



Investigation of CO methanation activities of ZSM-5 supported Ni catalysts using microchannel and conventional reactor

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Abstract

In this study, carbon monoxide methanation reaction in a microchannel reactor, which has come to a remarkable point in catalytic reactions in recent years, was investigated with Ni doped H-ZSM5 zeolite supported catalysts. All catalysts were prepared with impregnation method by using different solvents (water, ethanol, acetone and 1-propanol). Catalysts were also synthesized using surfactant (CTAB) in order to see the effect of using surfactant in the impregnation method. The physical properties of the catalysts were determined using various characterization techniques (N_2 physisorption, XRD, SEM, HRTEM). CO methanation activities were done by using both conventional and microchannel reactor at the same reaction conditions. According to the catalytic activity results, higher results were obtained in the activity experiments performed in the microchannel reactor. In terms of the preparation method, the catalysts prepared by the surfactant assisted impregnation method showed higher catalytic activity. The highest CO conversions were obtained from catalysts prepared using 1-propanol during the preparation of catalysts. In general, the best catalytic activity for CO methanation in the microchannel reactor was obtained from the catalyst prepared using 1-propanol solvent with the surfactant assisted impregnation method which gave %100 conversion to methane at 325 °C.

Keywords Methanation · Carbon monoxide · Microchannel reactor · Zeolite

Introduction

Today, in parallel with the increasing population and developing technology, the need for energy and fuel has increased. The exhaustion of available energy sources is currently the most difficult challenge facing the world. This situation has rapidly increased the trend towards alternative and renewable energy sources. Methane, which makes up the majority of natural gas, has a significant amount of potential for use in industrial settings as a result of its high heat of combustion (55.70 kJ/g), which is significantly superior to that of coal (39.30 kJ/g) and fossil oil (43.60 kJ/g). The

methanation reaction was discovered by Sabatier and Sendrens in 1902. In the presence of a nickel catalyst, hydrogen and carbon oxide react at elevated temperatures to produce methane and water. Carbon monoxide (CO) methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$) is a reaction concerning the generation of substituted natural gas (SNG), and the removal of trace carbon monoxide from a hydrogen stream for fuel cells, has piqued the scientific and industrial interests of many researchers (Hatta et al. 2023; Seemann et al. 2019).

The high surface-to-volume ratio brought about by the high surface area of microchannel reactors for catalytic reactions is one of the important advantages for microchannel reactors. This ratio is 10,000–50,000 m^2/m^3 for a reactor. This high rate is provided by parallel channels with microchannels. In this case, it can increase the reaction volume up to 90%. In conventional systems, the surface volume ratio remains around 1000 m^2/m^3 (Kawamura et al. 2006). The use of low reactants also provides an economic benefit for the chemical processes of expensive and rare reactants (Ouyang and Besser 2002). It is among the known advantages of microchannel reactors that they provide a significant increase in mass and heat transfer. It is also seen as an

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important gain that microreactors provide a safer working environment compared to traditional systems (Chen et al. 2004).

Zeolites are crystalline, microporous three-dimensional aluminosilicates, made of linked TO_4 tetrahedra ($\text{T} = \text{Si}, \text{Al}$), which were used as adsorbent, ion-exchangers, and catalyst. The general formula of zeolite can be written as $\text{M}_x/\text{n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot z\text{H}_2\text{O}$, where M is an extra-framework cation which needs to be balanced by the anionic charge of the framework. Chemically, zeolites differ in their Si/Al ratios in their ionic framework. This ratio is varied between 1, in type-A zeolite and infinite in silicalite, a type of modified crystalline silica which is free of aluminum. ZSM-5 and HY based catalysts are another important zeolites which have been widely used in the fuel-upgrading and production of many petrochemicals. As a catalyst, zeolite exhibits good performance for traditional application in the petrochemical industry and refinery (Azhari et al. 2022; Kianfar et al. 2020).

The studies in the literature have been examined in two ways: firstly, the methanation studies carried out in a micro-channel microreactor and the second one is the studies in which the CO methanation is examined over zeolite supported catalysts. We see in the studies in the literature that a series of catalysts doped with Rh and Ru have been prepared to be used in the methanation reaction by microreactor. In these studies, Ru and Rh were used as catalyst active components, while TiO_2 , ZrO_2 , CeO_2 , SiO_2 , Al_2O_3 were used as support components. The CO methanation was studied in the microreactor with Ru/Rh doped TiO_2 , $\text{TiO}_2/\text{ZrO}_2$ catalysts and Ru-doped TiO_2 was found as the most active and stable catalyst (Brooks et al. 2007). Rh and Ru doped Ni/CaO/ Al_2O_3 catalysts were prepared for selective methanation and tested in a microreactor. And over these catalysts the critical temperature of CO methanation decreased to 250 °C (Yong et al. 2007). Ru/ SiO_2 and Ru/ Al_2O_3 catalysts were prepared for selective methanation and activity results showed that the Ru/ SiO_2 catalyst was more active at 285 °C with 95% conversion. In addition, it was stated that the selectivity performance of the Ru/ SiO_2 catalyst was higher than the Ru/ Al_2O_3 catalyst (Görke et al. 2005). Ru supported CeO_2 and Al_2O_3 catalysts were also tested for selective CO methanation. It was observed that the Ru- Al_2O_3 catalyst was more active and selective than the Ru- CeO_2 catalyst, with a conversion rate close to 100% at 260 °C (Galletti et al. 2011). In another study the highest activity with the highest conversion rate of 97% CO at 400 °C observed from the Rh/ CeO_2 catalyst (Nicholaus et al. 2017).

When the zeolite-assisted CO methanation studies are examined, it is seen that USY (Ultra Stable Y-Zeolite), H-ZSM5, HNaUSY and 5A-type-zeolite types are mostly used as supports. Ni-impregnated USY (Ultra Stable Y-zeolite) supported catalysts used in methanation experiments.

This type of catalysts can compete with the high and expensive supports and catalysts in activity and selectivity for methanation reactions. The 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 amount of Ni added at 5%, 10% and 14% increases, it shows very serious increases in activity and selectivity (Westermann et al. 2015). In a study comparing the effect of zeolite support and SiO_2 support HZSM-5 supported Ru catalyst is more selective as a result of CO_2 methanation reactions over Ru/HZSM-5 and Ru/ SiO_2 catalysts. It has been stated that such zeolites with high Al content give effective results in catalytic reactions (Scirè et al. 1998). HNaUSY type zeolite supported Ni and Ce catalysts were also used in CO_2 methanation reaction. Activity studies showed that the activity and selectivity increased as the Ni ratio increased in zeolite supported catalysts. In addition, it has been stated that when Ce additive is added to Ni doped zeolites, it contributes positively to the activity and selectivity. Zeolite support provided higher stability and better dissociation with strong metal-surface interaction with acidity. In this case, it was emphasized that zeolite supports gave satisfactory results in such reactions (Graça et al. 2014). CO_2 methanation studies were done on 5A type zeolite supported Ni catalysts. It was stated that the highest activity result was in the catalyst with 6% by mass Ni doped. In addition, it has been stated that zeolites are suitable supports for methanation reactions with their pore sizes and acidity (Borgschulte et al. 2013). In a study comparing the effect of zeolite support and Al_2O_3 support zeolite supported Ru catalysts are more selective and active in selective CO methanation reactions than Al_2O_3 supported catalysts (Agustina et al. 2012). Calcination temperature of the catalysts is important. It has significant effects on structure properties as a result on activity properties. The ultra-stable Y-type zeolite supported Ni catalyst was calcined at 5 different temperature and used in CO methanation experiments. As a result of the activity experiments, it was stated that the most active catalyst among the 5% NiUSY catalysts calcined at 300 °C, 400 °C, 450 °C, 500 °C and 600 °C, respectively, was the catalyst calcined at 300 °C and the activity increased as the Ni addition rate increased (Bacariza et al. 2015).

In the methanation reaction studies with microchannel reactors in recent years, it has been seen that widely preferred catalysts such as Ru, Rh, Ti, Zr, Ce, Ni are used, on the contrary, there is no study done with zeolite supports. For this reason, it is thought that the use of acidified ZSM5 type zeolite support in methanation reactions in microchannel reactors will show promising results. With the results to be obtained from this study, firstly, low-cost catalysts for carbon monoxide methanation to be used in microchannel reactors and at a level that can compete with other common catalysts will be synthesized, and secondly, zeolite supports

with nickel active ingredient and acidity-enhanced zeolite will be used in microchannel reactors with proven effectiveness in catalytic reactions. As a result of the studies, the effects of both the surfactant, the type of solvent used in the impregnation method and the type of reactor to be used in the activity studies on the CO methanation activity results will be determined.

