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Lower-Temperature Catalytic Performance of Bimetallic Ni–Re/Al₂O₃ Catalyst for Gasoline Reforming to Produce Hydrogen with the Inhibition of Methane Formation

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The lower-temperature catalytic performance of bimetallic Ni–Re/Al₂O₃ catalyst for gasoline reforming to produce hydrogen with the inhibition of methane formation is studied. The complete conversion of gasoline with a very low methane concentration of near 0 in the product is achieved for steam reforming of gasoline on bimetallic Ni–Re/Al₂O₃ catalyst at a lower reaction temperature of 753 K. The high gasoline conversion of 100% with the low concentration of methane product is maintained very well during 700 h of time on stream for steam reforming of the gasoline fuel containing about 3.8 ppm sulfur at the lower reaction temperature. The low concentration of methane in the reforming product is effectively suppressed further by the addition of oxygen to the reaction system. Therefore, hydrogen generation from gasoline is feasible even at lower temperatures because of the unique high activity of the bimetallic Ni–Re/Al₂O₃ catalyst. Hydrogen production is enhanced by the inhibition of methane formation on the catalyst.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been considered as the most-appropriate power sources for future-generation vehicles because of their higher energy efficiency and lower emissions. Higher energy efficiency itself will lead to a reduction in carbon dioxide emissions. Atmospheric pollutants such as CO and NO_x will not be formed in the fuel cells. Hydrogen is the ideal fuel for PEMFCs. However, the hydrogen-fueled vehicle is less attractive because of the lack of hydrogen refuelling infrastructure and the low energy density of existing hydrogen storage technology. The alternative is to carry liquid fuels that have higher energy densities and convert them to a hydrogen-rich gas via an on-board fuel processor. Therefore, the successful development of a fuel-cell-powered vehicle will be directly dependent on the development of the on-board fuel processor. The liquid fuels may be methanol, gasoline, or diesel. Gasoline is the most commonly used transportation fuel in vehicles. The energy density of gasoline is higher than that of methanol, and gasoline is more readily available than methanol. Recently, some progress on the development of sulfur-tolerant and coke-resistant catalysts for steam reforming of transportation fuels such as a surrogate of diesel, desulfurized kerosene, and a mixture of MCH and toluene as model gasoline has been reported^{1–7}. Methane is a main side product for hydrogen generation from liquid fuel by reforming and it is a component of greenhouse gases. Methane formation

will also lead to a decrease in hydrogen concentration in the product. Methane concentration in the product is dependent on the performance of the catalyst used. Hydrogen production from hydrocarbons by catalytic partial oxidation or steam reforming generally requires high temperatures (1173 K). The automotive fuel processor is distinct from the larger industrial-scale stationary hydrogen generators. A feasible lower-temperature reforming process is more desirable for on-board hydrogen generation from gasoline. A noble metal Rh-based catalyst for the partial oxidation of C₁–C₁₀ hydrocarbons to produce hydrogen at lower temperatures of 773–873 K was recently reported by Newson et al.⁸ It is of importance that a green process be developed for the production of hydrogen from gasoline that inhibits methane formation at lower reaction temperatures. In the present paper, the enhancement of hydrogen production and inhibition of methane formation in the product by optimizing the reaction conditions for gasoline reforming are studied.

2. Experimental Section

2.1. Catalyst Preparation. Ni/Al₂O₃ was prepared by impregnating activated Al₂O₃ with Ni(NO₃)₂·6H₂O aqueous solutions, followed by drying at 383 K for 6 h and calcination at 773 K for 6 h. The specific surface area of the Al₂O₃ support is about 120.66 m²/g. The particle size of the Al₂O₃ support is 75 μm (about 200 meshes). Ni–Re/Al₂O₃ was prepared by impregnating the Ni/Al₂O₃ with NH₄ReO₄ aqueous solutions, followed by drying at 383 K for 6 h and calcination at 773 K for 6 h. The loadings of Ni and Re on the Ni–Re/Al₂O₃ catalyst are 10 and 2% respectively.

