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CO Methanation Over SAPO-34 Supported Ni Catalysts

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Highlights

- The effect of the preparation method on NiO/SAPO 34 catalysts was determined.
- Changing the solvent changed both physical and activity properties.
- The surfactant changed both physical and catalytic properties.

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Abstract

This study investigated carbon monoxide methanation with 15 %NiO doped SAPO-34 zeolite-supported catalysts. The SAPO-34 support was produced by hydrothermal synthesis, and nickel oxide was added to the support by impregnation and surfactant-assisted impregnation method, dissolved in different solvents (water, ethanol, acetone, and 1-propanol). Various characterization techniques, N_2 physisorption, XRD, SEM, TEM, and FTIR, were used to determine the physical properties of catalysts. XRD analysis showed that synthesizing the catalysts with surfactant reduced the crystallite size. The average crystal sizes of the catalysts synthesized using the impregnation and surfactant-assisted impregnation methods are between 11.3-7.1 nm and 8.9-7.1 nm, respectively. The N_2 physisorption analysis showed that the catalysts with the surfactant assisted impregnation method had higher surface areas among the catalysts produced by the two different preparation methods. It was observed that the surface area of the catalyst increased as the boiling point of the solvent increased. Scanning electron microscopy (SEM) analysis exhibited that the particle size of the catalysts with 1-propanol prepared by impregnation and surfactant-assisted impregnation methods are 118 nm and 86 nm, respectively. According to the results, surfactants cause to produce smaller particles. The CO methanation studies showed that the highest CO conversion values were reached with Ni/SAPO-34 catalyst using 1- propanol prepared by impregnation and other method, which gave 19.2% and 21.1% CO conversion to methane at 375°C, respectively. The low methane formation rates showed that most of the CO component was adsorbed on the surface, and some were converted to methane.
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1. INTRODUCTION

The polluting effects of CO and CO_2 gases on the atmosphere are well-known phenomena. By reacting these gases with H_2, it has become possible both to obtain an alternative fuel production and eliminate the harmful effects of these gases. Methanation reactions are frequently used to purify hydrogen in refineries and remove carbon oxides from gas mixtures in hydrogen or ammonia plants [1]. The choice of metal to be used as active component in catalytic reactions is important. Commonly used metals for methanation reaction include ruthenium (Ru), rhodium (Rh), iron (Fe), nickel (Ni), and cobalt (Co). Catalysts include such as Ru and Rh have the highest catalytic activity. However, their costs are quite high [2]. On the other hand, Fe has given low performance compared to other metals of selectivity despite its high activity [2]. Ni, frequently used among the catalysts, stands out with its high activity, selectivity and thermal stability. Although the performance of commonly used cobalt in catalytic reactions is close to Ni catalyst, it is more expensive than Ni [2]. In recent years, promising results have been revealed in the methanation studies in zeolite supports. In many studies, zeolites can be classified as synthetic and natural zeolites [3].

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Synthetic zeolites serve as ion exchanger, adsorbent and catalyst in the chemistry industry [4]. In the chemical industry, the usage areas of synthetic zeolites are much more than natural zeolites [4]. Synthetic zeolites are used as supports in many catalytic reaction processes. It has been tested in previous studies that zeolite support materials has the capacity to compete with supports and catalysts, which are expensive and have high activity and selectivity for methanation reactions. In addition, significant increases catalytic of Y-type catalyst with increased acidity were observed in the study and ZSM5, Y1-type, and CHA-type supports were widely used in catalytic reactions due to their acidity properties [4]. SAPO-34 (Silicoaluminophosphate) supports, also called chabazite which is the type of zeolite, have positive results in methanation reactions. It is obtained by adding Si to $AlPO_4$-34, which is neutral and has no catalytic activity under normal conditions. The amount of Si added to the SAPO-34 support material and the dispersion composition are the most important parameters in determining the pH and catalytic properties of the zeolite. The acidity of the zeolite support ensures that the electrons and protons are balanced. At the same time, it provides the formation of a superficial carboxyl group [5,6]. Some of the studies in which zeolites are used to support methanation studies have been summarized. A.Westermann et al. (2015) used Ni-impregnated USY (Ultra Stable Y-zeolite) supported catalysts in their methanation experiments. Previous studies have mentioned that the activities and selectivity of these catalysts for methanation reactions can compete with high and expensive materials. It has been stated in previous studies that USY low Si ratio acidic catalysts show high activity performance in catalytic reactions such as methanation. As a result of the methanation studies, it was stated that as the Ni content added at 5%, 10%, and 14% increases, the activity and selectivity increased significantly [7]. Carmen Bacariza et al. (2012) The calcination temperature of the catalysts was determined between 300 °C and 600 °C. The relationship between Ni ratio and calcination temperature and catalytic activity was investigated. The most active catalyst was determined to be NiUSY catalyst, calcined at 300 °C with 5% Ni doped. The activity increased as the Ni addition rate increased [8]. C. Italiano et al. (2019) performed methanation tests on CeO_2, Al_2O_3 and Y_2O_3 supported Ni catalysts. The reaction was carried out under 1 atm pressure and between 250-500 ºC. The highest performance Y_2O_3 supported Ni catalyst yielded nearly 100% CO conversion at 300 ºC, while the highest methane conversion value reached 350 ºC with a value close to 80%. In the study, it was emphasized that the catalytic performance depends on the state of the nickel-oxide interactions, so the weakly interacting Ni active sites of the Ni/CeO_2 catalyst are the catalyst that is most quickly deactivated due to the coke formation resulting from CO poisoning [9]. There are limited studies in the literature on carbon monoxide methanation using zeolite support. Some of these studies are given below. When the studies were examined, no study was found in which a similar zeolite type was used. In terms of zeolite type, our study will bring innovation to the literature. AM. Abdel-Magged et. al. (2013) investigated whether the pre-reaction treatments applied to Ru/zeolite catalysts have any effect on the performances of the catalysts in CO methanation studies. It has been determined that the calcination process applied before the reaction has a positive contribution to the selectivity and activity of the catalysts. It was found that as the calcination temperature increased, the Ru particle size decreased and accordingly the selectivity increased significantly [10]. S. Upasen et. al. (2022) they used nickel composed zeolite LTA4A and zeolite LTA5A supported catalysts for the CO_2 conversion to methane. When they examined the content of the product gas, they found that the amount of CO_2 was much higher than the amount of CH_4. They obtained the highest performance from the 5%Ni/LTA catalyst, with CO_2 conversion at 80%. They stated that as the mass ratio of Ni metal in the catalyst increased, the activity decreased [11]. H.X. Cao et. al. (2017) studied the CO methanation over the KIT-6 zeolite with different amounts of Ni and V. In CO methanation studies performed with 20Ni-2V/KIT-6 catalyst at 300 °C, the conversion rates of CO and CH4 were found to be 100% and 85%, respectively [12].