Experimental

H-ZSM5 supported catalysts containing 15% NiO were synthesized using both the conventional impregnation method and the surfactant assisted impregnation method. Four different solvents (water, ethanol, acetone and 1-propanol) were used during the preparation in order to see the effect of the solvent type used during the impregnation on the catalyst properties.

Catalysts preparation

Preparation of H-ZSM5

Sigma brand material with catalog number 96096 and CAS number 1318–02-1 as ZSM5 zeolite support was supplied within the scope of the project and used in the studies. In the study of Jhangirian et al., who conducted a study using the same zeolite support, the chemical structure of the zeolite support was stated as $0.6\text{K}_2\text{O}:4.0\text{Na}_2\text{O}:1.0\text{Al}_2\text{O}_3:2-2.1\text{SiO}_2:\text{XH}_2\text{O}$. It is reported that the pore diameter of the zeolite support is approximately 3 Å (Jhangirian et al. 2020). 1.0 g of ZSM5 (Zeolite, Sigma, cat no: 96096, CAS no: 1318–02-1) sample was ion exchanged (Na^+ ion will be replaced by NH_4^+) for 24 h at 50 °C with 10 mL of 1 M NH_4NO_3 solution. The process was repeated twice for the ion exchange to take place completely. The solid obtained after recovery by centrifugation was washed three times with deionized water. After drying at 100 °C for 20 h, it was calcined at 500 °C for 5 h. The most recently obtained zeolite was named H-ZSM5 (Vogt et al. 2015).

While preparing the catalysts, we followed the path we followed in our previous study (Derekaya et al. 2022). The same preparation steps both classical impregnation and surfactant assisted impregnation techniques were used.

Preparation of catalysts by impregnation method (Imp)

Precursors solution which includes nickel(II) nitrate and H-ZSM5 was prepared via using 0.383 g $\text{Ni}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$, 212.5 mg H-ZSM5 zeolite, and 25 mL 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 h.

The suspensions were first dried at 40 °C for 24 h, then at 100 °C for 24 h. After crushing and sieving, the materials were calcined at 500 °C for 3 h.

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 h, the solvent was controlled. The solutions were first dried until the solvent is completely removed at 40 °C then at 100 °C for 24 h. Then, after crushing and sieving, the samples were calcined at 500 °C for 3 h.

Catalysts characterization

Different techniques have been used to determine the physical properties of catalysts. These are X-Ray diffraction (XRD), N_2 physisorption, High resolution transmission electron microscopy (HRTEM), Scanning electron microscopy (SEM) techniques. Detailed information about the technical features of the devices used in characterization studies can be found in Derekaya F. (2022) [Derekaya et al. 2022].

Catalytic activity measurements for CO methanation

Activity studies in a classical vertical quartz glass reactor

The CO methanation studies are the same as the work we did in Derekaya F. (2022) (Derekaya et al. 2022a). Catalytic activity tests of the catalysts were carried out in a fixed bed quartz reactor at atmospheric pressure and temperatures between 125 °C and 375 °C. A quartz reactor with a length of 70 cm, a thickness of 1 mm and a diameter of 5 mm was used. Before the reaction, the catalysts were reduced in situ with pure H_2 at 500 °C for 1 h. The 10% vol. CO/ 90% vol. He, 100% vol. H_2 and 100% vol. He gases were used to prepare the desired feed gas composition. 1% vol. CO, 50% vol. H_2 and the remainder He feed gas composition was prepared. Aalborg brand mass flow meters were used to prepare the feed gas mixture. Gas flow rates were calibrated by passing the gas from the mass flow meter through a soap flow meter. The feed gas mixture was fed into the reactor at a total volumetric flow rate of 25 ml min^{-1} . According to the reactor dimensions and the total volumetric flow rate, the space velocity is $45,000\text{ h}^{-1}$. The amount of catalyst was calculated from the space velocity and volumetric flow rate of the feed gas mixture. Some calculation steps were followed to determine the amount of catalyst. For this, the

ratio of the volumetric flow velocity to the space velocity was first calculated. This value was then equalized to the volume of the reactor. As a result of this calculation, the reactor height to be filled with the catalyst was determined. All prepared catalysts have the same particle size as they are passed through a 150 mesh sieve. Therefore, approximately 25 mg of prepared catalysts was sufficient to fill the calculated height. The catalyst was filled into the reactor from the top of the reactor, supported vertically by glass wool. At each reaction temperature at which the conversion of CO to methane was to be determined, at least 30 min was waited for the methanation reaction to stabilize in the catalyst bed. Then, the reaction product composition was analyzed when the product analysis result was obtained at least three times in a row in gas chromatography. Feed and product gas compositions were analyzed by gas chromatograph (CLARUS 500, PerkinElmer) equipped with a thermal conductivity detector (TCD) with a separation column filled with carbosphere. In order to make the separation of hydrogen, carbon monoxide, methane and carbon dioxide gas components correctly, 50 °C temperature was chosen as the column temperature from the carbosphere operating temperatures. Detector temperature was determined as 125 °C.

The CO conversion was calculated using the equation given below.

$$\% \text{ CO Conversion} = \frac{[\text{CO}]_0 - [\text{CO}]_f}{[\text{CO}]_0} \times 100$$

Here $[\text{CO}]_0$ is the amount of CO in the feed, $[\text{CO}]_f$ is the amount of unreacted CO in the product stream. The concentration of methane in the product was determined by the calibration calculations made as a result of the analysis of 1% vol. CH_4 / 99% vol. He mixture before the activity tests.

Activity studies in microchannel reactor

Properties of the microchannel reactor The microchannel reactor was manufactured by MAGNUM Engineering company from AISI 316 material. The reactor consists of 2 stainless steel plates with dimensions of 100*90*15 mm. It consists of 1 gas inlet and outlet fittings, 1 copper sealing gasket and 4 standard connection elements. There are 48 channels of 0.17 mm depth, 0.50 mm channel width and 30 mm length on the plate. The schematic view of the microchannel reactor, image of the channels and Images of the microchannel reactor covering the channels with the catalyst and placing it in the furnace when it is in the closed position were given in supplementary information.

Coating of microchannel reactor with catalysts 25 mg of catalyst was turned into sludge using deionized water, and the coating process was carried out in the channels of the

microchannel reactor with the help of a brush. Then the solvent was removed by drying the water. The top cover was closed and after the gas inlet and outlet connections were made, it was placed in the horizontal furnace. It was ensured whether the reactor reached the designed reaction temperature by performing the catalyst coating process. Then, the system was operated under reaction conditions in the conventional reactor. All the steps given in Sect. 2.3.1 were used in the microchannel reaction.

Results and discussion

Characterization results

Fourier transform infrared and raman spectrometer (FTIR) and X-Ray diffraction analysis of H-ZSM5 zeolite support

FTIR analysis was performed to ensure the zeolite structure of H-ZSM5 which gave peaks at wave numbers of 522 cm^{-1} , 529 cm^{-1} , 975 cm^{-1} , 1631 cm^{-1} and 3300 cm^{-1} (Fig. 1). This result coincides with the peak values obtained as a result of previous studies (Varzaneha et al. 2014). At 522 cm^{-1} , 529 cm^{-1} values, Al-O, Si-O bond voltage peaks correspond to the peaks of 975 cm^{-1} Si-O-Si bond peaks. The peak occurring at 3300 cm^{-1} corresponds to the O-H bonds in the silanol groups (Innocenzi 2003; Sabah and Çelik 2002). The X-Ray diffraction pattern analysis result of the H-ZSM5 zeolite support was shown in Fig. 2. According to the XRD pattern drawn at low angle for HZSM5 shown in Fig. 2, diffraction peaks were obtained at reflection angles of 7.22°, 10.18°, 12.46°, 16.06°, 20.46°, 21.68°, 24°. These results are compatible with the ZSM-5 orthorhombic structure given in the literature (Zhao et al. 2019). Diffraction peaks were obtained at angles 2θ: 7.22°, 10.18°, 12.46°, 16.06°, 20.46°, 21.68°, 22.92°, 24°, 26.12°, 27.12°, 29.96°, 30.86°, 32.54°, 34°, 34.2°, 35.76°, 36.56°, 38.06°, 40.18°, 41.54°, 42.24°, 42.92°, 44.2°, 47.32°, 52.64°, 54.32°, 56.46°, 57.54°, 58.62°, 69.18°, 71.2°, 72.98° on H-ZSM5 zeolite support (JCPDS card No- 44-0003) (Fig. 2). These results are compatible with the results in the literature (Jhangirian et al. 2020). According to the study conducted by Jin et.al. the crystal structure of ZSM5 is in the MFI-type framework structure. Due to reasons arising from pretreatment, there are shifts in the exit positions of the peaks (Jin et.al. 2024).