2.2. Catalytic Tests and Product Analysis. Catalytic tests for steam reforming at a high WSV of gasoline were carried out with about 0.1–0.2 g of catalyst placed in a fixed-bed, continuous-flow quartz reactor. Catalytic tests for steam reforming at a lower WSV

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Table 1. Analysis Results of the Premium Gasoline Composition

density (g/cm ³ , 15 °C)	0.7458
total content of sulfur (ppm)	3.8
H:C ratio	1.746
average mol wt	91.3
research octane number (RON)	99.7
paraffin (P)	7.44
isoparaffin (I)	34.55
olefin (O)	18.49
naphthene (N)	2.33
aromatics (A)	37.20

of gasoline were carried out with about 4 g of catalyst placed in a fixed-bed, continuous-flow stainless steel reactor. Before the steam reforming reaction, the catalysts were first pretreated by flowing air at 873 K for 0.5 h and then reduced by H₂/N₂ at 793 K for 2 h. The flow rates of gasoline and water (H₂O) were controlled by liquid pumps, and the substances were preheated in an evaporator before being passed through the catalyst bed in the reactor. The flow rate of N₂ was controlled by a mass-flow rate controller. Two kinds of gasoline fuels, model and premium, were used for the catalytic tests. The premium gasoline fuel contains about 3.8 ppm sulfur, and the model gasoline is composed of about 75% methylcyclohexane (MCH) and 25% toluene without sulfur. The composition analysis results of the premium gasoline are shown in Table 1.

The reforming products were withdrawn periodically from the outlet of the reactor and analyzed by two on-line gas chromatographs, Shimadzu GC-14B and GC-8A, equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD), respectively. Hydrocarbon products were separated on a 4 mm × 1 m Porapak P column, and CH₄, CO, CO₂, H₂, and N₂ were analyzed on a 4 mm × 1 m active carbon column. Conversion, selectivity, and formation rates of products were calculated by an internal standard analyzing method. The method is presented briefly as follows. Even if the total flow rate changed at the outlet from that at the inlet of the reactor ($F_{\text{total}}^{\text{inlet}}$, $F_{\text{total}}^{\text{outlet}}$), the flow rate of nonreactive internal standard gas (F_{st}) was kept constant.

$$F_{\text{st}} = F_{\text{total}}^{\text{outlet}} X_{\text{st}}^{\text{outlet}} = F_{\text{total}}^{\text{inlet}} X_{\text{st}}^{\text{inlet}}$$

Here, X_{st} refers to concentration of the internal standard gas. The formation rate of product i (F_i) can be calculated as

$$F_i = F_{\text{total}}^{\text{outlet}} X_i^{\text{outlet}} = F_{\text{total}}^{\text{inlet}} \frac{X_i^{\text{outlet}}}{X_{\text{st}}^{\text{outlet}}}$$

The conversion of liquid hydrocarbon (C_{HC}) was calculated on the basis of carbon balance. It was calculated by dividing the sum of carbon in gaseous products by the carbon in the feed, as in eq 1.

$$C_{\text{gasoline}} = \frac{(F_{\text{CO}}^{\text{outlet}} + F_{\text{CO}_2}^{\text{outlet}} + F_{\text{CH}_4}^{\text{outlet}})}{F_{\text{gasoline}}^{\text{inlet}}} \quad (1)$$