Accroding to the literature survey in this study, the catalysts in which 15% NiO doped to SAPO-34 support, which did not used for methanation before, were synthesized via the two different impregnation method route. The one of the traditional impregnation and the other is surfactant assisted impregnation method. During prepartion, in addition to water, 3 different solvents (acetone, ethyl alcohol and 1-propanol) were used in order to see the effect of the solvent, which allows the impregnation process to form the structure of the catalyst, on both the characteristic and catalytic properties. The results obtained will contribute to the literature by revealing the effect of the preparation method, surfactant and solvent used.

2. MATERIAL METHOD

2.1. Catalyst Synthesis

Preparation of SAPO34 zeolite by Hydrothermal Synthesis Method: The hydrothermal synthesis method used to prepare SAPO34 was carried out using the following step given in H. Demir et al. (2011), [13]. As a result of the following steps, a mixture was obtained at the mole ratio of $Al_2O_3/P_2O_5/0.30 SiO_2/2.0TEAOH/50H_2O$.

Tetraethylammonium hydroxide (TEAOH) (25% aqueous solution) as a source of surfactant for SAPO-34 zeolite support, powdered silica (SiO_2) (Aldrich, 99,8%), aluminum isopropoxide (AIP) (Alfa Aesar, 98%), phosphoric acid (H_3PO_4) (Alfa Aesar, 98%) as a source of phosphorus (85% aqueous solution), 1 M NaOH solution was used as the base source. Deionized water was used as the solvent source.

In the preparation part of the SAPO-34 zeolite support solution, 55 g of AIP and 21.6 mL of TEAOH were mixed at 350 rpm for 1.5 hours at 50ºC. Mixing was done and after measuring the pH value as 13.9, 0.33 g of powdered silicon dioxide was added and mixed for 10 minutes. In the next step, the solution prepared with 2.5 mL of H_3PO_4 and 6.1 g of deionized water was titrated for 10 minutes. After titration, the pH value was measured as 6.97. Titration was applied with 1M sodium hydroxide solution until the pH of the solution was 7.40. The pH of the mixture, which was left to stir again for 1 hour, increased to 7.52. The prepared solution was left in the steel autoclave for hydrothermal synthesis at 200 °C for 48 hours. The autoclave taken from the oven was left to cool for 1 day. The sample was taken from the autoclave and aged with 300 mL of deionized water at 25 °C for 24 hours. To separate the liquid phase from the solution, 300 mL of the mixture was poured evenly into 6 tubes. Then the liquid phase was separated at 5000 rpm for 15 minutes. The tubes were filled with water again and the process was repeated 4 times. As a result of the process, a sample in gel form was obtained. The solid sample was powdered after drying at 100 °C for 24 hours. In the last step of the synthesis, calcination was done. The oven temperature was increased by 1 °C per minute to 550 °C. 100 cm^3 of dry air was passed for 8 hours to remove the burning surfactant from the pores.

Preparation of Catalysts by Impregnation Method (Imp): In studies with SAPO-34 zeolite-supported Ni catalysts, the effect of the mass ratio of Ni added on the activity was investigated, and it was determined that the highest activity results belonged to the catalysts with 15% Ni ratio. In the methanation studies conducted with catalysts include nickel ratio of 5%, 10%, 15%, and 20%. The activity gradually increases up to %15 Ni ratio. Contrary, the activity decreases after 15% Ni ratio due to the aggregation of nickel particles [14]. For these reasons, the mass ratio of Ni/Zeolite was determined as 15% in our studies.

Precursors solution which includes nickel(II) nitrate and SAPO-34 was prepared via using 0.383g $Ni(NO_3)_2x6H_2O$, 212.5 mg SAPO-34 zeolite, and 25mL solvent. The catalysts were dissolved with water, 1 Propanol, ethyl alcohol and acetone to investigate the effect of solvent on activity and material properties.The sample was mixed at 25 °C for 3 hours. The suspensions were first dried at 40 °C for 24 hours, then at 100 °C for 24 hours. After crushing and sieving, the materials were calcined at 500 ºC for 3 hours.