X-Ray diffraction analysis results of catalysts

X-Ray diffraction pattern analysis was performed to determine the crystal and average crystal sizes in the structure of the catalysts. In Fig. 3 and Fig. 4, the results of the X-Ray diffraction pattern analysis of the catalysts are shown. Due to the high intensities of the NiO peaks to the zeolite peaks,

Fig. 1 FTIR spectrum of HZSM5 zeolite

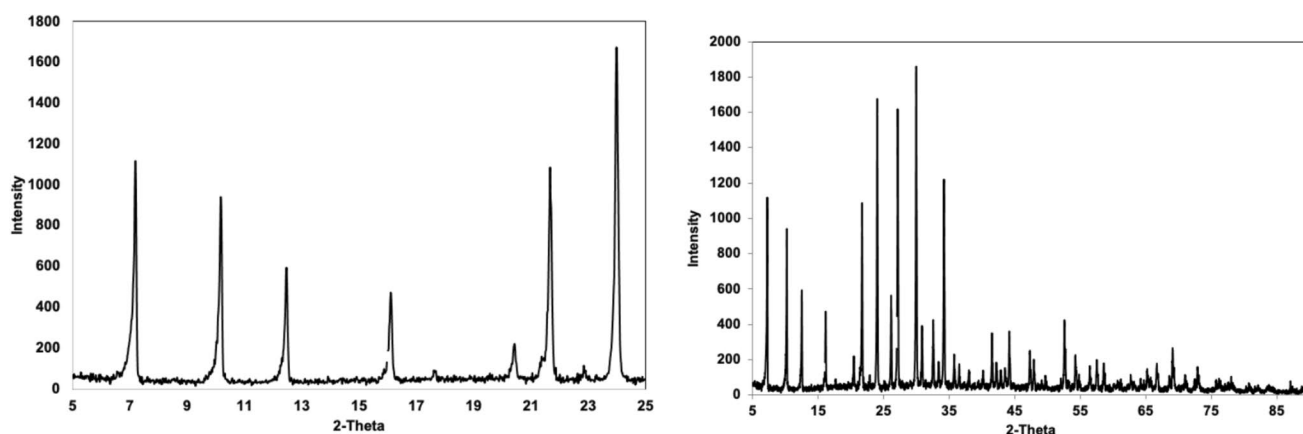
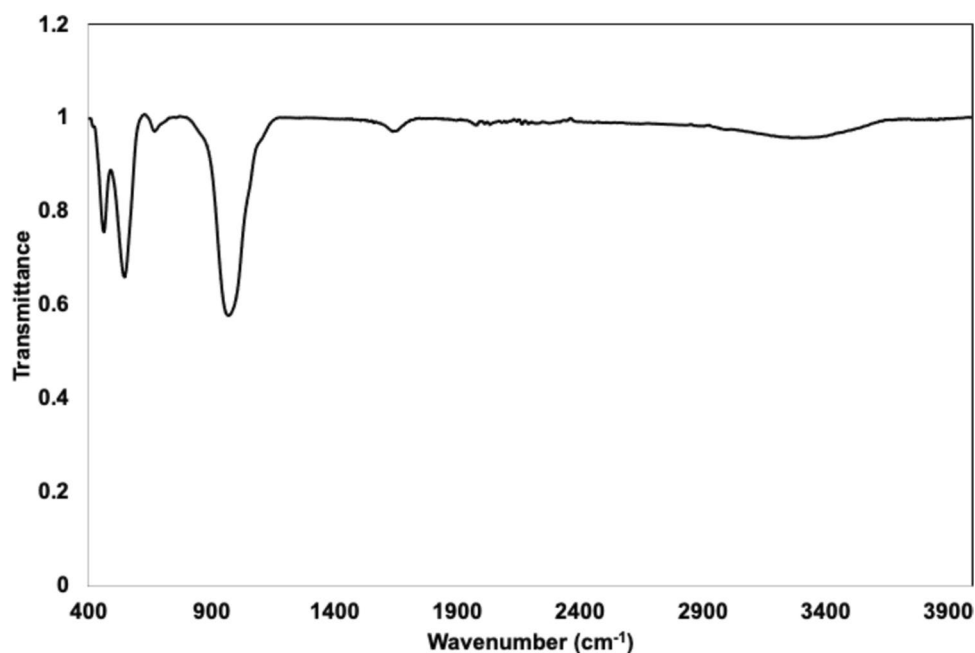


Fig. 2 XRD patterns of H-ZSM5 zeolite

some of the zeolite peaks were also observed at low intensities. The diffraction peaks of the zeolite support could be observed at $2\theta = 21.7^\circ$ and 30° angles. The diffraction peaks of the NiO crystal phase in the catalysts were obtained at $2\theta = 37.3^\circ$, 43.3° , 62.8° and 78.8° values (JCPDS Card No = 47–1049). It has been emphasized in previous studies that Ni largely suppresses the peaks of zeolites due to its high quality crystal structure and its high mass ratio of 15%, and that it is difficult to separate the characteristic peaks of the two structures due to possible overlapping of their peaks (Soghrati et al. 2018). Diffraction peaks of the NiO crystal phase were obtained from El-Kemary et al. It is very compatible with the results obtained in their study. According to the study, the diffraction data of the NiO crystal phase is listed as indexed as (111), (200), (220), (311), and (222)

crystal planes of the bulk NiO, according to the 2 theta angle output order. All the reflections can be indexed to face-centered cubic (fcc) NiO phase (El-Kemary et.al. 2013).

By using Scherrer equation crystal size of the catalysts were determined [$L = (K \cdot \lambda) / (\beta \cdot \cos \theta)$; L is a measure of the dimension of the particle in the direction perpendicular to the reflecting plane; λ is the X-Ray wavelength; β is the peak width; θ is the angle between the beam and the normal on the reflecting plane and K is a constant). Table 1 shows the average crystal sizes of the NiO crystal phase. Average crystal sizes were calculated from the strongest diffraction peak of $2\theta = 43.3^\circ$ of the NiO crystal phase. When the average crystal sizes were examined, the average crystal sizes of the catalysts prepared by the impregnation method varied between 114 Å and 112 Å. No

Fig. 3 X-Ray diffraction patterns of catalysts prepared by using impregnation method

