactivation after a 220 h continuous test using *iso*-octane with 100 ppm sulfur. For comparison, a nickel catalyst (12 wt.% Ni/Al_2O_3) was also tested using different levels of sulfur in *iso*-octane. The results indicated that the InnovaTek catalyst has a substantially improved sulfur resistance compared to the nickel catalysts currently used for steam reforming. In addition, a variation of the catalyst was also used to reduce CO concentration to $<1\%$ by water gas shift reaction.

Keywords: Steam reforming catalyst; Water gas shift catalyst; Natural gas; Gasoline; Diesel; Fuel processing and fuel cell

1. Introduction

Hydrogen is the fuel that powers polymer electrolyte membrane (PEM) fuel cells. The projected commercialization of PEM fuel cells requires a readily available hydrogen source [1,2]. Hydrogen can be supplied from a number of storage methods, such as liquid hydrogen storage, compressed hydrogen storage, and metal hydride. The most efficient way for storage is liquid hydrogen, which offers high storage density and allows fast refueling times, but this method suffers significant evaporative loss. Metal hydride provides a reliable method and permits loss-free hydrogen storage over time. However, metal hydride has low hydrogen storage density, and also requires an elevated temperature to release the hydrogen. New developments have been made to increase the hydrogen storage density from approximately 1.7 to 4.5 wt.% [3]. Another hydrogen storage medium is carbon nanotube. The results regarding the hydrogen storage capacity of nanotube are controversial and the practical application is questionable [4,5]. Hydrogen can also be extracted by reforming various readily available hydrocarbons, such as methanol, natural gas, gasoline, and diesel. Reforming has been intensively developed for both on board (vehicle), and off board (stationary, residential) applications [1,2,6–8].

Partial oxidation, autothermal reforming, and steam reforming are the primary methods used in reforming hydrocarbons to produce hydrogen for use in PEM fuel cells. Much effort in the development of fuel processors has been focused on the partial oxidation [7,9,10], and autothermal reforming [7,11–13] processes in

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which no indirect heating is required. Partial oxidation and autothermal reforming offer faster startup time and better transient response, but result in poor quality of feed to fuel cells. Compared with partial oxidation and autothermal reforming, catalytic steam reforming offers higher hydrogen concentrations (70–80% for steam reforming versus 40–50% for partial oxidation and autothermal reforming on a dry basis) in the crude reformate gas. In addition, with minimal parasitic power consumption, liquid water and hydrocarbon can be pumped to elevated pressures for a pressurized operation.

Since 1997 [14,15], InnovaTek has been developing fuel reformer technology based on the steam reforming process. Our system incorporates several unique technologies and is designed to generate the hydrogen to feed fuel cells ranging from 100 W to a few kW. The system consists of a microchannel catalytic steam reforming unit that is integrated with a micro-fuel injector, a micro-burner unit to provide heating energy for the reforming unit, and a reformate purification unit. The steam reforming reaction is a highly endothermic reaction and requires extensive heating. A microchannel reactor is engineered hardware that incorporates design features that provide rapid heat and mass transport, thus providing our system with quick startup time, high power density (W/L), and better dynamic response to hydrogen demand [14–16].

The catalytic steam reformer is a critical component of our system and the subject of this paper. Our goal is to develop a miniature reformer that can process various hydrocarbon fuels such as, gasoline, diesel, and natural gas. Due to the existing distribution and supply infrastructure these fuels are attractive choices [1,2,17,18] to generate hydrogen for use by fuel cells. However, gasoline has sulfur concentrations in the range of 50–300 ppm, and the concentration of sulfur in diesel grade fuel is higher (up to 0.5%) than that of gasoline. To reduce air pollution from sulfur dioxide, the sulfur content of fuels has been regulated with continuing efforts to reduce sulfur content in the US. The lowest level currently required by regulation is California reformulated gasoline at 30 ppm sulfur.

For many years, nickel has been the most suitable metal for steam reforming of hydrocarbons. The current steam reforming catalysts are mainly nickel supported on refractory alumina and ceramic magnesium aluminate. These supports provide high crush strength and stability [19]. However, coke formations [20] and sulfur poisoning [21,22] are two major problems associated with nickel catalyst. The formation of coke during the steam reforming of hydrocarbons results mainly from catalytic reactions. For nickel catalysts, filamentous carbon is formed at the surface of the metal particle by a consecutive process of formation, diffusion, and dissolution [19,21]. As the coke gradually is produced, the degradation of the catalyst is accelerated until the catalyst is disintegrated by coke and continuation of catalyzed reforming becomes impossible. Coking is an even more serious problem when reforming heavy hydrocarbon fuels such as gasoline and diesel.

The precious metal (ruthenium, rhodium)-based catalysts have been reported to be more effective catalysts for steam reforming by preventing the carbon deposition and proposed to replace conventional base metal for steam reforming in fuel cell applications [23]. Ruthenium-based (Ru/Al_2O_3) catalyst has been used for steam reforming of hydrocarbons while preventing the carbon deposition [24–26]. Suzuki et al. [26] has successfully conducted a long-term (8000 h) test of steam reforming of desulfurized kerosene ($C_{10}H_{22}$ with <0.1 ppm sulfur) using Ru/Al_2O_3-CeO_2 catalyst and reported that the sulfur resistance was dramatically improved through the addition of CeO_2 to Al_2O_3. When the same catalyst was used for steam reforming of kerosene (with 30–55 ppm sulfur), the conversion of kerosene was decreased to 85.5% after 25 h on stream.

Therefore, catalysts with improved sulfur and coke resistance for steam reforming of readily available hydrocarbons, such as gasoline and diesel are highly desirable. Such catalysts must also have high activity, selectivity, and durability. We have developed our proprietary ITC catalyst series for steam reforming of various hydrocarbons, including natural gas, *iso*-octane, retail gasoline, and surrogate diesel. Our catalyst is a bimetallic compound supported on the high surface area Al_2O_3 treated with oxide having oxygen ion conducting properties. We have also tested our catalyst for reducing the concentration of CO in the crude reformate using water gas shift reaction. The test results are reported in this paper.