Preparation of Catalysts by Surfactant Assisted Impregnation (SImp): The only difference of this method from the classical impregnation method is the addition of surfactant to the solution containing nickel nitrate and zeolite support.50 mg of CTAB (Cetyltrimethylammonium bromide, Sigma, 98 %) was added to the solutions with a molar ratio of (CTAB)/(Ni) of 0.1. After the sample was mixed at 25 °C for 3 hours, the solvent was controlled. The solutions were first dried until the solvent is completely removed at 40 °C then at 100 °C for 24 hours. Then, after crushing and sieving, the samples were calcined at 500 °C for 3 hours.

2.2. Catalyst Characterization

Rigaku MiniFlex brand device was used for X-Ray diffraction (XRD) analysis. Average crystal size and crystal phases were determined. Multi-point BET surface areas, average pore diameters, pore volumes and adsorption/desorption isotherms of catalysts were determined by N_2 measurements. Mean pore sizes were determined by the BJH method. Quantachrome Corporation/Autosorb-6 device was used for these analyses. Samples were degassed for one hour at 200°C before analysis. SEM was used to analyze the surface features, shape, and size of the catalysts. Philips FEI/ Quanta 400 F brand device was used for SEM analysis of the samples. The JEOL JEM 2100F high resolution transmission electron microscope (HRTEM) with an acceleration voltage of up to 200 kV was carried up for TEM analysis. The sample was dispersed in ethanol. A drop of the resulting suspension was dropped onto the C-film covered grid. It was determined qualitatively by the FTIR technique that the zeolites were synthesized correctly. Bruker IFS 66/S type HYPERION 1000 brand was used for this process. The FTIR system has light sources in the NIR, MIR and FIR ranges. IFS 66/S brand device was used for infrared tests and FRA 106/S brand device was used for Raman analysis.

2.3. Catalytic Activity Studies for CO Methanation

CO methanation reaction catalytic activity tests were performed in a conventional quartz tube reactor. The gas mixture formed from 10/90 CO/He, 100% H_2, 100% He was determined as the gases to be reacted. The feed gas mixture of 1% CO, 50% H_2 and the remainder He was sent to the reactor at a flow rate of 25 mL/min. 25 mg of catalyst was used in the experiments. The reactor was heated from 125ºC to 375ºC. The measurements of the feed gas mixture and the gas mixture formed as a result of the reaction were made with a Perkin Elmer Clarus 500 gas chromatograph with a thermal conductivity detector (TCD). The following calculations were used for the catalytic activity results in the methanation experiments:
The equation used to calculate the CO conversion is given below

$$\%\ \text{CO Conversion} = \frac{[CO]_0 - [CO]_f}{[CO]_0} \text{x}100 \qquad (1)$$

The amount of CO in the feed is denoted by $[CO]_0$ and unreacted CO by $[CO]_f$. The percentage of methane in the product was determined by calibration calculations with a 1% volume composition. CH_4 / 99% vol. Helium mixture was used before activity tests.

3. THE RESEARCH FINDINGS AND DISCUSSION

3.1. Characterization Results

Fourier transform infrared spectroscopy (FTIR): To qualitatively determine whether SAPO-34 can be synthesized, FTIR analysis was performed, and its compatibility with the data in the literature was determined. When the FTIR analysis results of SAPO-34 zeolite support were examined, peaks were observed at wave numbers of 491, 676, 1085, 1633, and 3400 cm^{-1}. Peaks at wave numbers of 491, 676 cm^{-1} correspond to Al-O, Si-O bond voltage peaks, and peaks with 1085 cm^{-1} correspond to Si-O-Si bond peaks. The peak occurring at 3400 cm^{-1} corresponds to the O-H bonds in the silanol groups [15] .The wave numbers of the observed bond voltage peaks were observed in the ranges defined in the literature [16]. Hossein A. et. al. (2018) wave numbers of SAPO-34 zeolite prepared by the hydrothermal synthesis method were determined as at 490 cm^{-1}, 640 cm^{-1}, 10.835 cm^{-1}, and 1100 cm^{-1} 1630 and 2360 cm^{-1}, 3450 cm^{-1} [17]. When FTIR analyses on zeolite supports in the past were examined, it was emphasized that the decrease in the peaks was the decrease in crystallization [16]. These results showed us that SAPO-34 was successfully synthesized.

X-Ray Diffraction Results (XRD): XRD diagram of the SAPO-34 showed the intense peak values at 18.42°, 20.44°, and 21.02°. However, the peaks with lower intensities were also seen at 9.44°, 15.9°, 22.72°, 24.58° and 27.66°. The specified peak values were consistent with the standard SAPO34 peaks determined as a result of the literature research. (JCPDS card no: 47-0617) [18]. The X-Ray diffraction patterns of catalysts are shown between Figures 1 - 3. In catalysts, the diffraction peaks due to the NiO in the catalysts were determined at 2θ= 37.2°, 43.3°, 62.8°, 75.5°, and 79.6°. In the literature studies, it has been determined that the peaks of NiO show a one-to-one agreement with the characteristic peaks given in previous studies (JCPDS card no. 47-1049) [16]. The intensities of the diffraction peaks can be discussed according to the effect of the preparation method. Diffraction peaks due to the zeolite support were suppressed by the NiO peaks due to the big crystal size of NiO. The synthesis methods and solvents types have no apparent effects on XRD peaks and peak intensities.

Table 1 shows the average crystal size of the SAPO-34 and catalysts. The average crystal size of SAPO-34 was 8.2 nm. Liangyuan Wei et al. (2021) synthesized NiO doped 13x type zeolite support. According to XRD measurements, the particle sizes of NiO were determined to be less than 3 nm [19]. The average crystal sizes of the catalysts prepared using the impregnation between 11.1 nm and 7.7 nm, and the average crystal sizes of the catalysts synthesized via the surfactant-assisted impregnation method vary between 8.9 nm and 7.1 nm. Although there was no significant effect of solvents on the average crystal sizes, it was observed that the average crystal sizes of the samples dissolved in water reached higher values in both preparation methods. The largest average crystal size values were obtained in catalysts prepared with both preparation methods. The average crystal size was larger in catalysts synthesized by the classical impregnation method and water was used as the solvent.

