



## The Effect of Preparation Method on the Activity of Bimetallic Ni-Fe Catalyst in Dry Reforming of Methane

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ARTICLE INFO	ABSTRACT
<p><b>Article History:</b> Received: 04 September 2021 Revised: 04 January 2021 Accepted: 04 January 2021</p> <p><b>Article type:</b> Research</p> <p><b>Keywords:</b> DRM, Fe/Ni Ratio, Ni-Fe Bimetallic Catalyst, Preparation Method, Sol-Gel</p>	<p>This paper investigates the effects of Fe/Ni ratio (0.5-2) and polyvinyl alcohol to total metal ratio (PVA/(Ni+Fe)=0.5-1.5) on the performance of bimetallic (Ni-Fe) catalysts in dry reforming of methane. The activity, stability, and H<sub>2</sub>/CO ratio of the catalysts are tested. The effects of both metal ratio and shell factor on the catalyst performance have been studied. The nickel-ferrite catalysts were prepared by the sol-gel method. Shell factor is employed for controlling the size of the particles. The samples were characterized by XRD, BET, SEM, and TGA. The catalysts were tested at 800°C in the micro-reactor with a feed ratio of CH<sub>4</sub>/CO<sub>2</sub>=1/1. The catalyst prepared with Fe/Ni=2 and PVA/(Ni+Fe)=0.5 ratio shows the best activity and stability with 30 h time on stream. It can be attributed to NiFe<sub>2</sub>O<sub>4</sub> as the only available phase after calcination and smaller crystal size at the optimum values of Fe/Ni and PVA/(Ni+Fe) ratio.</p>

### Introduction

Synthesis gas (syn-gas) is a mixture of hydrogen and CO gasses, a colorless, inodorous gas that burns at 574°C without flame. Syn-gas is produced by many methods, such as steam reforming, partial oxidation, and CO<sub>2</sub> reforming of hydrocarbons or coal [1, 2]. Hydrocarbons, especially methane, are inexpensive reactants that are widely used in the reforming process. In recent decades, many researchers have suggested dry reforming of the methane (DRM) method as a favorite technique to produce syn-gas. Since the method uses two inexpensive, and accessible gas, much attention is attracted to employing greenhouse gasses as reactants. However, the latter method is not proposed as an industrial technique. DRM produces H<sub>2</sub>/CO with a molar ratio equal to 1, and it is a very useful ratio for the carboxylation and hydrogenation process, and when combined with steam reforming of methane, it finds some applications for Fischer-Tropsch synthesis [1]. The main reaction of DRM is proposed as [3]:

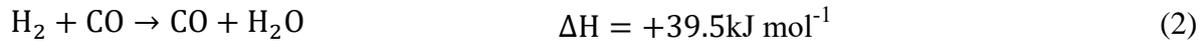


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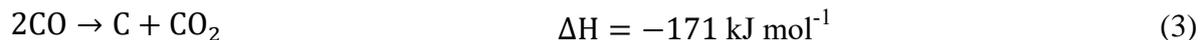




The endothermic reaction shows high activity at high temperatures. Some side reactions occur in DRM. The main side reaction is harmful and is considered the main determinative factor in decreasing  $H_2/CO$  from 1. This reaction is known as the reverse water-gas shift reaction (RWGS) [3].



Two other side reactions are occurring in the DRM. These reactions are the main reason for the coke deposition on the catalyst, Boudouard reaction (reaction 3), and methane decomposition (reaction 4) reaction, as illustrated below [4, 5]:



Since these two reactions drastically deactivate catalysts, many researchers are preparing catalysts with high resistance to coke deposition [1, 2, 4, 5].

There are three types of carbon in the reforming processes. Carbide carbon which has a high reactivity during the reaction is produced at  $250^\circ\text{C}$ . Amorphous carbon does not show high reactivity and is produced at  $250\text{-}600^\circ\text{C}$ . When the reaction temperature is above  $600^\circ\text{C}$ , graphite carbon is the main reason for catalyst deactivation [6].

The addition of the second metal to the catalyst, and synthesis of the bimetallic catalysts, is proposed as a useful method to prepare a catalyst with high resistance against carbon deposition. The other methods use perovskite-type and/or supports with alkaline properties for the reforming process [4, 5, 7, 8]. One of the advantages of perovskite-type catalysts is high resistance against carbon deposition in methane reforming [8, 9].

$NiFe_2O_4$  is a catalyst that employs two of the mentioned advantages; this catalyst has two metal sites along with a perovskite-type structure.  $NiFe_2O_4$  is an inverse  $AB_2O_4$  spinel with a perovskite structure. In  $AB_2O_4$ , spinel,  $A^{2+}$ ,  $B^{3+}$ , and oxygen atoms have an FCC structure but in an inverse structure. All of the  $A^{2+}$  and half of  $B^{3+}$  are placed in the octahedral structure, and the other  $B^{3+}$  are placed in the tetrahedral structure, so  $B(AB)O_4$  are formed during the reaction. Therefore, before the reaction,  $Fe^{3+}$  is located in the tetrahedral structure of the A atom, and octahedral B-sites and  $Ni^{2+}$  ions are located in the octahedral B-sites [9, 10].