2. Experimental

The ITC catalysts for our tests were prepared according to our proprietary formulations. The Al_2O_3 pellet (0.125 in.) catalyst support (Alfa Aesar, SA = 90 m^2/g) was ground and sieved. Particles in the range of 300–500 μm were treated and then used as catalyst support. The catalysts were prepared by impregnating with metal salt solutions and followed by drying at 150 °C for 30 min and calcinated in air at 600 °C for 1 h. The total metal loading was <1.5 wt.% of the supporting materials. The nickel catalyst used for comparison to our proprietary catalyst was prepared by impregnating nickel salt solution with Al_2O_3 (300–500 μm). Then it was dried at 150 °C for 30 min and calcined at 600 °C for 1 h. The same process was repeated once. The nickel concentration was 12 wt.%. Chlorides were used as all metal precursors for the preparation of catalysts.

The steam reforming reactions were conducted in a packed bed reactor. Typically, about 3–5 g of reforming catalyst was packed in a 0.5 in. stainless steel tube with a thermocouple inserted in the bottom of the tube. The thermocouples contacted the catalyst bed. The catalyst was activated by reduction in pure hydrogen (100 sccm) at 600 °C for 3 h. Liquid hydrocarbon and water were introduced and vaporized in a pre-heater, and then fed into the catalyst bed at atmospheric pressure. The steam/C ratio was varied for different hydrocarbons. The temperature of the catalyst bed was set and maintained using a temperature controller. For methane and natural gas reforming, the gas was fed into the reactor from pressurized gas cylinders with mass flow controller regulating the gas flow rates. All experiments were conducted at atmospheric pressure.

iso-Octane (>99%), toluene (>99.5%), dodecane (95%), and hexadecane (>99%) were purchased from Sigma–Aldrich and used in this investigation without further treatment. Retail regular-grade gasoline was obtained from Citgo gas station. 1,4-Thioxane (98%, Sigma–Aldrich) was added to the hydrocarbons as the sulfur compound. It was selected because it has boiling point close to the hydrocarbons and is highly soluble in these hydrocarbons that we used in this study. Presumably, the selection of this sulfur compound does not make difference due to the mechanism that sulfur interacts with catalysts [21]. Helium (high purity, GC carrier gas), hydrogen (pre-purified, reduction), methane (pre-purified), and natural gas (93.5% CH_4, 3.8% C_2H_6, 1.0% C_3H_8, 1.2% N_2, 0.5% CO_2, with other trace C_4–C_6 and <38 ppm sulfur compounds) were supplied by Oxarc.

The raw reformate was first cooled to condense the water. The dry product gas was then switched to either a gas chromatograph (SRI 8160C) equipped with both TCD and FID detectors to determine the reformate composition or to a gas collection setup to measure the gas flow rate. The GC separation columns are packed with silica gel and molecular sieve 5A. Lead acetate paper was initially used to detect the presence of H_2S by exposing the paper to the reformate gas stream. The conversion of hydrocarbons was calculated by dividing the sum of the carbons from C_1 products (CO, CO_2, and CH_4) by the total carbons in the feeding hydrocarbons.

3. Results and discussion

3.1. Steam reforming of iso-octane and gasoline

The product gas composition (dry basis) from steam reforming of *iso*-octane using our catalyst (ITC) at different temperatures is shown in Fig. 1. Carbon monoxide concentration increased from <5 to about 20% as the reforming temperature increased from 650 to 800 °C. The concentration of hydrogen dropped from its highest concentration of about 76 to 70% as the temperature increased from 650 to 800 °C. The conversion of *iso*-octane is also shown in Fig. 1. At 650 °C only about 25% of *iso*-octane was converted to C_1 products, while nearly 100% conversion was obtained at 800 °C. The time on stream (TOS) at every different temperature was 2 h.

At the same steam/C ratio and pressure as the above reaction, the equilibrium composition of an *iso*-octane/steam system at different temperatures was calculated and is shown in Fig. 2. The equilibrium composition was calculated using HSC Chemistry program [27]. When the amounts and temperatures of all reactants and their phases are specified, the amounts of products at equilibrium in isothermal and isobaric conditions are calculated based on the Gibbs energy minimization method. The system yields the highest hydrogen concentration at a temperature of about 650 °C. As the temperature increases, slight decreases

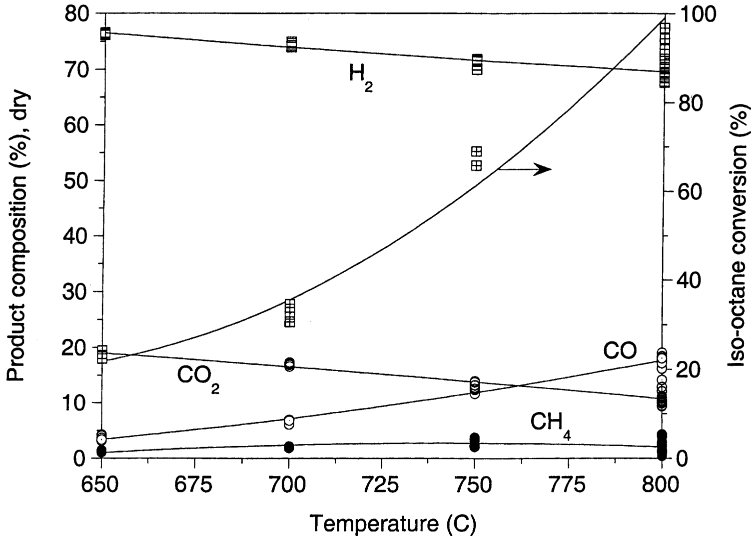

Fig. 1. Product composition (H_2, CO, CO_2, and CH_4) and *iso*-octane conversion for steam reformed *iso*-octane at different reaction temperatures using 8.0 g ITC catalyst; ratio of H_2O/C was 3.6; *iso*-octane feed rate was 0.28 g/min.

