Research Article GU J Sci 31(4): 1064-1077 (2018)

Gazi University

Journal of Science

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The CO Methanation Over The Rh and Ru Promoted NiO-CeO_2-ZrO_2 Catalysts

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Article Info

Received: 09/03/2017
Accepted: 01/06/2018

Keywords

Catalysts
Methanation
Surfactant
Carbonmonoxide

Abstract

In this study, Rh and Ru promoted NiO-CeO_2-ZrO_2 catalysts were prepared with different Rh and Ru loadings (3, 4, 5 (wt.%)) by using two different methods. N_2 phsisorption, X-Ray diffraction, scanning electron microscope with energy-dispersive (SEM-EDX) techniques were used in order to characterize the catalysts. Catalytic activities of the catalysts were tested for CO methanation. The selective CO methanation catalytic activity tests were made over the most active catalysts. The effect of the Rh and Ru loading and preparation method on the CO methanation was discussed. The Ru and Rh have different effect on the surface areas of the catalysts and identifiable peaks for Rh and Ru not observed from the XRD analysis. Because of the low ratio of Rh and Ru in catalysts structures, both Ru and Rh containing catalysts gave similar CO methanation activity results. The 50% conversion temperatures of the 3% Ru/NiO-CeO_2-ZrO_2 catalysts which were prepared by the co-precipitation and surfactant assisted co-precipitation are 191 °C and 185 °C, respectively. Selective CO methanation was made over the 3% Ru/NiO-CeO_2-ZrO_2 catalysts. Catalysts gave good activity until 300 °C. Because of the reversed water gas shift reaction activities of the catalysts were decreased after this temperature.

1. INTRODUCTION

Carbonmonoxide and carbondioxide methanation were studied over the nickel based catalysts by Sabatier and Senderens many years ago. Nickel catalysts can remove both CO and CO_2 by methanation reaction at 350 °C [1]. Several types of catalysts were used for the methanation of carbonoxides [1-3]. The studies showed that, because of the reverse water gas shift reaction, CO ratio increased at high temperatures. In order to increase the methanation rate and to suppress the reverse water gas shift reaction, the promoters are added to the methanation catalyst structure such as Rh, Ru, Pd, Pt [1]. The performace of CO methanation catalyst is affected by the metal loading and crystallite size [4]. After the literature survey, we found that Rh promote the CO methanation. Some researchers investigate the effect of rhodium on the water-gas shift performance [5-6]. According to these studies, the addition of rhodium to the zirconia supported CeO_2 enhances the CO conversion by the production of methane with CO methanation reaction [5]. And also over the Rh/CeO_2 catalyst, methane formation is observed during the Water Gas Shift Reaction (WGS) reaction. In the presence of large H_2 concentration in the feed, the outlet CH_4 concentration increased [6]. De Rogatis et.al. [7] and Birst et.al. [8] studied the ethanol steam reforming over the Rh/$Ce_{0.2}Zr_{0.9}O_2$-Al_2O_3 and Rh/$Ce_xZr_{1-x}O_2$ catalysts, respectively. In these studies the methane formation occurs via CO hydrogenation over the catalysts. The general result is that the incorporating of Rh in to the catalyst system gives a positive effect on the methanation reaction, because H_2 and CO or CO_2 easily chemisorbed and activated on the surface of the catalyst [9]. The methane formation requires dissociation of CO molecule and takes place on specific site(s) present on rhodium particles only [9].

In order to increase the stability and the performance of catalytic activity, there is great interest in the three metal-containing catalysts. In our previous study 50/25/25 NiO-CeO_2-ZrO_2 catalyst prepared by the surfactant assisted co-precipitation method has 50% CO conversion to methane at 198 °C [10]. Noble metals Rh and Ru were used as dopant to NiO-CeO_2-ZrO_2 catalyst in this research in order to decrease

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50% conversion temperature and to increase the methanation activity. These catalysts were prepared by two different methods with different Rh loadings.

2. EXPERIMENTAL

2.1. Catalysts Preparation

NiO-CeO_2-ZrO_2 (mol.% 50/25/25) catalyst with different Rh and Ru loadings (wt.% 3, 4, 5) were prepared by two precipitation method, which were described below. Characteristic properties were determined by using different techniques. Finally, methanation studies were carried out.

2.1.1. Co-precipitation

$Ni(NO_3)_2.6H_2O$ (Aldrich, 99.8%), $Ce(NO_3)_3.6H_2O$ (Fluka, 99.0%), $Zr(NO_3)_2.xH_2O$ (Sigma, 99%), $Rh(NO_3)_3$ (Aldrich, 99.8%), $Ru(NO)(NO_3)_3$ (Aldrich, 99.8%) were dissolved in distilled water to adjust the desired molar ratios. Total concentration of the metals in the final aqueous solution was 0.1 M. The Na_2CO_3 (1M) solution was added to the solution to adjust the pH of the solution to 8. The precipitates were aged for 3h at pH value of 8, and then filtered, washed with hot distilled water several times in order to remove excess ions. They were air dried overnight at 110 °C. Finally, catalysts were calcined in air at 500 °C for 3h. The co-precipitation technique was designated as "C".

2.2.2. Surfactant-assisted co-precipitation

6 mmol of cetiyltrimethylammoniumbromide (CTAB) was dissolved in 200 mL deionized water for 15 minutes by using a mechanical stirrer. Then the desired amount of metal salt solution was added to CTAB solution under vigorous stirring. After this solution was mixed at 0.5 h, sodium hydroxide solution was added to this solution at 0.2 mol/l flow rate until the pH value of the solution reached 10. Then the solution was mixed for 12 h, the precipitate was aged for 3 h at 90 °C. Then it was filtered, washed with hot distilled water several times in order to remove excess ions. They were air dried overnight at 110 °C. Finally, catalysts were calcined in air at 500 °C for 3h. The surfactant-assisted co-precipitation technique was designated as "S".