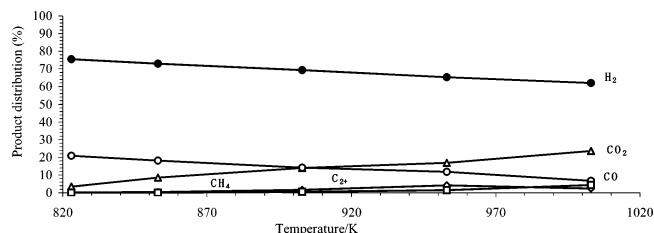
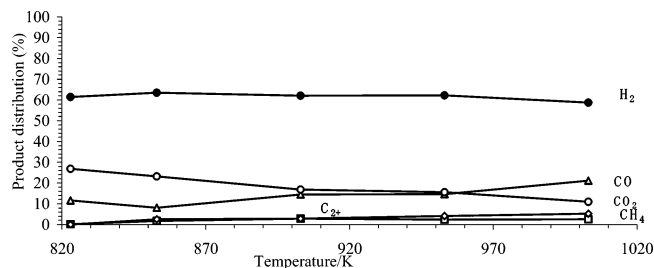
$F_{\text{gasoline}}^{\text{inlet}}$ is the flow rate of the gasoline feed and is controlled by a liquid pump. In the same way, H₂O conversion ($C_{\text{H}_2\text{O}}$) is calculated on the basis of oxygen balance by dividing the sum of oxygen in gaseous products by the oxygen in the feed, as in eq 2.

$$C_{\text{H}_2\text{O}} = \frac{(F_{\text{CO}}^{\text{outlet}} + 2F_{\text{CO}_2}^{\text{outlet}} - 2F_{\text{O}_2}^{\text{inlet}})}{F_{\text{H}_2\text{O}}^{\text{inlet}}} \quad (2)$$

$F_{\text{H}_2\text{O}}^{\text{inlet}}$ is the flow rate of water and is controlled by another liquid pump.

3. Results and Discussion

3.1. Dependence of Product Distribution on Reaction Temperature. The product distribution for steam reforming and oxidative steam reforming of the model gasoline fuel containing

**Figure 1.** Dependence of product distribution on reaction temperature for steam reforming of the model gasoline at a S:C ratio of 1.7:1 and a WSV of 12 h⁻¹.**Figure 2.** Dependence of product distribution on reaction temperature for oxidative steam reforming of the model gasoline at a S:O:C ratio of 1.7:0.8:1 and a WSV of 12 h⁻¹.

75% MCH and 25% toluene on Ni–Re/Al₂O₃ for a wide temperature range of 823–1003 K is investigated.

Dependence of product distribution on the reaction temperature for steam reforming of the model gasoline at a steam:carbon (S:C) ratio of 1.7:1 and a WSV of 12 h⁻¹ is shown in Figure 1. We can see from Figure 1 that the concentration of the hydrogen product is enhanced and the concentrations of CH₄ and C₂₊ hydrocarbons in the product are suppressed at lower reaction temperatures. The concentration of C₂₊ hydrocarbon products is 0 and the concentration of CH₄ product is near 0 for steam reforming at the lower temperatures below 823 K, as shown in Figure 1. Therefore, formation of the methane product is inhibited on the Ni–Re/Al₂O₃ catalyst at lower reaction temperatures. Steam reforming of gasoline is an endothermic reaction; partial oxidation of gasoline is an exothermic reaction. Oxidative steam reforming of gasoline may become an autothermal reaction, because the steam reforming reaction is combined with the partial oxidation reaction. The dependence of the product distribution on reaction temperature for oxidative steam reforming of the model gasoline fuel at a steam:oxygen:carbon (S:O:C) ratio of 1.7:0.8:1 and a WSV of 12 h⁻¹ is shown in Figure 2.

The concentrations of CH₄ and C₂₊ hydrocarbon components in the product are suppressed for oxidative steam reforming of the model gasoline fuel on Ni–Re/Al₂O₃ catalyst at lower temperatures, as shown in Figure 2. C₂₊ hydrocarbons are not formed, and the concentration of the CH₄ product is near 0 for oxidative steam reforming at a lower temperature of 823 K. However, it is different from the steam reforming reaction in that the concentration of the hydrogen product for oxidative steam reforming of the model gasoline fuel is not enhanced at lower temperatures. The concentration of hydrogen product for oxidative steam reforming of the model gasoline fuel changes little with reaction temperature, as shown in Figure 2. Gasoline conversion is dependent on the reaction temperature for both steam and oxidative reforming. The conversions of the gasoline for steam reforming and oxidative steam reforming at different temperatures are compared in Figure 3.