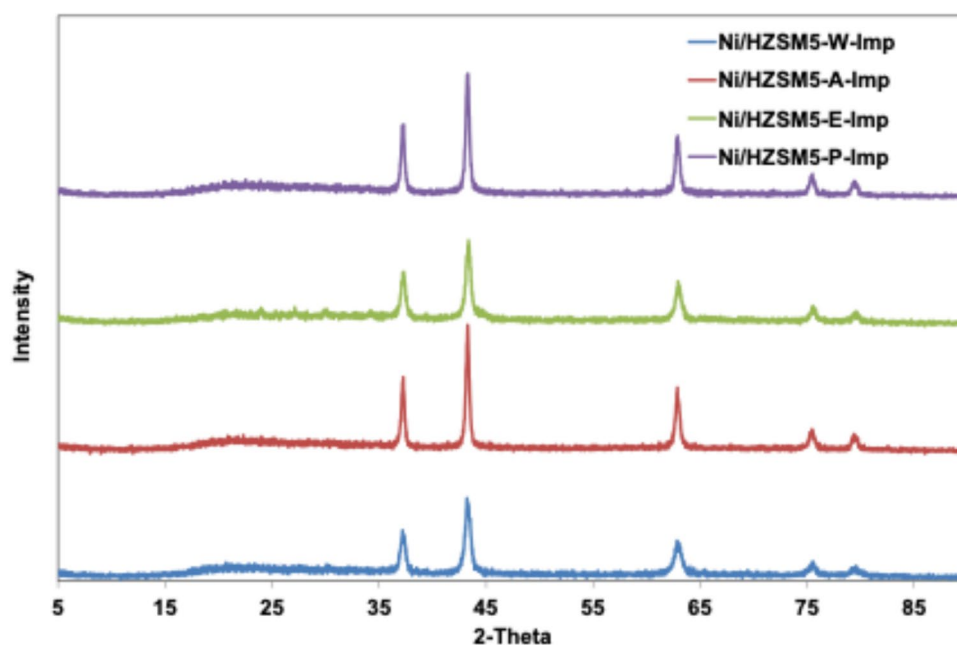
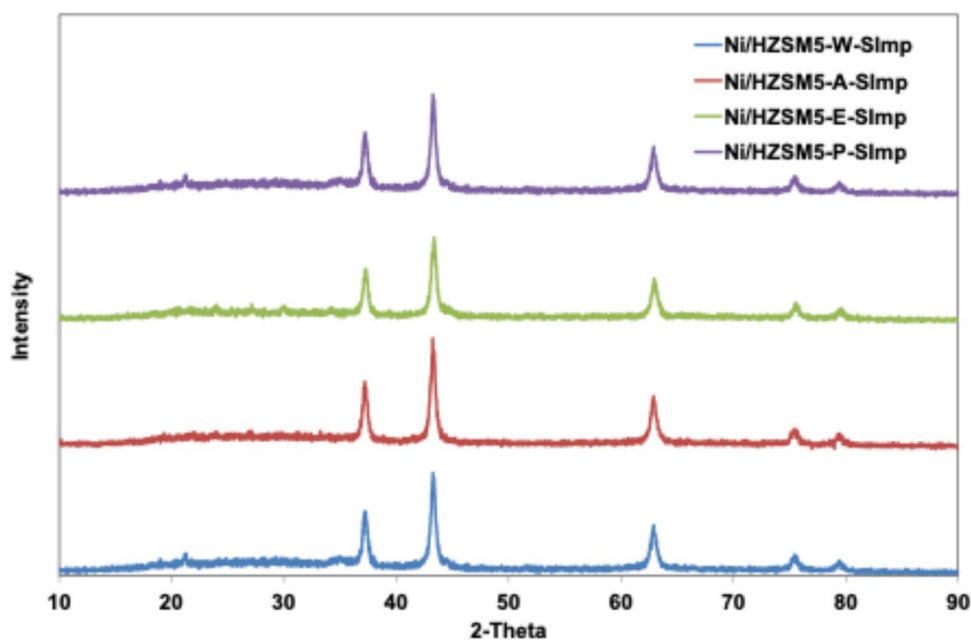


Fig. 4 X-Ray diffraction patterns of catalysts prepared by using surfactant assisted impregnation method



significant effect of the solvent on the average crystal size was observed. However, the average crystal sizes of the catalysts synthesized by the surfactant assisted impregnation method ranged from 89 Å to 86 Å. Depending on the preparation method, a significant decrease was observed in the average crystal sizes of the catalysts. The average crystal size of NiO close to the literature was obtained. In their study by Cui et al., the average crystal size of NiO in the H-ZSM5 supported catalyst containing 15% NiO without any different pretreatment was calculated as 10.1 nm. After treatment with alkaline solution, the average crystal

size of NiO decreased to between 7.3 nm and 6.7 nm (Cui et al. 2023).

N₂ physisorption analysis results

Multipoint surface areas, average pore diameters, pore volumes and N₂ adsorption/desorption isotherm types of catalyst and support materials were determined by N₂ physisorption analysis. The N₂ adsorption/desorption isotherms can be seen from supplementary information. Table 2 shows the surface areas of the catalysts and support material. The best

Table 1 Average crystal size of NiO obtained from X-Ray measurement

Catalysts	Solvent	Average Crystal Size (Å)	
		Impregnation Imp	Surfactant Assisted Impregnation SImp
Ni/H-ZSM5-W	Water	114	88
Ni/H-ZSM5-A	Acetone	113	88
Ni/H-ZSM5-E	Ethyl alcohol	112	87
Ni/H-ZSM5-P	1-propanol	113	86

results in the surface area were obtained with the catalysts prepared by the surfactant assisted impregnation method. The results show that water is the best solvent for obtaining high surface area. When the previous studies on the effect of solvents on the surface areas were examined, it was determined that the boiling point of the solvent had a significant effect on the analysis results (Zangeneh et al. 2013). The boiling points for water, 1-propanol, ethyl alcohol and acetone used in our study are 100 °C, 98 °C, 78 °C and 56 °C, respectively. When the BET surface areas of the catalysts are

examined, the order of surface area among the catalysts prepared by the impregnation method is water > acetone > ethyl alcohol, and the order of the catalysts prepared by the surfactant assisted impregnation method is water > 1-propanol > acetone. From this point of view, it was determined that the surface area of the catalysts increased as the boiling point of the solvent increased.

Table 3 shows the pore volume results obtained from N₂ physisorption analysis. Both the meso + micro pore volume and the total pore volume were higher in the catalysts prepared by the surfactant assisted impregnation method. The highest pore volume results were obtained in the catalyst prepared by ethyl alcohol and surfactant assisted impregnation method. In the catalyst prepared using classical impregnation and 1-propanol, high meso + micro pore volume and accordingly total pore volume were obtained. The macro pore volume is also larger in these two catalysts. The catalyst with the highest micro + meso pore volume ratio is the catalysts prepared using water and acetone with the classical impregnation method. It can be seen from Table 3 that the meso + micro pore volume of the catalyst prepared with the surfactant assisted impregnation method and using 1-propanol is as high as the other two catalysts. Average pore diameter distributions of the catalyst are shown in Table 4

Table 2 Surface areas of the catalysts

Catalysts	Solvent	Multipoint BET Surface Area m ² /g		Micropore Area, m ² /g	
		Impregnation Imp	Surfactant Assisted Impregnation SImp	Impregnation Imp	Surfactant Assisted Impregnation SImp
Ni/H-ZSM5-W	Water	17.0	25.0	22.8	33.5
Ni/H-ZSM5-A	Acetone	12.4	14.0	16.6	17.5
Ni/H-ZSM5-E	Ethyl alcohol	8.3	16.4	9.8	22.0
Ni/H-ZSM5-P	1-propanol	10.1	15.2	14.2	19.7
ZSM5		3			

Table 3 Micro + Meso Pore volumes of the catalysts obtained desorption data at P/P₀ = 0.96

Catalysts	Solvent	V _{0.96} , Micro + Meso Pore Volume cm ³ /g Liquid N ₂ volume		V _{0.99} , Total (Micro + Meso + Macro) Pore Volume cm ³ /g Liquid N ₂ Volume		% Micro + Meso Pore Volume	
		Impregnation Imp	Surfactant Assisted Impregnation SImp	Impregnation Imp	Surfactant Assisted Impregnation SImp	Impregnation Imp	Surfactant Assisted Impregnation SImp
Ni/H-ZSM5-W	Water	0.060	0.148	0.082	0.382	73	39
Ni/H-ZSM5-A	Acetone	0.039	0.073	0.065	0.140	60	52
Ni/H-ZSM5-E	Ethyl alcohol	0.055	0.547	0.107	1.971	51	28
Ni/H-ZSM5-P	1-propanol	0.527	0.061	1.250	0.104	42	59
HZSM5		0.0012		0.021		43	

Table 4 Average pore diameters of catalysts obtained by using the BJH desorption method

Catalysts	Solvent	Average Pore Diameter, nm	
		Impregnation Imp	Surfactant Assisted Impregnation SImp
Ni/ZSM5-W	Water	2.13, 3.3, 3.7, 7.5, 27.4	2.13, 2.7, 3.7, 6.4, 9.2
Ni/ZSM5-A	Acetone	2.13, 3, 4.2, 5.5, 7.5, 16.5	2.13, 3, 4.2, 5.5, 9.2, 29.5
Ni/ZSM5-E	Ethyl alcohol	2.13, 3, 3.7, 4.8, 7.5, 16.8	17.8
Ni/ZSM5-P	1-propanol	1.9, 2.4, 3, 3.7, 16.75, 182 >	2.4, 3, 4.2, 5.4, 9.2, 28.4
ZSM5		109	

and. The pore diameter distribution can be seen from the figures which were given in supplementary information. Table 4 shows that the catalysts have more than one average pore diameter. In accordance with the pore volume results, average pore diameters in the mesopore size of the catalysts were obtained.