2.3. Catalyst Characterization

Different techniques were used in order to determine the physical properties of the catalysts; namely, X-ray diffraction (XRD), N_2 phsisorption, scanning electron microscopy (SEM). BET, multipoint surface areas, pore volumes and pore diameters of the catalysts were evaluated by using Quantochrome Autosorp 1C/MS device. Before the analysis, samples were outgassed at 300 °C for 1 h. Average pore sizes were determined by using the BJH method. X-ray diffraction patterns were obtained using a PHILIS PW 1840 diffractometer. A rigaku rotating anode X-ray diffractometer system generating CuKα radiation was used to obtain XRD patterns. Surface morphology and composition was determined by using scanning electron microscopy.

2.4. Activity Measurements

Catalytic activities of the catalysts were determined for the CO methanation reaction. Before the catalytic measurements fresh catalysts were reduced in situ under pure H_2 atmosphere for an hour at 500 °C. Catalytic activity measurements for the CO methanation reaction were carried out in a fixed bed quartz tubular reactor. The 25 mg of catalyst was used in the activity experiments. The feed composition that was used in the reaction experiments was set as 1% CO, 50% H_2 and remaining He. Temperature range of the reactor was changed from 125 °C to 375 °C. The flow rate of the feed gas was 25 mL/min. Analysis of the reactor effluent was performed by an on-line Perkin Elmer CLARUS 500 gas chromatograph equipped with a thermal conductivity detector (TCD). The chromatograph column packing was carbosphere and the column temperature was maintained at 50 °C. (The detailed calculation procedure is given at Derekaya et.al. (2014) for the % CO conversion) [10].

Selective CO methanation catalytic activities of the catalysts were made on the same reaction system described above. Before the selectivity measurements catalysts were in-situ reduced under pure H_2 atmosphere for an hour at 500 °C. And 25 mg catalyst was used. A 1% CO, 25% CO_2, 50% H_2 and remaining He feed gas composition was used. Temperature range of the reactor was changed from 100 °C to 600 °C.

3. RESULTS AND DISCUSSION

3.1 Characterization Results

The BET surface areas, average pore diameter, pore volume results obtained from N_2 phsisorption measurements are shown in Table 1. Catalysts showed different behavior according the type of the promoter. Surface areas of the catalysts increased with increasing Ru ratio in the catalysts structure but surface area values were decreased by increasing Rh amount. Preparation method has a great effect on the physical properties of the catalysts. In recent studies, materials called surfactants were used in the preparation techniques to obtain catalysts with better properties. The content of surfactant template influences the textural properties of the catalysts. It was known that anionic and cationic surfactants have an important role on pore size distribution [11, 12]. As it might be expected catalysts prepared by the surfactant assisted co-precipitation method gave higher surface area values. Table 1 and Figure 1 also show the average pore diameters of the catalysts. Catalysts prepared by the co-precipitation method have both uniform and broad peaks. On the other hand, catalysts prepared by the surfactant assisted co-precipitation method have different behavior. These catalysts have average pore diameter which is focused on two values on the scale. Because of the small pores, these catalysts gave larger surface are values. This result can be supported by Zou et.al. [13]. They found that when surfactants are involved in the precipitation process much higher surface areas could be obtained [13]. The highest surface area value was obtained from 3-RhNiCeZr-S catalyst. The amount of the Rh on the average pore diameter has negligible influence. All catalysts have average pore diameter in the mesopore diameter scale (2nm<d_{avr}<50nm). According to the pore volume results, catalysts prepared by the co-precipitation method have higher meso+micro pore volume. All catalysts have Type IV adsorption/desorption isotherm in the BDDT classifications, which is the characteristic curve for mesoporous materials (Figure 2). The existence of the mesoporous structure gave the optimum pore size in helping to adsorb the reactant gases on the surface of the catalyst itself [14].

Table 1. *Physical properties of the catalysts obtained from N_2 phsisorption measurements*

Catalysts	Multipoint BET Surface Area, m^2/g		Average Pore Diameter nm		Mikro+Meso Pore Volume, cc/g, STP		Total Pore Volume cc/g, STP	
	C[1]	S[2]	C	S	C	S	C	S
3% Ru-NiCeZr[3]	46	67	17.7	4.9, 28.3	176	116	188	124
4% Ru-NiCeZr	48	77	17.9	4.9, 28.3	165	103	172	106
5% Ru-NiCeZr	62	83	17.9	4, 29	234	111	261	115
3% Rh-NiCeZr	73	81	18	5.6, 17.4	293	133	427	138
4% Rh-NiCeZr	66	79	17.2	4.8, 16.9	243	122	266	126
5% Rh-NiCeZr	42	68	12.4	4.8, 17.7	103	118	110	124

[1] :Co-precipitation method

[2] :Surfactant assisted co-precipitation method

[3] : $NiO-CeO_2-ZrO_2$

Figure 3-6 shows the x-ray diffraction patterns of the catalysts. All catalysts gave three identifiable peaks which were due to the CeO_2, CeZroxide and NiO. The peaks due to the CeO_2 were observed at 2θ= 29.3°, 33.9°, 48.7°, 56°; the peaks due to the CeZroxide were observed at 2θ= 70.6°, 75.7° and 79.3°; the peaks due to the NiO were observed at 2θ= 37.4°, 43.5°, 63°. The NiO and CeO_2 crystalline diffraction peaks are small and broad peaks due to the high dispersion of this crystal phases on the catalyst structure [15]. Because of lower amount of Rh and Ru, no separate phase of rhodium and ruthenium were found from

XRD analysis. Concentrations of Rh and Ru in the catalysts are below the XRD detection limit [16-20]. The average crystallite sizes of the NiO, CeO_2 and ZrO_2 were calculated by using the Debye Scherrer equation over the peaks which has highest intensity. The average crystallite sizes of the NiO and CeO_2 obtained from the catalysts were not changed with the preparation method and values are equal to 90 Å and 104 Å, respectively. The preparation method has different effect on the average crystallite size of the ZrO_2. The average crystallite size of the ZrO_2 prepared by the co-precipitation method and the surfactant assisted co-precipitation method are 83 Å, 99 Å, respectively.

