



## CO<sub>2</sub> Methanation over Ni-Sepiolite Catalysts

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### Abstract

In this study, it was aimed to develop new catalysts to increase the conversion of environmentally harmful carbon dioxide gas to methane which is a valuable fuel. By using a natural clay mineral sepiolite (SEP) as support material; 6-8% (weight-weight) Ni-containing catalysts were prepared by impregnation. Catalysts were characterized by XRD and FT-IR analysis. Reaction conditions of catalytic hydrogenation of carbon dioxide for methane production were determined as: H<sub>2</sub>/CO<sub>2</sub> = 4 molar ratio, the temperature range of 300-600°C at atmospheric pressure. The output gas mixture was analyzed using the μGC. The activities of the catalysts were determined in terms of carbon dioxide conversion and methane selectivity. 6%Ni/SEP and 8%Ni/SEP provided 65.76% and 68.42% carbon dioxide conversion at 400°C, respectively. In addition, both catalysts exhibited high methane selectivity at 300 and 400°C (>98%).

**Keywords:** CO<sub>2</sub> methanation, Sepiolite, Nickel, Impregnation, Catalyst.

## Ni-Sepiolit Katalizörler Üzerinde CO<sub>2</sub> Metanasyonu

### Öz

Bu çalışmada çevreye zararlı karbondioksit gazının değerli bir yakıt olan metana dönüşümünü artırmak için yeni katalizörlerin geliştirilmesi amaçlandı. Destek malzemesi olarak doğal bir kil minerali olan sepiolit (SEP) kullanılarak; %6-8 (ağırlık-ağırlık) Ni içeren katalizörler emdirme yöntemiyle hazırlandı. Katalizörler, XRD ve FT-IR analizi ile karakterize edildi. Karbon dioksitin katalitik hidrojenasyonu ile metan üretimi için reaksiyon koşulları şu şekilde belirlendi: H<sub>2</sub>/CO<sub>2</sub> = 4 molar oranı; atmosfer basıncında 300-600°C sıcaklık aralığı. Çıkış gaz karışımı μGC kullanılarak analiz edildi. Katalizörlerin aktiviteleri karbondioksit dönüşümü ve metan seçiciliği açısından belirlendi. %6Ni/SEP ve %8 Ni/SEP, 400°C'de sırasıyla %65,76 ve %68,42 karbondioksit dönüşümü sağladı. Ek olarak, her iki katalizör de 300 ve 400°C'de (>%98) yüksek metan seçiciliği sergiledi.

**Anahtar Kelimeler:** CO<sub>2</sub> metanasyonu, Sepiyolit, Nikel, Emdirme, Katalizör.

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## 1. Introduction

Due to its environmental effects, the issue of converting carbon dioxide into valuable products is becoming more important today. Methane, as the main component of natural gas, has an important place in energy consumption in daily life. The conversion of carbon dioxide to methane by catalytic hydrogenation represents only one reaction of the Fischer-Tropsch synthesis, which is a highly complex process. Therefore, catalyst selection and optimization of reaction conditions are very important to increase conversion of carbon dioxide to methane (Stangeland, Kalai, Li, & Yu, 2017).

Ni catalysts, known to increase efficiency in hydrogenation reactions, are used to obtain methane (Jayan, Anand, & Stephen, 2017).

Sepiolite (SEP) is a suitable clay mineral for using as catalyst support with its porosity, high stability, suitable surface area, tetrahedral and octahedral layers and fibrous structure and the presence of surface Si-OH groups (Kurtaran Ersal, 2013), (Corma, García, Leyva, & Primo, 2004).

Studies about development of sepiolite supported Ni catalysts and use them in carbon dioxide methanation is very few in the literature (Cerdá-Moreno, Chica, Keller, Rautenberg, & Bentrup, 2020). The SEP supported catalysts in this study were prepared with different nickel contents from the literature. In addition, the efficiency of SEP catalysts in the conversion of carbon dioxide to methane was investigated in the temperature range of 300-600°C, unlike the literature examining the range of 250-450°C (Cerdá-Moreno et al., 2020).

In this study, SEP catalysts containing 6% and 8% Ni by weight were prepared using the impregnation method. XRD and FT-IR characterization studies were carried out for catalysts and investigated their efficiency in carbon dioxide methanation process at atmospheric pressure.

