



## Regular Article

## Investigating the Activity of the Supported Bimetallic Ni-Co Catalysts on the Dry Reforming of Methane

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### ABSTRACT

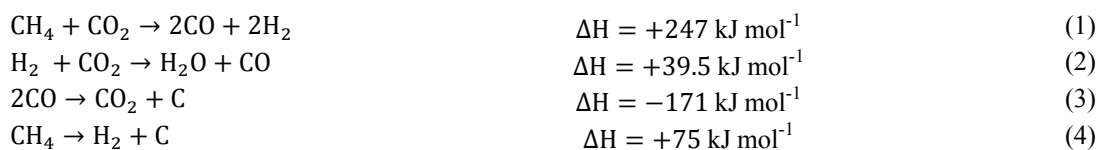
In this work, the effect of the Si/Al ratio on the activity of zeolite supported bimetallic (Ni-Co) catalysts for Dry Reforming of Methane (DRM) has been studied. Samples are prepared with impregnation and sol-gel methods and then calcined at 550 °C for 2 h. The catalysts were characterized by XRD, XRF, FESEM, BET and TGA. All samples were tested in a micro reactor at three different temperatures (i.e. 700, 750, and 800 °C). Micro reactor test results showed that 800 °C was the proper temperature for DRM. The catalyst with 5 wt % of Ni and 2.5 wt % of Co supported on  $\gamma$ -Alumina have shown a higher H<sub>2</sub>/CO ratio than other samples. For the zeolite supported catalysts when Ni/Co=2/1, the surface area and pore volume decreased but the H<sub>2</sub>/CO ratio increased by increasing the Si/Al ratio. Reverse the Water Gas Shift (WGS) reaction was not very active when the catalyst and support showed a basic property. Also, the stability of the catalysts has been tested for 30h on stream.

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### 1. Introduction

The Dry Reforming of Methane (DRM) is one of the important processes that produces the mixture of H<sub>2</sub> and CO, also known as syngas with the molar ratio of 1:1. One of its important applications is in the Fischer-Tropsch synthesis for the production of liquid

hydrocarbon. The reforming of CO<sub>2</sub> is a reaction that consumes CO<sub>2</sub> and CH<sub>4</sub> which are two harmful greenhouse gasses. On the other hand, these gasses are inexpensive and very easy to access [1, 2]. The DRM consists of the following reactions [3]:



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The reaction 1 is a primary reaction of DRM. The second reaction is the Reverse Water Gas Shift (RWGS) reaction, an undesirable reaction and the reason for decreasing the H<sub>2</sub>/CO ratio. Boudouard reaction (reaction 3) and methane decomposition reaction (reaction 4) are the main effects of the coke formation that occurs between 633 and 700 °C according to thermodynamics. As it is clear from these equations, DRM is an endothermic reaction so this reaction must occur at high temperatures to obtain high H<sub>2</sub>/CO ratios. In this condition, the carbon deposition on the catalysts is increased, and catalysts lose their activities [3-5]. In the DRM reaction, the support and the active site have the most effect on the catalyst performance [3]. Several methods are suggested to decrease the deposition of carbon on the Ni-based supported catalyst [1]. To mention a few, adding the second metal, changing the catalyst preparation method, or using the support with strong Lewis basicity can be named [2, 6, 7]. Higher H<sub>2</sub>/CO ratios are achieved on the catalysts with high acidic properties. However, in this situation, the carbon deposition increases, but when the catalyst has some basic properties, the H<sub>2</sub>/CO ratio is lower than the acidic catalyst, but the deposition of carbon on the catalyst is less than the other one. So the addition of the second metal, especially a precious metal, is one of the best methods for developing the catalyst resistance against the carbon deposition [2].

Many types of research have been done on the effect of adding a second metal to the Ni supported catalysts such as Rh [8], Pt [9, 10], Pd [11] and Ru [12]. However, this metal is expensive and not cost effective for use as a second metal for DRM [3, 13].

Cobalt is one of the non-noble metals that is

used as a second metal in the Ni-based catalyst. Cobalt-based catalysts have high stability and good resistance against the carbon deposition [1, 14, 15]. For the bimetallic Ni-Co catalysts, the Ni/Co ratio has the highest impact on the activity of the Ni/Co supported catalysts [15]. Koh et al. have suggested that the rate of the coke formation decreases when the catalyst has cobalt as an active site since cobalt has a good activity for the oxidation of coke. Therefore, the deposited carbon on the catalyst is oxidized to CO or CO<sub>2</sub> [14]. This catalyst has an inverted AB<sub>2</sub>O<sub>4</sub> spinel structure [16] and the behavior of this structure in the dry reforming of methane remains unknown.

