Short communication

Steam reforming of gasoline promoted by partial oxidation reaction on novel bimetallic Ni-based catalysts to generate hydrogen for fuel cell-powered automobile applications

Linsheng Wang*, Kazuhisa Murata, Megumu Inaba

National Institute of Advanced Industrial Science and Technology, AIST Tsukuba Central 5, Tsukuba, Ibaraki 305-8565, Japan

Abstract

Steam reforming of gasoline fuels combined with partial oxidation reaction on ZSM-5-supported Ni-based bimetallic catalysts and Al_2O_3-supported Ni-Re bimetallic catalysts with different Ni/Re ratios for hydrogen generation at a relatively lower reaction temperature was studied. The ZSM-5-supported Ni-Ce and Ni-Mo bimetallic catalysts exhibited a higher activity than the Ni/ZSM-5 catalyst for the oxidative reforming of gasoline. Steam reforming of gasoline to produce hydrogen was remarkably promoted by partial oxidation reaction by addition of molecular oxygen to the reaction system on ZSM-5-supported Ni-Ce catalyst. Al_2O_3-supported Ni-Re catalyst with suitable Ni/Re ratios exhibits unique high activity and sulfur tolerance because of the alloying of Ni with Re to form a new active sites for oxidative steam reforming of gasoline to generate hydrogen. The crystal structure of Al_2O_3-supported bimetallic Ni-Re catalyst and monometallic catalysts of Ni and Re were characterized by XRD method. Structured changes resulting from the alloying of Ni with Re were found.
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1. Introduction

The rapid development of proton-exchange membrane (PEM) fuel cell technology has stimulated the research in small reforming process systems for on-board vehicle applications. The energy efficiency of a car with a PEM fuel cell propulsion system based on gasoline as fuel will be higher than the efficiency of a car with an internal combustion engine. The replacement of the internal combustion engine with an electric motor associated with a fuel cell will be one of the most attractive alternatives for the elimination of emissions from the internal combustion engines because pollutants such as NO_x can be avoided if the reforming process is performed at relatively low temperatures on active catalysts. Recently some progress on development of sulfur-tolerant and coke-resistant catalysts for steam reforming of transportation fuels, such as a surrogate of diesel, a desulfurized kerosene and a mixture of MCH and toluene as model gasoline [1–7]. However, gasoline is the most commonly used transportation fuel in the vehicles. In the present paper, production of hydrogen from regular gasoline, high-grade gasoline and model gasoline by oxidative steam reforming on Ni-Re/Al_2O_3 and Ni/CeZSM-5 catalysts is reported.

2. Experimental

2.1. Catalyst preparation

Ni/CeZSM-5 was prepared by impregnating the CeZSM-5 with $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solutions, then followed by drying at 383 K for 6 h, and calcination at 773 K for 6 h and at 1023 K for 6 h. Ni/ZSM-5 and CeZSM-5 were prepared

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* Corresponding author.
  E-mail address: linsheng.wang@aist.go.jp (L. Wang).

by impregnating NH$_4$ZSM-5 (SiO$_2$/Al$_2$O$_3$ = 38) with Ni(NO$_3$)$_2$·6H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O aqueous solutions, respectively, then followed by drying at 383 K for 6 h and calcination at 773 K for 6 h. The loadings of Ni and Ce are about 5 and 2 wt.%, respectively. Ni-Re/Al$_2$O$_3$ was prepared by impregnating the Ni/Al$_2$O$_3$ with NH$_4$ReO$_4$ aqueous solutions, followed by drying at 383 K for 6 h and calcination at 773 K for 6 h. Ni/α-Al$_2$O$_3$ was prepared by impregnating α-Al$_2$O$_3$ with Ni(NO$_3$)$_2$·6H$_2$O aqueous solutions, then followed by drying at 383 K for 6 h and calcination at 773 K for 6 h.