## 2. Material and Method

### 2.1. Catalyst Preparation

#### 2.1.1. Pretreatment of Sepiolite

Raw SEP in stone form was obtained from Eskişehir region. Grinding, washing, filtering and drying processes were applied to the raw SEP, respectively. It was calcined at 900°C. After calcination, it was treated with nitric acid solution to increase porosity and remove impurities. Finally it was washed until neutral, filtered and dried in an oven (Yurdakul, 2015).

#### 2.1.2. Synthesis of Impregnated Catalyst

Calculated amount of nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) solution was added onto the pretreated SEP. After mixing and drying it was calcined at 500°C for 4 hours under dry air flow. Impregnated catalysts were named as 6%Ni/SEP and 8%Ni/SEP based on their Ni content (Xie et al., 2017), (Esen, 2016).

### 2.2. Characterization

XRD patterns of catalysts were recorded by using a Rigaku MiniFlex600 X-Ray diffractometer in the  $2\theta$  range of 5°–80° (Cu  $K\alpha$  radiation at 40Kv, step size: 0.04°).

FT-IR (Fourier transform infrared) spectroscopy was performed to detect functional groups with a Thermo Science Nicolet IS10. ATR technique was used and spectra were recorded between 4000-650  $\text{cm}^{-1}$  wavenumbers.

### 2.3. Reaction Conditions

Reaction studies were carried out in Microactivity Effi system using a quartz reactor (ID: 10 mm, OD: 12 mm, L: 370 mm).  $\text{N}_2$  was used as the carrier gas. The  $\text{H}_2/\text{CO}_2 = 4$  molar feed ratio was used and the total gas flow rate was 40 mL/min. 0.5 grams of catalyst (SiC was added until it filled 2 mL volume) was put into the reactor for each experiment, and the in-situ reduction was performed at 400°C under  $\text{H}_2$  flow (30 mL/min) for 1 hour before each experiment. The prepared Ni/SEP catalysts were used in the conversion of carbon dioxide to methane at atmospheric pressure and the temperature of 300, 400, 500, 600°C. The composition of the gas products were determined by the online  $\mu\text{GC}$  directly connected to the Microactivity Effi system. A very small amount of liquid product were not analyzed and not included in the  $\text{CH}_4$  selectivity calculation.

### 2.4. Conversion and Selectivity of Catalysts

The following equations were used to calculate the carbon dioxide conversion ( $X_{\text{CO}_2}$ ) (Eq. 1) and methane selectivity ( $S_{\text{CH}_4}$ ) (Eq. 2) of catalysts, respectively (Quindimil, Bacariza, González-Marcos, Henriques, & González-Velasco, 2021):

$$X_{\text{CO}_2} (\%) = \frac{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}}{F_{\text{CO}_2, \text{in}}} \cdot 100 \quad (1)$$

$$S_{\text{CH}_4} (\%) = \frac{F_{\text{CH}_4, \text{out}}}{F_{\text{CH}_4, \text{out}} + F_{\text{CO}, \text{out}} + F_{\text{C}_2\text{H}_4, \text{out}} + F_{\text{C}_2\text{H}_6, \text{out}} + F_{\text{C}_3\text{H}_6, \text{out}} + F_{\text{C}_3\text{H}_8, \text{out}}} \cdot 100 \quad (2)$$

Where  $F_{X, \text{in}}$  and  $F_{X, \text{out}}$  (mL/min) symbolize the amount of X species in feed and product, respectively. The amount of catalyst loaded into the reactor and discharged at the end of the reaction were weighed. There were no significant difference between the two measurements which amount of catalyst at before and after reaction. Further the  $\text{H}_2/\text{CO}_2 = 4$  molar ratio was used in the feed. Therefore possible C accumulation was neglected. C(s) is not included in the selectivity calculations.

## 3. Results and Discussion

### 3.1. Characterization Results

The XRD diffraction patterns and FT-IR spectra of the catalysts are shown in Fig. 1 and Fig. 2, respectively.