The advantage and novelty of this study is its ability to investigate the performance of the AB<sub>2</sub>O<sub>4</sub> spinel structure in the activity of the bimetallic Ni-Co catalyst in the dry reforming of methane. In addition, the effect of this type of structure on the deposition of carbon on the catalyst must also be answered according to its perovskite structure.

Also, the effects of different Si/Al ratios on the support have been investigated. Several characterization methods including XRD, XRF, BET, TGA and SEM/EDX were used to correlate the catalyst performance with their specified properties and elucidate the effects of different Si/Al ratios and preparation methods.

## 2. Samples preparation

### 2.1. Zeolite preparation

#### 2.1.1. Synthesis of the silicate-1 seeds

The silicate-1 seeds were prepared using the same exact method as the one used before [2]. To prepare the Silicate-1 seeds, TPAOH: TEOS: H<sub>2</sub>O: C<sub>2</sub>H<sub>5</sub>OH with the molar ratios of 3:10:1500:40 were used. Tetra Ethyl Ortho Silicate (TEOS 99 %, MERCK), which was

used as a silica source, and tetrapropylammonium hydroxide (TPAOH, 40 wt % solution in water), which was used as a template, were added to the mixture of deionized water and ethyl alcohol respectively while the solution stirred. To obtain a homogenized and clear solution, that mixture is stirred for an hour at room temperature. The mixture is treated hydrothermally at 130 °C for 5 h. Then, silicate-1 seeds are prepared and directly used for the synthesis of ZSM-5.

### 2.1.2. Synthesis of Na-ZSM-5 (different Si/Al ratios)

For the preparation of the zeolite samples with different Si/Al ratios, SiO<sub>2</sub>: Al<sub>2</sub>O<sub>3</sub>: NaOH: H<sub>2</sub>O with the molar ratios of 100: x: 6: 1500 are used, following the procedure described by [2]. First, Al (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O as an aluminum source and sodium hydroxyl (NaOH, Merck 99.99 %) were solved in deionized water and stirred until a clear solution was achieved. The TEOS was used as a silica source, silicate-1 that was prepared previously and 1, 6 diamino hexane (99.5 %, MERCK) was dropped into the mentioned solution. After 2 h., the mixture was transferred into the autoclave and kept at 160 °C for 2h. The prepared solid was then dried in the oven for 12 h and calcined in an electric furnace at 550 °C for 6 h to remove the template and produce the zeolite crystal.

## 2.2. Catalyst preparation

### 2.2.1. Ni-Co/ZSM-5 catalysts

The supported bimetallic Ni-Co catalyst is prepared on the supports by loading 5 wt % of Ni and 2.5 wt % of Co (Ni/Co ratio equal to 2). Ni (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (99.99 %, MERCK) and Co (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (99.99 %, Asog) as the metal precursors and all zeolite samples are

prepared by the dry impregnation method. Ni (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and Co (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O are dissolved in distilled water separately and stirred until homogenous solutions are obtained. The Co salt solution is added slowly to the other solution while the solution is stirred. At the final stage the zeolite powders that have various Si/Al ratios were added to this solution slowly (NCZ(x)). All catalysts are dried overnight at 110 °C and then calcined at 550 °C for 6 h. The catalyst samples are named as NCZ(x) where x is the Si/Al ratio.

### 2.2.2. Ni-Co/SiO<sub>2</sub>

The Ni-Co/SiO<sub>2</sub> (NCS) catalyst is prepared by the sol-gel method [15, 17]. Appropriate amounts of TEOS (Merck) and Ethanol (commercial grade, 96 %) are mixed at 50 °C and stirred vigorously. Then, a mixture of ammonia (Merck, 25 %) and distilled water is added dropwise to the initial solution over 3 h. A very small amount of citric acid (0.1 M, Kaveh industry) is added to the solution and mixed for 10 min. Then a certain amount of an aqueous solution of Ni and Co precursors with the stoichiometric ratio of Ni/Co=2 was added at 50 °C and mixed vigorously for 15 minutes. Then, the pink gel is prepared. This gel is dried in the oven at 110 °C overnight and then calcined for 2 h at 550 °C.

