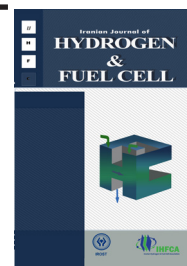


Iranian Journal of Hydrogen & Fuel Cell

IJHFC

Journal homepage://ijhfc.irost.ir



Hydrogen production via steam reforming of LPG on Ni/Zeolite catalysts

Nahid Khandan ^{1,*}, Mahmoud Ziarati ², Reza Karkeabadi ², Mohammad Ali Ghafouri Roozbahani²

¹ Department of chemical technologies, Iranian Research Organization for Science & Technology (IROST), P. O. Box 3353-5111, Tehran, Iran

² Faculty of Chemistry and Chemical Engineering, Malek Ashtar University of Technology, Lavizan, Tehran, Iran

Article Information

Article History:

Received:

13 July 2015

Received in revised form:

8 August 2015

Accepted:

22 August 2015

Keywords

Steam reforming

LPG

Ni/ zeolite catalyst

Hydrogen production

Abstract

Steam reforming is one of the most important processes for producing hydrogen from hydrocarbon fuels such as LPG and has attracted much attention due to its high efficiency and economy. In this study, the LPG steam reforming reaction was investigated on nickel catalysts supported on four various zeolites (H-Y, Na-Y, HZSM5 and Ferrierite). The catalytic tests were performed in a tubular fixed bed stainless steel reactor (I.D. 10 mm) at 650°C. Results revealed that type of support and specific surface area have significant effects on the activity and selectivity of the prepared catalyst. In this way, the Ni/Na-Y catalyst exhibited the highest surface area (696.4 m²/g) among the prepared catalysts. Also, this catalyst showed a low degree of coke formation; and consequently, high stability in the LPG steam reforming process. Ultimately, the catalytic results showed that the Ni/Na-Y catalyst possessed the highest LPG conversion (95.7 %), H₂ yield (48.6%) and stability in this reaction.

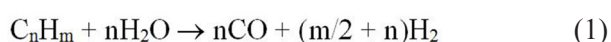
1. Introduction

In recent years, along with population growth, decreasing available energy sources and increasing air pollution and consequently increasing severity of environmental legislation, the use of hydrogen as an

energy carrier in connection with renewable energy production has been increased substantially [1-6]. Nowadays the commercial process of hydrogen production is based on fossil fuels, although these fuels are not renewable they draw the roadmap of hydrogen applications to the year 2050. There are

*Corresponding author. Tel:+98-912 6131380,
Email: khandan@irost.org

three main processes to produce hydrogen from hydrocarbons: partial oxidation, steam reforming and auto thermal reforming. Research in the field of hydrogen production methods has shown that the steam reforming process gives the maximum yield of hydrogen and it is also economical [7-9]. Steam reforming of hydrocarbons can be described by the following reaction:



The main beneficial side reaction that may occur is the water gas shift reaction (WGS) which increases the hydrogen production:



There is an unfavorable side reaction that causes the creation of coke and hydrogen. Although, this reaction helps the production of hydrogen it decreases the activity of the catalyst due to coke; and consequently, it must be avoided.

LPG is a mixture of hydrocarbons, predominantly propane and n-butane, whose composition depends on the source, recovery processes, and season. It can be a mixture of either predominantly butane or predominantly propane with small amounts of propylene and butylene. The advantage of LPG compared to heavier hydrocarbon feed stocks, like naphtha or diesel, as a source of hydrogen is being cleaner and containing a higher weight percent of hydrogen. Also, depending on seasonal demand, refinery operations often result in a surplus of different feed stocks. For example, LPG demand soars in winter due to increased heating requirements, whereas it is usually in surplus throughout the summer [10, 11].

The development of new catalysts is one of the most important and effective ways to address problems related to the sustainable production of hydrogen. In previous research on LPG steam reforming catalysts metal oxide supports, such as Al_2O_3 , ZrO_2 , and La_2O_3 , were applied for this process [13-16]. Zeolite has particular properties of high surface area and surface acidity, interconnected pore/channel system, uniform porosity, accessible pore volume,

high adsorption capacity, ion-exchange ability, and shape/size selectivity which make it convenient for using as a catalyst and catalyst supports [12, 17].