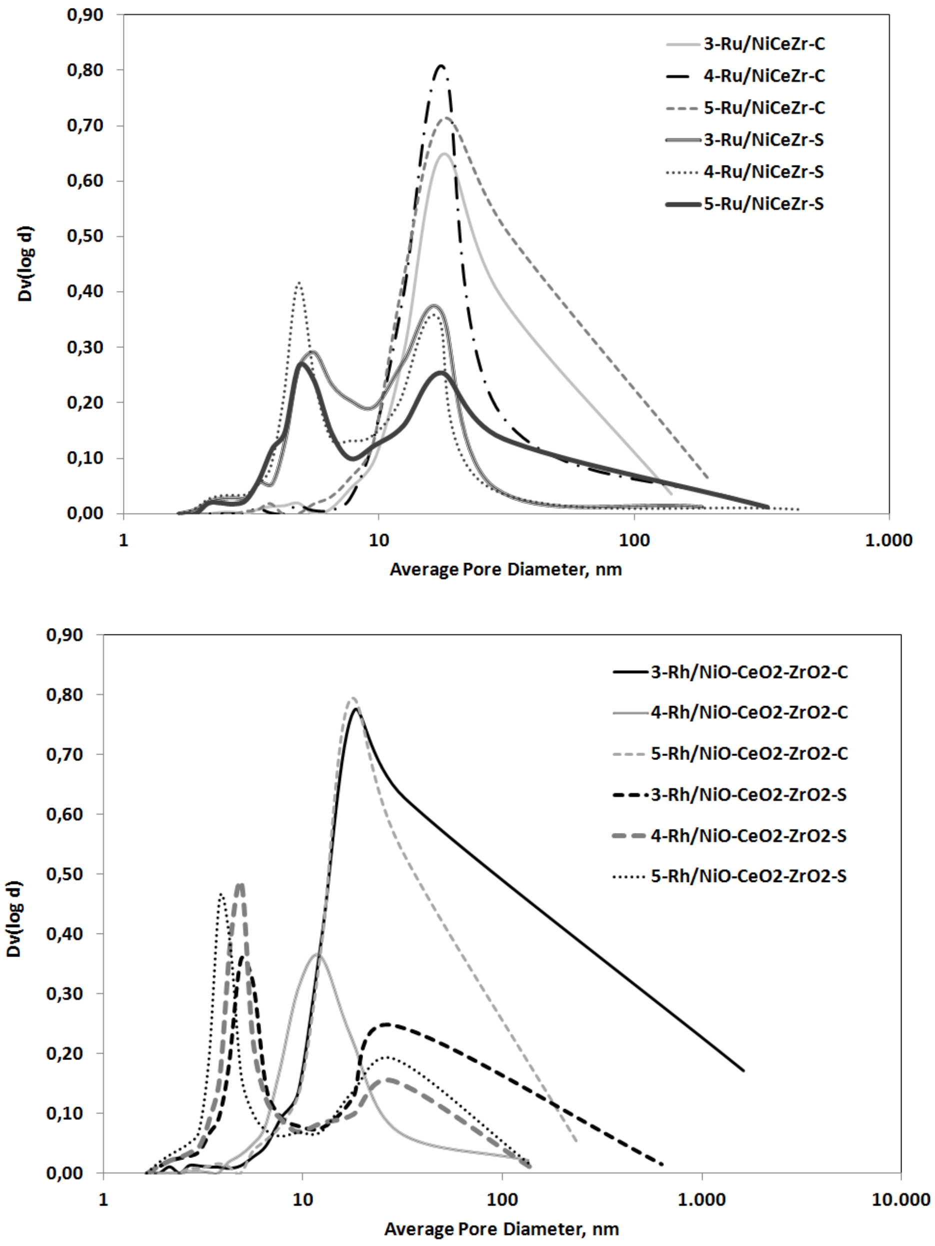

Figure 1. *Average pore dimater results of the catalysts*

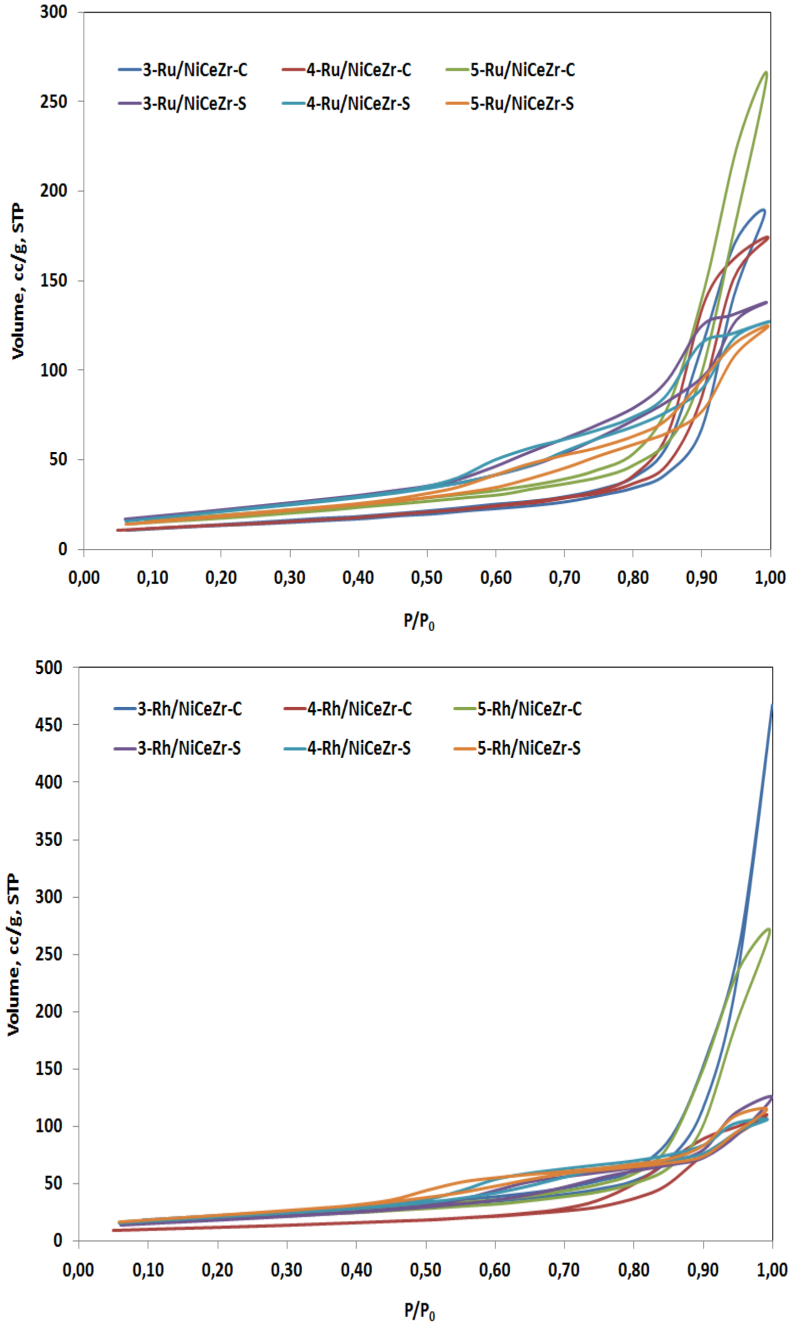

Figure 2. *N_2 adsorption/desorption isotherms of the catalysts*

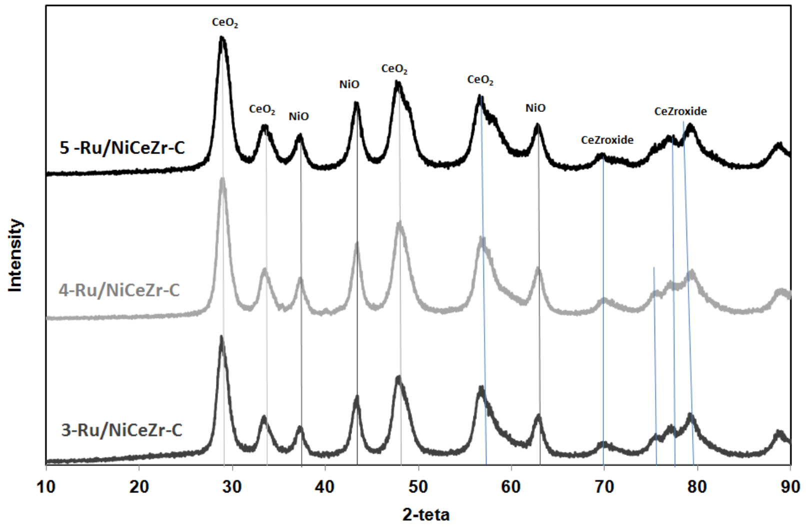