### 2.2.3. Ni-Co/Al<sub>2</sub>O<sub>3</sub>

This catalyst is prepared with sol-gel (NCA1) and impregnation (NCA2) methods [18]. For the NCA1 sample, Al, Ni and Co precursors (Merck, 99.99 %) are dissolved separately in distilled water. Then Al and Ni solutions are mixed at 50 °C. Then a very small amount of citric acid (0.1 M, Kaveh industry) is added dropwise, this mixture is stirred vigorously

under the constant reflux for 5 h at 50 °C. Afterwards, the Co solution is added and again the second mixture is stirred under the constant reflux for 5 h. at the same temperature. For the final stage, this mixture is kept at room temperature for 12 h. for aging until the pink gel is achieved. For the NCA2 sample,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Engelhard, S.S=181 m<sup>2</sup>/g) is used as a support. Ni and Co precursors are dissolved in distilled water separately. Then the two mixtures are mixed and stirred vigorously. This mixture is heated under the constant reflux condition. Then, the alumina is added to the prepared gel to produce the pink gel. Both samples are dried overnight at 110 °C in the oven and calcined for 2 h at 550 °C.

### 2.3. Catalyst characterization

X-ray diffraction patterns are performed by X-ray diffractometer using Philips Xpert with Cu K $\alpha$  radiation ( $\lambda=1.54052$  Å) to indicate the sample phase. Phase identifications are performed by comparing the pattern spectra in the database. Using Scherrer formula for calculating the crystal size for all samples, examined by the XRD device [19] and X-ray fluorescence (XRF) analysis, is carried out with a Hirox EAGLE II XRF spectrometer for the determination of the metal content in samples. FESEM (TSCANS) is used to determine the morphology of samples. The surface area of samples is determined by the BET test (Quantachrome Chem-BET-3000) using the N<sub>2</sub> adsorption – desorption method. The TGA analysis (PL-TGA) is applied to measure the deposition of coke on the samples used in the stability test. The sample was heated up to 700 °C along with the O<sub>2</sub> flow with a ramp of 10 °C min<sup>-1</sup>.

### 2.4. Catalytic activity

The DRM reaction is carried out in a fixed-bed quartz micro reactor (I. D=2 mm, length=50 cm). The catalyst length for all tests is constant and chosen as 2 cm. for all tests, the mass of the catalyst is 0.05 g diluted with 0.25 g of the quartz seed to avoid the formation of hot spots in a micro reactor. First, samples are heated to 700 °C and reduced in situ with hydrogen flow (30 ml/min) for 3 h and kept under this condition for 1 h. Then H<sub>2</sub> is cut, and the reaction feed contains CO<sub>2</sub>/CH<sub>4</sub>/He=1/1/8 (molar ratio) with GHSV=12000 mL.g<sup>-1</sup>.h<sup>-1</sup> added. The reactions occurred at atmospheric pressure and different temperatures (700-800 °C). The product from the reactor is analyzed with a gas chromatograph equipped with Propack Q and Molecular sieve columns, and the detector is TCD [2, 20].

## 3. Results and discussion

### 3.1. XRD analysis results

XRD patterns of all samples are shown in Figure 1. For all zeolites samples, it is clear that all samples had a peak at  $2\theta = 20-30^\circ$ . This peak is related to the ZSM-5 (JCPDF 84-385) crystal. The crystalline structure cannot be completed by increasing the Si/Al ratio, and samples with an amorphous structure and 5NCZ (30) have a better crystalline structure than the other zeolite samples. In all samples, NiO (JCPDF 4-835) and Co<sub>3</sub>O<sub>4</sub> (JCPDS 42-1467) are detected, so it seems that dispersion of active sites cannot be improved by increasing the Si/Al ratio. One reason for the amorphous zeolite being prepared by this method, is that 2 h is not enough as the hydrothermal treatment time for the synthesis of zeolite. So when the time of the thermal treatment is increased, the amount of crystallization is also increased, and ZSM-5 samples have a sharper peak in XRD patterns,

this result is entirely in agreement with the results obtained by [2, 21].

The calculated average sizes of the NiO crystallite using Scherrer equation are 80 nm, 17 nm, 51 nm, 48 nm and 41 nm for NCA1, NCS, 5NCZ (30), 5NCZ (45) and 5NCZ (60) respectively. The average sizes of the Co<sub>2</sub>O<sub>4</sub> crystallite are about 54 nm, 30 nm and 13 nm for 5NCZ (30), 5NCZ (45) and 5NCZ (60) respectively. It seems that by increasing the Si/Al ratio in zeolites samples, the sizes of

NiO and Co<sub>2</sub>O<sub>4</sub> are decreased. In the XRD patterns of NCS, NiO and Co<sub>2</sub>O<sub>4</sub> the phases are indicated and the result is consistent with other researches [14, 15, 18]. The pattern of NCA1 prepared by the sol-gel method has an amorphous structure, and no sign of NiO or cobalt oxides is observed but in NCA2 that is prepared by the impregnation method, NiAl<sub>2</sub>O<sub>4</sub>, and CoAl<sub>2</sub>O<sub>3</sub> phases are observed. It seems that the active site on NCA1 had a better dispersion than the that in NCA2.