The conversion of the gasoline for oxidative steam reforming is evidently higher than that for steam reforming at the lower

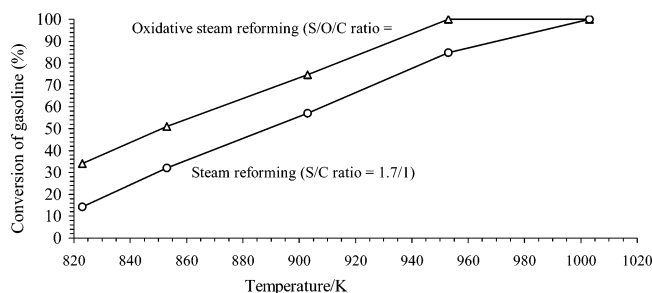


Figure 3. Dependence of the model gasoline conversion on reaction temperature for steam reforming and oxidative steam reforming at a WSV of 12 h⁻¹.

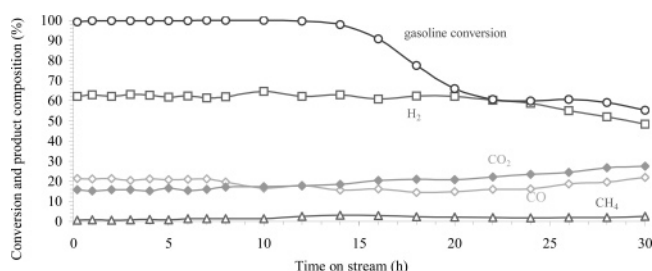


Figure 4. Conversion and product composition with time on stream for gasoline reforming with a S:O:C ratio of 1.7:0.8:1 on Ni/Al₂O₃ catalyst at 953 K and a WSV of 3 h⁻¹.

reaction temperatures. Therefore, the addition of oxygen is effective at promoting the conversion of gasoline at lower reaction temperatures. This indicates that the steam reforming of gasoline is promoted by the partial oxidation reaction. In addition, the lower reaction temperatures lead to the lower gasoline conversions both for steam reforming (S:C = 1.7:1) and oxidative steam reforming (S:O:C = 1.7:0.8:1) at a high WSV of 12 h⁻¹, as shown in Figure 3. A lower gasoline WSV should be required for achieving a higher conversion for the reforming at lower temperatures.

3.2. Performance of the Bimetallic Ni–Re/Al₂O₃ Catalyst for Reforming of Gasoline. Ni/Al₂O₃ is a traditional catalyst system for steam reforming of hydrocarbons. Recently, we reported the Re/HZSM-5 catalyst for dry reforming⁹ and the bimetallic Ni–Re/Al₂O₃ catalyst for steam reforming³ of hydrocarbons. The Re-containing catalyst is a novel, highly active catalyst system for reforming reactions of hydrocarbons to produce hydrogen. The catalytic performance of the bimetallic Ni–Re/Al₂O₃ catalyst and traditional monometallic Ni/Al₂O₃ catalyst for oxidative reforming of the premium gasoline fuel is shown in Figures 4 and 5, respectively.

The oxidative steam reforming tests were conducted at 953 K and a WSV of 3 h⁻¹ with a S:O:C ratio of 1.7:0.8:1. A

comparison between Figures 4 and 5 shows that the activity of the bimetallic Ni–Re/Al₂O₃ catalyst is maintained much better with time on stream than that of the monometallic Ni/Al₂O₃ catalyst for the oxidative steam reforming of the sulfur-containing gasoline fuel. Therefore, the bimetallic Ni–Re/Al₂O₃ catalyst exhibits a much-better coking resistance and sulfur tolerance than the monometallic Ni/Al₂O₃ catalyst, because of the interaction between Ni and Re. The structures of Ni/Al₂O₃, Re/Al₂O₃, and Ni–Re/Al₂O₃ are checked by XRD. The structure differences between the bimetallic catalyst of Ni–Re/Al₂O₃ and the monometallic catalyst of Re/Al₂O₃ or Ni/Al₂O₃ are shown in Figure 6.