Bordes-Richard et al. [11] investigated the effect of the preparation method on the activity of  $NiFe_2O_4$ . They prepared this catalyst by impregnation, co-precipitation, and sol-gel method with Fe/Ni ratio equal to 2. They used polyacrylic acid as a shell factor in the sol-gel method. The sol-gel method is not widely reported in the preparation of  $NiFe_2O_4$  catalysts by researchers. The main purpose of their work has been to investigate the effects of the preparation method of activity of  $NiFe_2O_4$  in DRM. They observed that the sample prepared by the sol-gel method showed a better activity, as well as a high  $H_2/CO$  ratio compared to the other samples. They did not report any stability test in their work, so there is no information about the performance of the catalyst after a long time on stream [11].

The shell factor is a polymer molecule or so-called surfactant molecule with a large size and has one hydrophilic end, and the other end is hydrophobic. In other words, these molecules have one polar end, and the other end is non-polar. Dissolution of these substances in aqueous or organic solvents causes the formation of micellar structures. Depending on the type of organic or aqueous solvent used during the catalyst fabrication process, the micelles formed are called inverted micelles and micelles, respectively. When this molecule is dissolved in an aqueous medium, the hydrophilic parts are inclined towards the water and their hydrophobic end is strongly repelled by water molecules; therefore, by adding appropriate amounts of these

substances to aqueous solvents, molecular aggregates are formed. In these molecular assemblies, the hydrophilic head is inclined outward (the aqueous medium) and the hydrophobic ends of the molecules are positioned toward each other. Such a structure is called a conventional micelle. Now, if these molecules are added to an organic solvent, due to the polarity of the solvent, the hydrophobic end is oriented towards the solvent and the hydrophilic heads are gathered together. Such a structure, which is observed in organic solvents, is called the inverse micelle structure. Depending on the amount of active surface molecule, the size of the micelles becomes smaller or larger, causing the particles they form to become smaller or larger [12, 13].

In the current paper, NiFe<sub>2</sub>O<sub>4</sub> catalysts with different Fe/Ni ratios were prepared by the sol-gel method to investigate the effect of the metal ratio on the activity of bimetallic catalysts. To investigate the effect of PVA on the structure and activity of the catalyst, the samples have been prepared by employing PVA as a shell factor and different ratios of PVA/ (Ni+Fe). So, this paper investigates the effect of both metal ratio and shell factor in the dry reforming of methane.

## Experimental

### Catalyst preparation

In this experimental study, Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Fe (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (MERCK, 99%) and PVA (Polyvinyl Alcohol, MERCK, MW=72000) are used as precursors. In the first step, the desired amounts of PVA, and Ni and Fe salts, according to Table 1, were separately solved in the hot distilled water and stirred until homogeneous solutions are obtained. The metal solutions were then added to the PVA solution and stirred vigorously to form a brown mixture. The droplets of HNO<sub>3</sub> (MERCK, 0.2M) were added to the solution while mixing until the color was converted to light green. In the end, this solution was dried in an electric oven for 12h at 100 °C and calcined at 500°C for 4h to prepare a dark brown catalyst. The catalysts were named xNyF(z), in which x, y, and z, show Ni, Fe, and PVA/(Ni+Fe) ratios, respectively.

**Table 1.** List of the prepared catalysts.

Ni/Fe	PVA/(Ni+Fe)	Catalyst
1/2	0.5	1N2F (0.5)
1/1	0.5	1N1F (0.5)
1/2	1	1N2F (1)
1/2	1.5	1N2F (1.5)
1/1	1.5	1N1F (1.5)
2/1	1.5	2N1F (1.5)
2/1	0.5	2N1F (0.5)
1/1	1	1N1F (1)
2/1	1	2N1F (1)

### Catalyst Characterizations

The catalyst samples were analyzed by X-ray diffraction patterns or XRD test (Philips PW3040 instrument) equipped with Cu K $\alpha$  radiation (1.54 Å) to identify the relevant crystal phases. The phases in the catalyst were determined by comparison with the reference peak of the materials (JCPDSs). The average crystal size of samples was calculated by the Scherrer equation [14]. FESEM was used to investigate the morphology of the catalyst (TSCANS instrument). The BET method is commonly applied to calculate the specific surface area based on nitrogen adsorption isotherm measurements at 77 K (Quantachrome Chem-BET-3000). Usually, data in the relative pressure range from 0.05 to 0.3 are used. 0.2 g of catalyst sample was used for BET Test and before the test, a sample was degassing at 150 for 1h. To measure carbon deposition on the catalyst for the stability test, TGA (thermal gravimetric analysis) test was employed by the PL-TGA instrument.

