Konversi 13(2) (2024) 57-60

KONVERSI
Homepage:
https://ppjp.ulm.ac.id/journal/index.php/konversi

Regeneration of Ni/Al_2O_3 catalyst in CO_2 methanation

Rima Melati, Robert Junaidi*, Mustain Zamhari

Department of Chemical Enginering, Sriwijaya State Polytechnic,Palembang 30139, Indonesia

ARTICLE INFO

Article history:
Received: 14 July 2024
Received in revised form: 09 October 2024
Accepted: 16 October 2024

Keywords:
Catalyst, CO_2, methane

ABSTRACT

CO_2 emissions are one form of greenhouse gas (GHG) emissions that contribute to global warming. CO_2 contributed 175.62 million tons in 2021, impacting greenhouse gas levels. One strategy to reduce the concentration of CO_2 in the atmosphere is to convert CO_2 gas into useful chemicals. One example of this is the hydrogenation of CO_2 to produce methane, which can serve as an alternative to LPG. The aim of this research is to produce methane gas by developing a fixed bed reactor in a simple manner. The catalyst Ni/Al_2O_3 with 20 grams and five regenerations could produce CH_4 up to 49.73% compared to 39.06% for those with 10 grams. However, the H_2 gas remaining is higher for those with 10 grams (1.454 ppm compared to 1.042 ppm). Also, The CO_2 gas remaining is higher for those with 10 grams (58.18% compared to 47.92%). The results of this study can be the basis for developing energy policies, encouraging investment in clean energy technologies, and supporting the reduction of greenhouse gas emissions for energy sustainability and resilience.

1. Introduction

Fossil fuels, which are the primary source of energy supply, have significant drawbacks. When fossil fuels are burned, there are substantial emissions of CO_2 (carbon dioxide), which can contribute to the greenhouse effect [1]. The increase in greenhouse gas concentrations in the Earth's atmosphere leads to excessive greenhouse effects. When greenhouse gases like CO_2 are trapped in the atmosphere, they can cause the greenhouse effect by retaining heat from the sun, thereby increasing global temperatures. The energy sector is the largest contributor to greenhouse gas emissions, with approximately 175.62 million tons of CO_2 emitted in 2021. CO_2 has high stability, making it difficult to convert into other substances, such as formic acid and ethylene, by breaking down the C=O structure. Therefore, additional strong energy is required to drive the conversion of CO_2 [1].

Several researchers have already made efforts to reduce CO_2 emissions, one of which involves utilizing CO_2 in methanol production [2]. It has also been found that CO_2 can replace the use of formic acid in the leather tanning process [3]. CO_2 has been utilized using in situ methods in hydrogenation processes with nickel talate catalysts to enhance steam-based oil recovery [4]. The research focused on CO_2 methanation using a Ni/Al_2O_3 catalyst at an optimum temperature of 400°C, achieving a CO_2 conversion of approximately 3% over three continuous cycles lasting 74 hours [5].

Previous study has focused on the catalytic conversion of carbon dioxide into methane [6]. In the study conducted by Zhong et al., a simple approach was used to convert CO_2 into methane using a Ni/Al_2O_3 catalyst that had been heated for 2 hours prior to reaction to open the pore structure of the commercial catalyst [7].

The results showed that they successfully achieved a high methane conversion rate of 98% at a temperature of 300°C. The research conducted catalytic tests and concluded that the Ni catalyst could produce methane with a maximum yield of 17.63% at nearly 400°C [8]. The Ni catalyst was chosen because Ni has properties comparable to noble metals while being relatively inexpensive [5]. The study demonstrated the utilization of CO_2 in methane production, achieving an optimal methane yield of 13.56% at 60°C [5].

Based on the results obtained, it appears that the conversion of CO_2 remains quite low, especially when using extreme temperatures and lengthy reaction times. Therefore, to improve the methane conversion yield, the amount of zinc metal promoter will be varied—specifically, 10 grams and 20 grams—and the commercial Ni/Al_2O_3 catalyst will be activated to open its pores. This catalyst activation will be denoted as Ni_R1, and the regeneration/recycling of the catalyst will be represented as (Ni_R2 - Ni_R5), conducted at a temperature of 100°C over 60 minutes.

2. Materials and Methods

2.1. Tools

Beaker, graduated cylinder, Erlenmeyer flask, spatula, catalyst container, water bath, stirring rod, and a set of PFR (Packed Bed Reactor) tools.

* Corresponding author. Tel.: +6281278314339
Email: robert.junaidi@polsri.ac.id
http://dx.doi.org/10.20527/k.v13i2.19951

This open access article is distributed under a Creative Commons Attribution (CC-BY-SA) 4.0 license

2.2. Materials

Ni/Al_2O_3 catalyst, NaOH, Zinc (Zn) promoter, Aquadest (distilled water), and Deionized water.