Figure 3. *X-Ray diffraction patterns of the Ru/ NiO-CeO$_2$-ZrO$_2$ catalysts prepared by the co-precipitation method.*

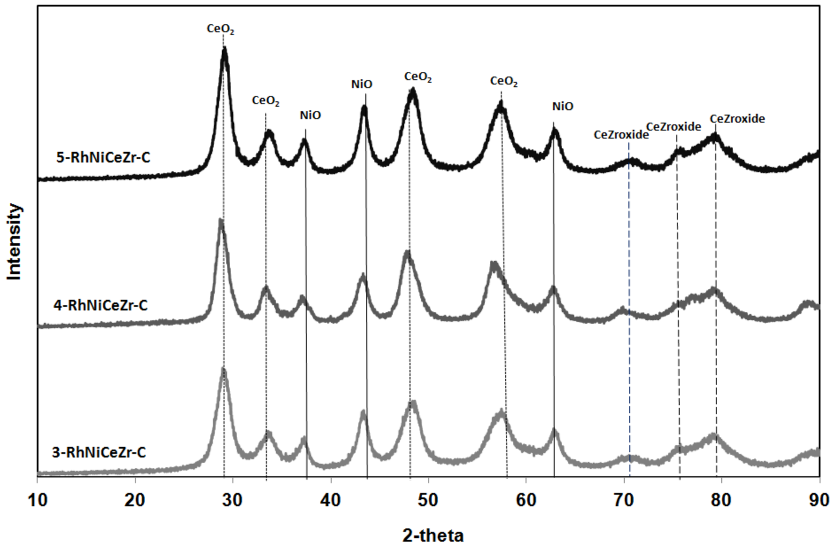

Figure 4*. X-Ray diffraction patterns of the Rh/ NiO-CeO$_2$-ZrO$_2$ catalysts prepared by the co-precipitation method*