## Activity Test

The DRM was carried out in a fixed-bed quartz reactor (ID = 2 mm and L=50 cm) under atmospheric pressure and 800°C as shown in Fig. 1. The temperature detector placed in the center of the catalyst bed was used for monitoring the temperature of the reactor. 50 mg catalysts were diluted by 0.25 g quartz (30-60 mesh) and fixed between two quartz wool. The length of the catalyst bed was 2cm [3]. To convert the metal oxide to the active metal, the catalysts were first reduced in situ by hydrogen flow (30ml/min) from room temperature to 400°C with the ramp of 5°C/min and kept for 30 min [15, 16]. Following the preliminary step, the H<sub>2</sub> flow was disconnected, then a feed flow containing CH<sub>4</sub>/CO<sub>2</sub>/He=1/1/8 with GSHV=12 L.g<sup>-1</sup>h<sup>-1</sup> was supplied to the catalyst and heated from 400 °C to 800 °C with the ramp of 5°C/min [15]. The feed and product gasses were analyzed on-line by a gas chromatograph equipped with a thermal conductivity detector along with Propack Q and Molecular sieve columns [3]. Conversions of methane and carbon dioxide and yields of hydrogen and carbon monoxide were determined as follows:

$$X_{\text{CH}_4} = \frac{C_{\text{CH}_4, \text{initial}} - C_{\text{CH}_4, \text{final}}}{C_{\text{CH}_4, \text{initial}}} \quad (5)$$

$$X_{\text{CO}_2} = \frac{C_{\text{CO}_2, \text{initial}} - C_{\text{CO}_2, \text{final}}}{C_{\text{CO}_2, \text{initial}}} \quad (6)$$

$$Y_{\text{H}_2} = \frac{C_{\text{H}_2, \text{final}}}{2C_{\text{CH}_4, \text{initial}}} \quad (7)$$

$$Y_{\text{CO}} = \frac{C_{\text{CO}, \text{final}}}{C_{\text{CH}_4, \text{initial}} + C_{\text{CO}_2, \text{initial}}} \quad (8)$$

$$\frac{\text{H}_2}{\text{CO}} = \frac{n_{\text{H}_2(\text{out})}}{n_{\text{CO}(\text{out})}} \quad (9)$$

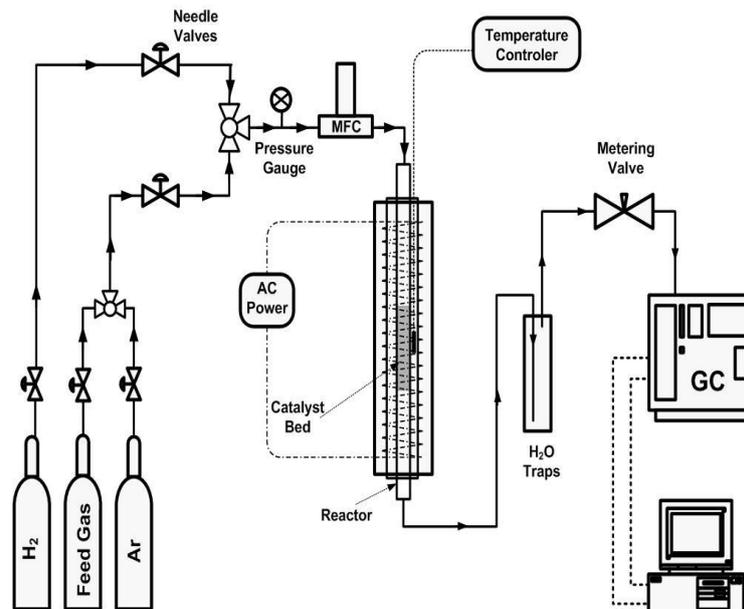


Fig. 1. Schematic of the experimental setup [8]

## Results and Discussion

### XRD Analysis

Fig. 2 presents the XRD patterns of 5 samples. In all samples,  $\text{NiFe}_2\text{O}_4$  spinel (JCPDS 10-0325) is formed, but in some of the samples, the other oxide phase was detected. Results, show that by increasing PVA/(Fe+Ni) ratio at constant Fe/Ni, NiO (JCPDF 4-835),  $\text{Fe}_2\text{O}_3$  (JCPDS 33-0664) and  $\text{Fe}_3\text{O}_4$  (JCPDS 75-1610), were formed during catalyst preparation (Fig. 1). These metal oxides weren't participating in catalyst structure, so active sites were reduced in the catalyst.