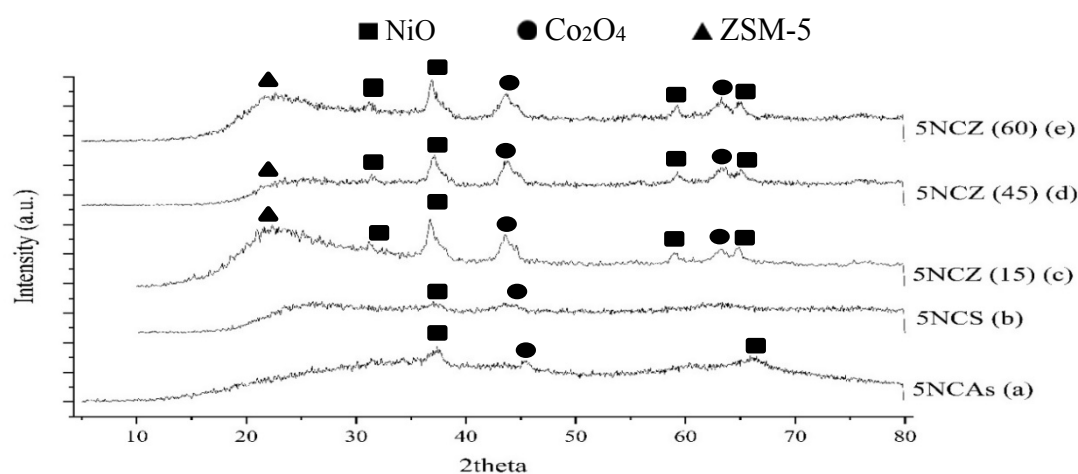


Figure 1. XRD patterns of catalyst samples.

### 3.2. XRF analysis results

The results of the XRF analysis are shown in Table 1. As it can be seen in this table, the theoretical and experimental values indicate almost the same results. The similarity of the outcomes of the theory and experimentation

shows that substances that has been used in this research are correct, and both the Si/Al ratios and the amount of the Ni-loading (5 wt %) and Co loaded (2.5 wt %) are in accordance with the amount of the theory that is used for the preparation of catalysts.

Table 1

XRF and BET test results of the fresh catalyst.

Catalyst	Ni (%)	Co (%)	Si/Al	BET (m <sup>2</sup> /g)	V <sub>P</sub> (cm <sup>3</sup> /g)
NCS	4.9	2.49	—	125.2	96.1
NCA1	5.2	2.51	0	74.3	16.9
NCA2	5.1	2.48	0	90.1	19
5NCZ(30)	4.8	2.51	28	12.2	4.85
5NCZ(45)	4.7	2.3	42	9.2	2.1
5NCZ(60)	5.1	2.4	56	7.9	1.8