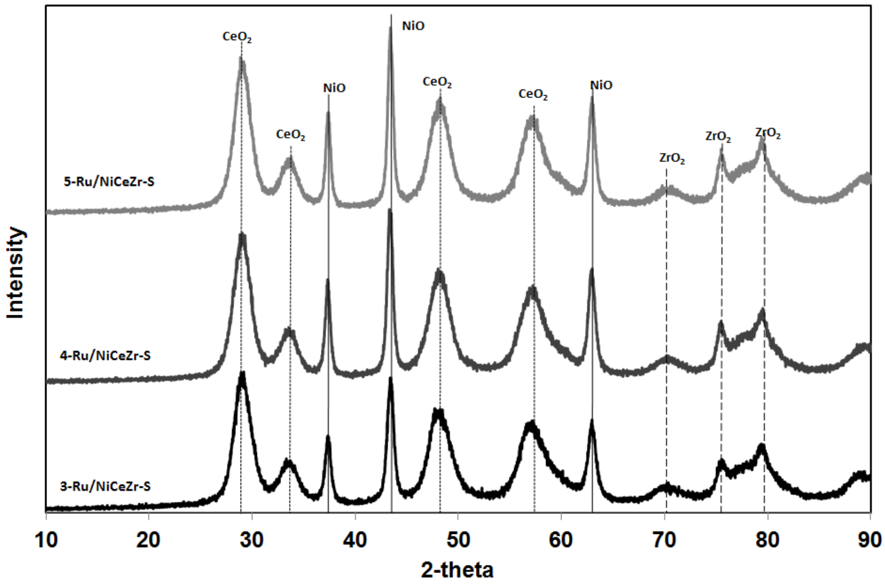

Figure 5. *X-Ray diffraction patterns of the Ru/ NiO-CeO_2-ZrO_2 catalysts prepared by the surfactant assisted co-precipitation method*

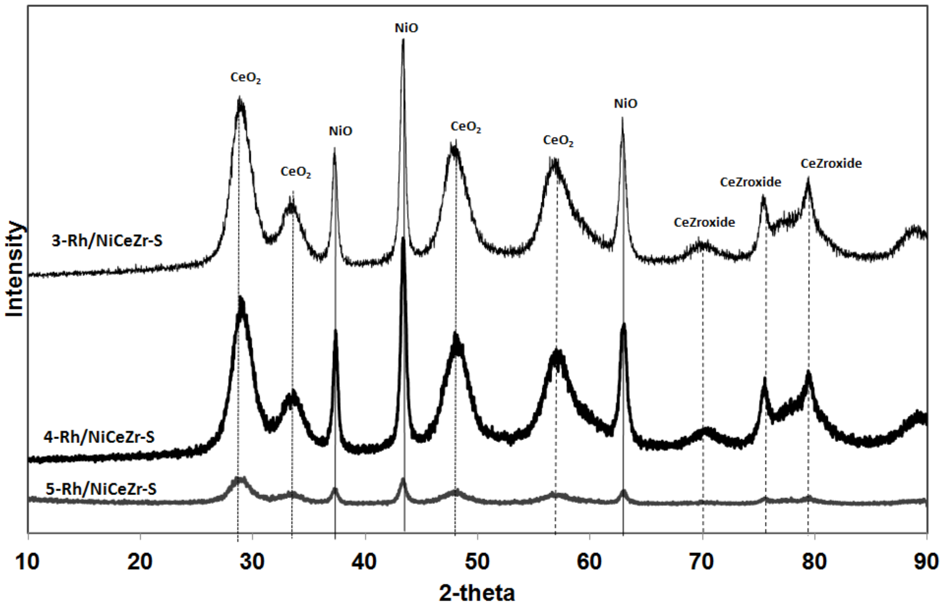

Figure 6. *X-Ray diffraction patterns of the Rh/ NiO-CeO_2-ZrO_2 catalysts prepared by the surfactant assisted co-precipitation method*

From EDX measurements % weight concentration of each elements present in the catalyst were obtained and listed in Table 2. The desired Rh loadings were achieved over all catalysts. On the other hand the desired Ru loadings could not be obtained over the all catalysts. SEM photographs were taken for the most active catalysts for the CO methanation which are 3-RuNiCeZr-S and 3-RuNiCeZr-C catalysts. The SEM photograph of the catalyst that was prepared by the co-precipitation method shows that the particles shapes and sizes are similar. On the other hand, over the catalyst that prepared by the surfactant assisted co-precipitation method most of the particles are small. Besides the small particles large clusters were obtained. This structure might be responsible for the higher activity. (see Figure 7 and Figure 8).

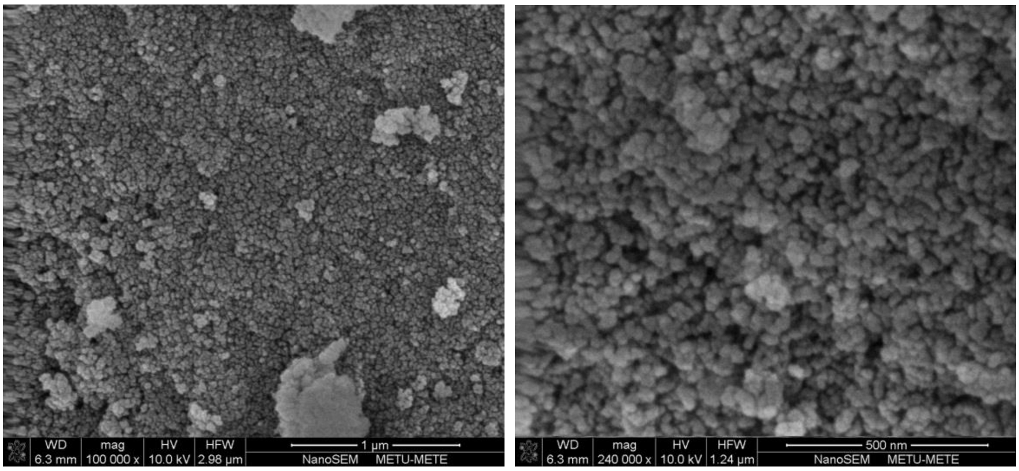

Figure 7. *SEM images of the3 Ru/ NiO-CeO$_2$-ZrO$_2$ catalysts prepared by the co-precipitation method*

