THE ACTIVITY OF ZEOLITE-SUPPORTED NICKEL CATALYST IN CO_2 HYDROGENATION TO PRODUCE CH_4

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Abstract

The utilization of CO_2 by converting it into different products is a very important and remerkable research area because of CO_2s harmful environmental effects. In this study, the natural zeolite was impregnated with nickel, which is known for its effectiveness in catalytic hydrogenation reactions. The prepared 15%Ni/Zeo catalyst was characterized by XRF, XRD, FT-IR, SEM and TGA techniques. The activity of catalyst was investigated in the CO_2 methanation. Catalytic activity studies were performed by a Microactivity Effi reactor system. The catalyst was reduced in-situ with H_2 for 1 hour at 400°C before the reaction. The H_2/CO_2 molar ratio was set to 4. The experimental studies were carried out at atmospheric pressure and the temperatures of 300, 400, 500 and 600°C. 15%Ni/Zeo is the most effective in CO_2 methanation at 400°C with 66.36% CO_2 conversion and 99.33% CH_4 selectivity. Characterization studies and catalytic activity results showed that zeolite is a suitable support for CO_2 methanation.

Keywords: CO_2, Nickel-zeolite, Hydrogenation, CH_4

1 INTRODUCTION

CO_2 is one of the most important greenhouse gases with its increasing rate in the atmosphere in recent years. The usage, storage or evaluation of carbon dioxide by converting it into different products has been a remarkable research topic in recent years. CH_4 is the largest component of natural gas and is an important fuel. Therefore, the conversion of CO_2 to CH_4 is significiant research [1].

The Fischer-Tropsch (FT) process is used to convert syngas to high C-number products and consists of a series of complex catalytic reactions [2]. The conversion of CO_2 to CH_4 takes place by hydrogenation of CO_2 and is part of the FT process. The catalysts used in the FT process vary according to the demanded product [3]. In general, high yield Ni catalysts are preferred in hydrogenation reactions to obtain CH_4 from CO_2 [4].

Zeolites have chemically active nanostructures [5] and are often preferred as support materials due to their properties such as porosity, crystal structure and thermal resistance. In addition, metal contents in natural zeolites can increase the efficiency of the catalyst.

There are a few studies in the literature in which Ni-containing catalysts prepared using commercial zeolites are used in CO_2 methanation [6–8]. However, no study was found in which the Ni catalyst prepared with the untreated natural zeolite support was used in the same reaction.

In this study, the untreated natural clinoptilolite zeolite supported catalyst with 15% Ni content was prepared, characterized and used in the production of CH_4 from CO_2.

2 EXPERIMENTAL

2.1 Synthesis of Catalyst

Natural zeolite with clinoptilolite properties was obtained from Balıkesir, Turkey. The impregnation method was used in the preparation of the catalyst. Calculated amount of nickel nitrate ($Ni(NO_3)_2.6H_2O$) was dissolved in water and added onto the natural zeolite. The solution was stirred, dried and the remaining solid powder was calcined with a stream of dry air at 500°C for 4 hours [9]. The final material was named as 15% Ni/Zeo.

2.2 Characterization

A Rigaku ZSX100 Primus X-Ray Fluorescence (XRF) device was used to determine bulk composition of catalyst.

The X-Ray Diffraction (XRD) patterns of fresh and used catalysts were recorded by using a Rigaku MiniFlex600 X Ray diffractometer in the 2θ range of 5° - 80° (Cu Kα radiation at 40Kv, step size: 0.04°).

Fourier Ttransform Infrared Spectroscopy (FT-IR) was performed with a Thermo Science Nicolet IS10 by using ATR technique. Spectra was recorded between 4000 cm^{-1} and 650 cm^{-1} wavenumbers.

The Scanning Electron Microscopy (SEM) of sample were recorded by a ZEISS-SUPRA 50 VP scanning electron microscope at 20 kV.

The Thermogravimetric (TG) analysis of the catalyst used was recorded with the Perkin Elmer STA6000 device in the temperature range of 30-900°C.