The focus of this work is to benefit from the unique properties of zeolites as a support for this catalytic reaction. For this purpose nickel catalysts supported by various types of zeolites (Na-Y, H-Y, ZSM5 and Ferrierite) were synthesized and investigated in steam reforming of LPG.

2. Experimental

2.1 Catalyst preparation

Nickel nitrate, $(Ni(NO_3)_2 \cdot 6H_2O)$, and zeolites including Na-Y, H-Y, ZSM5 and Ferrierite were purchased from the Merck and Zeolyst company, respectively. Catalysts were synthesized via the precipitation-sedimentation method [18, 19]. In detail, aqueous solutions of nickel nitrate (1M) and Na_2CO_3 (1M) were prepared at room temperature and simultaneously added drop wise to a suspension of the considered zeolite under continuous stirring at 70 °C. During precipitation, pH of the suspension was monitored and adjusted to 7 ± 0.2 by changing the rate of Na_2CO_3 solution addition to the suspension. After that, the precipitate was aged for 30 min at room temperature and under 300 rpm, then it was filtered three times and washed with distilled water. Washed precipitate was dried for 14 h at 110 °C and then calcined under air flow for 4h at 700 °C. Nickel contents of all catalysts were the same at 8 wt.%.

2.2 Catalyst Characterization

A PW-1800 Philips X-ray diffraction with Cu $K\alpha$ radiation source was used for X-ray measurement. Spectra were measured with a step size of 0.02° over a 2θ range of $4^\circ - 70^\circ$. The BET surface area and pore volume of the catalysts were measured by a multipoint N_2 adsorption-desorption method at liquid N_2 temperature (77K) using a Quant SORB1 apparatus. Prior to analysis all samples were out-gassed under vacuum to remove water. The

weight changes of catalyst precursors were recorded by using thermo-gravimetric analysis (TGA) 5500B ACME equipment. For this purpose, samples were placed in a Pt cell and heated from room temperature to 800 °C at a heating rate of 10 °C min⁻¹ under air atmosphere.

2.3 Catalyst testing

Catalytic performance tests were carried out in a stainless steel fixed bed reactor (I.D. 10 mm) located in a furnace capable of heating to 1200°C and equipped with a PID controller. A schematic of the experimental setup is shown in Figure 1. Before starting the reaction, the catalyst (1.0 g) was reduced in situ at 650°C and gas (a mixture of 10 vol.% of H₂ and 90 vol.% of N₂) flow rate of 60 ml/min for 2 hours, and after reduction a feed gas mixture of steam and LPG (including 95% Butane and 5% Propane) with a molar ratio = 3/1 was entered to the reactor. The steam reforming reaction was carried out at 650°C. After process stabilization, product stream was analyzed on line using a gas chromatograph (manufactured by Agilent Company) equipped with a sample loop and a thermal conductivity detector. To measure the amount of products we had to use two GC columns called Molecular Sieve (for hydrogen and carbon monoxide) and Plot-Q (for other products). Performance of the catalysts were evaluated in terms of three parameters:

$$\text{Conversion} = \frac{(\text{LPG}_{\text{in}} - \text{LPG}_{\text{out}}) \text{ mol}}{(\text{LPG}_{\text{in}}) \text{ mol}} * 100 \quad (3)$$

$$\text{Selectivity} = \frac{(\text{Product}) \text{ mol}}{(\text{LPG}_{\text{in}} - \text{LPG}_{\text{out}}) \text{ mol}} * \frac{1}{\text{stoichiometry coefficient of the product}} * 100 \quad (4)$$

$$\text{Yield} = \frac{\text{Conversion} * \text{Selectivity}}{100} \quad (5)$$

In equation (5), conversion and selectivity are shown as a percentage.