### 3.3. BET

The BET test was used to obtain the specific

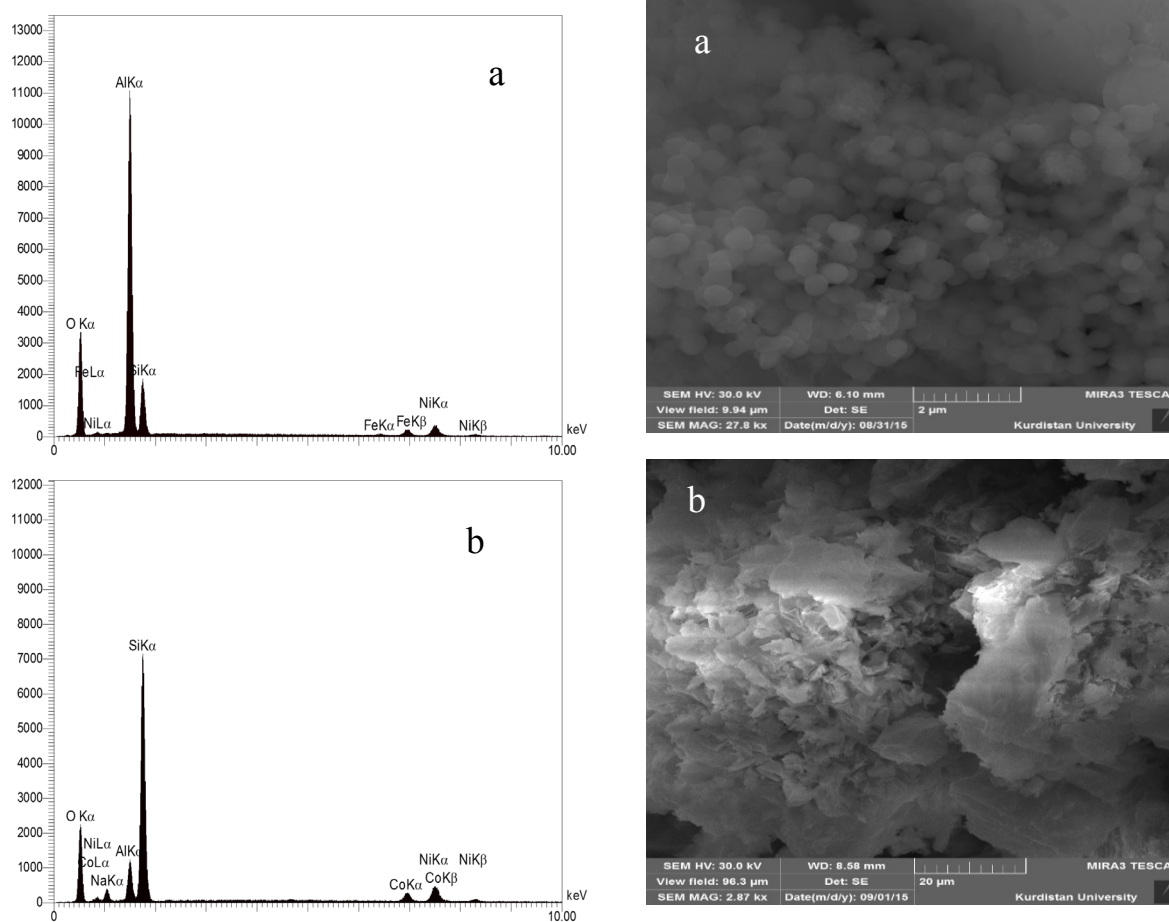
surface area and pore volume, of which the results are reported in Table 1. As it can be

seen in Table 1, when the Si/Al ratio increased from 30 to 60, the specific surface area and pore volume decreased. The high amount of the surface area and pore volume was for the NCS sample. Between zeolite samples, 5NCZ (30) had a high surface area and pore volume, which might be attributed to the well-crystallized structure during 2 h of elucidating that was suitable for the hydrothermal treatment with the hierarchical approach for this sample. Conversely, for the other two Ni/ZSM-5 samples, this time is not enough to accomplish the crystallization. These results are in agreement with the results that were reported by other researchers [21, 22]. They suggested that when the Si/Al ratio increased, fewer aluminum species were present, resulting in the decreased crystalline pore volume and specific surface area [22].

### 3.4. SEM/EDX analysis

SEM images in Figure 2 show the morphology of the 5NCZ (30) and NCA1 samples. According to this figure, NCA1 has amorphous structures. 5NCZ (30) has well spherical crystals with the crystal size in the range of 45-450 nm which agrees with the XRD results.

5NCZ (30) is amorphous. Because the aging time during the zeolite preparation process is about 2 hours, which causes the growth of the molecular network of the catalyst structure to be incomplete and leads to the formation of an amorphous irregular structure, so in SEM images, the amorphous irregular structure which is seen causes the crystal boundary in the 5NCZ (30) sample to appear indistinct. These results are in line with the results reported by other researches [21, 23].



**Figure 2.** SEM-EDX analysis of the fresh catalyst. (a) 5NCZ (30), (b) 5NCA1.

The EDX analysis is used to confirm that the materials used in this research were the right ones. Also, dispersion of the used materials is uniform as shown in Figure 2. In addition, no impurity is observed and only the essential species (Al, Si, Ni and Na) exist. The appearance of Na<sub>2</sub>O in EDX results has been attributed to the Na-form of ZSM-5 zeolites in the support.