2.3. Methods

2.3.1. Catalyst activation

Prepare a 4M NaOH solution and weigh 50 grams of the Ni/Al_2O_3 catalyst. Then, mix the 4M NaOH solution and the catalyst in an Erlenmeyer flask and heat it in a water bath for 2 hours, denoted as Ni_R1

2.3.2. CO_2 methanation

Weigh 10 g and 20 g of Zn, then prepare a 4M NaOH solution. Ni_R1 and Zn are placed into the collection tube. The methanation apparatus is connected to the power supply, and the temperature is set to 100°C. The NaOH solution is periodically flowed through a transparent tube to prevent drastic temperature spikes in the reactor, followed by alternating the flow of CO_2 gas with the NaOH solution. When the pressure in the reactor decreases or stabilizes, open the valve connected to the gas collection container. The collected gas will then be analyzed using a Multi Gas Detector Analyzer, with the catalyst used in the first reaction denoted as Ni_R2.

2.3.3. Catalyst regeneration

Nickel catalyst is considered the best catalyst choice in the CO2 methanation process due to its relatively lower cost and catalytic properties similar to those of noble metals [9]. Ni_R2 catalyst that has been used is then regenerated by rinsing the Ni/Al_2O_3 catalyst with deionized water and vacuum-drying it. After drying, the catalyst can be reused. We performed this catalyst regeneration process five times, denoted as Ni_R3 through Ni_R5.

2.4. The analysis of the gas products generated is conducted using a multi gas detector analyzer

The analysis of the gas product is conducted using a Multi Gas Detector Analyzer with a self-testing method for approximately 5 minutes, until it shows a reading of 0 on the display. The gas collection container is connected to the gas sensor device. The analysis can be performed under constant conditions on this equipment.

3. Results and Discussion

From the gas analysis using the Multi Gas Detector Analyzer, three gas components were identified in the gas collection we conducted. These include carbon dioxide (CO_2) and hydrogen (H_2), which were produced due to the failure of these two gases to react and form methane (CH_4). The percentages of the gas components can be seen in the following Table 1.

Based on Figure 1, which was taken from Table 1, it can be observed that the graph shows a direct proportionality of the CH_4 produced. This indicates that the activation of the commercial catalyst (Ni_R1) can form pore structures on the catalyst, and the regeneration of the catalyst (Ni_R2 - Ni_R5) also plays a crucial role in increasing the CH_4 gas due to the increasingly fine and wider pore structures each time the catalyst is regenerated [10].

Table 1. Research results data

Catalyst Treatment	Amount of Zn Promoter (grams)	Test Results (%)		
		CH_4	CO_2	H_2
Ni_R1	10	29.43	67.56	1.703
Ni_R2		31.79	65.30	1.607
Ni_R3		35.24	61.95	1.510
Ni_R4		37.92	59.28	1.492
Ni_R5		39.06	58.18	1.454
Ni_R1	20	32.67	64.44	1.588
Ni_R2		36.12	61.08	1.499
Ni_R3		43.60	53.80	1.296
Ni_R4		47.00	50.59	1.102
Ni_R5		49.73	47.92	1.042

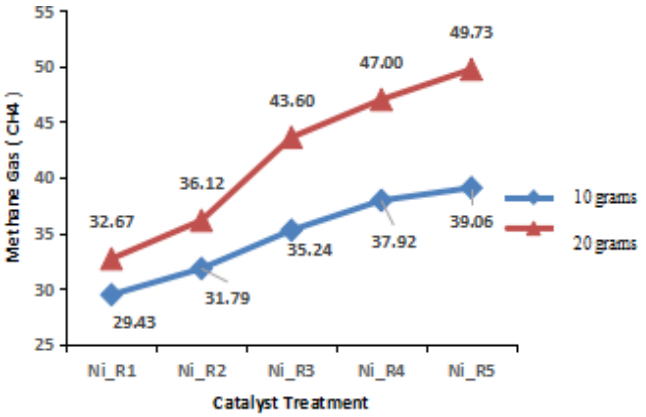

Fig. 1. The produced methane gas (CH_4)

The methane gas results obtained in this study align with previous research, which indicated an increase in methane gas production with a methane percentage reaching 98% [7]. This result was achieved at a high temperature of 300°C over a duration of 4 hours. In contrast, the research [11] reported a methane percentage of 13.56% at 60°C. Furthermore, a study conducted by TM Putri in 2023 showed a methane yield of 12.54% at 60°C. From these studies, it can be seen that at the relatively low temperature of 60°C, the percentage of methane gas produced is also relatively low.Increasing the pressure up to a certain point can enhance the reaction efficiency within the general temperature range [12]. In this research, we used a pressure of 12.5 atm.In particular, increased reaction pressure is beneficial to suppress CO and ethane formation.[13]

Therefore, in this study, a temperature of 100°C was chosen, as this temperature is the boiling point of water, facilitating the formation of H_2 to rise to the surface and react with Carbon Dioxide. It can be observed again in Figure 1 that the percentage of methane gas shows an increase; however, the increase is not significant across each catalytic treatment and promoter variation. This is believed to be due to human error during the process.