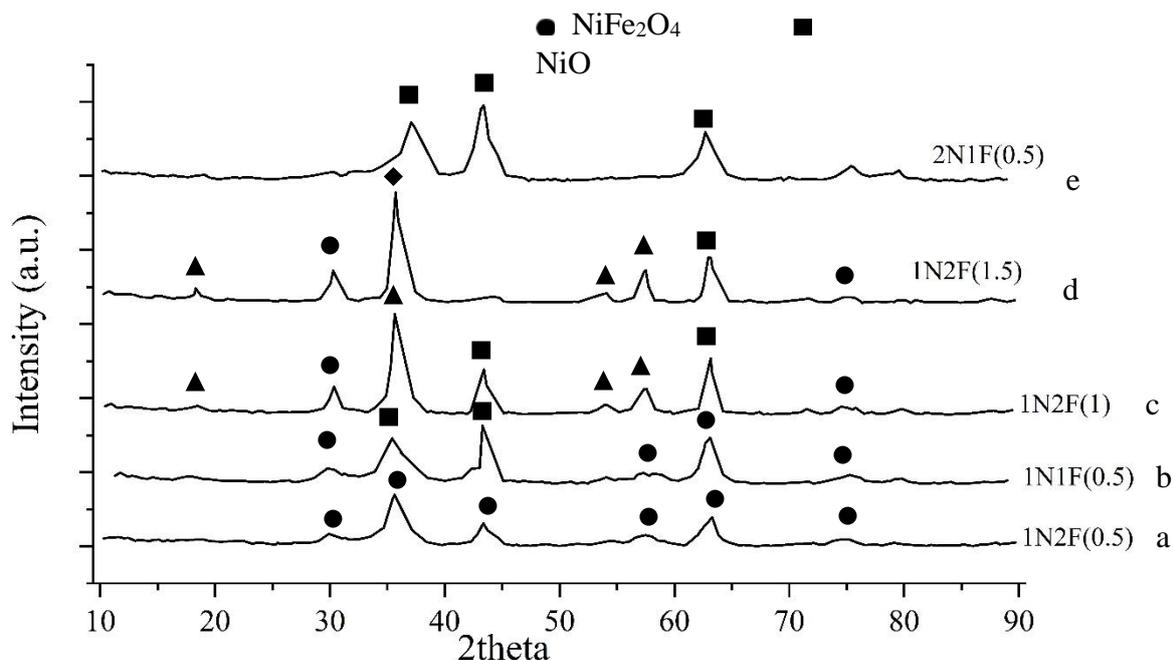


Fig. 2. XRD of all samples

Comparing other samples in Fig. 1, by decreasing Fe/Ni from 2 to 0.5 in constant PVA/(Fe+Ni) = 0.5 ratios, other than  $\text{NiFe}_2\text{O}_4$  spinel, just NiO was formed during catalyst preparation. It seems that by increasing Ni species, the NiO phase does not participate in catalyst structure. So the formation of NiO is the main reason for decreasing active sites. These metal oxides, Ni oxide, and Fe oxides may be one of the reasons for the deactivation of the catalyst during reforming. Scherrer formula calculated the size of all phases in samples. For 1N2F (0.5) (Fig. 2a), only  $\text{NiFe}_2\text{O}_4$  was detected, and the crystal size between 6-10 nm was varied. For 1N1F (0.5) (Fig. 2b), the size of  $\text{NiFe}_2\text{O}_4$  was 17 nm. For the 1N2F (1) (Fig. 2c) size of  $\text{NiFe}_2\text{O}_4$  was 22 nm. For 1N2F (1.5) (Fig. 2d) size of  $\text{NiFe}_2\text{O}_4$  was 34 nm. For 2N1F (0.5) (Fig. 2e) peak of  $\text{NiFe}_2\text{O}_4$  was not detected in the sample.

When PVA is dissolved in water, its polar head has a partial negative charge, and then it is placed next to the positive metal base and micelles are formed. Now, with increasing the amount of PVA, the size of the micelle is larger and more metal is placed in its formed space, causing that in addition to  $\text{NiFe}_2\text{O}_4$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  bases are also placed inside the micelle space and after oxidation by  $\text{HNO}_3$  and after calcination, they remain oxidized in the catalyst and reduce the active metal surface of the catalyst.

On the other hand, by increasing PVA/(Ni+Fe) ratio or Fe/Ni ratio, the crystal size was increased. So rising in PVA amount or Fe/Ni ratio during catalyst preparation harms crystal size. For preparing a catalyst with a smaller crystal size, Fe/Ni ratio and PVA/(Ni+Fe) ratio must be 2 and 0.5 respectively. Using the sol-gel method and PVA as a shell factor, a catalyst

is obtained with a smaller crystal size than the other method that was reported by other researchers [11, 17]. The size and type of crystal size are changed by adding a high amount of PVA for the preparation of the samples. Bordes-Richard et al. [11] have shown that in the catalyst that was prepared by the sol-gel method using polyacrylic acid as a shell factor to produce NiFe specie in the catalyst structure when  $Fe/Ni=2$  and  $PAA/(Ni+Fe)=0.5$ , the unit size is between 11-14 nm. The primary phase is  $NiFe_2O_4$  [11].

### FESEM Analysis

FESEM analysis was presented in Fig. 3 for 1N2F (0.5), and 2N1F (0.5) for observing the effect of excess Ni loaded on catalyst structure. 1N2F (0.5) (Fig. 3b) has a pores structure with small crystals, but 2N1F (0.5) (Fig. 3a) has a uniform structure with a high crystal size.