### 3.5. Catalyst activity

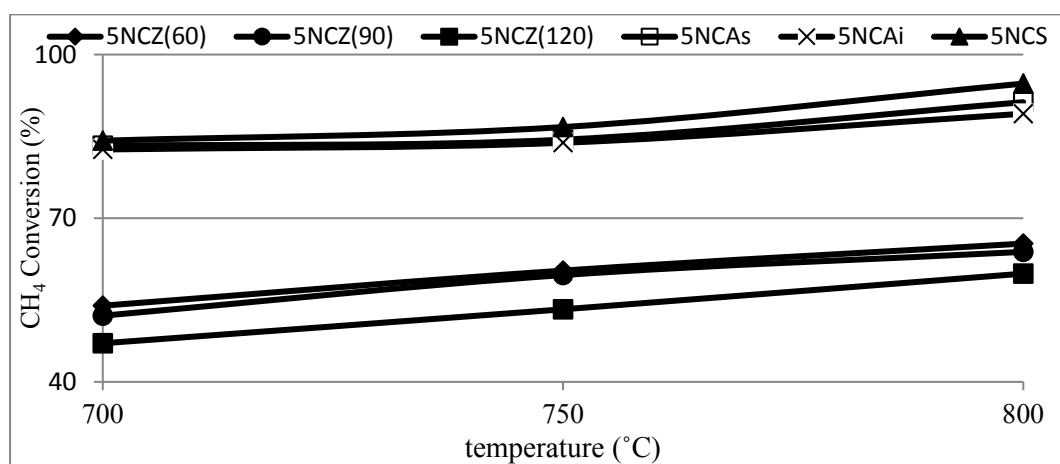
The activity test was done with the feed containing CH<sub>4</sub>/CO<sub>2</sub>= 1/1 (molar ratio) at the atmospheric pressure. The conversions of CH<sub>4</sub>, CO<sub>2</sub> and the H<sub>2</sub>/CO ratio that were obtained by gas chromatograph have been shown in Figures 3-4 and Table 2. Considering that the dry reforming of

methane is an endothermic reaction, increasing temperature has direct effects on the equilibrium conversions. Therefore, when temperature increases, the conversion of methane, CO<sub>2</sub> and also the H<sub>2</sub>/CO ratio will move to higher values. This result is fully confirmed by figures 3 and 4. All samples except 5NCZ (60) had better CO<sub>2</sub> conversions than the CH<sub>4</sub> conversions, and the H<sub>2</sub>/CO ratio was lower than 1, it seems that RWGS is the main reason for this phenomenon. For 5NCZ (60), the methane conversion was higher than the CO<sub>2</sub> conversion. For this catalyst, RWGS had a lower activity than other samples which is the main effect of increasing the H<sub>2</sub>/CO ratio by increased temperature during the reaction.

**Table 2**

Activity result of all samples.

Catalysts	Temperature (°C)								
	700			750			800		
	X <sub>CH<sub>4</sub></sub>	X <sub>CO<sub>2</sub></sub>	H <sub>2</sub> /CO	X <sub>CH<sub>4</sub></sub>	X <sub>CO<sub>2</sub></sub>	H <sub>2</sub> /CO	X <sub>CH<sub>4</sub></sub>	X <sub>CO<sub>2</sub></sub>	H <sub>2</sub> /CO
NCS	94.21	97.56	0.88	96.71	98.86	0.91	98.68	99.26	0.97
NCA1	93.28	96.32	0.86	94.4	97.54	0.87	95.27	98.77	0.93
NCA2	92.60	98.27	0.80	95.37	98.85	0.86	97.16	99.42	0.91
NCZ(30)	56.96	65.81	0.26	60.39	70.08	0.33	65.34	74.35	0.48
NCZ(45)	52.12	54.54	0.27	59.57	65.90	0.36	63.83	72.72	0.5
NCZ(60)	47.07	39.81	0.32	53.30	47.89	0.38	59.83	53.16	0.52



**Figure 3.** Methane conversion vs.the reaction temperature for all samples.

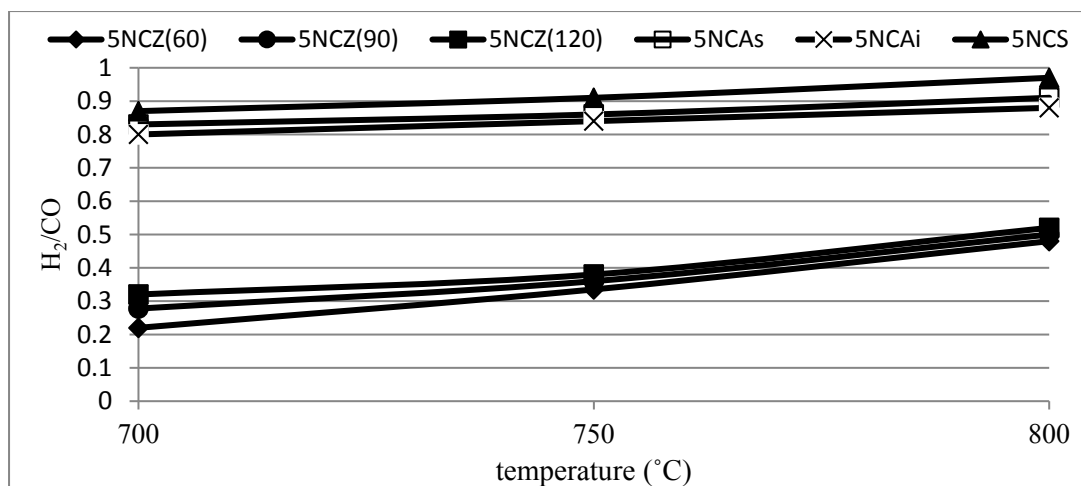


Figure 4. H<sub>2</sub>/CO ratio vs. the reaction temperature for all samples.