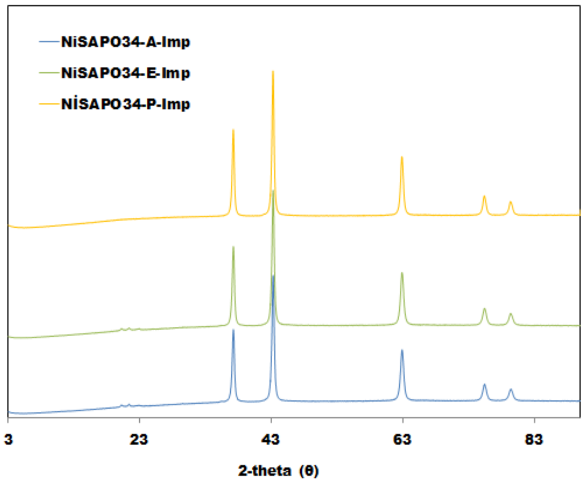

Figure 1. *X-Ray diffraction diagram of SAPO 34 zeolite supported Ni catalyst prepared by the Impregnation Method (Imp) (W: water, A: acetone, E: ethyl alcohol, P:1propanol)*

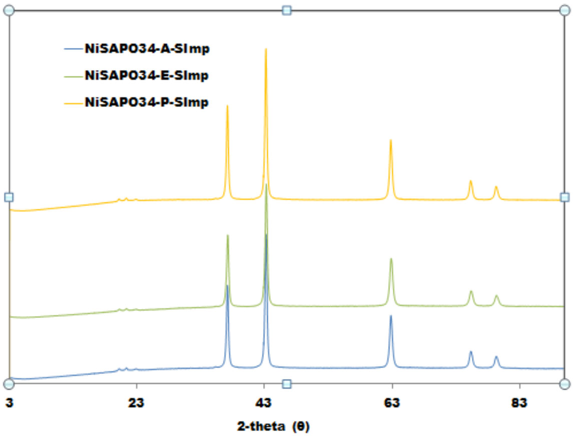

Figure 2. *X-Ray diffraction diagram of SAPO 34 zeolite supported Ni catalyst prepared by the surfactant-assisted impregnatiom method (SImp) (W: water, A: acetone, E: ethyl alcohol, P:1propanol)*

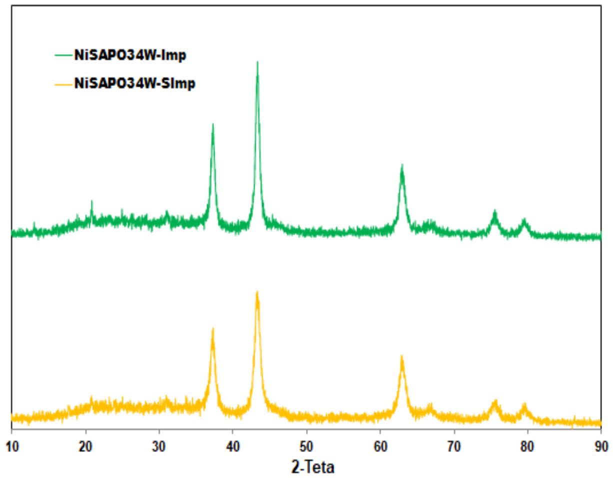

Figure 3. *X-Ray diffraction diagram of SAPO34 zeolite supported Ni catalyst by the Impregnation Method (Imp) (W: water)*

Multipoint Surface Area Results: Synthesis methods are very effective on shaping surface areas. According to the BET surface area measurements, it was observed all catalysts synthesized by the surfactant-assisted impregnation method had higher surface areas than the all catalysts synthesized by the classical impregnation method. The previous studies show that the boiling point of the solvent used during the preparation of catalysts had a significant effect on surface area. The boiling points for water, 1propanol, ethyl alcohol, and acetone used in our study are 100 ºC, 98 ºC, 78 ºC and 56 ºC, respectively. Among the catalysts, for those produced by the impregnation method, the order is water>1 propanol> ethyl alcohol> acetone, and among the catalysts synthesized by the surfactant-assisted impregnation method, the order is water> ethyl alcohol> 1-propanol> acetone. Results are given in Table 2. Senliang Xi et al. (2021) The BET surface area Ni-doped SAPO-34 zeolite support by synthesized was determined as 215.59 m^2/g [20]. It has been determined that the surface areas of the catalysts prepared with the highest boiling points and very close to each other with water, and 1-propanol have higher surface areas, and the surface areas of the catalysts prepared with acetone and ethyl alcohol, In addition, a significant increase in the surface area of the catalysts prepared with water was detected among the catalysts prepared with SAPO-34. As the boiling points of the solutions increased, a significant increase was found in the surface areas of the prepared catalysts.

Pore Volume Results: The micro+mesopore volume results of the catalysts at P/P_0= 0.96 showed that the samples synthesized via the surfactant-supported impregnation method have higher micro+mesopore volumes than the catalysts prepared by the impregnation method. When the micro+mesopore volumes of the samples are compared over the solvent used during the preparation, the ranking among the catalysts prepared via the impregnation method is water>1-propanol >acetone>ethyl alcohol, and the sequence in the catalyst synthesized by the surfactant-assisted impregnation method is water>1-propanol> ethyl alcohol > acetone. It was determined that there was a linear relationship between the boiling point of the solvent and the volume values. The same result was obtained for the total pore volume (Tables 3-4).