2.3 Methanation of CO_2

Possible reactions that can occur in the hydrogenation of CO and CO_2 have been shared in the literature [4,10]. The reaction of CO_2 methanation (R1) is as follows:

$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ $\Delta H_{298K} = -165$ kJ/mol (R1)

The efficiency of the 15%Ni/Zeo catalyst in the methanation of CO_2 was determined using the MicroActivity Effi reactor. The reduction and reaction were carried out in-situ consecutively. The catalyst was placed in a stainless steel reactor and reduced for 1 hour under H_2 flow rate of 30 mL/min. Experimental studies were carried out at the temperatures of 300, 400, 500 and 600°C and atmospheric pressure. The H_2/CO_2 molar feed ratio was used as 4 and the gas hourly space velocity (GHSV) was maintained at 3600 mL/h.gcat. The composition of the gaseous products was determined online by the µGC device. A very small amount of liquid product was ignored.

2.4 Equations

The CO_2 conversion (X_{CO2}) and CH_4 selectivity (S_{CH4}) equations used in this study are as follows:

$$X_{CO2} = ((F_{CO2,in} - F_{CO2,out})/F_{CO2,in})*100 \quad (1)$$

$$S_{CH4} = (F_{CH4,out}/(F_{CH4,out}+F_{CO,out}+F_{C2H4,out}+F_{C2H6,out}+F_{C3H6,out}+F_{C3H8,out}))*100 \quad (2)$$

Where $F_{X,in}$ and $F_{X,out}$ (mL/min) symbolize the amount of X in inlet and outlet, respectively.

3 RESULTS

3.1 Characterization Results

The XRF results of fresh catalyst are shown in the Table 1.

Table 1. The chemical composition of 15%Ni/Zeo

Component	wt. %
SiO_2	54.89
NiO	18.72
Al_2O_3	9.14
CaO	3.01
K_2O	2.76
Fe_2O_3	1.15
Others	0.81
LOI[a]	9.52

[a] Loss on ignition.

As it is seen from Table 1, the three main components of the catalyst are SiO_2, NiO and Al_2O_3 respectively. The NiO component was determined as 18.72%. According to the XRF results, it was clarified that the desired 15%Ni/Zeo catalyst was successfully synthesized.

The XRD diffraction patterns of fresh and used catalyst are shown in the Figure 1.

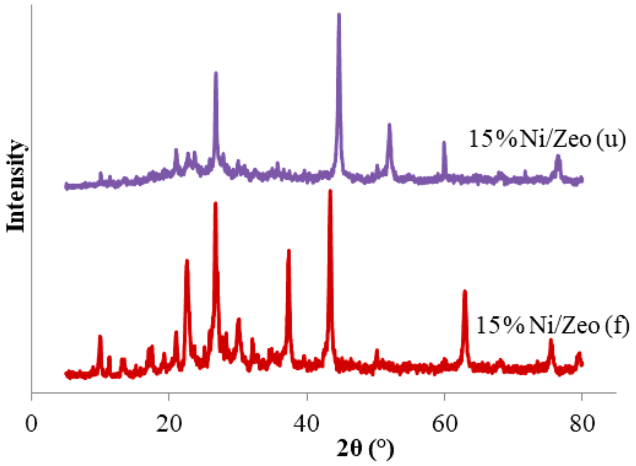

Figure 1. XRD patterns of fresh and used 15%Ni/Zeo

The clinoptilolite phases are observed at 2θ = 11, 14, 16, 20, 30, 33, 35 and 37,5° values in the Figure 1 [11]. The peak seen at 2θ = 26° corresponds to quartz SiO_2 phase [12] and it is also consistent with XRF results. Almost all of these peaks were detected in the fresh catalyst. It is understood that the natural zeolite used contains clinoptilolite. The peaks at 2θ = 37, 43 and 63° indicate the NiO phase in the fresh catalyst [6–8,13–15]. On the other hand, the metallic Ni peaks were observed at 44.5, 52 and 76.6° in the used catalyst [15,16].

The FT-IR spectra of the 15%Ni/Zeo is given in the Figure 2.