Scanning electron microscope analysis (SEM) results

Scanning electron microscopy (SEM) images of 15% NiO/H-ZSM5 catalyst synthesized by the impregnation method using 1-Propanol given in Fig. 5 and scanning electron microscopy (SEM) images of 15% NiO/H-ZSM5

catalyst synthesized by the surfactant assisted impregnation method using 1-Propanol given in Fig. 6. When the figures are examined, it is seen that small spherical particles are dispersed on the large surface particles. The diameters of the small spherical particles were measured on the figures and calculated by taking the average. While the average particle size of the catalyst prepared by the normal impregnation method was 42 nm, the average particle size of the catalyst prepared by the surfactant-assisted impregnation method was calculated as 63 nm. The particle size increased with the impregnation method with surfactant. More SEM images are provided in the supplementary file.

Fig. 5 Scanning electron microscopy (SEM) images of 15% NiO/H-ZSM5 catalyst synthesized by the impregnation method using 1-propanol

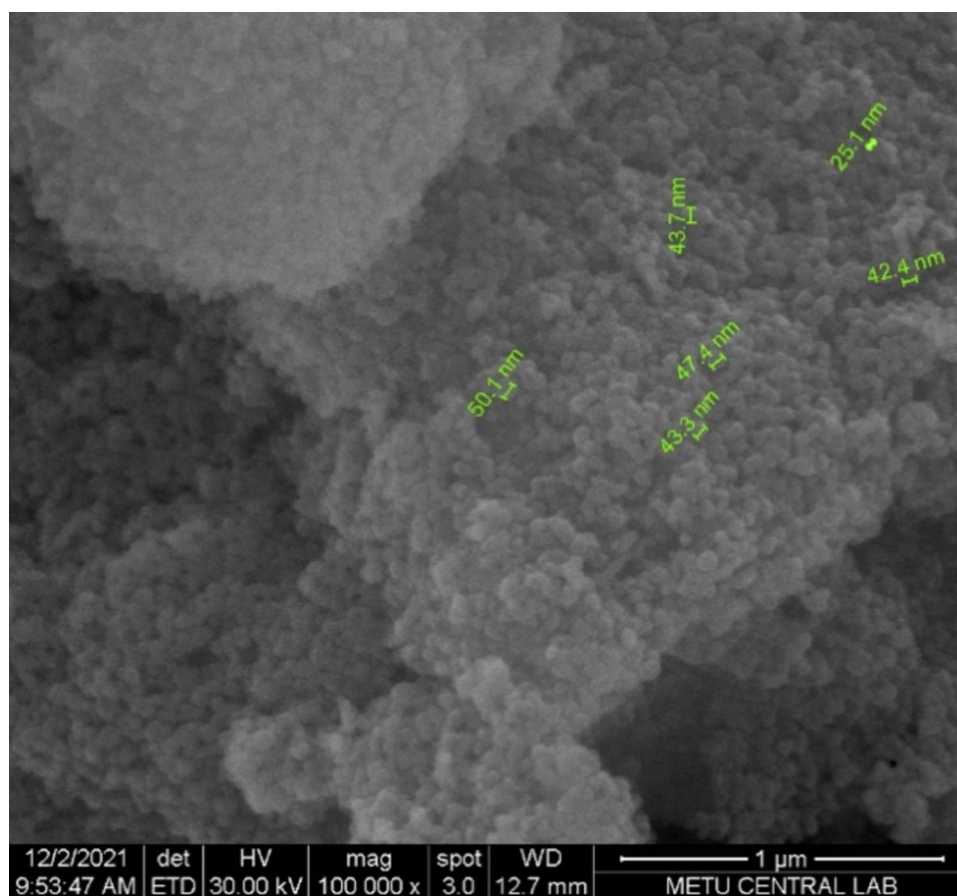
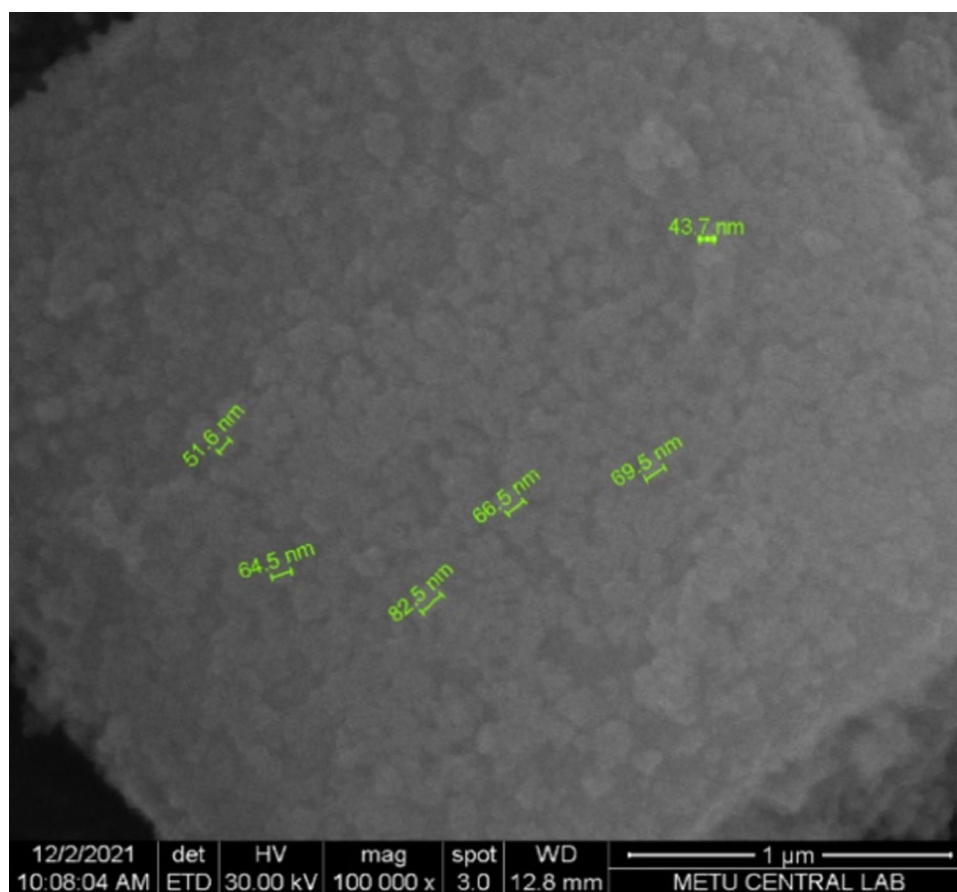


Fig. 6 Scanning electron microscopy (SEM) images of 15% NiO/H-ZSM5 catalyst synthesized by surfactant assisted impregnation method using 1-propanol



High resolution transmission electron microscope (HRTEM) results

In Figs. 7, 8, images of 15% NiO/H-ZSM5 catalysts in which 1 propanol obtained from high resolution transmission electron microscope is used as solvent. When the images of the 15% NiO/H-ZSM5 catalyst are examined, it is seen that the

black coloured regions are more in the catalysts prepared by the classical impregnation method, while the catalyst synthesized with the surfactant-assisted impregnation method has both more dark gray colored documents and more black colored regions more homogeneously dispersed. In this case, the surfactant allowed the NiO crystal phase to be more homogeneously dispersed on the zeolite support and

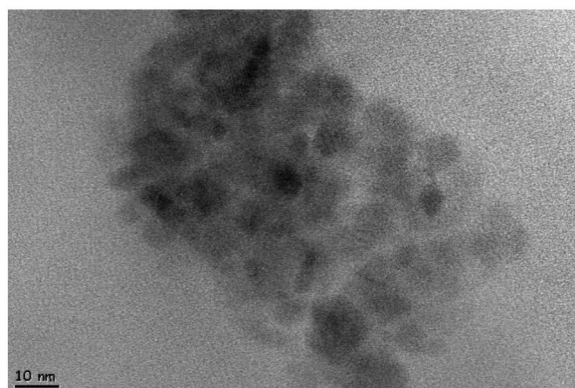
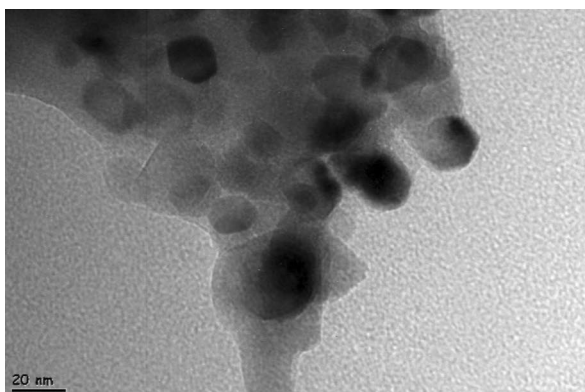