Average Pore Diameter Results: The average pore diameters of the catalysts prepared using both methods were observed between 2nm and 50nm. Accordingly, all catalysts were found to be mesoporous. The use of SAPO-34 support materials used in catalysts allowed the catalysts to have more than one average pore diameter and smaller diameter pores. Senliang Xi et al. (2021) was determined that the mean pore diameter of Sapo 34 zeolite support was 4.4 nm. It was emphasized that the Ni-doped SAPO 34 zeolite supports were detected between 2 and 50 nm [20]. Accordingly, the formation of small-sized pores also led to higher surface areas. Average pore diameter results are given in Table 5.

Table 1. *Average crystal sizes of catalysts and support material*

Catalyst/Support	Solvent	Average Crystal Size (nm)	
		Impregnation method (Imp)	Surfactant assisted impregnation method (SImp)
NiO/SAPO34-W	Water	11.3	8.9
NiO/SAPO34-A	Acetone	7.6	7.1
NiO/SAPO34-E	Ethyl alcohol	7.8	7.2
NiO/SAPO34-P	1-propanol	7.7	7.1
SAPO-34	8.2		

Table 2. *Multi-point BET surface area results obtained as a result of N_2 physisorption analysis of catalysts*

Catalyst/Support	Solvent	Multi-Point Surface Area Result m^2/g	
		Impregnation Method Imp	Surfactant Impregnation Method SImp
NiO/SAPO34-W	Water	102.8	107.5
NiO/SAPO34-A	Acetone	15.2	16.4
NiO/SAPO34-E	Ethyl alcohol	17.7	18.3
NiO/SAPO34-P	1-propanol	25.7	16.7
SAPO-34	112.5		

Table 3. *Micro+Mesopore Volume results calculated from the desorption data at $P/P_0=0.96$ obtained as a result of the N_2 physisorption analysis of the catalysts*

Catalyst/Support	Solvent	Micro+Meso Pore Volume ($V_{\mu+m}$), 0.96, cm^3/g Liquid N_2 volume	
		Impregnation Method Imp	Surfactant Impregnation Method SImp
NiO/SAPO34-W	Water	0.2653	0.3070
NiO/SAPO34-A	Acetone	0.0662	0.1282
NiO/SAPO34-E	Ethyl alcohol	0.0509	0.1314
NiO/SAPO34-P	1-propanol	0.0772	0.1340
SAPO-34	-	0.0582	

Table 4. *Total Pore Volume results calculated from the desorption data at P/P_0= 0.99 obtained as a result of the N_2 physisorption analysis of the catalysts*

Catalyst/Support	**Solvent**	**Total (Micro+Mezo+Macro) Pore Volume ($V_{t0.99}$), cm^3/g Liquid N_2 volume**	
		Impregnation Method Imp	**Surfactant Impregnation Method SImp**
NiO/SAPO34-W	Water	0.3996	0.4453
NiO/SAPO34-A	Acetone	0.0891	0.1289
NiO/SAPO34-E	Ethyl alcohol	0.0785	0.1314
NiO/SAPO34-P	1-propanol	0.1271	0.1342
SAPO34	-	0.0803	

Table 5. *Average pore diameter results obtained using BJH desorption method as a result of N_2 physisorption analysis of catalysts*

Catalyst	**Solvent**	**Average Pore Diameter, nm**	
		Impregnation Method Imp	**Surfactant Impregnation Method SImp**
Ni/SAPO34-W	Water	2.13, 3, 3.75, 5.5, 30.2	1.9, 2.4, 3, 3.7, 4.8, 17.5
Ni/SAPO34-A	Acetone	2.41, 3.77, 6.4, 12.2	2.41, 3.73, 5.5, 9.37, 17.28
Ni/SAPO34-E	Ethyl alcohol	2.15, 3.76, 6.43, 16.87	2.69, 3.76, 6.39, 9.29, 17.01
Ni/SAPO34-P	1-propanol	1.9, 2.69, 3.78, 7.66, 17.24	1.9, 2.41, 4.23, 7.59, 12.05
SAPO 34	-	18.9, 37,53, 96,1	

N_2 adsorption/desorption isotherms : The N_2 adsorption/desorption isotherms of the prepared catalysts were evaluated according to the types in the BDDT classification. The isotherms are similar to the isotherm type IV. Lihui Yu et al. (2022). 3A, 4A, 5A, 13X, and ZSM-5 are Ni-doped to the zeolite supports by the impregnation method. The pore structure and properties of these catalysts were determined by N_2 adsorption/desorption analysis. According to the BDDT classification of isotherm types, IV. It was found to overlap with the isotherm type [21]. The average pore diameters of all samples vary between 2 nm and 50 nm, indicating that they are mesoporous. The catalysts synthesized by both preparation methods have more than one pore diameter and are mesopore in nature IV. It confirms that it is similar to the isotherm type.

Electron Microscopy (SEM and HRTEM) Results : Scanning electron microscopy (SEM) images of 15% NiO/SAPO34 catalyst synthesized by the impregnation method using 1-Propanol shown in Figure 4 and scanning electron microscopy (SEM) images of 15% NiO/SAPO34 catalyst synthesized by the surfactant-assisted impregnation technique using 1-Propanol shown in Figure 5. A homogeneous spherical particle structure was obtained in the catalysts. The diameters of the small spherical particles were measured on the figures and calculated by taking the average. While the average particle size was calculated as 118 nm in the catalysts synthesized by the impregnation technique, the average particle size was calculated as 86 nm in the surfactant-supported catalyst. In this case, smaller particles were obtained in catalysts prepared with surfactant. Hossein A. Et.al. (2017) synthesized SAPO-34 zeolite support using hydrpthermal synthesis method [22]. The produced zeolite supports are doped with Ni and Ce by impregnation method.