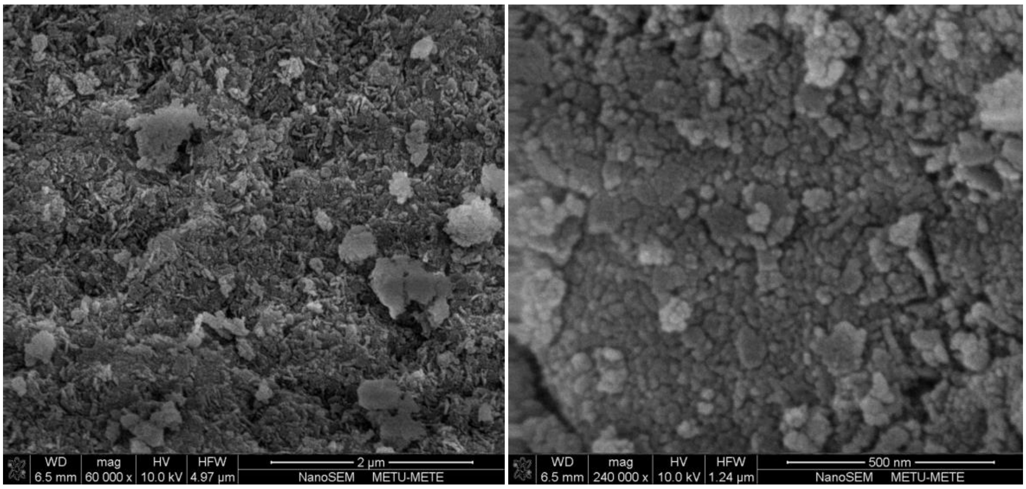

Figure 8. *SEM images of the3 Ru/ NiO-CeO$_2$-ZrO$_2$ catalysts prepared by the surfactant assisted co-precipitation method*

Table 2. *Weight percentage data obtained from the EDX analysis*

Preparation method	C	S	C	S	C	S	C	S	C	S
Catalysts	Rh		Ru		Ni		Zr		Ce	
3% Rh-NiCeZr	3.40	3.71	-	-	32.4	34.3	14.8	12.5	49.5	49.5
4% Rh-NiCeZr	4.44	4.31	-	-	34.1	34.4	12.8	13.0	48.7	48.3
5% Rh-NiCeZr	5.65	5.89	-	-	32.7	34.2	13.4	11.7	48.1	48.2
3% Ru-NiCeZr	-	-	0.33	1.01	35.3	38.0	13.9	11.8	50.5	49.2
4% Ru-NiCeZr	-	-	0.68	0.74	35.1	36.0	13.4	13.3	50.9	50.0
5% Ru-NiCeZr	-	-	0.97	1	34.5	36.4	13.7	10.9	50.9	51.7

3.2. Catalytic Activity Results

The aim of these catalysts is to convert CO present in the hydrogen rich gas mixture to methane. At the end, when CO removed, the poisoning effect of CO on the Pt catalysts of the PEMFC will be eliminated. Figure 9 shows the % CO conversion to CH_4 as a function of reaction temperature. Catalytic activities of the catalysts were determined and compared by using 50% conversion and 100% conversion temperatures which are given in Table 3. The catalyst, which has lowest 50% conversion temperature, is qualified as the most active catalyst for CO methanation. The 50% conversion temperatures of the catalyst prepared by surfactant assisted co-precipitation method are lower. This result can be connected with the characterization result. Catalyst prepared by the surfactant assisted co-precipitation method has larger surface area. The effect of the surfactant used in the preparation step as template, on the surface area, pore size, pore volume is great which can be supported by other studies [11-13]. Larger surface area leads to formation of much more active sites that are needed during the reaction. When surface area is large, the distribution of active size that is responsible for the reaction will be high. The increase in Rh and Ru loadings lead to an increase in the 50% conversion temperatures of the catalysts. For CO methanation, according to the type of catalyst preparation method, the 3-Ru/NiCeZr-C and 3-Ru/NiCeZr-S catalysts are determined as the most active catalysts. According to the catalytic activity results the change in the amount of the dopant has no great effect on the activity since the dopant values are very low and the ratios of the dopants are very close. All of CO is converted to CH_4 after 225 °C over the all catalysts. Catalytic activities can be connected with the characterization results. This result can be connected with surface area, since surface area decreased as Rh loading increased. The decrease in activity can be connected also with the also particle size. Kasuma et.al. concluded that increase in Rh loading caused in increase in particle size [21]. The difference in Rh loading significantly changed product selectivity of CO_2 hydrogenation over Rh catalysts supported on SiO_2 [21]. On the other hand, Surisetty et.al. found different results over the MWCNT-supported alkali modified MoS_2 catalysts for higher alcohols synthesis from CO hydrogenation [22]. Because of the synergic interaction of the rhodium with the molybdenum species, CO conversion increased linearly as a function of Rh loading on MoS_2-K/MWCNT [22].