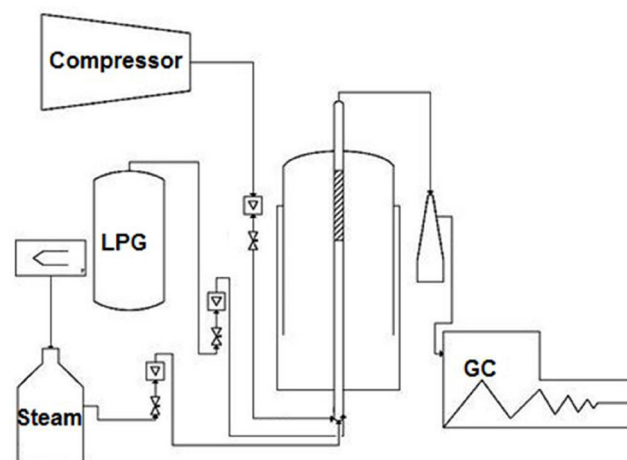


Figure 1. Schematic of the experimental set-up.

3. Results and discussions

Figure 2 shows XRD patterns of the prepared catalysts. As can be seen, the diffraction peaks related to NiO ($2\theta = 34.8, 44.3$ and 61.8°) showed high intensity, indicating well crystallized NiO in these catalysts. BET surface areas of the catalysts are presented in Table 1. These results indicate that Ni/Na-Y has the highest surface area and pore volume ($696.4 \text{ m}^2/\text{g}$ and $0.42 \text{ cm}^3/\text{g}$), and the lowest surface area belongs to Ni/Ferrierite ($379.5 \text{ m}^2/\text{g}$) with a pore volume of $0.24 \text{ cm}^3/\text{g}$. Also, results of catalytic tests are summarized in Table 1.

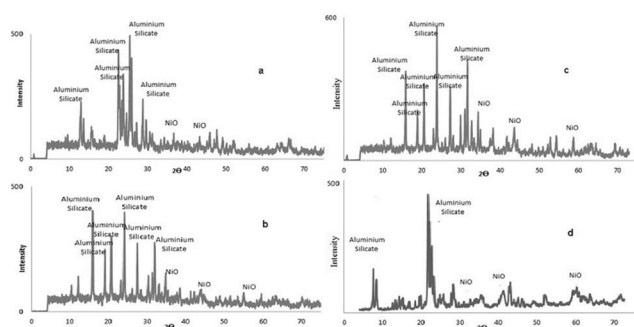


Figure 2. XRD patterns of the catalysts a) Ni-Ferrierite, b) Ni/H-Y, c) Ni/Na-Y, d) Ni/H-ZSM5.

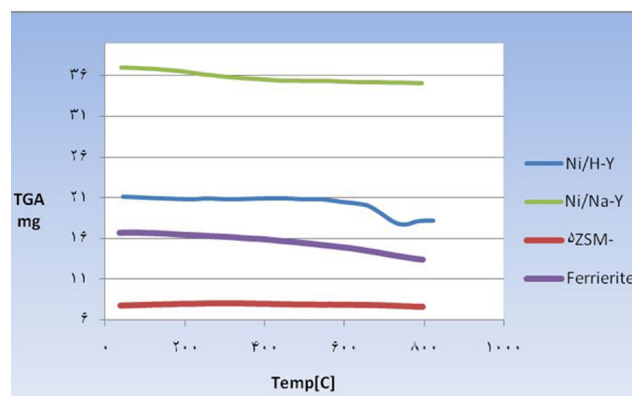
Table 1. Results of BET Analysis and Catalytic Tests of the Prepared Catalysts

Catalyst	BET surface area (m ² /gr)	Pore volume (cm ³ /g)	Conversion (%)	Selectivity (%)			Yield (%)
				H ₂	CO ₂	CO	
Ni/H-Y	603.24	0.35	57.65	70.33	13.68	15.99	40.55
Ni/Na-Y	696.41	0.42	95.71	50.78	34.11	15.11	48.6
Ni/ZSM5	425.0	0.28	47.65	55.71	13.89	17.12	26.54
Ni/Ferrierite	379.5	0.24	41.82	53.15	0.42	18.1	22.23

The catalytic results showed that the H₂ selectivity is rather high for all prepared catalysts. However, the Ni/H-Y showed the highest H₂ selectivity in comparison with the lowest H₂ selectivity of Ni/Na-Y. As can be seen, the highest conversion was obtained by Ni/Na-Y while the Ni/Ferrierite catalyst exhibited the lowest conversion among the prepared catalysts. The higher conversion of Ni/Na-Y catalyst is related to its higher surface area, which can improve the nickel dispersion and increase the number of available active sites for reactants.