While the average particle size of SAPO 34 was determined as 126 nm, the average particle sizes of Ni–Ce/SAPO-34 catalysts synthesized with the impregnation method varied between 125 nm and 122 nm [18].

High-resolution transmission electron microscope HRTEM images of 15% NiO/SAPO34 catalysts are shown in Figures 6 and 7. The distribution of homogeneous NiO particles in the catalyst can be seen very clearly. When the 50 nm scaled images were compared, it was determined that the preparation of the catalysts with surfactant caused the NiO crystal phase to be dispersed more homogeneously within the SAPO34 support pores.

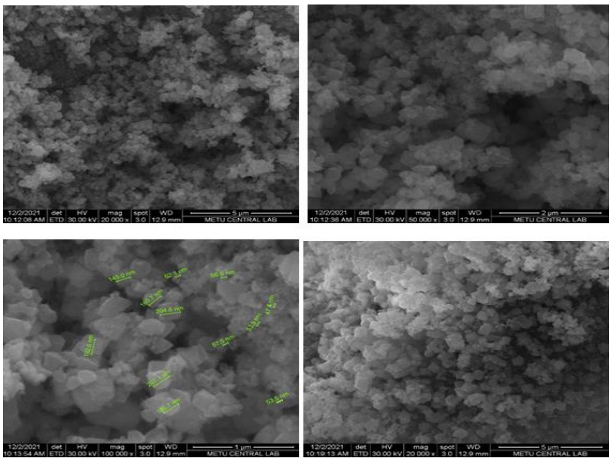

Figure 4. *Scanning electron microscopy (SEM) images of 15% NiO/SAPO34 catalyst ynthesized by the impregnation method using 1-Propanol*

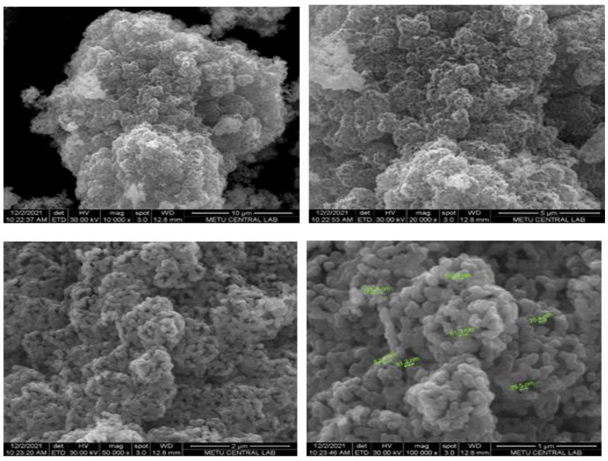

Figure 5. *Scanning electron microscopy (SEM) images of 15% NiO/SAPO34 catalyst synthesized by surfactant assisted impregnation method using 1 Propanol*

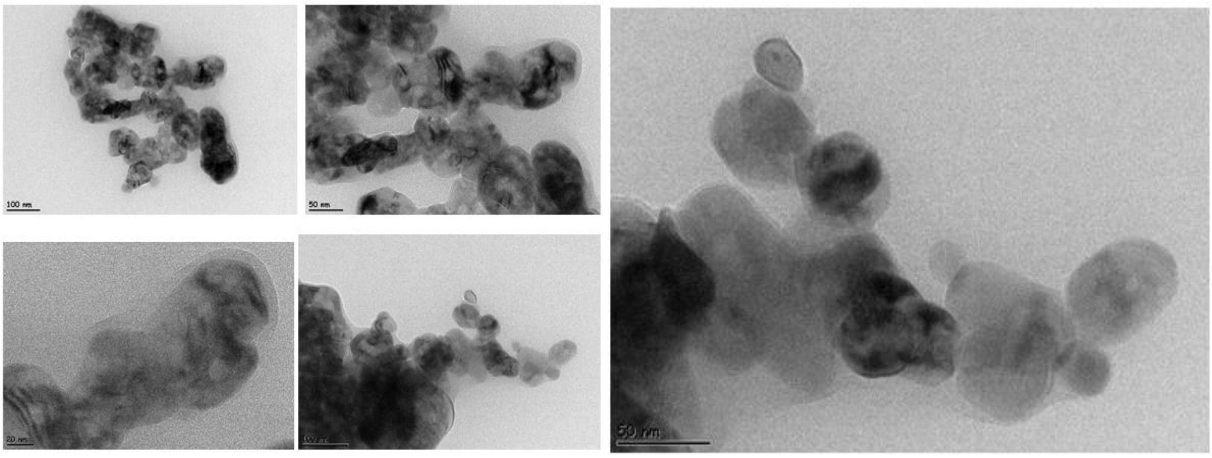

***Figure 6.** High resolution transmission electron microscopy images (HRTEM) of 15% NiO/SAPO34 catalyst synthesized by the impregnation method using propanol*