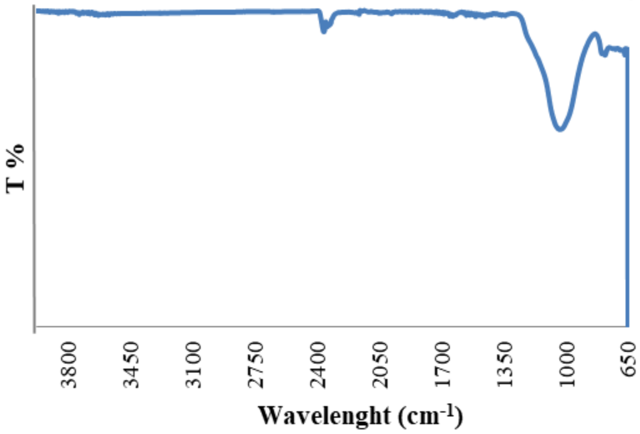

Figure 2. FT-IR spectra of 15%Ni/Zeo

The 791 cm^{-1} band is due to Si-O-Si vibrations indicating the presence of the quartz phase [17,18]. The 1004 cm^{-1} band is an indicator of the T-O bonds in the structure of the material (T = Al, Si) [19]. The bending vibration of water are observed at 1635 cm^{-1} [19]. And finally, the 3620 cm^{-1} band indicates the presence of structural OH groups.

The SEM micrograph of the 15%Ni/Zeo is given in the Figure 3.

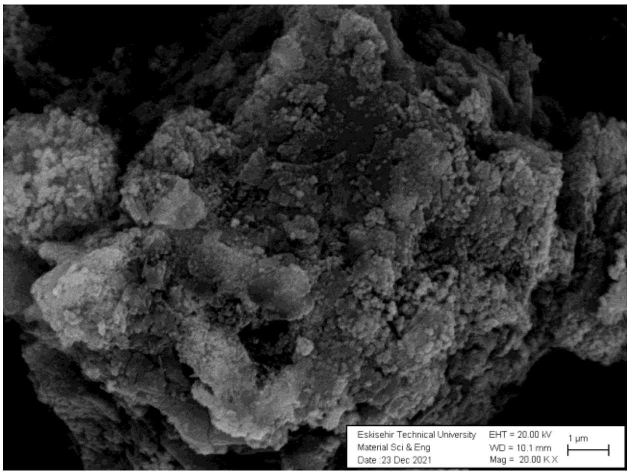

Figure 3. SEM micrograph of fresh 15%Ni/Zeo

The NiO particles was uniformly dispersed on the zeolite surface in the Figure 3. The different stone-like structures are observed in the SEM image of 15%Ni/Zeo catalyst that can be associated with the use of the support material as received. Hence, it is determined that the SEM image of the catalyst is compatible with the literature [11,20].

The TG curves of fresh and used 15%Ni/Zeo catalyst were given in the Figure 4.

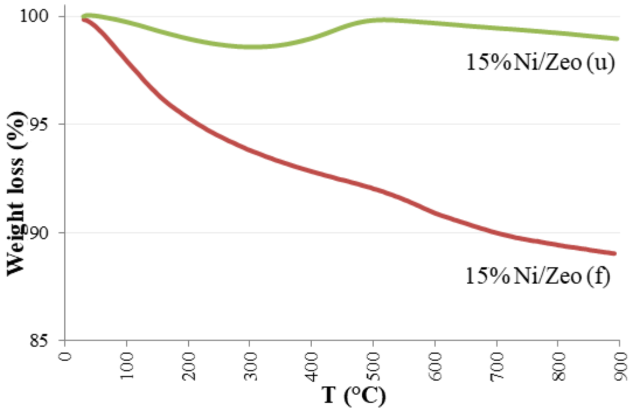

Figure 4. TG curves of 15%Ni/Zeo

The fresh catalyst lost about 11% of its mass at 900°C. The high mass loss can be attributed as normal as the natural zeolite without pretreatment. The mosture in the catalyst structure is removed below at 400°C and the OH group at 400-700°C [11,19]. The mass losses in the used catalyst up to 300°C are due to the removal of moisture and volatile components absorbed on the catalyst. The C species begin to leave above 300°C. The significant weight gain observed in the range of 300-500°C is due to metallic Ni oxidation, which suppresses the combustion of carbon species [21,22]. The amorphous carbon is oxidized at lower temperature in the range of 250-350°C. The mass losses at temperatures higher than 550°C are due to the oxidation of inert carbon (graphitic carbon) [23]. The used catalyst lost only 1.04% of its mass at 900°C. Therefore, it can be said that the accumulation of C on the catalyst is ignorable.