in both H_2 and CO_2 concentration and increases in CO concentration are due to a reverse water gas shift reaction. These results are similar to the experimental results shown in Fig. 1. The small amount of methane present in the product as shown in Fig. 1 may be due to the methanation reaction [22] ($3H_2 + CO \leftrightarrow CH_4 + H_2O$, $4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O$) at a lower temperature after removal of the product gas mixture

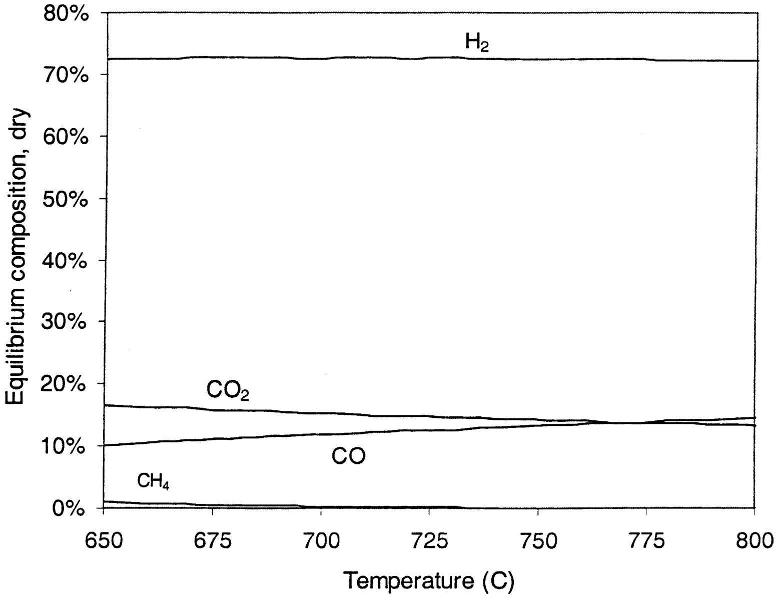

Fig. 2. Equilibrium composition of H_2, CO, CO_2, and CH_4 at different temperatures for steam/*iso*-octane system; ratio of H_2O/C was 3.6; pressure was 1 atm.

from the catalyst bed. Similar result is also observed during autothermal reforming of *iso*-octane [28].

Despite the high hydrogen and low CO concentrations, a low reaction temperature, for instance 650 °C, is not desirable because of low conversion of *iso*-octane. Our experimental results have shown that a complete conversion of *iso*-octane requires the reaction temperature to be close to 800 °C.

The stable performance of the catalyst during a 70 h run has led us to conduct a longer-term test of the durability of the catalyst during steam reforming of *iso*-octane. The reaction temperature was set at 800 °C to ensure a complete conversion of *iso*-octane. Fig. 3 shows the product composition over a 300 h test. The hydrogen concentration was sustained at about 70% throughout the test, while CH_4 concentration was very low, typically $<1\%$. The catalyst maintained its activity and selectivity for the entire 300 h.

After stable performance of the catalyst was demonstrated for steam reforming of *iso*-octane, 50 ppm sulfur was added to the *iso*-octane to test for sulfur tolerance. Fig. 4 shows the product composition for a 160 h test with the ITC catalyst. The hydrogen concentration is about 65% on the dry basis. The presence of hydrogen sulfide (H_2S) was indicated by the darkening of lead acetate paper exposed to the product gas. This darkening occurred shortly after initiating the reaction. The H_2O/C ratios, reaction temperatures, and space velocities were the same for this test as that shown in Fig. 3. However, the concentrations of both methane and CO are higher than those shown in Fig. 3. The presence of sulfur and inappropriate injection of both liquid water and fuel are two possible causes. The large scatter of experimental data shown in Fig. 4 was predominantly caused by inappropriate liquid injection.

As a comparison, a nickel catalyst was also tested at the same conditions for the steam reforming of *iso*-octane with 50 ppm sulfur. The nickel catalyst had high activity initially, but it quickly lost its activity (Fig. 5). The concentration of methane increased from 0 to over 10% in 8 h, while hydrogen concentration dropped by over 10% during the same time period. The total product gas flow rate also significantly decreased, indicating a decrease in conversion of *iso*-octane. After 8 h, it became difficult to feed the reactants due to fouling of the reactor tube by carbon formation. Using a commercial nickel catalyst for steam reforming of low sulfur bearing kerosene (0.1 ppm sulfur), Suzuki et al. [26] has reported that the conversion of kerosene decreased to 72.3% after 24 h on stream and suggested that deactivation of the nickel catalyst was

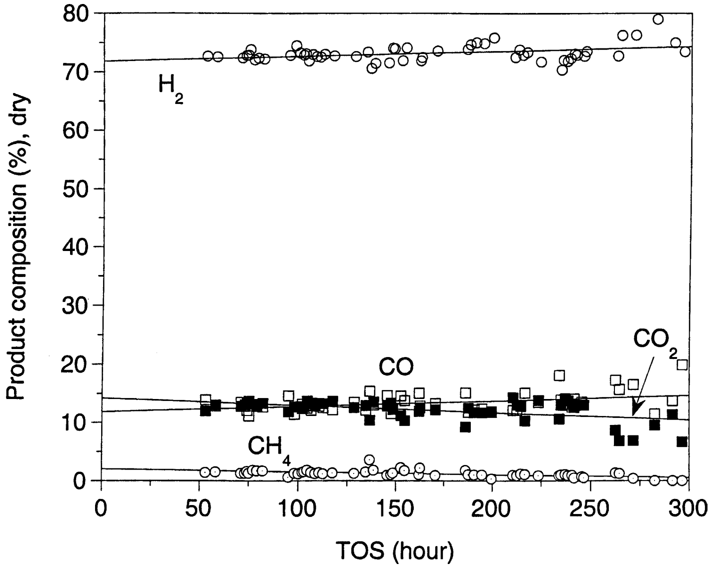

Fig. 3. Product composition (H_2, CO, CO_2, and CH_4) for steam reformed *iso*-octane using 5.0 g ITC catalyst at 800 °C; ratio of H_2O/C was 3.6; *iso*-octane feed rate was 0.11 g/min.