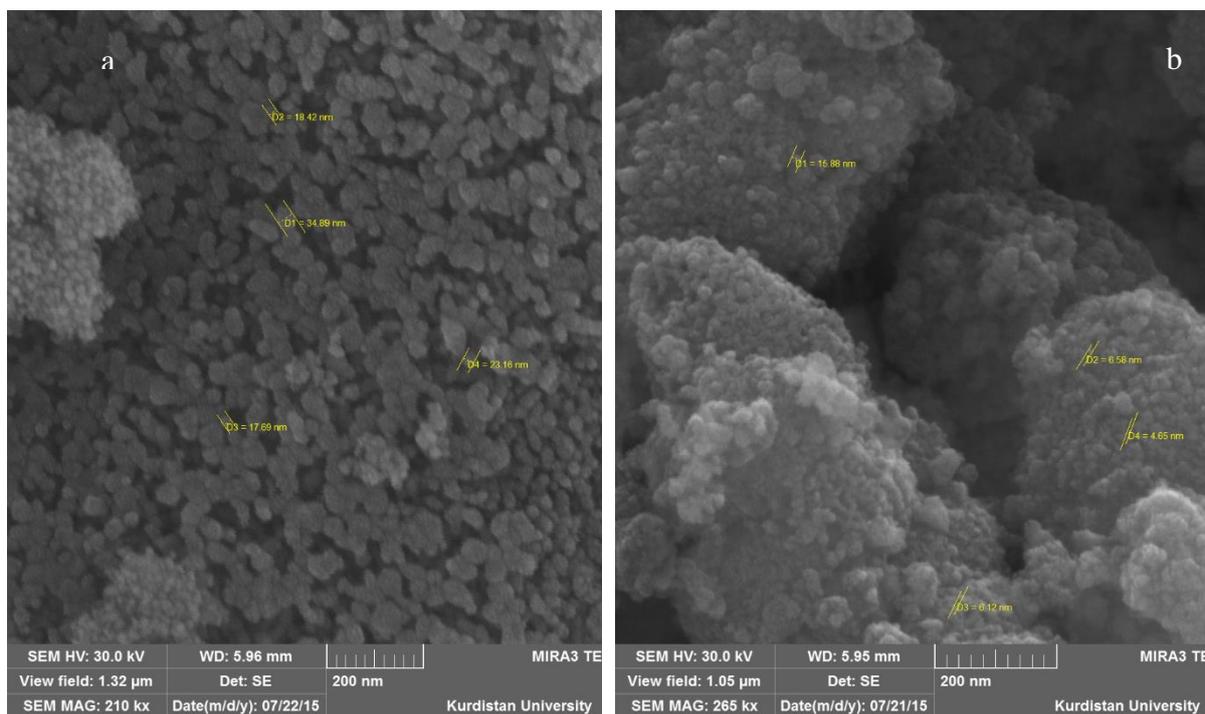


Fig. 3. FESEM micrograph of (a) 2N1F (0.5), (b) 1N2F (0.5)

### BET Analysis

Surface area and pore volume were calculated by BET test for sample 1N2F (0.5) because the primary phase of this catalyst is  $NiFe_2O_4$ . The result shows that the surface area and pore volume of the catalyst is  $63.49 \text{ m}^2/\text{g}$  and  $14.46 \text{ cm}^3/\text{g}$  respectively. The catalyst was prepared by the sol-gel method described by Bordes-Richard et al. [11] and had a lower surface area (surface area for their catalyst calcined at  $500^\circ\text{C}$  was  $32 \text{ m}^2/\text{g}$ ) than this catalyst. Using heavier surfactant (PVA) must be the main reason for increasing surface area.

### Catalyst Activity

Dry methane reforming was an endothermic reaction, so this reaction had a low activity at a low temperature. This reaction was carried out at  $800^\circ\text{C}$  with the feed containing  $CH_4/CO_2=1/1$  with  $GHSV=12 \text{ Lh}^{-1}\text{g}^{-1}$  at atmospheric pressure. Before the reactor test, the catalysts were reduced by hydrogen flow at  $400^\circ\text{C}$ . According to Borges et al. [16], the TPR curve of the

NiFe<sub>2</sub>O<sub>4</sub> catalyst has three peaks, the peak of which is at 360 °C for nickel reduction. The second and third peaks at 536 °C and 800°C are related to Fe reduction.