Fig. 7 High resolution transmission electron microscopy images (HRTEM) of 15% NiO/H-ZSM5 catalyst synthesized by impregnation method using 1-propanol

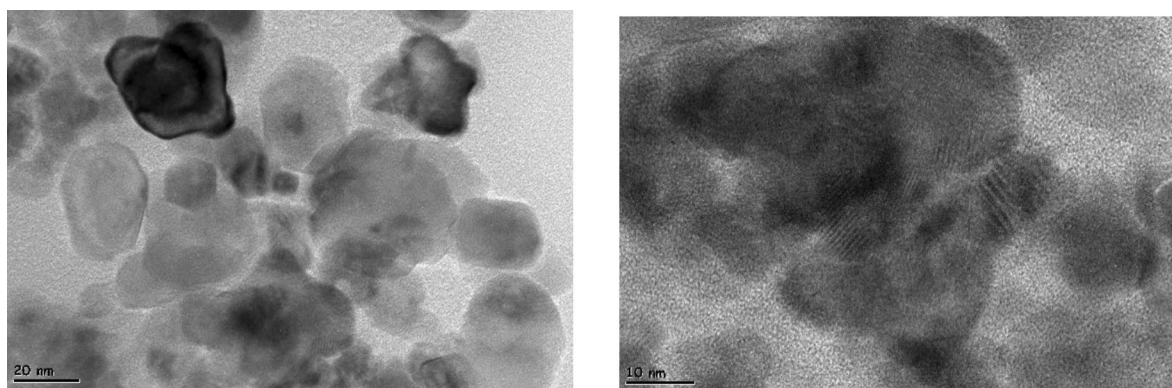


Fig. 8 High resolution transmission electron microscopy images (HRTEM) of 15% NiO/H-ZSM5 catalyst synthesized by surfactant assisted impregnation method using 1-propanol

penetrated more into the pores. This is a desired result. However, the surface area results obtained from SEM images and N_2 physisorption analysis lead us to the conclusion that NiO is collected on the H-ZSM5 support surface. At the same time, SEM images showed that spherical NiO particles were formed on the zeolite flat structures. Looking at Fig. 6, it is seen that there are dark-coloured areas within the support pores. This leads us to the conclusion that some NiO was able to enter the pore structure. More HRTEM images are provided in the supplementary file.

Catalytic activity results for CO methanation reaction by using two different reactor type

The CO methanation activity experiments of the catalysts were carried out in both conventional differential reactor and microchannel microreactor. In our study, in order to convert the NiO crystal phase into metallic Ni crystal phase, the catalysts were in-situ reduced with 100% H_2 gas at 500 °C for 1 h before the reaction. By looking at the studies in the literature, it was determined that this temperature was sufficient to obtain metallic Ni with the reducing gas used. Fedorov et al. (2020) used NiO and CuO-NiO catalysts with 10% H_2 /90% Ar gas mixture in their TPR- H_2 study, and they determined that depending on the heating rate, NiO gave a reduction peak of 333 °C at low heating rate, and 549 °C at high heating rate (Fedorov et al. 2020). In another study, TPR- H_2 study was carried out for $CuCo_2O_4$ -NiO catalyst and it was determined that the reduction peak for NiO was at 469.3 °C and Ni^{+2} was reduced to Ni^0 at this temperature (Wang et al. 2023). Gong et al. In their study, zeolite Y was subjected to ion exchange with different cations and was used for the decomposition reaction of ammonia by adding nickel to its structure. In their study, reduction temperatures were determined in the TPR- H_2 study they conducted on zeolite-supported catalysts. All catalysts started to reduce after a temperature of approximately 300 °C (Gong et al.

2024). In their study by Miskan et al., Nickel supported on fibrous Zeolite-Y was used for dry reforming of methane. Reduction in zeolite-supported catalysts started at approximately 300 °C and was completed at 410 °C. The maximum temperature of reduction was determined to be approximately 343–350 °C (Miskan et al. 2024). According to this result, the reduction temperature made in situ before the reaction for the catalysts in our study is sufficient for the reduction of nickel oxide to metallic nickel. At the same time, it is understood that the nickel in the structure cannot use hydrogen in the reduction process for itself during the reaction.

In order to compare the results obtained and to show the reactor difference, four different catalyst activity results are shown in separate figures. Catalytic activities of the catalysts have been shown between Figs. 9–12. According to the GASEQ program, there is 100% CO conversion in the temperature range of 25–400 °C. As can be seen in the study by Jiajian et al., the equilibrium conversion at low temperatures is 100% [Jiajian et al. 2012]. Figure 9 shows the catalytic activity results obtained from catalysts prepared by using water as solvent during preparation. Catalytic activities of catalysts increased after 325 °C. The best results were obtained at 375 °C. The best activity results were obtained as a result of activity studies using microchannel reactor. The best result was determined as 27% CO conversion at 375 °C in the tested catalyst in the microchannel reactor prepared by the surfactant assisted impregnation method. An increase of 13% was obtained in the catalytic activity of the catalyst prepared by the surfactant-assisted impregnation method using a microchannel reactor, and 3% as a result of the catalytic activity of the catalyst prepared by the classical impregnation method. Figure 10 shows the catalytic activity results for the CO methanation of catalysts prepared using acetone as a solvent. Catalytic activities of the catalysts increased after 275 °C. The best results were obtained at 375 °C. The best activity results were obtained as a result of

Fig. 9 The CO methanation activities of the catalysts prepared by using water(W) as solvent (1% CO, 50% H₂ remain He feed condition; 25 mg catalysts, S.V: 45,000 h.⁻¹, 25 ml/min). (Imp: for impregnation method; SImp: for surfactant assisted impregnation; CR: conventional reactor; MCR: microchannel reactor)

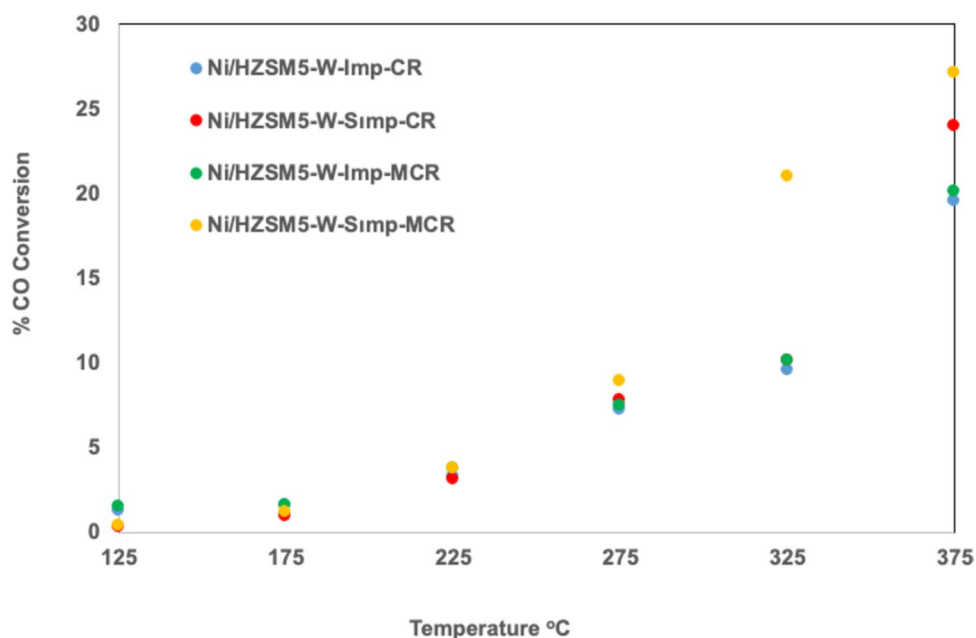
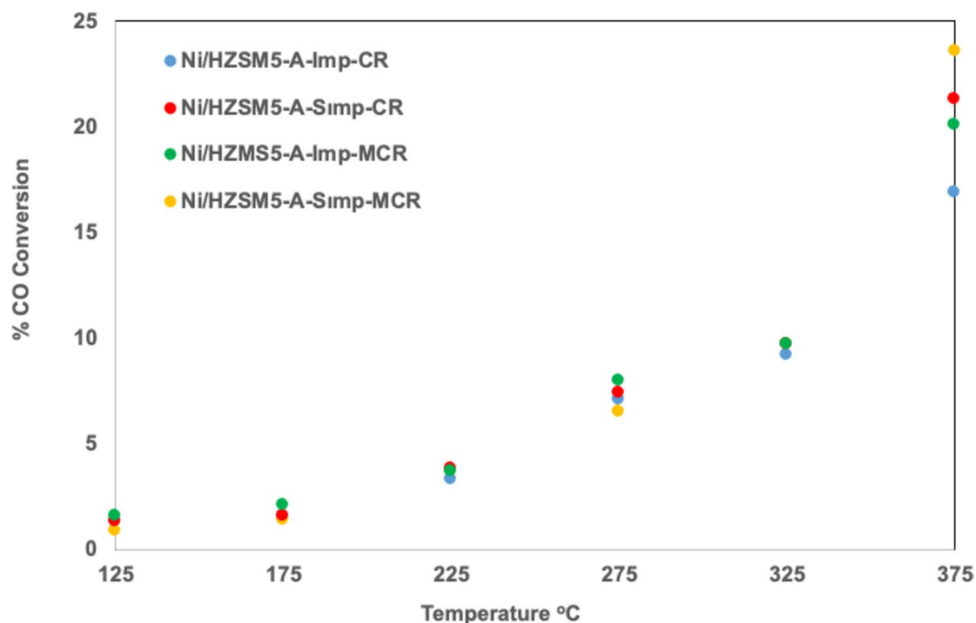