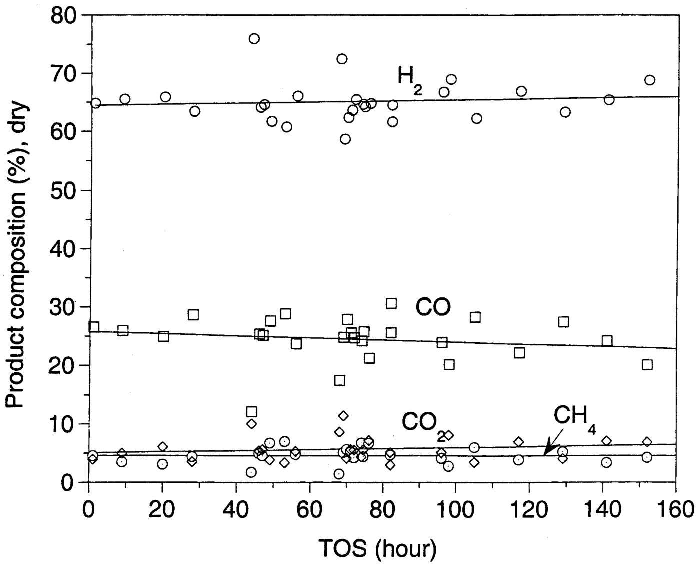

Fig. 4. Product composition (H_2, CO, CO_2, and CH_4) for steam reformed *iso*-octane with 50 ppm sulfur using 5.0 g of ITC catalysts at 800 °C; ratio of H_2O/C was 3.6; *iso*-octane feed rate was 0.11 g/min.

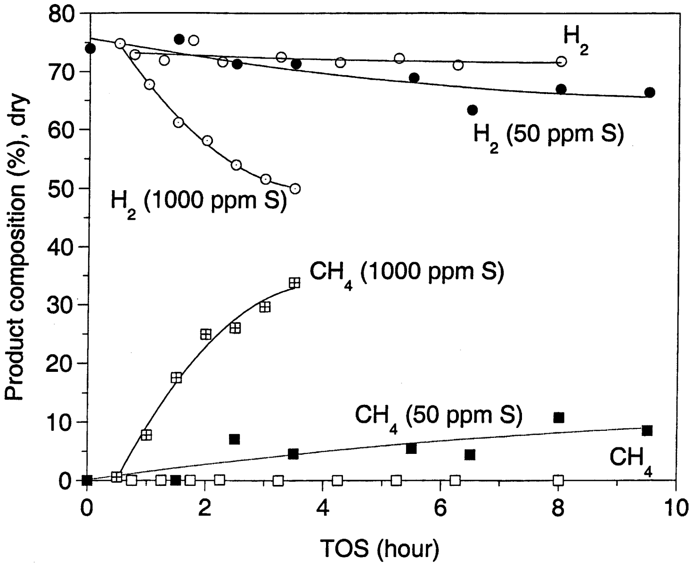

Fig. 5. Comparison of product composition (H_2 and CH_4) for steam reformed pure *iso*-octane and *iso*-octane with 50 and 1000 ppm sulfur using 5.0 g of Ni/Al_2O_3 catalysts at 800 °C; ratio of H_2O/C was 3.6; *iso*-octane feed rate was 0.11 g/min.

predominantly caused by carbon deposition. In our study, the sulfur concentration of 50 ppm is much higher. Both sulfur poisoning and coke formation are believed to degrade the performance of nickel catalyst with sulfur poisoning being predominant cause. The sulfur poison may also accelerate the coke formation. This conclusion is validated by another independent test with the same nickel catalyst, which shows that stable hydrogen product distribution and flow rate were obtained during steam reforming of pure *iso*-octane (without sulfur) over the same time period of 8 h on stream (Fig. 5). Sulfur is well known to readily poison nickel catalysts by the formation of stable surface metal sulfides and thereby prevent reactants (steam, fuel) from adsorbing at the surface. It also results in sulfating the support. Typically, the content of sulfur needs to be reduced to 0.2 ppm or lower to avoid poisoning nickel catalyst [19,21,22]. Deactivation of nickel catalysts by sulfur poisoning has also been reported for both partial oxidation [10] and autothermal reforming [13].

We further tested the ITC catalyst by increasing the sulfur concentration of the *iso*-octane to 100 ppm. Fig. 6 shows the product composition for a 220 h test. The concentration of hydrogen remained at about 70% (dry) during the entire 220 h, while methane concentration was <1% during the same time period. The CO concentration of slightly less than 20% on dry basis is lower than that shown in Fig. 4. A higher H_2O/C ratio (=4.0) shifted the water gas shift reaction ($H_2O + CO \leftrightarrow CO_2 + H_2$) toward producing more hydrogen, thus lowering CO concentration.

A 120 h intermittent run of *iso*-octane steam reforming with 1000 ppm sulfur using the ITC catalyst was also conducted. The concentration of hydrogen dropped from its average 73.8% for the first 10 h to an average 69.6% for the last 10 h. The methane concentration increased from 2 to 7% during the 120 h test. The organic sulfur component (thioxane) was converted to H_2S that was detected by lead acetate paper shortly after the reaction started. The same test was also conducted with nickel catalyst. The nickel catalyst exhibited a rapid deactivation due to sulfur poisoning. The hydrogen concentration dropped from 74.8 to 50%, while methane concentration increased from 0.6 to 33.8% in 3.5 h (Fig. 5).