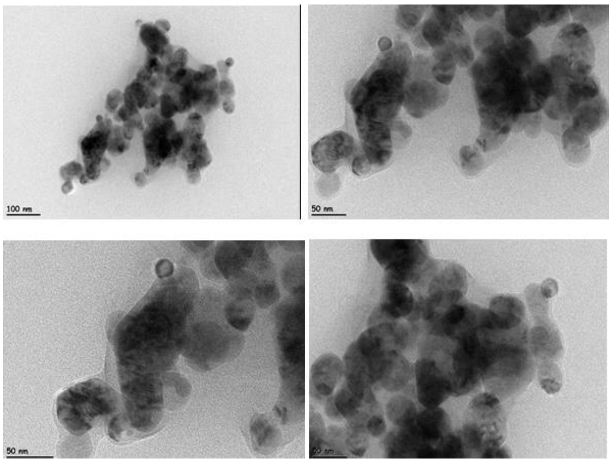

***Figure 7.** High resolution transmission electron microscopy images (HRTEM) of 15% NiO/SAPO-34 catalyst synthesized by surfactant assisted impregnation method using 1 propanol*

3.2. CO Methanation Activity Results

The catalytic activities of the synthesized catalysts were determined by CO methanation reaction. The effects of the support type, solution type and preparation method, on catalytic activity were investigated by catalytic activity studies. The catalytic activity test system was used in the catalytic activation studies of the catalysts. Activity studies were carried out by gradually increasing the temperature from 125 ^{o}C to 375 ^{o}C. The concentration of the reactant gases was obtained using gas mixtures of 10/90 CO/He, 100% H_2, 100% He. The feed gas mixture of 1% CO, 50% H_2 and the remainder He was passed through the reactor bed at a 25 mL/min flow rate. 25 mg of catalyst was used in the experiments. Activity experiments were carried out in a quartz tube reactor. As a result of the methanation experiments, the most active catalyst was determined by determining the lowest 50% CO conversion temperature. The products formed as a result of the reaction were analyzed with a gas chromatography device.

The maximum CO conversion values of the catalysts are shown in Table 6. The activity results of the SAPO-34 supported catalysts can be compared over the effect of preparation method and the effects of solvents used during the impregnation methods. Results showed that the activity performances of all catalysts prepared by the surfactant-assisted impregnation method were higher than those prepared by the impregnation method. It was determined that 1-propanol and water catalysts contributed significantly to the activity compared to other catalysts. In both preparation methods, catalysts synthesized using water and 1-propanol as solvents have close activity results and were at the highest values. E.Jwa. et al. (2013) No significant CH_4 conversion was found between 180 °C and 260 °C of 10% Ni-doped β-zeolite catalyst prepared by wet impregnation method. However, as it approaches 300 °C, it has been determined that the CO conversion increases up to 95% [23]. The highest CO conversion was gained from the catalyst prepared with using 1-propanol as a solvent, and the surfactant assisted impregnation method with %21.2. In Figure 9, the second-highest conversion was obtained from the catalyst prepared by the surfactant-assisted impregnation method, again with 21.1%, using water as the solvent. Among the catalysts synthesized by the impregnation method, the highest CO conversions were obtained from catalysts synthesized via using water and 1-propanol as solvents at 375°C temperature as 19.6% and %19.2, respectively that are given in Figure 8. In addition, the highest CO conversions of all catalysts are shown in Table 6. When the results were compared with the literature, catalysts containing nickel oxide and Sapo-34 zeolite could not be found directly. Therefore, results were obtained on catalysts containing similar active and support components with similar structure. In the studies in the literature, it was determined that high CO conversions were obtained at both low and high reaction temperatures, depending on the catalyst structure. Hong-Xia C. et al. (2017) have reached 93% CO conversion and 66% CH_4 conversion values at 400 °C in their CO methanation studies with 10% Ni-doped KIT 6 zeolite supported catalyst. Catalytic activity results were significantly better than the results of our study. The most important reason for this may be that both the zeolite support and the surface areas of the catalysts were much higher than the catalyst in our study. [12]. Wenli G. (2021) et al. They achieved 100% CO conversion performance at 290 °C with Ni-Fe catalyst doped SBA 16 type zeolite support. In this study, when the SEM and HRTEM images of the data were examined, it was seen that the catalysts fully penetrated into the support material and dispersed more homogeneously compared to our study. This is thought to be the difference between the activities. [24]. Jiangwei L. (2021) et al. conducted CO methanation experiments with SiO_2-supported Ni catalyst. As a result of the activity studies, they reached CO conversion value of 88.7% at 350 °C [25]. Zeolite was used as support material in our study. In this study, SiO_2 was used as support material. The use of different types of supports explains the difference between performances.

Figures 10 and 11 show the CH_4 formations obtained over the catalysts as a function of reaction temperature. All catalysts did not give methane until to rich the 325%C. The % CH_4 formation values are very low below the 10%. When these results are compared with the % CO conversion results, that can be concluded that all of the CO does not convert to the CH_4. That means some of the CO adsorbed chemically on the catalysts structures. In the product stream of the reaction mixture, the other carbon-based product were not seen. The highest CH_4 formation value was obtained over the Ni/SAPO34 catalysts prepared using the acetone and surfactant-assisted impregnation method.