When temperature is increased from 700 °C to 800 °C, the methane and CO<sub>2</sub> conversions, and the H<sub>2</sub>/CO ratio increase as well. The NCS sample had a high activity and higher H<sub>2</sub>/CO ratio than other samples. 5NCZ and 5NCA1 that were prepared by the sol-gel method had high activities; it seems that the sol-gel method prepares a better catalyst with the high dispersion of the active site. Catalysts show that as the Si/Al ratio increases from 30 to 60, the conversions of both CO<sub>2</sub> and CH<sub>4</sub> increase, but the H<sub>2</sub>/CO ratio decreases. It seems that when the process needs the removal of CH<sub>4</sub> and CO<sub>2</sub>, the catalyst with acidic properties is used but for producing the high H<sub>2</sub>/CO ratio, the catalyst must have a basic property.

In order to have proper performance in bimetallic catalysts, the second metal must play a positive role in the reforming process and should also help the catalyst have a high resistance to the carbon deposition. The NiCo<sub>2</sub>O<sub>4</sub> catalyst is a perovskite catalyst type that is an inverted spinel of the overall structure of AB<sub>2</sub>O<sub>4</sub>. In this structure, A<sup>2+</sup> atoms and part of B<sup>3+</sup> atoms are in the octahedral structure and the rest of B<sup>3+</sup> are in the quadrilateral structure, so during the reforming process, the structure is broken and

re-formed as B(AB)O<sub>4</sub> [16]. This helps the cobalt atoms here, which are B, with the help of the A atoms, which are nickel, to play a role beyond the promoter in the catalyst, and as a secondary active phase in the reforming process alongside the primary active phase of nickel, in the reforming process progresses. As a result, the activity and conversion of methane and carbon dioxide are improved. In addition, due to the presence of abundant oxygen in the structure as well as the release of oxygen during the remodeling of B(AB)O<sub>4</sub>, the deposition of carbon on the catalyst is reduced, which inactivates the catalyst structure [13].

In all tested temperatures for each sample, the concentration of H<sub>2</sub> is less than that of the CO that can be attributed to the Reverse Water Gas Shift Reaction (RWGS). This result is consistent with other researches [5]. Estephane et al. reported that the bimetallic Ni-Co catalyst with 7 wt % of the total metal loading and Ni/Co=2 supported with industrial ZSM-5 with Si/Al=23 and S.A.=284 m<sup>2</sup>/g and carried out a DRM test with CH<sub>4</sub>/CO<sub>2</sub>=1/1 at 700 °C with GHSV=60000 Lh<sup>-1</sup>g<sup>-1</sup>, which lost activity after 12 h. Methane conversion decreased 13.5 % after this time. It seems that the



creation of  $\text{NiCo}_2\text{O}_4$  and deposition of graphitic carbon on the catalyst are the two main reasons for the deactivation of the catalyst [24].

### 3.6. Stability test

The stability test is performed for zeolite samples at  $800\text{ }^\circ\text{C}$  because at this temperature the catalysts have a high activity and high ratio of  $\text{H}_2/\text{CO}$  with a feed containing  $\text{CH}_4/\text{CO}_2 = 1/1$  for 30 h. The methane conversion results and  $\text{H}_2/\text{CO}$  ratio for the stability tests are presented in Figure 5 and 6. The results show that all zeolite samples have good activity and stability during 30 h on

stream (TOS). It can be concluded that the deposition of carbon on the surface of the catalyst is small, resulting in the stable conversion and  $\text{H}_2/\text{CO}$  ratio. The amount of carbon deposition on 5NCZ (30) that was examined by TGA was 3 wt %. However, under these conditions, the catalyst had a good activity and stability, it seems that the type of carbon deposition on the catalyst was not the reason for having a deactivated catalyst. In addition, the high stability of this particular sample during TOS can be related to the small size of Ni. Another reason for the high activity of these samples is the added Co as the second active site.