Results of catalytic tests indicate that decomposition of LPG has an effective role on products, selectivities and hydrogen is produced via this reaction in addition to the two main reactions, especially in the Ni/H-Y catalyst. TGA analysis (Fig. 3) confirms that decomposition of LPG on Ni/Na-Y is slower than the others; and consequently, has the lowest H₂ selectivity. Also, results showed higher CO₂ selectivity of Ni/Na-Y compared to other catalysts. It can be interpreted that this catalyst enhances the rate of the water gas- shift reaction.

Results of yield calculations demonstrated that despite having the lowest H₂ selectivity, the Ni/Na-Y catalyst had the highest efficiency to produce hydrogen. Therefore, the Ni/Na-Y catalyst is the most effective catalyst for producing of hydrogen by steam reforming of LPG.

**Figure 3. TGA analysis of zeolite-based catalysts after a reaction time of 8 h.**

To investigate stability of the catalysts, TGA analysis was used to measure the amount of coke formed on the catalysts. Deposition of coke on the catalyst surface causes pore filling and covering of the active sites which may reduce the specific surface area of the catalyst. Consequently, it can affect performance of the catalyst.

Results of the TGA analysis are given in Figure 3. The amount of coke formed on Ni/H-Y and Ni/Na-Y were 9.5% and 4.5%, respectively. This difference may be because of the higher acidity of the H-Y zeolite. The amount of coke formed on Ni/ZSM5 and Ni/Ferrierite were 5% and 20.5%, respectively. The high amount of coke formed on Ni/Ferrierite caused the lowest stability among all catalysts. Ni/Na-Y had the lowest amount of coke formed and had higher stability during this process. Changes of catalysts' activities versus reaction time, (Fig. 4), confirms this conclusion. This figure shows that activity of Ni/Na-Y changes less versus time than those of the other catalysts. Therefore, it is more stable than the others.

Considering the results, it can be concluded that:

1. The large pore zeolite of Y and small pore zeolite of Ferrerite indicated the highest and the lowest efficiencies of hydrogen production, respectively. Therefore, large pore zeolites such as Y are more appropriate for steam reforming of LPG.
2. Stronger acidity of zeolites enhances coke formation. Therefore, zeolites having weak acidity sites are preferred for production of hydrogen via

steam reforming of LPG.

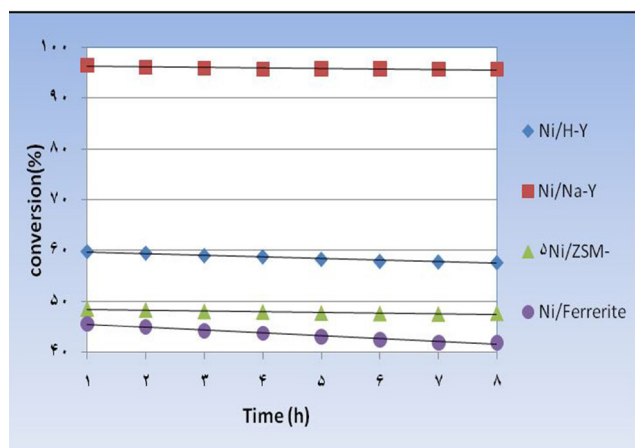


Figure 4. Activities of catalysts versus reaction time.