Table 3. *50 % Carbon monoxide conversion temperatures of the catalysts*

Catalysts	$T_{1/2}$ Temperature °C	
Preparation Method	C	S
3% Rh-NiCeZr	197	195
4% Rh-NiCeZr	198	193
5% Rh-NiCeZr	199	198
3% Ru-NiCeZr	191	185
4% Ru-NiCeZr	196	186
5% Ru-NiCeZr	198	190

Since the best CO methanation activity was obtained over the 3-Ru/NiCeZr-C catalyst prepared by the co-precipitation method, selective CO methanation was also studied over this catalyst. In order to see the effect of the preparation method, the selectivity of the 3-Ru/NiCeZr catalyst prepared by the surfactant assisted co-precipitation method was also determined. Figure 10 shows the catalytic activity results obtained from the selective CO methanation measurements. According to the results CH_4 was formed via both CO and CO_2 methanation until 350 °C and subsequently methanation was continued over the CO_2 methanation reaction after 350 °C. When we compare the activity results obtained from the selective CO methanation studies, CO_2 methanation showed different behavior in this study. According to studies in the literature CO_2 methanation is started after CO methanation is completed [23, 24].

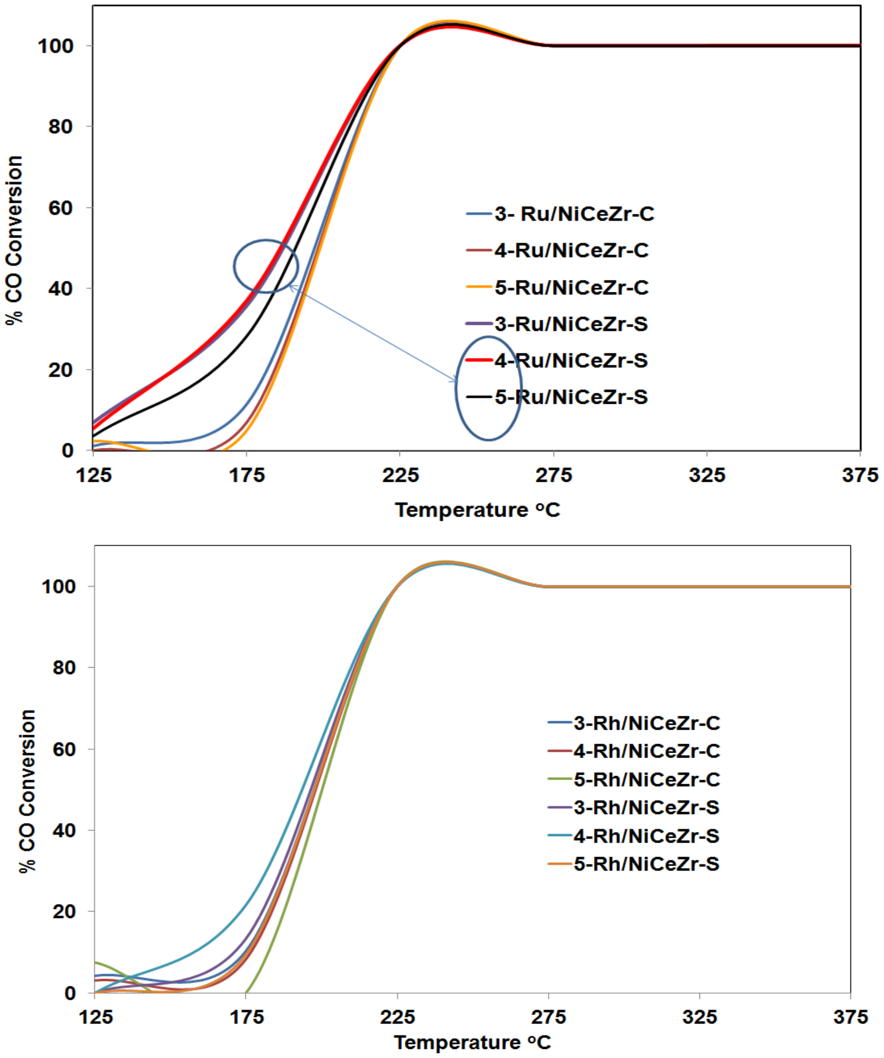

Figure 9. *CO methanation activities of the catalysts as a function of the reaction temparature (1% CO, 50% H_2 and rest He: 45000; Space Velocity: 45000 h^{-1}, 25 mg catalysts)*

In general, the maximum CH_4 formation is obtained between the temperatures 300 °C-350 °C. Between these temperatures the maximum conversion in H_2 is also obtained. After 350 °C the H_2 conversion and CH_4 formation were decreased because of the reversed water gas shift reaction (RWGS: $CO_2 + H_2 \leftrightarrow CO + H_2O$) [25]. The conversion of CO_2 is continued after 350 °C. As a result of the RWGS reaction the amount of the CO in the effluent gas mixture was increased. If we compare the catalytic activities of the 3-Ru/NiCeZr-C and 3-Ru/NiCeZr-S catalysts over the % CO in the effluent gas mixture, the 3-Ru/NiCeZ-S is most active catalysts since the CO percentage goes to zero at 200 °C. On the other hand the 3-Ru/NiCeZ-C is suitable only at 300 °C since % CO is at lowest value at this temperature. In general, selective CO methanation can be study over the 3-Ru/NiCeZr-C and 3-Ru/NiCeZr-S only between the temperatures 200-300 °C since the % CO in the effluent gas mixture is at lowest value.