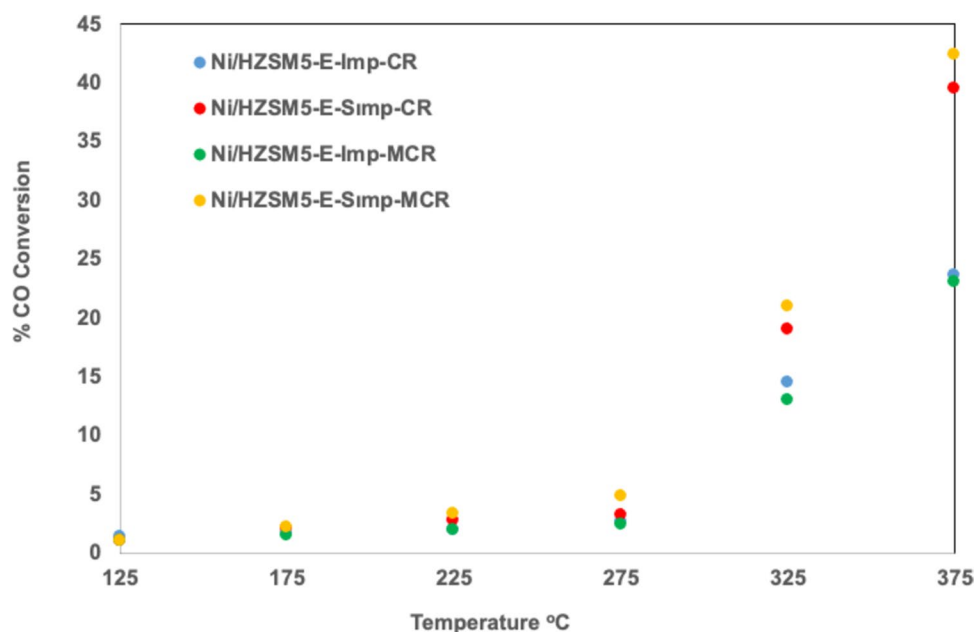
Fig. 10 The CO methanation activities of the catalysts prepared by using acetone (A) as solvent (1% CO, 50% H₂ remain He feed condition; 25 mg catalysts, S.V: 45,000 h.⁻¹, 25 ml/min). (Imp for impregnation method, SImp for surfactant assisted impregnation, CR conventional reactor, MCR microchannel reactor)



activity studies using microchannel reactor. The best result was determined as 24% CO conversion at 375 °C in the tested catalyst in the microchannel reactor prepared by the surfactant assisted impregnation method. An increase of 11% was obtained in the catalytic activity of the catalyst prepared by the surfactant-assisted impregnation method using a microchannel reactor, and 19% as a result of the catalytic activity of the catalyst prepared by the classical impregnation method. Figure 11 shows the catalytic activity results for the CO methanation of catalysts prepared using ethyl alcohol as a solvent. Catalytic activities of the catalysts

increased after 275 °C. The best results were obtained at 375 °C. The best activity results were obtained from catalysts with surfactant assisted impregnation in both reactors. However, the highest catalytic activity result was obtained as a result of activity studies using a microchannel reactor in the catalyst prepared by the surfactant-assisted impregnation method. The 43% CO conversion was obtained in the catalyst at 375 °C. While an increase of 7% was obtained in the catalytic activity of the catalyst prepared with the surfactant-assisted impregnation method using a microchannel reactor, no increase was obtained as a result of the catalytic

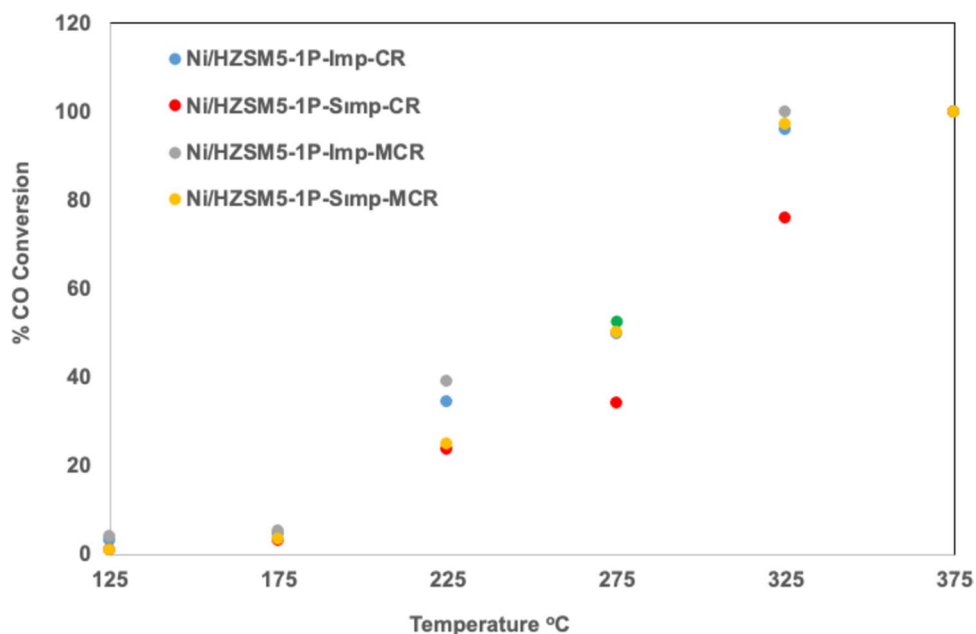
Fig. 11 The CO methanation activities of the catalysts prepared by using ethyl alcohol (E) as solvent (1% CO, 50% H₂ remain He feed condition; 25 mg catalysts, S.V: 45,000 h.⁻¹, 25 ml/min) (*Imp* for impregnation method, *SImp* for surfactant assisted impregnation, *CR* conventional reactor, *MCR* microchannel reactor)



activity of the catalyst prepared by the classical impregnation method. Figure 12 shows the catalytic activity results for the CO methanation of catalysts prepared using 1-propanol as solvent. Among all catalysts prepared in this study (including those prepared with water, ethyl alcohol and acetone as solvents), the highest CO conversion results were obtained from these catalysts both in the conventional reactor and in the microchannel reactor. Catalytic activities of catalysts increased after 225 °C. The best results were obtained at 375 °C. It gave 100% CO conversion at 375 °C in four catalysts. The catalysts showed very close CO

conversion activities to each other. Among the catalysts, the partially best activity result was obtained from the catalyst, which was prepared by the classical impregnation method and whose activity was tested in a microchannel reactor. According to the results obtained at 325 °C, the effect of the reactor type was investigated and an increase of 28% was obtained in the catalytic activity of the catalyst prepared with the surfactant assisted impregnation method using the microchannel reactor, while the catalytic activity of the catalyst prepared by the classical impregnation method could not be increased. According to the catalytic activity results, the