Peaks observed in Fig. 1 in the range of  $2\theta = 21^\circ$  and  $26^\circ$  indicate the presence of the quartz  $\text{SiO}_2$  phase (Kurtoğlu et al., 2018). In addition, the peaks observed at  $2\theta = 35^\circ$  and  $67^\circ$  in both samples also represent  $\text{SiO}_2$  (Xie et al., 2017), (Shi et al., 2017), (Lu et al., 2015) and  $2\theta = 37^\circ, 43^\circ, 63^\circ, 75^\circ$  and  $80^\circ$  peaks are interpreted as NiO (Darouhegi Mofrad, Rezaei, & Hayati-Ashtiani, 2019; Dong et al., 2020; Graça et al., 2014; Jiang, Huang, Dong, Qin, & Ji, 2018; Quindimil, De-La-Torre, Pereda-Ayo, González-Marcos, & González-Velasco, 2018). The characteristic peak of raw SEP expected to be observed at  $2\theta = 7.3^\circ$  ( $12.04\text{Å}$ ) (Akçay, 2004; Güngör et al., 2006; Meşe, Kantürk Figen, Coşkun Filiz, & Pişkin, 2018) was not observed in the samples.

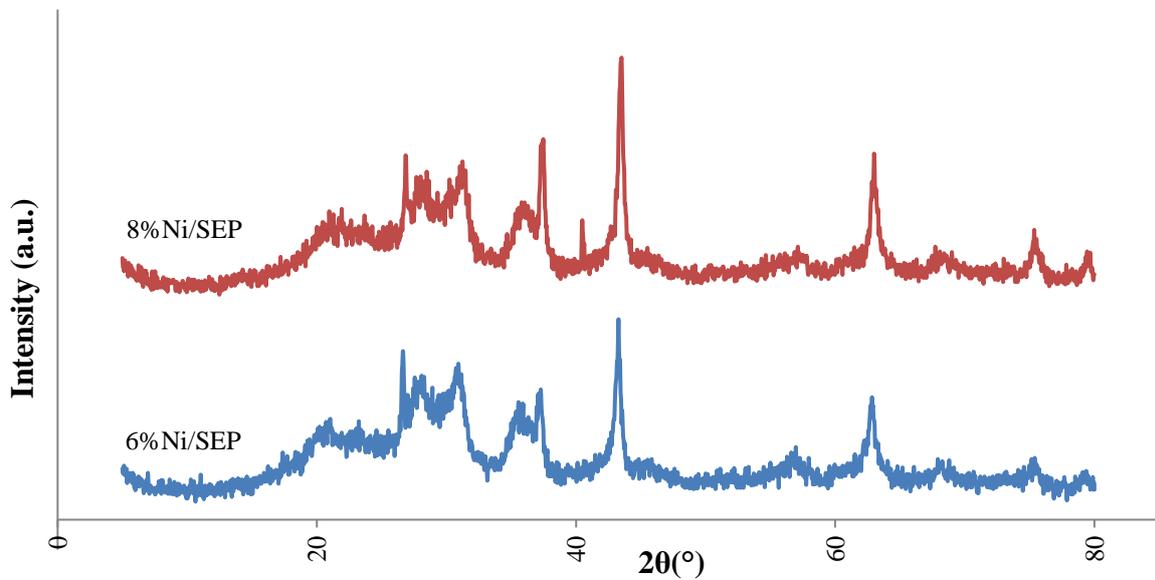


Fig. 1. XRD patterns of catalysts

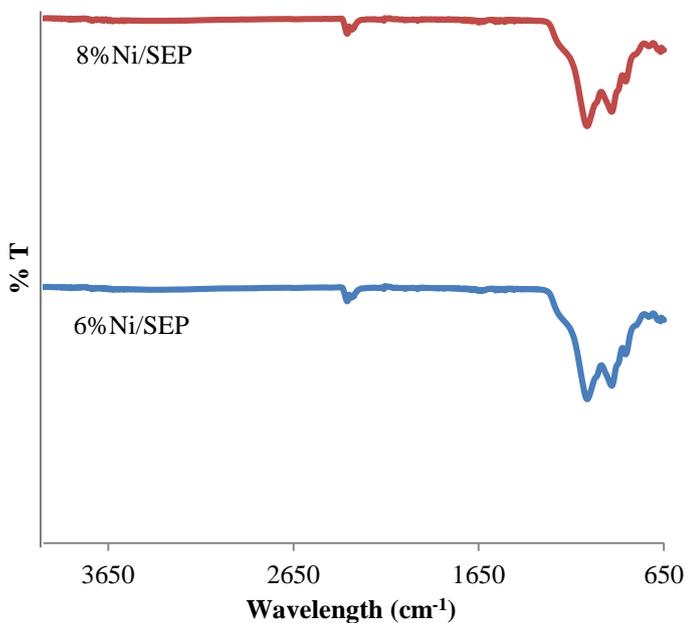


Fig. 2. FT-IR spectra

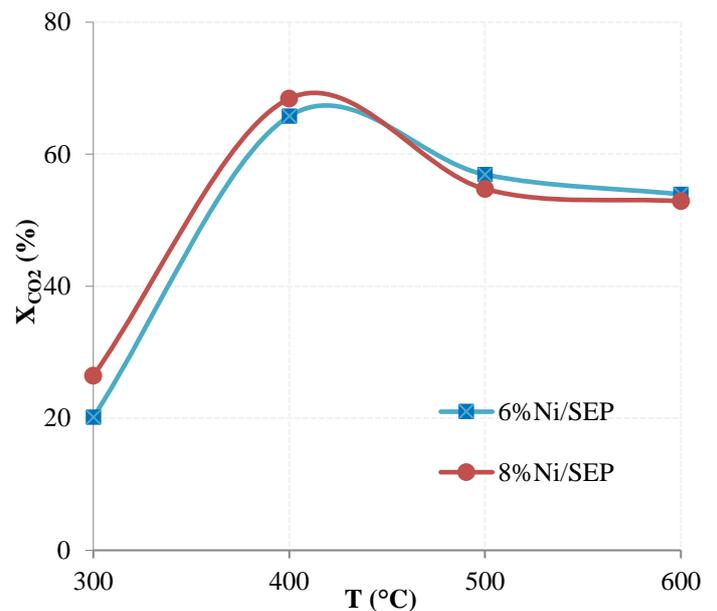
This is thought to be due to the pre-treatment of the raw SEP and followed by impregnation.

As seen in Fig. 2, the FT-IR spectra of the samples are almost the same. The  $3570\text{ cm}^{-1}$  band seen in both samples shows the vibrations of the structural  $\text{-OH}$  groups (Meşe et al., 2018). The  $1614\text{ cm}^{-1}$  band can be interpreted as H-O-H vibrations in the water molecule (Meşe et al., 2018), (Kıpçak & Kalpazan, 2020).