Most of our catalyst tests were conducted using a 0.5 in. stainless steel tube, since it provides an easy way to load and unload the catalyst. As we discussed above, our strategy is to use a microchannel reactor design to develop a miniature fuel reformer with improved performance. The steam reforming reaction is a highly endothermic reaction and is heat transport limited. The microchannel reactor offers rapid mass and heat transport through the engineered design and also minimize diffusional resistance induced by limitation of mass transfer. This provides a higher activity per unit volume than a conventional reactor. Therefore, it allows for higher space velocity, resulting in lower catalyst volume requirements and an overall

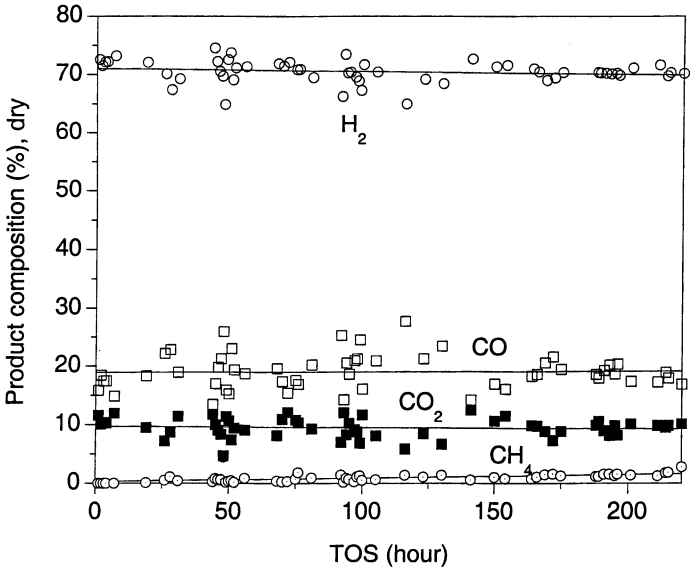

Fig. 6. Product composition (H_2, CO, CO_2, and CH_4) for steam reformed *iso*-octane with 100 ppm sulfur using 5.0 g ITC catalyst at 800 °C; ratio of H_2O/C was 4.0; *iso*-octane feed rate was 0.10 g/min.

more compact reactor design. We have also tested the ITC reforming catalyst within our microchannel reactor. A micro-burner was integrated into the reactor, and the reaction was heated by catalytic combustion of methane. The reactor was made of two stainless steel plates with machined channels (catalyst bed) and manifolds (the passage of reactant and product). The reaction temperature was controlled by the flow rate of methane to the burner. A hydrocarbon mixture simulating gasoline (60% *iso*-octane, 20% toluene, and 20% dodecane) with 476 ppm sulfur was used for the test. During the first 20 h, the concentration of CH_4 was very low (<1%), after that, it increased and stabilized at 3–4%. The test was terminated after 67 h due to leakage induced by oxidative erosion of sealing material. The high concentration of CH_4 after first 20 h may have been caused by a low H_2O/C ratio or/and methanation due to the failure of microchannel reactor sealing. An improved sealing mechanism is needed for the reactor that is operated at high temperature (800–850 °C).

The results of testing of our ITC catalyst with retail gasoline are shown in Fig. 7. Gasoline normally contains some sulfur compounds in concentrations ranging from 50 to 300 ppm. During the entire testing period, the catalyst maintained its high selectivity and activity. The product hydrogen concentration was above 70% (dry basis). The low CO concentration for the test was a result of a high steam/C ratio (=6.6). The test was conducted intermittently for 50 h without any noticeable deactivation of the catalyst. A wide range (from 2.6 to 5) of H_2O/C ratio was also used to reform the gasoline. At reaction temperature of 800 °C, a low H_2O/C ratio of 2.6 resulted in an incomplete gasoline conversion to C_1 product and coke formation. A typical gasoline contains >55% paraffinic, <10% olefinic, <35% aromatic hydrocarbons. Steam reforming of aromatic hydrocarbons requires a higher temperature than that of paraffinic hydrocarbons similar to the reported results for autothermal reforming [13]. In addition, steam reforming of olefinic and aromatic hydrocarbons existing in gasoline also require a higher H_2O/C ratio than that required by *iso*-octane to avoid the coke formation and subsequent catalyst deactivation. The results of recent tests have shown that a H_2O/C ratio of about 4.0–4.5 and temperature above 835 °C may be required for the complete conversion (to C_1 product) of gasoline.

3.2. Steam reforming of hexadecane, $C_{16}H_{34}$

Hexadecane was used as a surrogate for diesel fuel to test our catalyst for reforming heavier hydrocarbons. Fig. 8 shows the product gas composition and

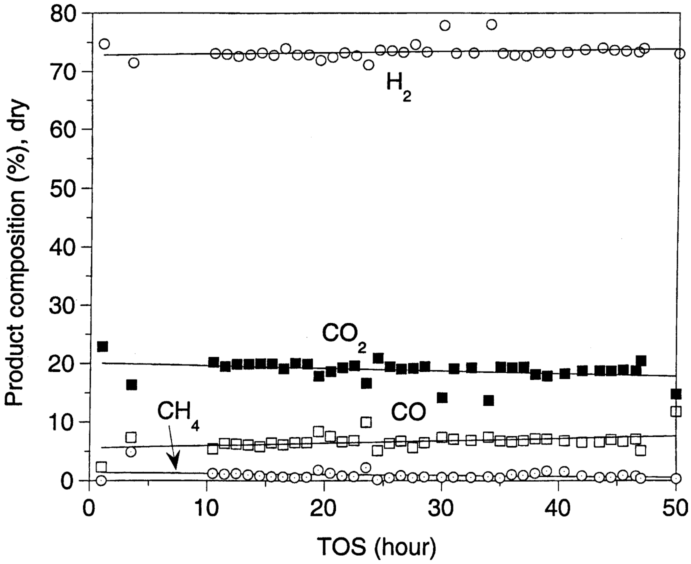

Fig. 7. Product composition (H_2, CO, CO_2, and CH_4) for steam reformed retail gasoline (regular grade) using 3.0 g ITC catalyst at 800 °C; ratio of H_2O/C was 6.6; gasoline feed rate was 0.12 g/min.