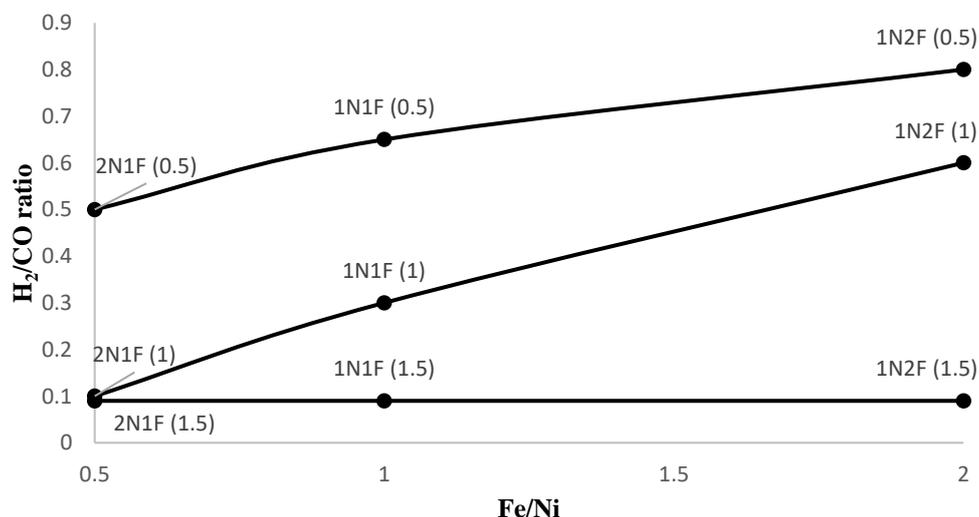
Table 2 shows the results of the reaction activity test. In some catalysts such as 1N2F (0.5), 1N2F (1), 2N1F (0.5), and 1N1F (1), methane conversion is higher than CO<sub>2</sub> conversion, but in the other samples, these phenomena are inverted. In all samples, H<sub>2</sub>/CO ratio was very much lower than 1; it seems that reverse water Gas shift(RWGS) has been very active in this catalyst because Fe was a good active site for RWGS[18]. For better comparison, the results can be divided into two parts. One part shows the effects of the Fe/Ni ratio, and the other indicates the effects of the PVA/(Ni+Fe) ratio on methane and CO<sub>2</sub> conversion and yield and H<sub>2</sub>/CO ratio.

**Table 2.** Activity result of all samples

Catalysts	%X <sub>CH<sub>4</sub></sub>	%X <sub>CO<sub>2</sub></sub>	%Y <sub>CO</sub>	%Y <sub>H<sub>2</sub></sub>	H <sub>2</sub> /CO
1N2F (0.5)	74.54	73.65	51	69	0.8
1N1F (0.5)	66.25	71.77	43	18	0.65
1N2F (1)	61.86	44.62	40	19	0.6
1N2F (1.5)	22.92	29.44	5	7	0.09
1N1F (1.5)	17.20	24.15	8	10	0.09
2N1F (1.5)	19.59	13.17	8	4	0.09
2N1F (0.5)	44.67	37.30	12	34	0.5
1N1F (1)	29.76	28.42	15	25	0.3
2N1F (1)	14.64	20.51	9	10	0.1

By increasing Fe/Ni ratio at the constant PVA/(Ni+Fe) ratio, methane and CO<sub>2</sub> conversion increased. When PVA/(Ni+Fe) =1, the rate of methane and CO<sub>2</sub> conversion by increasing Fe/Ni is higher than two other ratios of PVA/(Ni+Fe). 1N2F (0.5) shows higher methane and CO<sub>2</sub> conversion than the other samples. These results can be attributed to the smaller crystal size and presence of the effective phase (only the NiFe<sub>2</sub>O<sub>4</sub> phase was detected in XRD patterns).

Fig. 4 shows the effect of the Fe/Ni ratio on H<sub>2</sub>/CO ratio production during reforming at different PVA/(Ni+Fe) ratios. As shown in this Figure, by increasing Fe/Ni ratio from 0.5 to 2, H<sub>2</sub>/CO ratio is increased rapidly except for PVA/(Ni+Fe) =1.5; it seems that adding excess Ni or Fe does not affect syn-gas production.



**Fig. 4.** the effect of Fe/Ni ratio on H<sub>2</sub>/CO ratio for different PVA/(Ni+Fe) ratio(0.5,1,1.5)

According to XRD patterns for 1N2F (1.5) in Fig. 2d, the main phase of the catalyst is Fe oxide such as Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> which reduces the active sites of the catalyst; this is the main reason for the low activity of this catalyst. It seems that a high amount of PVA or high PVA/(Ni+Fe) ratio is not suitable for the preparation of an active catalyst containing NiFe<sub>2</sub>O<sub>4</sub>.

Also, 1N2F (0.5) shows a high  $H_2/CO$  ratio. The best Fe/Ni ratio for the preparation of  $NiFe_2O_4$  catalyst with the sol-gel method is equal to 2.

Fig. 5 shows the effect of the PVA/(Ni+Fe) ratio at different Fe/Ni ratios on  $H_2/CO$ . The results for methane and  $CO_2$  conversion have shown in Table 2. By increasing the PVA/(Ni+Fe) ratio from 0.5 to 1.5, conversions are decreased. On the other hand, a low PVA/(Ni+Fe) ratio must be used for prepared  $NiFe_2O_4$  spinel catalysts. The best PVA/(Ni+Fe) ratio for the prepared catalyst equals 0.5.