2.2. Catalytic tests and product analysis

Catalytic tests were carried out with about 300–500 mg of catalyst placed in a fixed bed continuous-flow quartz 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 H$_2$/N$_2$ at 773 K for 2 h. Flow rates of gasoline and water (H$_2$O) were controlled by liquid pumps and preheated in an evaporator before passing through the catalyst bed in the reactor. The flow rate of N$_2$ was controlled by a mass flow rate-controller. The products were withdrawn periodically from the outlet of reactor and analyzed by a two on-line gas chromatographs, Shimadazu 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 CH$_4$, CO, CO$_2$, H$_2$ and N$_2$ 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 reactor (F_{Total}^{intlet}, F_{Total}^{outlet}), the flow rate of non-reactive internal standard gas (F_{st}) is kept constant.

$$F_{st} = F_{Total}^{outlet} X_{st}^{outlet} = F_{Total}^{inlet} X_{st}^{inlet}$$

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

$$F_i = F_{Total}^{outlet} X_i^{outlet} = F_{st} \frac{X_i^{outlet}}{X_{st}^{outlet}}$$

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 feed as

Eq. (1).

$$C_{HC} = \frac{F_{CO}^{outlet} + F_{CO_2}^{outlet} + F_{CH_4}^{outlet}}{F_{HC}^{inlet}} \quad (1)$$

F_{HC}^{inlet} is the flow rate of liquid hydrocarbon feed and controlled by a liquid pump. In the same way, H$_2$O conversion (C_{H_2O}) is calculated on the basis of oxygen balance and calculated by dividing the sum of oxygen in gaseous products by the oxygen in feed as Eq. (2).

$$C_{H_2O} = \frac{F_{CO}^{outlet} + 2F_{CO_2}^{outlet} - 2F_{O_2}}{F_{H_2O}^{inlet}} \quad (2)$$

$F_{H_2O}^{inlet}$ is the flow rate of water and controlled by another liquid pump.

2.3. XRD characterization

The samples of Ni/Al$_2$O$_3$, Re/Al$_2$O$_3$ and Ni-Re/Al$_2$O$_3$ were firstly treated by air at 873 K for 0.5 h and reduced by H$_2$/N$_2$ at 573 K for 2 h and then was in the stream of steam reforming for 8 h before XRD characterization.

3. Results and discussion

3.1. Catalytic performance of ZSM-5-supported Ni-based catalysts for oxidative steam reforming of mixture fuel of MCH and toluene as model gasoline to produce hydrogen

Conversions of gasoline and H$_2$O, formation rates and composition of hydrogen-rich gas product and CO conversion (X_{CO}) for steam reforming of a mixture fuel of 75% MCH and 25% toluene as a model gasoline on ZSM-5-supported monometallic and bimetallic catalysts are listed in Table 1. It is clear in Table 1 that the ZSM-5-supported Ni catalyst exhibits better activity than the Ru/ZSM-5 catalyst. In addition, addition of second metals such as Ce and Mo is effective to promote the activity of Ni/ZSM-5. Ni/CeZSM-5 and Ni/MoZSM-5 catalysts exhibit evidently higher activity than the Ni/ZSM-5 catalyst for the oxidative steam reforming reaction.

Table 1
Conversion, formation rates and composition of product for integration of AR and WGS reaction on different catalysts

Catalyst	Conversion (%)		Formation rate (μ mol s^{-1}g^{-1})				Product composition (%)				X_{CO} (%)
	HC	H$_2$O	H$_2$	CO	CO$_2$	C$_1$–C$_3$	H$_2$	CO	CO$_2$	C$_1$–C$_3$	
Ni/ZSM-5	48.9	12.1	66.0	7.0	23.1	9.6	62	6.6	21.9	9.1	77
Ni/CeZSM-5	59.3	16.7	83.9	10.9	26.5	10.4	64	8.3	20.1	7.9	71
NiMo/ZSM-5	58.9	10.0	57.2	27.8	10.0	5.3	57	27.8	10.0	5.3	26
Ni/MgZSM-5	24.6	2.5	17.5	5.5	11.2	2.8	47.3	14.9	30.3	7.6	67
NiRe/ZSM-5	37.3	6.8	44.4	9.4	15.0	5.5	59.7	12.7	20.2	7.4	61
Ru/ZSM-5	23.4	1.1	14.4	5.5	9.4	4.0	43.2	16.5	28.2	12.0	63

T = 853 K; WSV of fuel = 4 h^{-1}; fuel: 75% MCH + 25% C$_7$H$_8$; S/C/O = 1.7/1/0.3.