By comparing the XRD patterns of Ni/Al₂O₃, Re/Al₂O₃, and Ni–Re/Al₂O₃ catalysts, we can clearly find that the crystal structure of the bimetallic Ni–Re/Al₂O₃ catalyst is different from that of the monometallic catalyst of Ni/Al₂O₃ or Re/Al₂O₃ because of the interaction of Ni and Re. The XRD results indicate that a new bimetallic active phase may be formed by alloying Ni with Re, which is more active than the monometallic catalyst.

3.3. Achievement of Complete Conversion of Gasoline with a Low Methane Concentration of Near 0 in the Product for Gasoline Reforming. Because of the unique high activity of the bimetallic Ni–Re/Al₂O₃ catalyst for gasoline reforming, hydrogen generation from gasoline by steam reforming is still feasible even at a lower temperature of 753 K. Figure 7 shows the time-on-stream results for steam reforming of the premium gasoline fuel containing about 3.8 ppm organic sulfur on the bimetallic Ni–Re/Al₂O₃ catalyst at a lower reaction temperature of 753 K and a lower gasoline WSV of 0.3 h⁻¹.

A high gasoline conversion of 100% with a low methane concentration of near 0 in hydrogen-rich product is obtained for steam reforming of the premium gasoline fuel on Ni–Re/Al₂O₃ catalyst at a lower temperature of 753 K and a lower gasoline WSV of about 0.3 h⁻¹. Complete conversion of gasoline into hydrogen-rich gas and inhibition of methane formation in the product are significant for highly efficient utilization of gasoline fuel and for the reduction of greenhouse gas emissions. Such a low reaction temperature also makes this a more feasible option for application as an automotive fuel processor for on-board hydrogen generation from gasoline. The high gasoline conversion of 100% with the low methane concentration of near 0 in hydrogen-rich product is maintained very well even after 700 h of time on stream. This indicates that the bimetallic Ni–Re/Al₂O₃ catalyst exhibits promising coking resistance for steam reforming of gasoline at a lower temperature of 753 K. The amount of coke deposited on the used catalyst after 700 h of time on stream was analyzed by the TG-DTA method. The amount of coke

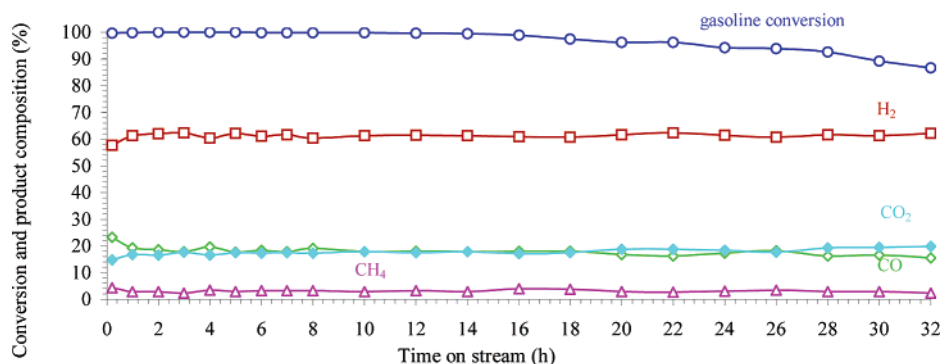


Figure 5. Conversion and product composition with time on stream for gasoline reforming with a S:O:C ratio of 1.7:0.8:1 on Ni–Re/Al₂O₃ catalyst at 953 K and a gasoline WSV of 3 h⁻¹.