In brief, for preparing the best  $NiFe_2O_4$  catalyst, the high Fe/Ni ratio and low PVA/(Ni+Fe) ratio must be used. So, a 1N2F (0.5) catalyst sample was used to investigate the stability of the catalyst.  $NiFe_2O_4$  samples in the other papers have shown a lower activity and  $H_2/CO$  ratio compared to the catalyst prepared in this work.

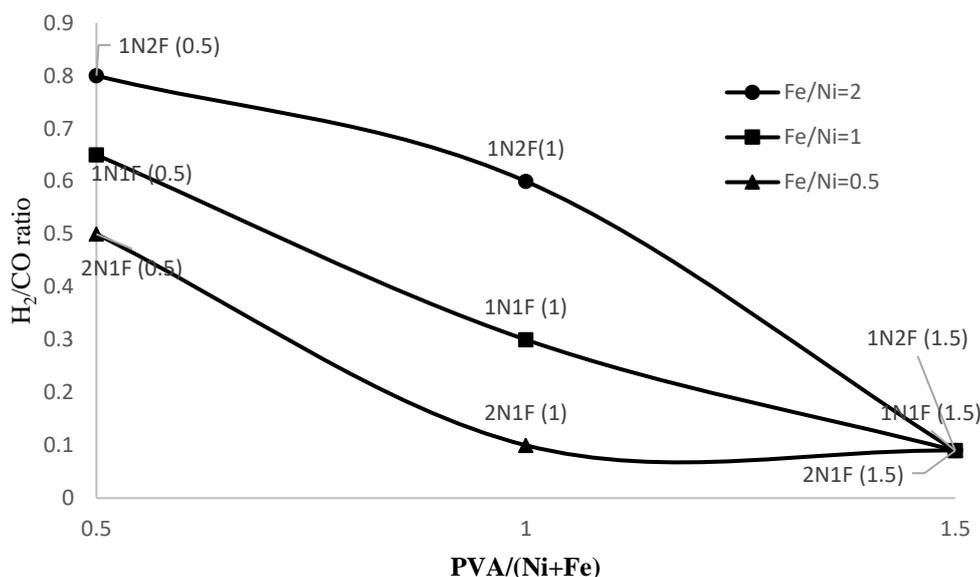


Fig. 5. the effect of PVA/(Ni+Fe) ratio on  $H_2/CO$  ratio

Bordes-Richard et al. [13] have examined this catalyst at  $800^\circ C$  with the feed containing  $CH_4/CO_2=2/1$  and a flow rate of 90 ml/min without pre-reduction and found that the samples prepared by the sol-gel method show a high activity than the samples prepared by hydrothermal or co-precipitation. When the catalyst is reduced by  $H_2$ -flow, conversion and  $H_2/CO$  ratio have been improved. All samples were deactivated for a short time except for the sample prepared by the sol-gel method. The higher rate of deactivation related to the catalyst prepared by co-precipitation was about 47.9% for methane, and it had a lower rate for samples prepared by the sol-gel method about 2.7% for 30min at  $800^\circ C$  [11].

### Stability Test

The stability test for 1N2F (0.5) has been carried out for 30h TOS, at the atmospheric pressure and  $800^\circ C$ , and the feed containing  $CO_2/CH_4=1/1$  with GHSV=12 Lh-1g-1. This sample shows a high and stable activity during the time of reaction, and no deactivation was observed during this time. The TGA test examined the amount of carbon deposition on the catalyst after the stability test. The weight loss of the used catalyst after the deactivation test is about 4%. The stability result and TGA graph are present in Figs. 6 and 7.

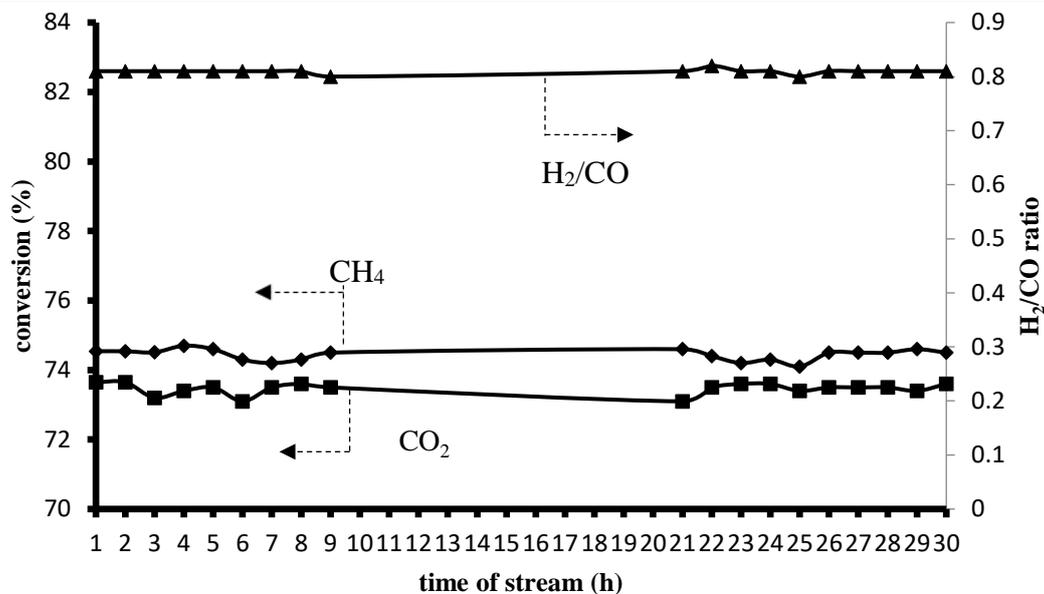


Fig. 6. Conversion and H<sub>2</sub>/CO ratio vs. TOS (h)