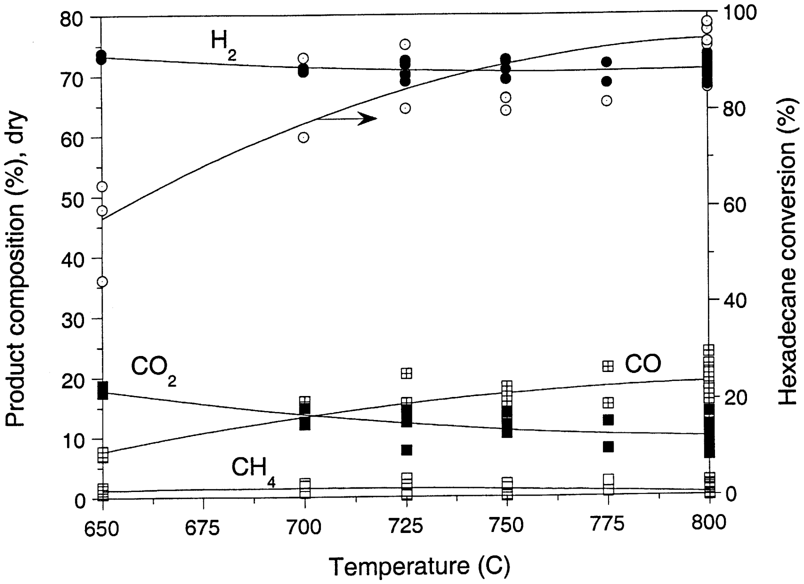

Fig. 8. Product composition and hexadecane conversion for steam reformed hexadecane at different temperatures using 5.0 g ITC catalyst at 800 °C; ratio of H_2O/C was 2.7; hexadecane feed rate was 0.14 g/min.

conversion of hexadecane at the different temperatures. The time on stream (TOS) at every different temperature was 2 h. The product composition has a trend similar to the steam reforming of *iso*-octane shown in Fig. 1. The concentrations of both H_2 and CO_2 decreased as the temperature increased, while CO concentration increased with increase of temperature. The increase of CO concentration is attributed to reversed water gas shift reaction that is favored at high temperature. About 45% of hexadecane was converted to C_1 product at temperature of 650 °C. A nearly complete conversion was obtained at about 800 °C. At 700 °C, the conversion of hexadecane was slightly less than 80%, but only about 40% of *iso*-octane was converted to C_1 product at the same temperature as shown in Fig. 1, indicating that hexadecane is readily reformatted by steam due to its long chain structure. During a 73 h test, the hydrogen concentration stayed at about 70% (Fig. 9). There was virtually no methane produced during the test period. The comparison of product gas composition with one calculated from thermodynamics (70.7% H_2, 16.9% CO, 12.3% CO_2, 0% CH_4) indicates that the reforming reaction reached its equilibrium conversion in our tests.

The catalyst has also shown high hydrogen selectivity for the steam reforming of hexadecane. Hexadecane is a 16-carbon heavy hydrocarbon, coke formation due to cracking and various intermediate reactions is believed to be more likely than for *iso*-octane during the steam reforming. Hydrocarbons with low number of carbon, such as CH_4, C_2H_4, and C_2H_6 may also be produced during hexadecane reforming. However, our 73 h test results showed that neither coke nor light hydrocarbons were produced by the reaction.

The results also indicate that a low steam/C ratio may be feasible for reforming heavier hydrocarbons as hexadecane. The low steam/C ratio required less energy for pumping, heating and recycling excess water, thus increasing overall system energy efficiency.

3.3. Steam reforming of natural gas

The ITC catalyst was also examined for its performance in reforming natural gas, which is a more likely choice for fuel cells used in residential applications. The first test was conducted at different temperatures for steam reforming of methane, the major compound of natural gas. The steam/C ratio was 3.0, and the methane gas hourly space velocity was 12,000 h^{-1}. At 750 °C, nearly complete conversion of methane was obtained, while only 30% conversion was achieved when the reaction temperature decreased to 550 °C

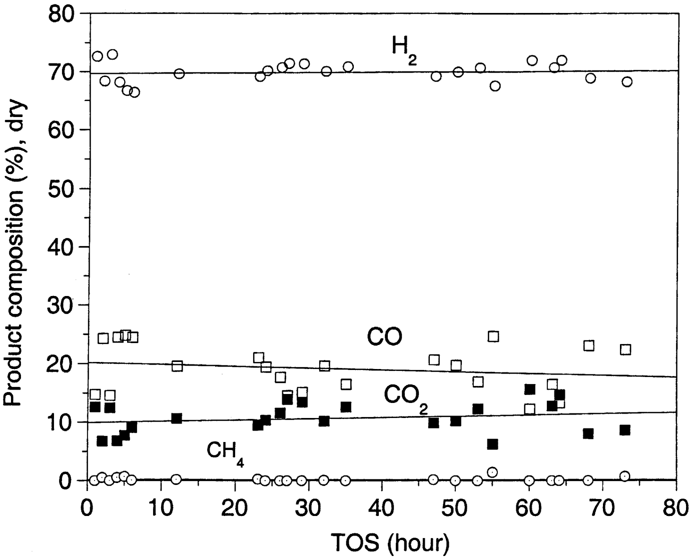

Fig. 9. Product composition (H_2, CO, CO_2, and CH_4) for steam reformed hexadecane using 5.0 g ITC catalyst at 800 °C; ratio of H_2O/C was 2.7; hexadecane feed rate was 0.14 g/min.