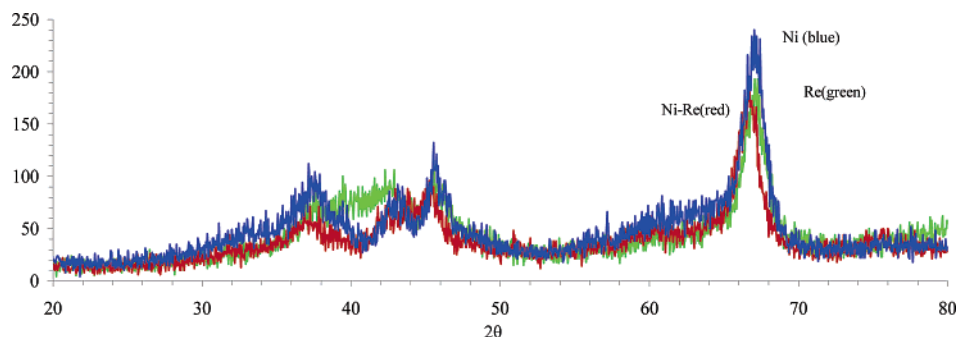


Figure 6. Comparison of XRD patterns of Ni-Re/ Al_2O_3 , Re/ Al_2O_3 , and Ni/ Al_2O_3 catalysts.

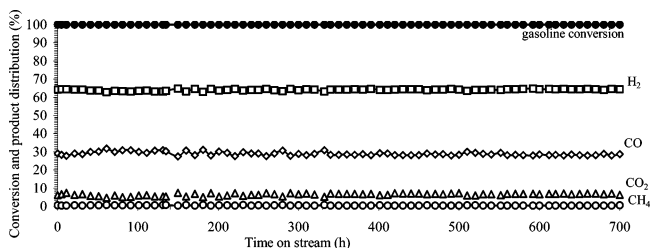


Figure 7. Gasoline conversion and product distribution with time on stream for steam reforming of the premium gasoline at a gasoline WSV of 0.3 h^{-1} and 753 K with a S:C ratio of 1.7.

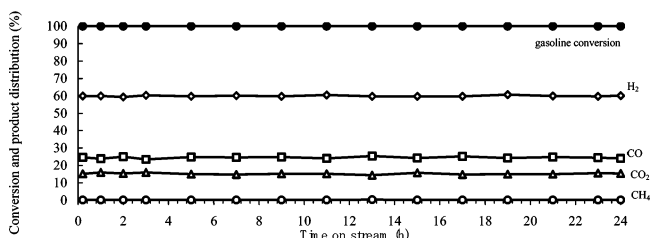


Figure 8. Conversion and product distribution with time on stream for oxidative steam reforming of gasoline (S:O:C = 1.7:0.8:1) on Ni-Re/ Al_2O_3 at a gasoline WSV of 0.3 h^{-1} and 753 K.

deposited on the catalyst is about 0.3% of the converted gasoline fuel. The catalyst also exhibits a promising sulfur tolerance, even at the lower reaction temperature, because of its long lifetime for steam reforming of the gasoline fuel containing about 3.8 ppm sulfur.

3.4. Effect of Oxygen Addition on Product Distribution.

The dependence of product composition on the mole ratio of steam:oxygen:carbon (S:O:C) in reactants was also investigated. Conversion and product distribution with time on stream for oxidative steam reforming of gasoline on Ni-Re/ Al_2O_3 at a lower reaction temperature of 753 K and the different ratios of S:O:C are shown in Figures 8 and 9. Autothermal reforming becomes possible with the combination of steam reforming and the partial oxidation reaction. The addition of oxygen to the reaction system also leads to a change in product distribution. We can see by the comparison between Figures 8 and 9 that the concentration of CO decreases and the concentration of CO_2 increases in the product with an increase in the O:C ratio from 0.8 to 1.4. However, a higher O:C ratio also leads to a lower concentration of hydrogen in product.

The concentrations of methane in the products for steam reforming, oxidative steam reforming, and partial oxidation of gasoline are compared in Figure 10.