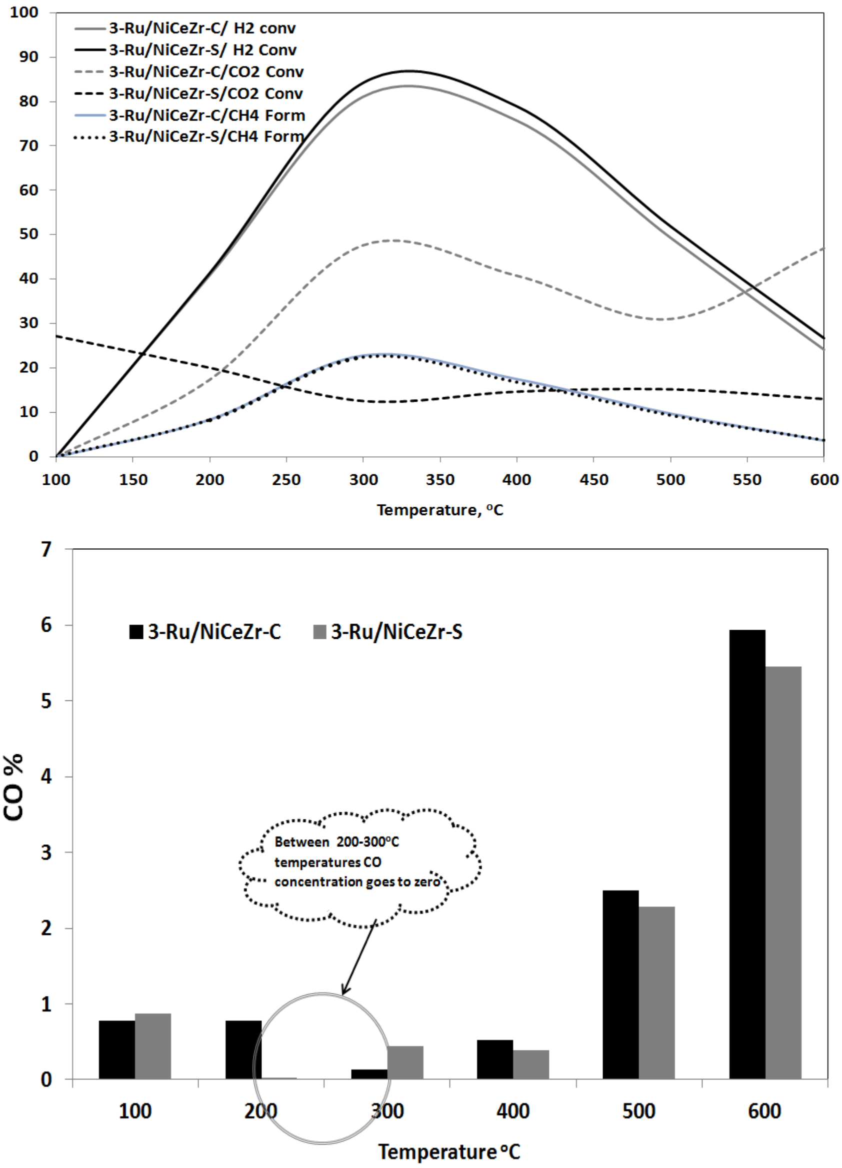

Figure 10. *Activity results as a function of the temperature for the selective CO methanation over the NiCeZr-S (1% CO, 25% CO_2 , 50% H_2 , and rest He; Space Velocity: 45,000 h^{-1} ; 25 mg of catalysts)*

Addition of Ru in to the catalyst structure slightly increased the selective CO methanation activity of the $NiO\text{-}CeO_2\text{-}ZrO_2$ catalyst because CO methanation was continued until to 350 °C. At the earlier study CO methanation was continued until to 200 °C over the $NiO\text{-}CeO_2\text{-}ZrO_2$ catalyst [10]. Effect of the Ru on the selective CO methanation activity can be supported by the Liu et. al. [26]. Xiong et.al. combined the achievement in the activity to the high dispersion of Ru particles with smaller size [27].

4. CONCLUSION

In this study the effect of the Rh and Ru as promoter on the CO methanation activity of the $NiO\text{-}CeO_2\text{-}ZrO_2$ catalyst was studied. Effects of the amount of Rh and Ru and type of the preparation method on the characteristics and catalytic activities of the $NiO\text{-}CeO_2\text{-}ZrO_2$ were investigated. Catalysts prepared by the surfactant assisted method gave highest surface area values and ~~gave~~ average pore diameters in compare with the catalysts prepared by the co-precipitation method. Diffraction peaks for the Rh and Ru were not observed from the XRD measurements since their ratio in the catalysts structures are not in the detection limit of the XRD. The desired ratio of the Rh was observed over the Rh containing catalysts according to the EDX results. All catalysts were tested for the CO methanation reaction. Most active catalysts for the CO methanation found that the catalysts were prepared by the surfactant assisted co-precipitation method since they gave the lowest 50% CO conversion temperature. The increase in Rh and Ru loadings lead to an increase in the 50% conversion temperatures of the catalysts. The selective CO methanation reaction were studied over the most active catalysts for the solo CO methanation reaction. Over the 3-Ru/NiO-CeO_2-ZrO_2 catalysts prepared by both two method all CO converted to CH_4 until to 300 °C, after this temperature CO ratio in the effluent gas mixture was increased due to the reverse water gas shift reaction. The CO_2 also converted to CH_4 during the CO methanation and continued very slowly with reverse water gas shift reaction after CO methanation completed. As a result the 3-Ru/NiO-CeO_2-ZrO_2 catalysts were suitable for selective CO methanation reaction between the 200-300 °C reaction temperatures.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial supports of the Gazi University BAP 18/2011-02.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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