(Fig. 10). Since methane is the major compound in natural gas, it is likely that complete conversion of natural gas also requires a reaction temperature of about 750 °C or higher. The product gas composition for steam reforming of methane at different temperatures is also shown in Fig. 10. At 750 °C, hydrogen concentration reaches equilibrium at about 77%. At the same temperature, the equilibrium composition for CO and

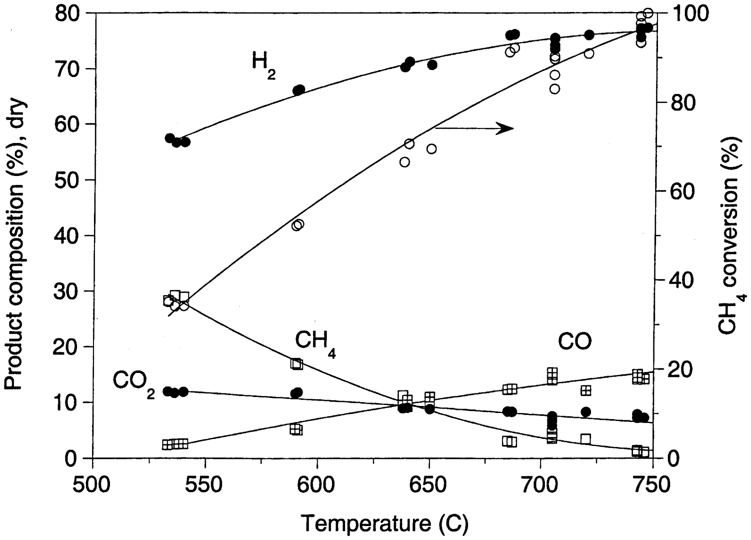

Fig. 10. Percent conversion and product composition (H_2, CO, CO_2, and CH_4) for steam reformed methane at different temperatures using 1.45 g ITC catalyst; ratio of H_2O/C was 3.0; methane feed rate was 300 ml/min.

CO_2 are 14 and 8.5%, respectively. These equilibrium concentrations are very close to the experimental concentrations obtained.

Accordingly, we conducted natural gas steam reforming tests at 760 °C with steam/C ratio of 3.0. The catalyst showed sustained performance for the entire 150 h test period (Fig. 11). The product gas concentration is very closed to the equilibrium composition that is calculated based on methane at the same conditions ($H_2O/C = 3.0$, and 1 atm pressure). No carbon formation was observed on the used catalyst. These results show that the ITC catalyst can also be used for steam reforming of natural gas.

This test was terminated after 153 h on stream due to the development of a leak in the reactor tube. Due to limited heat conduction, the temperature at the outside of reactor tube was considerably higher (about 150 °C) than that of the catalyst bed in order to maintain the reaction temperature of 760 °C. The long exposure time of the reactor tube to high temperature and the highly reducing gas environment were probable causes for the failure. This shows the necessity to use much higher quality and priced materials for the reactor. Our microchannel reactor design allows us to overcome this problem. The microchannel design significantly increases the surface area for heat conduction, and also minimize diffusional resistance induced by limitation of mass transfer, providing a higher activity per unit volume than a conventional reactor. Therefore, it allows for high space velocity, resulting in lower catalyst volume and a compact reactor design. A microchannel design will also allow a quick startup and dynamic response to hydrogen demand.

3.4. Water gas shift reaction

It is well recognized that the concentration of CO in the reformate gas has to be dramatically reduced to be suitable for a PEM fuel cell (i.e. 20 ppm or less). As an option for CO cleanup, the integration of a water gas shift reaction into our reformer is being considered. A commercial high temperature water gas shift catalyst was compared (C12; $Fe/Cr/Al_2O_3$, from Sud-Chemie, KY) with the ITC-HTS catalyst (same as ITC reforming catalyst but with slightly higher metal loading) prepared in house. The tests were evaluated by conducting the reaction at different temperatures and space velocities. The shift reactor was connected to the reforming reactor; so, the feed to the shift reactor was the crude reformate from the *iso*-octane reforming reaction. Typically, the composition of wet reformate was around 42.3% H_2, 0.9% CH_4, 9.2% CO, 7.5% CO_2, and

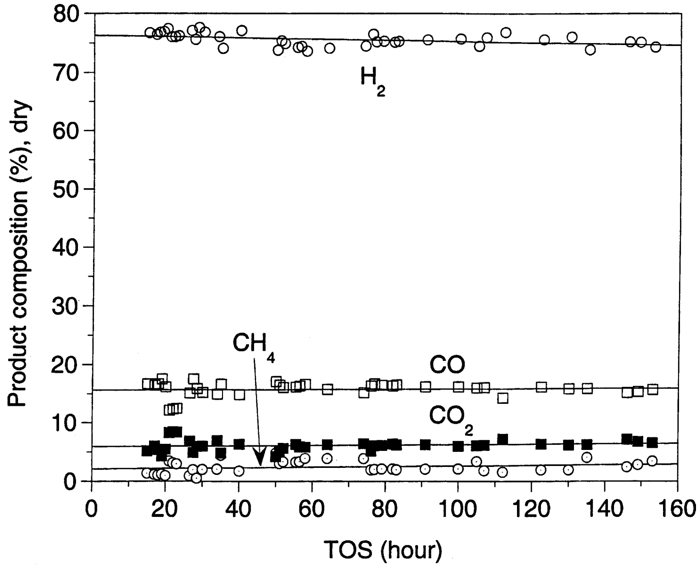

Fig. 11. Product composition (H_2, CO, CO_2, and CH_4) for steam reformed natural gas using 1.45 g ITC catalyst at 760 °C, ratio of H_2O/C was 3.0; natural gas feed rate was 300 ml/min.