Table 2
Effect of S/O/C ratio on conversion, formation rates and composition of product for steam reforming of a model gasoline on Ni/CeZSM-5

The ratio of S/C/O	Conversion (%)		Formation rate (μ mol s^{-1}g^{-1})				Product composition (%)				X_{CO} (%)
	HC	H_2O	H_2	CO	CO_2	C_1–C_3	H_2	CO	CO_2	C_1–C_3	
1.7/1/0	38.3	26.7	65.6	7.0	14.8	8.3	68.6	7.3	15.4	8.7	68
0/1/0.8	39.1	−11.5	25.5	12.0	14.2	4.8	45.1	21.2	25.1	8.5	54
1.7/1/0.3	42.3	16.4	57.3	7.6	17.6	8.0	63.3	8.4	19.5	8.8	70
1.7/1/0.5	59.3	16.1	83.9	10.9	26.5	10.4	63.7	8.3	20.1	7.9	71
1.7/1/0.8	69.1	2.8	90.8	12.8	32.8	9.3	62.3	8.8	22.5	6.4	72
1.7/1/1.4	67.5	−12.0	54.4	10.2	35.7	7.4	50.5	9.5	33.1	6.9	78

T = 853 K; WSV of fuel = 4 h^{-1}; composition of fuel: 75% MCH + 25% C_7H_8.

However, the product selectivity for oxidative steam reforming reaction on Ni/CeZSM-5 and Ni/MoZSM-5 catalysts are quite different. Syngas (H_2 and CO) is the major product for oxidative reforming reaction on Ni/MoZSM-5 catalyst, and H_2 and CO_2 are the major products for oxidative steam reforming reaction on Ni/CeZSM-5 as shown in Table 1. The role of Ce addition is to enhance the acidity and the hydrothermal stability of Ni/ZSM-5 catalyst. The role of acid sites of catalyst is to promote the oxidative steam reforming reaction by promoting the cracking of C–C bonds of liquid hydrocarbon feed. We can also see from Table 1 that the activity of Ni/ZSM-5 is evidently suppressed by addition of alkali metal such as Mg. This is because the activity of Ni/ZSM-5 is suppressed by the addition of Mg.

3.2. Promotional effect of partial oxidation reaction on steam reforming of gasoline on ZSM-5-supported Ni-Ce catalyst

The results for partial oxidation, steam reforming and oxidative steam reforming of mixture of hydrocarbon fuel of 75% MCH and 25% toluene as a model gasoline on Ni/CeZSM-5 catalyst are summarized in Table 2.

Steam reforming of the hydrocarbon fuel is effectively enhanced by the partial oxidation reaction on Ni/CeZSM-5 catalyst. Conversions for oxidative steam reforming are evidently higher than the value for steam reforming reaction. Hydrogen concentration in oxidative steam reforming product is also higher than the value in partial oxidative product. Conversion of hydrocarbon fuel is increased from 38.3% to

69.1% with increasing in the C/O ratio from 1/0 to 1/0.5, as shown in Table 2. Therefore, the enhanced hydrocarbon conversion and the production of hydrogen are achieved by the coupling of steam reforming and partial oxidation reaction.

3.3. Oxidative steam reforming of premium gasoline to generate hydrogen on bimetallic Ni-Re/Al$_2$O$_3$ catalysts

Conversions of gasoline and H_2O, formation rates and composition of hydrogen-rich gas product and CO conversion (X_{CO}) for oxidative steam reforming of premium gasoline containing about 3.8 ppm sulfur on bimetallic Ni-Re/Al$_2$O$_3$ catalysts with different Ni/Re ratio are listed in Table 3. It is indicated from the data in Table 3 that 5% Ni/Al$_2$O$_3$ is inactive for oxidative steam reforming of the high-grade gasoline fuel, although a little hydrogen is produced by partial oxidation reaction.

However, the bimetallic Ni-Re/Al$_2$O$_3$ catalysts with Ni/Re ratios of 5/2 and 5/5 exhibit an evident activity for oxidative steam reforming of gasoline to produce hydrogen. The bimetallic Ni-Re/Al$_2$O$_3$ catalyst with Ni/Re ratio of 5/2 exhibits a little bit higher activity than the bimetallic Ni-Re/Al$_2$O$_3$ catalysts with Ni/Re ratio of 5/5 for oxidative steam reforming of gasoline, as shown in Table 3. Ten percent of Ni/Al$_2$O$_3$ catalyst exhibits a lower activity for oxidative steam reforming of gasoline to produce hydrogen. Moreover, the catalyst activity is remarkably enhanced by adding the second metal such as Re to the 10% Ni/Al$_2$O$_3$ catalyst for oxidative reforming of gasoline. High conversions of gasoline and H_2O are achieved on the bimetallic Ni-Re/Al$_2$O$_3$

Table 3
Effect of Ni/Re ratio of Ni-Re/Al2O3 on conversion, formation rates and composition of product for oxidative steam reforming of gasoline