The adsorption force at the  $1010\text{ cm}^{-1}$  is due to the  $\text{SiO}_2$  bending vibrations of the tetrahedral layer. The peak seen at  $784\text{ cm}^{-1}$  in both samples can be interpreted as Si-O vibrations in the quartz  $\text{SiO}_2$  phase which also detected in the XRD (Kıpçak & Kalpazan, 2020). The wavelengths of  $850\text{ cm}^{-1}$  and  $703\text{-}720\text{ cm}^{-1}$  represent Si-O vibrations originating from SEP (Meşecikli Cansev, 2014).

### 3.2. Catalytic Activity Results

The carbon dioxide conversions of the catalysts in the methanation process were calculated according to Eq. 1 and are shown in Fig. 3.

Fig. 3.  $\text{CO}_2$  conversion of catalysts

The 6%Ni/SEP and 8%Ni/SEP catalysts showed similar  $X_{\text{CO}_2}$  results with minor differences (Fig 3). 6%Ni/SEP yielded 20.18% and 65.76% carbon dioxide conversion at 300 and 400°C, respectively. 8%Ni/SEP provided 26.45% and 68.42%  $\text{CO}_2$  conversion at 300 and 400°C, respectively. Higher Ni content of 8%Ni/SEP catalyst increased the carbon dioxide conversion at 300 and 400°C. Therefore, it can be said that 8% Ni/SEP for 300 and 400°C is more effective in terms of  $X_{\text{CO}_2}$ . 6% Ni/SEP yielded slightly higher carbon dioxide conversion than 8% Ni/SEP at 500 and 600°C (6%Ni/SEP provided 56.81% and 53.95% conversions; 8%Ni/SEP provided 54.73% and

52.87% conversions at 500 and 600°C, respectively). However, both catalysts reached their highest  $X_{CO_2}$  values at 400°C.