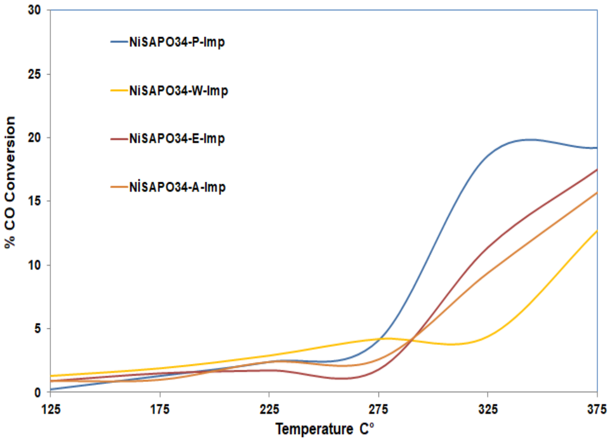

Figure 8. *Activity results of SAPO-34 supported 15% Ni catalysts synthesized by surfactant assisted impregnation (SImp) (W: water, A: acetone, E: ethyl alcohol, P: 1propanol)*

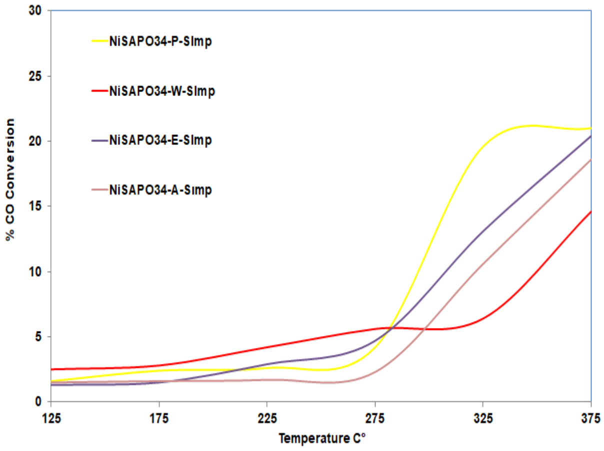

Figure 9. *Activity results of SAPO-34 supported 15% Ni catalysts synthesized by surfactant assisted impregnation (SImp) (W: water, A: acetone, E: ethyl alcohol, P: 1propanol)*

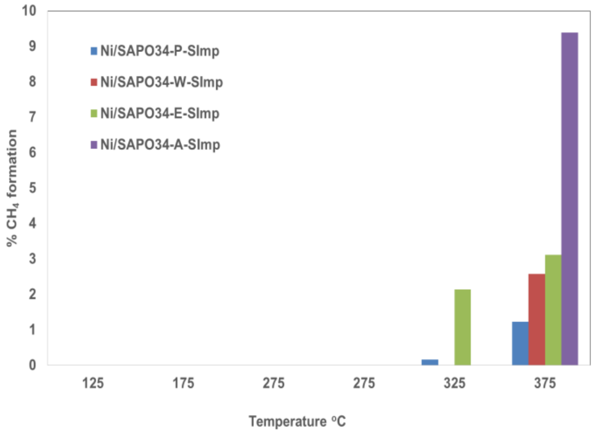

Figure 10. *Methane formations over the catalysts*

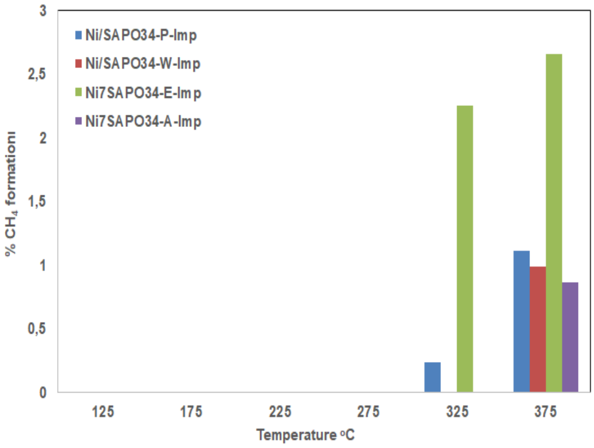

Figure 11. *Methane formations over the catalysts*

Table 6. *The maximum % CO conversion of all catalysts*

Catalyst	**Solvent**	**% CO CONVERSION**	
		Impregnation Method **Imp**	**Surfactant Assisted Impregnation Method** **SImp**
Ni/SAPO34-S	Water	19.6	21.1
Ni/SAPO34-A	Acetone	15.7	18.6
Ni/SAPO34-E	Ethyl alcohol	12.7	14.6
Ni/SAPO34-P	1-propanol	19.2	21.2

4. RESULTS

In this study, CO methanation was carried out using NiO doped Sapo34 supported catalysts. Here, effects of surfactant and the solvents used during the impregnation on the characteristic and catalytic propertied of 15% NiO/SAPO34 catalysts were investigated. The CTAB was used as surfactant, and water, ethyl alcohol, acetone and 1-propanol were used as solvents. FTIR and XRD analysis results of the SAPO 34 zeolite support were consistent with the results of studies in the literature. From XRD analyses of the catalysts, the solvents did not significantly affect the average crystal sizes of the catalysts. However, when the effect of the preparation method is examined, the average crystal sizes of the catalysts synthesized by the surfactant-assisted impregnation method gave lower results. N_2 phsisorprtion analysis showed that all of the catalysts prepared by the surfactant-assisted impregnation method had higher surface areas than the catalysts synthesized by the classical impregnation method. All catalysts have spherical particules on the surface and the average particle size was changed according to the preparation method. From SEM analysis, average particle sizes for impregnation and the other methods are found as 118 nm and 86 nm, respectively. HRTEM microphotographs showed more homogeneouseneous distribution of the active component NiO was observed in NiO/SAPO34 prepared by the surfactant-assisted impregnation method and 1-propanol as solvent compared to the same catalyst synthesized by the impregnation method. 15%NiO/SAPO34 catalysts prepared using both methods and with 1-propanol as solvent were found as most active catalysts between the catalysts for CO methanation reaction. The same rate of methane formation with CO conversion could not be obtained. The presence of methane, unreacted CO, and no CO_2 in the product distribution indicates that some of the CO are adsorbed on the catalyst surface.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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