Ni/Re	Conversion (%)		Formation rate (μ mol s^{-1}g^{-1})				Product composition (%)				X_{CO} (%)
	HC	H_2O	H_2	CO	CO_2	C_1–C_3	H_2	CO	CO_2	C_1–C_3	
5/0	23.2	−8.4	2.5	3.2	4.5	3.2	18.6	23.9	33.6	23.9	58.4
5/2	68.4	11.7	52.4	8.1	18.0	6.1	61.9	9.6	21.3	7.2	68.9
5/5	79.2	4.8	38.4	8.7	12.2	14.7	51.9	11.8	16.5	19.9	58.3
10/0	60.2	5.7	36.9	5.2	14.7	8.4	56.6	8.0	22.5	12.9	73.9
10/1	87.2	17.0	64.9	11.0	20.8	9.2	61.3	10.4	19.6	8.7	65.3
10/2	95.3	18.2	67.4	12.4	21.0	11.5	60.0	11.0	18.7	10.2	63.0
10/5	75.1	13.6	57.0	10.2	18.5	6.7	61.7	11.0	20.0	7.3	64.5

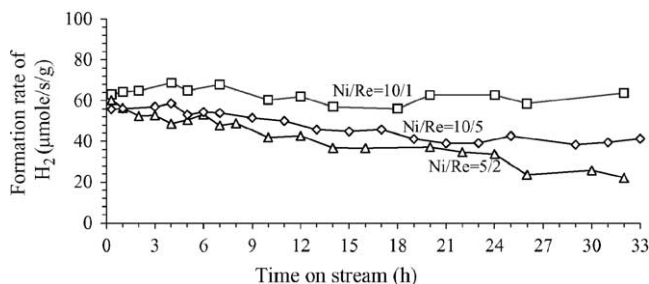T = 853 K; WSV of gasoline: 2.4 h^{-1}; S/C/O = 1.7/1/0.5; fuel: premium gasoline.

Fig. 1. Formation rate of hydrogen for oxidative steam reforming of premium gasoline on bimetallic Ni-Re/Al$_2$O$_3$ catalysts with different Ni/Re ratios.

catalyst with Ni/Re ratio of 10/2 for oxidative steam reforming of gasoline.

Formation rate of hydrogen with time on stream for oxidative steam reforming of premium gasoline containing about 3.8 ppm sulfur on the Ni-Re/Al$_2$O$_3$ catalysts with different loadings of Ni and Re is shown in Fig. 1. It is indicated from the Fig. 1 that activity maintenance of the Ni-Re/Al$_2$O$_3$ catalysts is well for oxidative steam reforming of premium gasoline because the sulfur concentration in the premium gasoline is not high. In addition, the Ni-Re/Al$_2$O$_3$ catalysts with higher Ni loadings exhibit the better activity maintenance for the oxidative steam reforming reaction.

3.4. Structure changes resulted from alloying of Ni with Re characterized by XRD

The unique high activity of Ni-Re/Al$_2$O$_3$ for steam reforming reaction is most possibly because of the alloying of Ni with Re to form the new active bimetallic Ni-Re sites for the reaction. To find the structure difference of the bimetallic Ni-Re/Al$_2$O$_3$ from that of monometallic Ni/Al$_2$O$_3$ and Re/Al$_2$O$_3$, the structures of Ni/Al$_2$O$_3$, Re/Al$_2$O$_3$ and Ni-Re/Al$_2$O$_3$ are checked by XRD. The structure differences between Ni/Al$_2$O$_3$ and Ni-Re/Al$_2$O$_3$ and between Re/Al$_2$O$_3$ and Ni-Re/Al$_2$O$_3$ are shown in Figs. 2 and 3. By comparing the XRD patterns of Ni/Al$_2$O$_3$, Re/Al$_2$O$_3$ and Ni-Re/Al$_2$O$_3$ catalysts, it is clearly found that the crystal structure of the bimetallic Ni-Re/Al$_2$O$_3$ catalyst changes because of alloying of Ni with Re. Therefore, the XRD results support our pro-
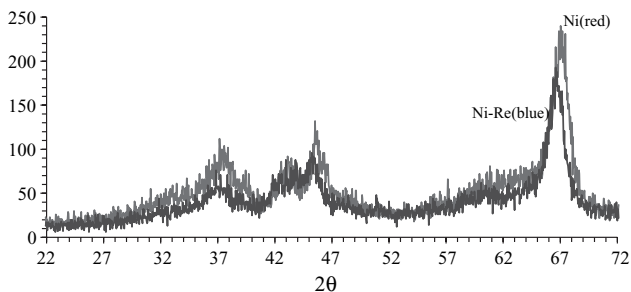