4. Conclusions

In this study, steam reforming of LPG on Ni/H-Y, Ni/Na-Y, Ni/ HZSM5 and Ni/ Ferrierite was investigated. The Ni/Na-Y catalyst showed the highest activity in steam reforming of LPG. This catalyst exhibited a high LPG conversion of 95.71% and a high H₂ yield of 48.6%. According to TGA results, the Ni/Na-Y catalyst showed the lowest amount of carbon formation and the highest catalytic stability in steam reforming of LPG. Therefore, it can be concluded that among the considered catalysts, Ni/Na-Y is the best catalyst to produce hydrogen via steam reforming of LPG.

5. References

[1] Udengaard N. R., "Hydrogen production by steam redorming of hydrocarbons", Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem., 2004, 49(2):906.

[2] Armor J. N., "The multiple roles for catalysis in the production of H₂", Applied Catalyst, 1999, 176: 159.

[3] Terada J., "Development of Hydrogen Production Technology by Thermochemical Water Splitting IS Process Pilot Test Plan", Journal of Nuclear Science and Technology, 2007, 44: 477.

[4] Spath M. K. M. P. L. and Amos W.A., "Update of Hydrogen from Biomass — Determination of the Delivered Cost of Hydrogen", National Renewable Energy Laboratory, 2003: 1.

[5] Lin M. H., "Hydrogen production from coal by separating carbon dioxide during gasification", Fuel, 2002, 81: 2079.

[6] Stiegel M. R. G. J., "Hydrogen from coal gasification: An economical pathway to a sustainable energy future", International Journal of Coal Geology, 2006, 65: 173.

[7] Song C., "Fuel processing for low-temperature and high-temperature fuel cells: Challenges, and opportunities for sustainable development in the 21st century", Catalyst Today, 2002, 77: 17.

[8] Wei T. K., Energy Security Challenges for the 21st Century: A Reference Handbook, 2005.

[9] Ke C. S. and Subramani V., Hydrogen and Syngas Production and Purification Technologies, 2010.

[10] Mohammad J. G., Rakib A., JimLim C., Said S.E., Elnashaie H. and Ghiasi B., "Steam reforming of propane in a fluidized bed membrane reactor for hydrogen production", International journal of hydrogen energy, 2010, 35: 6276.

[11] Laosiripojana S. A. N., "Hydrogen production from steam and autothermal reforming of LPG over high surface area ceria", Journal of Power Sources, 2006, 158: 1348.

[12] Chica A., "Zeolites: Promised Materials for the Sustainable Production of Hydrogen", Hindawi Publishing Corporation, Article ID 907425, 19 pages, 2013.

[13] Malaibari Z., Amin A., Croiset E. and Epling W., "Performance characteristics of Mo-Ni/Al₂O₃

catalysts in LPG oxidative steam reforming for hydrogen production", *International Journal of Hydrogen Energy*, 2014, 39(19):10061.

[14] Laosiripojana N., Sutthisripok W., Charojrochkul S. and Assabumrungrat S., "Steam reforming of LPG over Ni and Rh supported on Gd-CeO₂ and Al₂O₃: Effect of support and feed composition", *Fuel*, 2011, 90(1): 136.

[15] Matsumura T., "Steam reforming of methane over nickel catalysts at low reaction temperature", *Applied Catalysis A: General*, 2004, 258:107.

[16] Laosiripojana W. S., Charojrochkul S. and Assabumrungrat S., "Steam reforming of LPG over Ni and Rh supported on Gd-CeO₂ and Al₂O₃: Effect of support and feed composition", *Fuel*, 2011, 90:136.

[17] Inokawa S. N., Kameshima Y. and Miyake Y., "Difference in the catalytic activity of transition metals and their cations loaded in zeolite Y for ethanol steam reforming", *International Journal of Hydrogen Energy*, 2010, 35:11719.

[18] Aghaziarati M., Soltanieh M., Kazemeini M. and Khandan N., "Synthesis of tetrahydrofuran from maleic anhydride on Cu-ZnO-ZrO₂/H-Y bifunctional catalysts", *Catalysis Communications*, 2008, 9:2195.

[19] Xiancai L., Zhihua L. and Fei H., "Studies on nickel-based catalysts for carbon dioxide reforming of methane", *Applied Catalysis A: General*, 2005, 290:81.