Fig. 12 The CO methanation activities of the catalysts prepared by using 1-propanol (1P) solvent (1% CO, 50% H₂ remain He feed condition; 25 mg catalysts, S.V: 45,000 h.⁻¹, 25 ml/min) (*Imp* for impregnation method, *SImp* for surfactant assisted impregnation, *CR* conventional reactor, *MCR* microchannel reactor)



microchannel reactor showed the designed increase in catalytic activity. In general, higher results were obtained in the activity experiments performed in the microchannel reactor. In terms of the preparation method, the catalysts prepared by the surfactant assisted impregnation method showed higher catalytic activity. The highest CO conversions were obtained from catalysts prepared using 1-propanol during the preparation of catalysts. In general, the best catalytic activity for CO methanation in the microchannel reactor was obtained from the catalyst prepared using 1-propanol solvent with the surfactant assisted impregnation method. Depending on the characterization results, the activity of the catalyst prepared using the surfactant-assisted impregnation method and 1-propanol can be evaluated. Among the catalysts prepared by the surfactant-assisted impregnation method, the micro-mesopore volume ratio of the catalyst prepared with 1-propanol is higher. At the same time, this catalyst has the lowest meso + micro and total pore volume compared to catalysts prepared with other surfactants. Micropore surface areas of catalysts prepared by surfactant-assisted impregnation method are higher. This has resulted in higher catalytic activity from these catalysts. However, the order of magnitude obtained due to catalyst preparation in micropore areas was not achieved in catalytic activity. The average NiO crystal size in the structure of the catalysts prepared by the surfactant-assisted impregnation method is smaller than that of the catalyst prepared by the classical impregnation method. At the same time, the smallest average crystal size was obtained from the catalyst prepared by 1-propanol and surfactant-assisted impregnation method. In this case, it can be concluded that the high activity of the catalyst prepared using the surfactant-assisted impregnation method and 1-propanol in CO methanation is due to the small crystal size. In the literature, there are no studies in which the CO methanation is carried out with both the classical vertical reactor and the microchannel reactor and the results are compared. Therefore, results from some studies have been added to the discussion. In the literature, the activities of the reactions studied using microchannel reactors have increased. In our study, compared to the classical reactor, working on CO methanation in a microchannel reactor increased the activity at certain rates depending on the catalyst type. Görke et al. (2005) studied the selective methanation by using the microchannel reactor over Ru/SiO₂ and Ru/Al₂O₃ catalysts. They observed that the microchannel reactor is an excellent tool for studying the reaction network of methanation of CO in presence of oxygen, CO₂ and hydrogen without heat transfer limitation (Görke et al. 2005). Galletti et al. (2011) studied the CO selective methanation over 3% Ru based catalysts supported on γ -Al₂O₃ and CeO₂. 3% Ru- γ -Al₂O₃ catalyst showed best performance. By covering the microchannels of plates with 5 mg cm⁻² catalysts they observed that CO did not convert to methane but CO₂

methanation was occurred. In order to increase the activity, the covering of microchannels with catalysts was doubled. And they observed that, the residual CO decreased to 100–150 ppmv at 310 °C, but large amount of methane produced to the CO₂ methanation which lead to decrease in selectivity (Galletti et al. 2011). Men et al. (2007) studied selective methanation of carbon oxides in a microchannel reactor. They used Ni/ CaO/Al₂O₃ in this study under conditions with different feed compositions, the solo-methanation or co-methanation, methanation in the presence or absence of steam. The experiments demonstrate that the microchannel reactor is an excellent tool for studying the reaction pathway by varying feed composition and reaction temperature (Men et al. 2007). A direct comparison cannot be made with studies in the literature. In this study, it was aimed to examine the effect of CO on the methanation reaction with both classical and microchannel reactors, depending on the effect of the solvent used in the catalyst preparation stage on the structural properties of the catalyst. The results showed that the catalysts prepared using 1-propanol were better than other catalysts. The effect of the active component in the catalyst structure on the methanation reaction activity is very important. High conversions are achieved in the methanation of both CO and CO₂ from Ru-containing catalysts. A ruthenium-doped fibrous silica-mordenite (Ru-FSMOR) catalyst was prepared for CO methanation. The Ru-FSMOR catalyst showed improved catalytic capacity at 450 °C, with 84% conversion of CO. The highest activity was due to the high surface area, basicity, and the presence of uniformly distributed Ru, which served as CO and H₂ adsorption sites, significantly improve the CO methanation activity (Hussaina et al. 2023). The selective CO methanation in CO₂-rich H₂ atmospheres were studied over the 2.2 wt.% Ru/zeolite catalyst. The effect of the in-situ calcination before the activation step were examined. Calcination in synthetic air, followed by the standard activation procedure in reaction gas, cause a decrease in mean Ru particle size. The increase in dispersion goes along with a distinct increase in selectivity of the Ru/zeolite catalyst for CO methanation at extremely low concentrations of CO (100 ppm) (Abdel-Mageed et al 2013). In another study, the transition metal Mo, which is in the same row as Ru in the periodic table, was used. Methane transformation into light olefins using methanol as co-reactant over 3Mo/HZSM5-x catalysts of Si/Al ratios ranging from 25 to 250 under varied reaction conditions were studied by Liu et al. 3Mo/HZSM5-160 (Si/Al = 160) shows the highest methane conversion rate, light olefins selectivity, and catalytic stability. By increasing the Si/Al ratio the amount and strength of the acid sites in the catalyst were decreased. And this enhances the olefin-based cycle (Liu et al. 2024). The Ni-based catalysts supported on the hollow ZSM-5 zeolites were used for CO₂ methanation. NiO is present in the structure of this catalyst at a mass ratio of 15% but the

catalyst has only been tested in the CO₂ methanation reaction. According to their results the highest CO₂ conversion and CH₄ selectivity in compare with the traditional Ni/ZSM5 catalysts were due to the strong basicity of the hollow supports as well as the presence of silicon hydroxyls. And the hollow structure of the support with alkaline treatment was an important consideration of high-performance Ni-based catalysts for CO₂ methanation (Cui et al. 2023). Catalytic methanation of CO and CO₂ over Ni-zeolite catalysts were investigated by plasma-assisted catalytic hydrogenation and compared with the conventional catalytic hydrogenation. Methanation of CO and CO₂ were increased in the presence of plasma. They found that Ni particles were dispersed more uniformly after the plasma reaction, which may partly explain the enhanced methanation rate in the presence of plasma (Jwa et al. 2013).

Conclusion

In this study, H-ZSM5 supported catalysts containing 15% NiO were prepared for the methanation reaction of carbon monoxide by the classical impregnation method. Within the scope of the study, the effects of using surfactant in the impregnation method on the characteristic properties of the solvent used in the impregnation process and therefore on the catalytic activity properties were investigated. In order to examine the effect of the reactor type used on the methanation reaction of CO, the catalysts were tested in both a vertical conventional glass reactor and a microchannel reactor. XRD analysis showed diffraction peaks originating from the NiO crystal phase. Due to the high intensities of the NiO peaks to the zeolite peaks, some of the zeolite peaks were also observed at low intensities. According to the average crystal size results calculated using XRD analysis results, no significant effect of the solvent on the average crystal size was observed. Depending on the preparation method, a significant decrease was observed in the average crystal sizes of the catalysts. From N₂ physisorption analysis, the best results in the surface area were obtained with the catalysts prepared by the surfactant assisted impregnation method and water is the best solvent for obtaining high surface area. It was determined that the surface area of the catalysts increased as the boiling point of the solvent increased. From catalysts a uniform pore diameter could not be obtained. HRTEM results showed that the surfactant allowed the NiO crystal phase to be more homogeneously dispersed on the zeolite support and penetrated more into the pores. Preparation of catalysts with the surfactant-assisted impregnation method allowed obtaining larger micropore areas, which resulted in higher catalytic activity from these catalysts. A similar situation occurred with the average crystal sizes obtained from XRD analysis results. The average size of the NiO crystal in the

catalysts prepared by the surfactant-assisted impregnation method was smaller than the results obtained from the catalysts prepared by the classical impregnation method. This situation had a positive reflection on the catalytic activity. Higher catalytic activity was obtained from smaller crystals. It can be concluded that the high CO methanation activity in this study obtained from the catalyst prepared by 1-propanol and surfactant-assisted impregnation method is due to the small crystals formed in the catalyst structure. These crystals on the inner surface form active sites. The formation of small crystals leads to the conclusion that metal/metal oxides do not agglomerate on the inner surface and therefore have high dispersion. According to the catalytic activity results, higher results were obtained in the activity experiments performed in the microchannel reactor. In general, for this study, it can be concluded that the preparation of 15% NiO/H-ZSM5 catalyst by the impregnation method using surfactant and 1-propanol is positive for the methanation of CO.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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