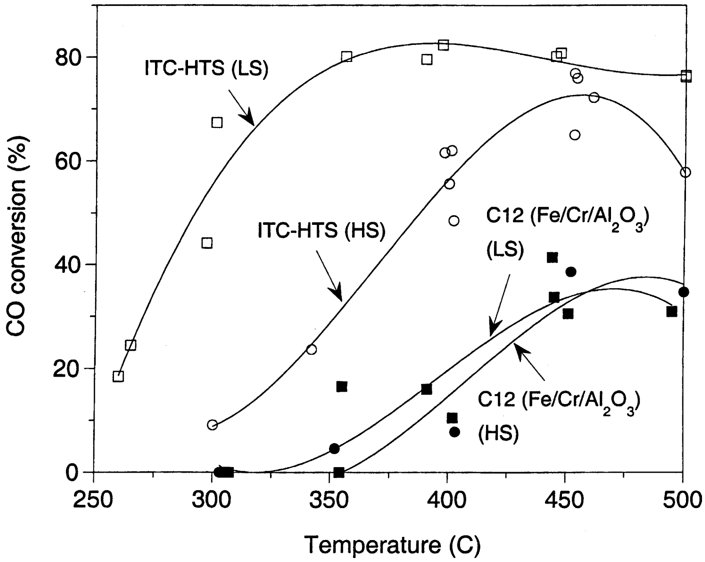

Fig. 12. CO conversions for water gas shift reaction using ITC-HTS and commercial C12 (Fe/Cr/Al_2O_3) catalysts at different temperatures. The tests were conducted at both high space (HS, dry GHSV = 66,000 h^{-1}) and low space (LS, dry GHSV = 12,000 h^{-1}) velocities; the feed to the water gas shift reactor was the product of steam reforming of *iso*-octane.

40.1% H_2O. At both higher and lower space velocities, the ITC-HTS catalyst had higher CO conversion than the commercial C12 catalyst. For ITC-HTS catalyst over 80% CO was converted (Fig. 12) at lower space velocity (dry GHSV = 12,000 h^{-1}) when the reaction temperature reached 350 °C, while at higher space velocity (dry GHSV = 66,000 h^{-1}) only about 30% CO was converted at the same temperature of 350 °C.

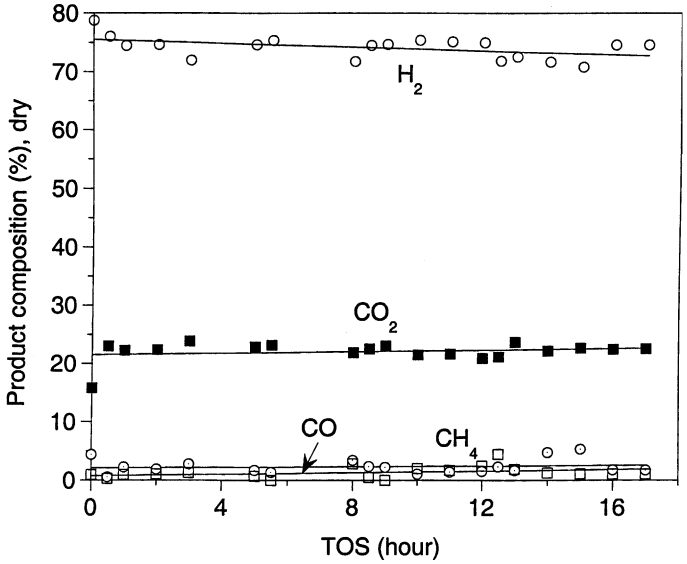

Fig. 13. Composition of H_2, CO, CO_2, and CH_4 after *iso*-octane steam reforming and water gas shift reactions; 3.0 g ITC-HTS catalyst at 400 °C; 3.5 g ITC-LTS catalyst at 250 °C; steam reforming feed rate of 0.11 g/min and H_2O/C of 3.6 with 3.0 g ITC catalyst.

The conversion of CO at both higher and lower space velocities followed the similar trend: it increased as increases of temperatures, then decreased as further increase of temperatures. The highest CO conversion of 76 and 82% occurred at about 450 °C for higher space velocity and at about 400 °C for lower space velocity. After these the CO conversion decreased with the increases of temperature due to reverse water gas shift reaction that is favored at high temperatures. For C12 catalyst, the space velocity does not have significant impact on the CO conversion at the temperatures ranging from 300 to 500 °C. The highest CO conversion was about 40% at 450 °C as shown in Fig. 12.

A test was conducted integrating both high temperature water gas shift and low temperature water gas shift reactors with our reforming reactor. Fig. 13 shows the product composition for a 17 h test. The feed to the water gas shift reactor was the raw reformate from *iso*-octane reforming reaction. The CO concentration was reduced to $<1\%$ (dry basis) by the water gas shift reaction during 17 h test (Fig. 13). The operating temperatures were 400 and 250 °C for high temperature water gas shift reaction and low temperature water gas shift reaction, respectively. In order to further decrease the CO concentration, a selective oxidation of CO by oxygen (from air) is required.

4. Conclusion

InnovaTek has developed a proprietary catalyst formulation for the steam reforming of various hydrocarbons, such as *iso*-octane, surrogate gasoline and diesel. The catalyst has shown very stable performance for the steam reforming of *iso*-octane for over 300 h. No carbon deposition was found during the entire test period. The sulfur tolerance of our catalyst has been evaluated with the addition of sulfur in these hydrocarbons. The sustained performance (over 200 h) of the catalyst in reforming fuels with 100 ppm sulfur to produce hydrogen at nearly maximum stoichiometric concentrations is a significant milestone in our development effort. Reduction of CO concentration to $<1\%$ has been accomplished using our water gas shift catalysts. This achievement will allow further development of our fuel processing technology for multiple fuel types.

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