Fig. 2. Comparison of XRD patterns of bimetallic Ni-Re/Al$_2$O$_3$ and monometallic Ni/Al$_2$O$_3$ catalysts.
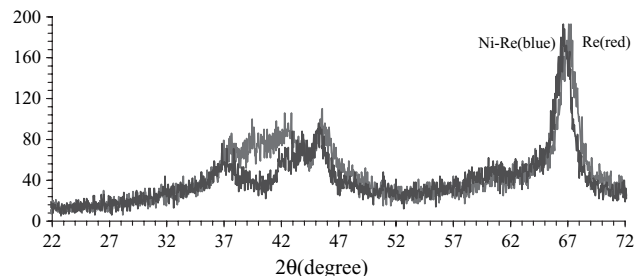

Fig. 3. Comparison of XRD patterns of bimetallic Ni-Re/Al$_2$O$_3$ and monometallic Re/Al$_2$O$_3$ catalysts.
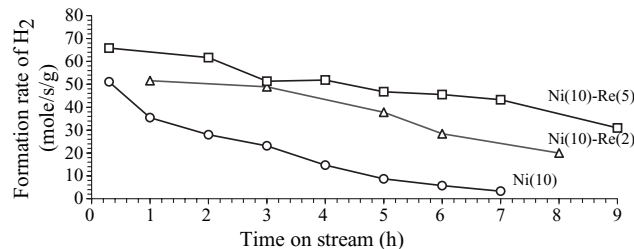

Fig. 4. Formation rate of hydrogen with time on stream for oxidative steam reforming of regular gasoline on bimetallic Ni-Re/Al$_2$O$_3$ catalysts and monometallic Ni/Al$_2$O$_3$ catalyst.

posed model for alloying of Ni with Re to form a new active phase for oxidative steam reforming of gasoline.

3.5. Sulfur tolerance enhancement of Ni-Re catalyst by alloying of Ni with Re for oxidative steam reforming of regular gasoline

Formation rate of hydrogen with time on stream for oxidative steam reforming of regular gasoline containing 29.9 ppm sulfur on bimetallic Ni-Re/Al$_2$O$_3$ catalysts with different loading of Ni and Re and on monometallic Ni/Al$_2$O$_3$ catalyst is shown in Fig. 4.

It is clear in Fig. 4 that the activity of the monometallic Ni/Al$_2$O$_3$ catalyst declined quickly with time on stream. However, the activity maintenance of the bimetallic Ni-Re/Al$_2$O$_3$ catalysts with different loadings of Ni and Re is much better than that of the monometallic Ni/Al$_2$O$_3$ catalyst for oxidative reforming of the regular gasoline. This indicate that the sulfur tolerance of the bimetallic Ni-Re/Al$_2$O$_3$ catalyst with different loadings of Ni and Re is remarkably enhanced by alloying of Ni with Re.

4. Conclusions

It is effective to enhance the activity of ZSM-5-supported Ni catalyst by the addition of a second metal such as Ce or Mo. Steam reforming of gasoline to produce hydrogen is remarkably promoted by partial oxidation reaction by addition of the molecular oxygen to the reaction system on ZSM-5-supported Ni-Ce catalyst. Alumina-supported Ni-Re catalyst

exhibits the unique high activity and the sulfur tolerance because of the alloying of Ni with Re to form bimetallic Ni-Re active sites for oxidative steam reforming of gasoline.

Acknowledgements

References

[1] Q. Ming, T. Healey, L. Allen, P. Irving, Catal. Today 77 (1999) 51.
[2] T. Suzuki, H. Iwanami, T. Yomohiro, Int. J. Hydrogen Energy 25 (2000) 119.
[3] L. Wang, K. Murata, M. Inaba, Appl. Catal. A: Gen. 257 (2004) 43.
[4] L. Wang, K. Murata, M. Inaba, Appl. Catal. B: Environ. 48 (2004) 243.
[5] D.J. Moon, K. Sreekumar, S.D. lee, B.J. Lee, H.S. Kim, Appl. Catal. A: Gen. 215 (1996) 1.
[6] K. Murata, L. Wang, M. Saito, M. Inaba, I. Takahara, N. Mimura, Energy Fuels 18 (2004) 122.
[7] L. Wang, K. Murata, M. Inaba, Ind. Eng. Chem. Res. 43 (2004) 3228.