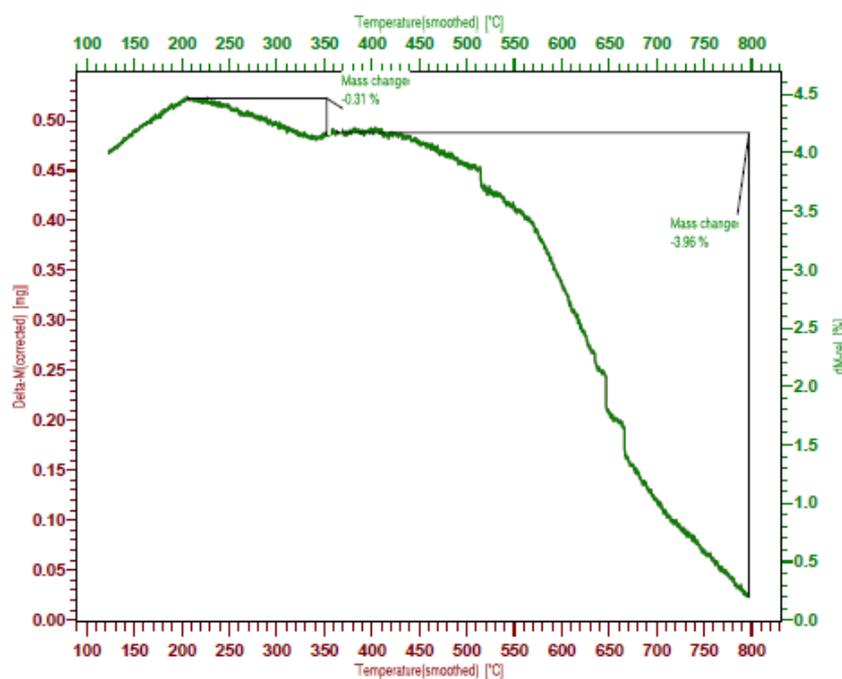


Fig. 7. TGA result for the catalyst used for the stability test

## Conclusion

The effect of PVA/(Ni+Fe) and Fe/Ni ratio on the activity of NiFe<sub>2</sub>O<sub>4</sub> catalyst prepared by the sol-gel method is investigated in this research. XRD patterns show that the crystal size of the catalyst decreased by increasing PVA/(Ni+Fe) and Fe/Ni ratio, and the presence of the other oxide phases increased. The sample prepared by Fe/Ni=2 and PVA/(Ni+Fe) =0.5 (1N2F (0.5)) has a smaller crystal size with uniform and maximum presence of NiFe<sub>2</sub>O<sub>4</sub> phase in catalyst structure in comparison with the other samples. Activity results show that methane, CO<sub>2</sub> conversion, and H<sub>2</sub>/CO ratio decreased by increasing PVA/(Ni+Fe) and Fe/Ni ratio. 1N2F (0.5) also shows high and stable activity during dry methane reforming for 30h. No deactivation was found in the DRM process for 1N2F (0.5).



## Nomenclature

PVA	Polyvinyl Alcohol
Ni	Nickle
Fe	Iron
DRM	Dry Reforming of Methane
CH <sub>4</sub>	Methane
CO <sub>2</sub>	Carbon Dioxide
CO	Carbon Monoxide
H <sub>2</sub>	Hydrogen
XRD	X-ray Diffraction
BET	Brunauer-Emmett-Teller Surface Area Analysis
SEM	Scanning electron microscope
TGA	Thermal Gravimetric Analysis
Syn-gas	Synthesis gas
RWGS	Reverse water-gas shift reaction
MW	Molecular Weight
x	Nickel ratio in Catalyst
y	The iron ratio in Catalyst
z	PVA ratio in Catalyst
N	represent Nickel in Catalyst
F	represent Iron in Catalyst
JCPDSs	Joint Committee on Powder Diffraction Standards
GSHV	The gas hourly space velocity
%X <sub>CH<sub>4</sub></sub>	Methane Conversion percentage
%X <sub>CO<sub>2</sub></sub>	Carbon Dioxide Conversion percentage
%Y <sub>CO</sub>	Carbon Monoxide Yields percentage
%Y <sub>H<sub>2</sub></sub>	Hydrogen Yields percentage

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