The calculated methane selectivity of the catalysts by using Eq. 2 in the temperature range of 300-600°C is given in Fig. 4.

Both catalysts provided almost completely methane selectivity (>98%) at 300 and 400°C. However, the selectivity began to decrease when 400°C was exceeded. This can be explained by the fact that endothermic reactions in the carbon dioxide hydrogenation process such as Reverse Water-Gas Shift (RWGS) ( $CO_2 + H_2 \rightleftharpoons CO + H_2$ ) and methane cracking ( $CH_4 \rightleftharpoons C + 2H_2$ ) begin to occur with increasing temperature.

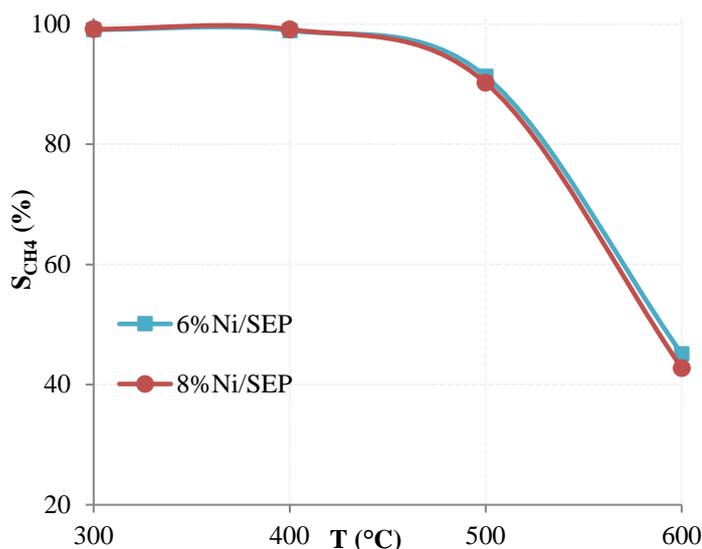


Fig. 4. CH<sub>4</sub> selectivity of catalysts

When Figures 3 and 4 are examined together, it is seen that the optimum operating temperature for both catalysts is 400°C.

#### 4. Conclusions and Recommendations

The characterization results of the catalysts are compatible with the literature and it seems appropriate to use SEP as a catalyst support.

Very few Ni-containing SEP catalysts have been used in the methanation of carbon dioxide in the literature. Therefore, the results are remarkable. Both catalysts showed the highest efficiency at 400°C. There are many studies in the literature in which carbon dioxide methanation was carried out at 400°C (Cerdá-Moreno et al., 2020), (Xie et al., 2017), (Danaci et al., 2016), (Li et al., 2018). In this regard, the determined operating temperature is consistent.

In the literature, there is a study in which 5%Ni/sep catalyst prepared by the incipient wetness impregnation (IWI) method is used in the methanation of carbon dioxide (Cerdá-Moreno et al., 2020). In (Cerdá-Moreno et al., 2020), 5%Ni/sep catalyst provided 73% carbon dioxide conversion and 97% methane selectivity at 400°C ( $H_2/CO_2=4$ , atmospheric pressure). In our study, 6%Ni/SEP reached 65.76% ( $X_{CO_2}$ ) and 98.93% ( $S_{CH_4}$ ) values at the same temperature. The differences between the results are interpreted to be due to differences in used SEP, catalyst preparation, amount of catalyst, reduction temperature and GHSV.

8%Ni/SEP achieved a higher CO<sub>2</sub> conversion than 6%Ni/SEP at 400°C. This result is expected due to the higher Ni content of 8%Ni/SEP.

The selectivity curves of both catalysts are almost identical and are above 98% at temperatures of 300-400°C. Therefore, the  $X_{CO_2}$  curves are decisive. According to Fig. 3, the optimum condition in this study is the use of 8%Ni/SEP at 400°C (Applicable when all the other conditions are constant: 0.5 grams of catalyst, same reduction conditions,  $H_2/CO_2 = 4$ , atmospheric pressure, GHSV = 3600 mL.gcat<sup>-1</sup>.h<sup>-1</sup> etc.).

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