The concentration of methane in the product for oxidative steam reforming is much lower than that in the product for steam

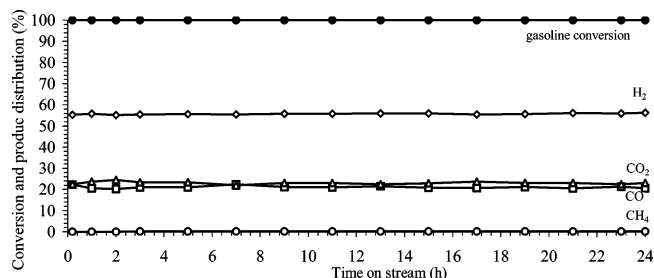


Figure 9. Conversion and product distribution with time on stream for oxidative steam reforming of gasoline (S:O:C = 1.7:1.4:1) on Ni-Re/ Al_2O_3 at a gasoline WSV of 0.3 h^{-1} and 753 K.

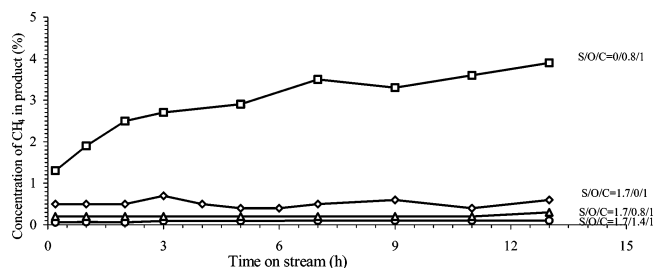


Figure 10. Effect of oxygen addition on methane concentration in the product for gasoline reforming on Ni-Re/ Al_2O_3 at a gasoline WSV of 0.3 h^{-1} and 753 K.

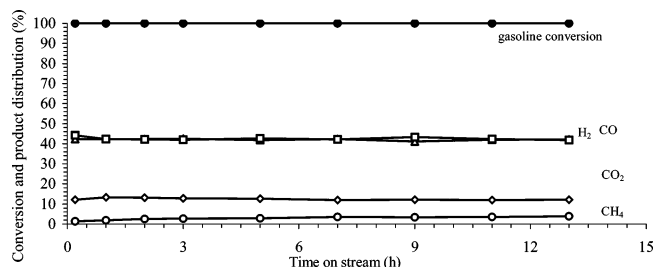


Figure 11. Conversion and product distribution with time on stream for partial oxidation of gasoline (S:O:C = 0.0:0.8:1) on Ni-Re/ Al_2O_3 catalyst at a gasoline WSV of 0.3 h^{-1} and 753 K.

reforming, although the concentration of methane in the product for the partial oxidation of gasoline is higher than that for steam reforming. The addition of oxygen to the steam reforming reaction system is effective in suppressing the formation of methane. The concentration of methane in the product is remarkably suppressed further by increasing the O:C ratio in reactants, as shown in Figure 10. Therefore, the formation of methane is minimized only by combining steam reforming with partial oxidation. Conversion and product distribution with time on stream for the partial oxidation of gasoline on Ni-Re/ Al_2O_3 at 753 K is shown in Figure 11.

We can see from Figure 11 that hydrogen concentration in the product for the partial oxidation of gasoline is also lower

than that in the product for oxidative steam reforming or steam reforming of gasoline.

4. Conclusion

Gasoline reforming for hydrogen generation is feasible on Ni–Re/Al₂O₃ even at lower temperatures because of the unique high activity of the bimetallic catalyst system. The complete conversion of gasoline with the low methane concentration of near 0 in the product is achieved on the Ni–Re/Al₂O₃ catalyst

for steam reforming of gasoline at 853 K and a gasoline WSV of 0.3 h^{−1}. The high gasoline conversion of 100% with the low methane concentration of about 0.3% in product is maintained very well during 700 h of time on stream. The methane concentration is suppressed further by the addition of oxygen to the reaction system in the product for oxidative steam reforming.

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