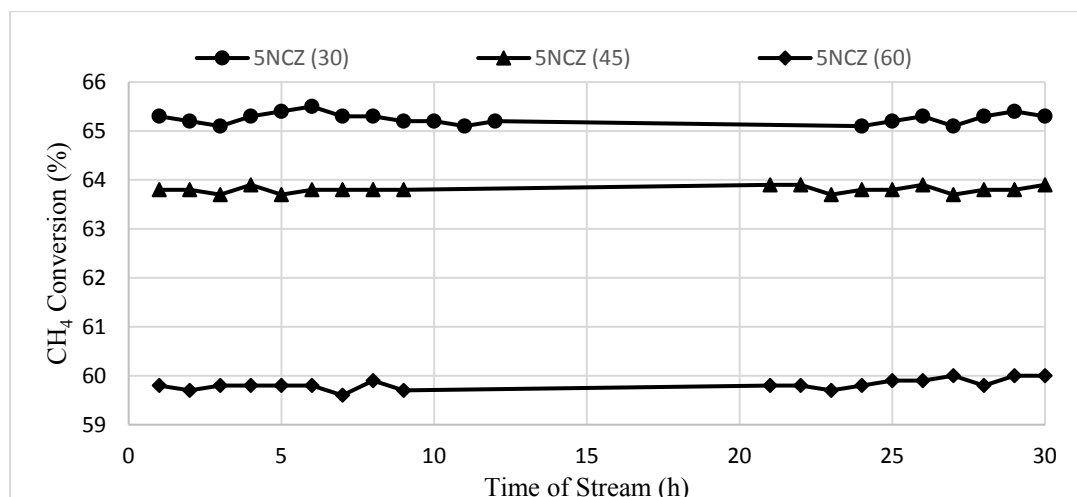


Figure 5. Methane conversion of stability results vs. the time of stream

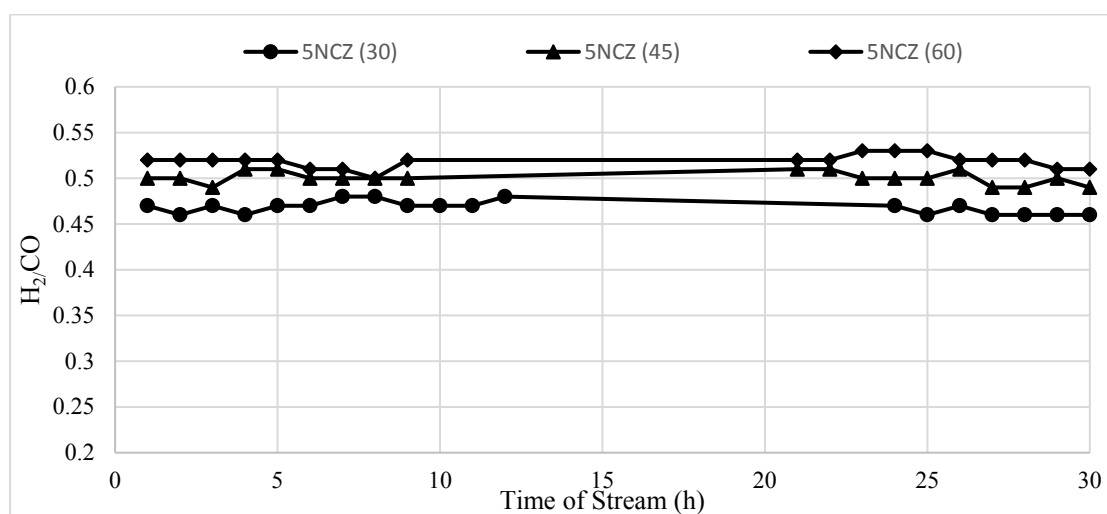


Figure 6. Ratio of  $\text{H}_2/\text{CO}$  during the stability test. The test was carried out at  $800\text{ }^\circ\text{C}$  and 1 atm.

#### 4. Conclusions

Bimetallic Ni-Co/ZSM-5 with the ratio of Ni/Co=2/1 and different ratios of Si/Al (0-∞) are successfully prepared. Various tests are performed, and considering the results, we can conclude that Ni-Co supported on silica has a better activity and higher H<sub>2</sub>/CO ratio than other samples. Also, the specific surface area and pore volume of ZSM-5 decrease when the Si/Al ratio increases. Further, no deactivation is observed during the TOS and 5NCZ (X) samples show the highest stability after 30 h. Last but not least, the results indicate that the synthesis time and Si/Al ratio play important roles in creating the well-crystallized structure of Ni-Co/ZSM-5 catalysts.

#### Acknowledgement

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