3.2 The Catalytic Activity Results

The catalytic activity results of 15%Ni/Zeo in terms of X_{CO2} (Equation 1) and S_{CH4} (Equation 2) are shown in Figures 5 and 6, respectively.

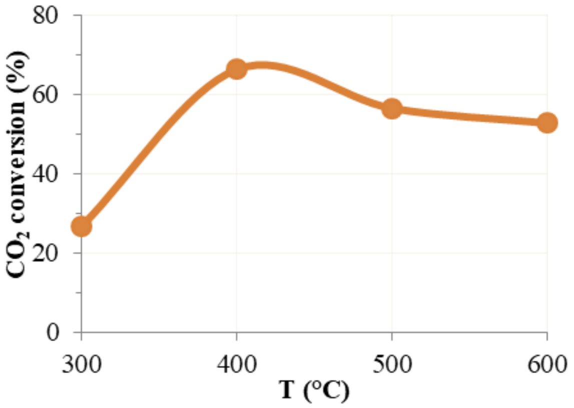

Figure 5. CO_2 conversion of 15%Ni/Zeo

15%Ni/Zeo reached the highest X_{CO2} at 400°C (66.36%). The commercial zeolite supported Ni catalysts was achieved 71% X_{CO2} at 400°C [6] and 65.5% at 450°C [7] in the literature. Because of the exothermic character of CO_2 methanation, X_{CO2} is reduced at 500 and 600°C. It was determined that the optimum temperature for 15%Ni/Zeo was 400°C in terms of X_{CO2} in the temperature range of 300-600°C.

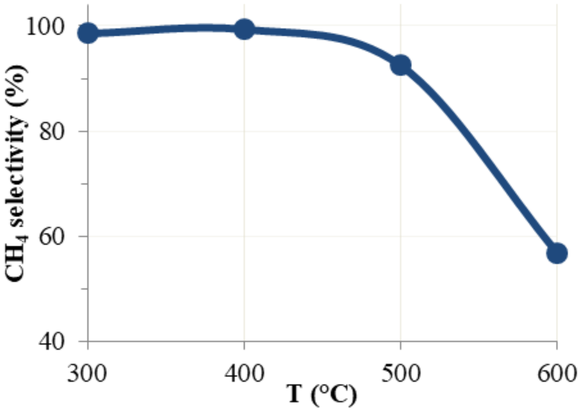

Figure 6. CH_4 selectivity of 15%Ni/Zeo

According to Figure 6, the S_{CH4} is almost 100% at 300 and 400°C. But the S_{CH4} gradually decreases as different endothermic reaction products appear above 400°C. The Ni-commercial zeolite catalysts was exhibited 95% S_{CH4} at 400°C [6] and 94.2% at 450°C [7] in the literature. In this study, the S_{CH4} is higher than the literature at 400°C. In terms of S_{CH4} for 15%Ni/Zeo in the temperature range of 300-600°C, the most suitable temperature was determined to be 400°C.

4 CONCLUSIONS

The untreated natural zeolite supported 15% Ni catalyst showed similar efficiency with the commercial zeolite supported Ni catalysts in the literature in terms of X_{CO2} in CO_2 methanation. It also provided about 100% S_{CH4} at 300 and 400°C. According to the XRD diffraction pattern, it was observed that the addition of Ni has no effect on the structure of the natural zeolite. The negligible mass loss was observed in the TG analysis of the used catalyst. This means that very small amount of C is deposited on the catalyst. The highest X_{CO2} and S_{CH4} values were achieved in the CO_2 methanation reaction carried out at 400°C. The positive structural properties and activity results show that the 15%Ni/Zeo is a suitable and potential catalyst for CO_2 methanation.

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