After analysis using the Multi Gas Analyzer Detector, results for CO_2 and H_2 gas were obtained (Figures 2 and 3), which failed to react with methane gas. However, the percentages of CO_2 and H_2 gas experienced a decline, which is inversely proportional to the increasing percentage of methane

gas, as shown in Figure 1. The reduction in CO_2 results over a longer reaction time occurs because CO_2 can react to form CH_4, as the Ni nanoparticle catalyst is highly active in reducing CO_2 to methane [10].

In addition to CO_2, H_2 gas also showed a decrease in every catalytic treatment. H_2 gas at 100°C for 60 minutes experienced a decline, which aligns with the results showing a decrease in H_2 gas in this study [14]. The reduction in H_2 is attributed to the failure to form methane due to insufficient adsorption of H_2 gas by the Ni nanoparticles.

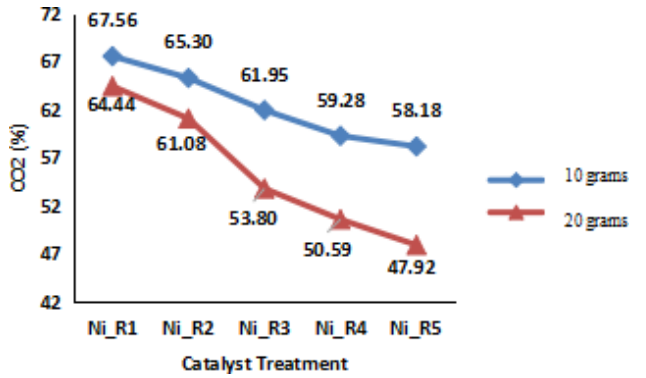

Fig. 2. CO_2 gas that failed to form methane gas

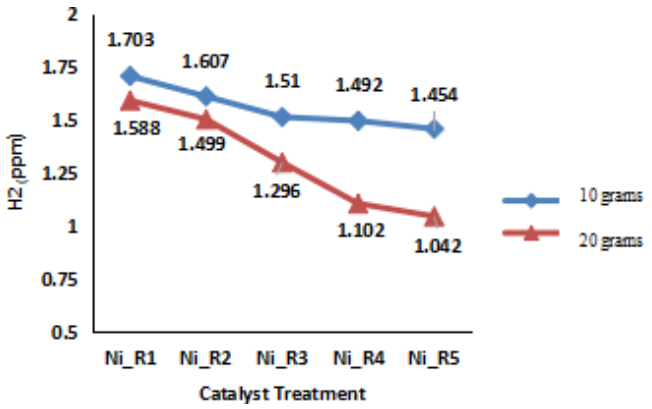

Fig. 3. H_2 gas that failed to form methane gas

The commercial Ni/Al_2O_3 catalyst has large particles without pore structure [7]. When this commercial catalyst is reacted, almost no methane is produced within the first 3 hours. However, when the catalyst is activated (Ni_R1), there is a significant increase in methane production in less than 1 hour, which continues to increase up to 98% within 4 hours. Additionally, two extra treatments, (Ni_R4 & Ni_R5), were added in this study. Upon analysis, the percentage of methane gas continued to increase in these treatments, which supports the findings by [10] regarding the enhancement of methane production after catalyst regeneration treatment.

The addition of lanthanum as a promoter significantly enhances the activity of Ni/Al_2O_3 in the methanation of Carbon Dioxide (CO_2) [12]. The role of Zn as a promoter capable of producing H_2 from high-temperature water. The methane gas production increases with the addition of the promoter, as the increase in the amount of Zn promoter enhances the catalyst's activity in CO_2 methanation [9].

In this study, variations of 10 grams and 20 grams of the promoter were used; this significant difference in amounts was intended to observe the spike in the produced methane gas. The most optimal methane gas yield was found in sample 10 during the fifth catalyst regeneration (Ni_R5) with the use of 20 grams of the Zn metal promoter, reaching 49.73%. With the use of 20 grams of Zn in Ni_R5, the catalyst's activity became increasingly active, resulting in a methane gas percentage that was over 10% higher compared to the use of 10 grams of the promoter.

The methane gas results from Figure 1 indicate that the methanation reaction proceeds very well and is directly proportional to the increase in the amount of Zn promoter, which aids the reaction process, resulting in a greater yield of methane gas alongside the catalyst regeneration.Catalytic conversion of CO2 into methane can reduce global warming and provide a solution to the energy depletion crisis [15].

4. Conclusion

Based on the results of the research conducted, the following conclusions can be drawn. The highest percentage of methane gas production was obtained from sample 10, which utilized a promoter amount of 20 grams during the regeneration of catalyst Ni_R5. This sample yielded an impressive 49.73%. When this result is compared with findings from previous studies and analyzed through the corresponding graph, a clear direct proportionality is observed. This suggests that our research has the potential to continue and achieve even higher percentages in future experiments. In every comparison of treatments (Ni_R1 - Ni_R5) and the addition of the Zn metal promoter (10 grams and 20 grams), all percentages showed an increase, starting from 3.24% for Ni_R1, 4.33% for Ni_R2, 8.36% for Ni_R3, 9.08% for Ni_R4, and 10.47% for Ni_R5. Thus, the greater the amount of Zn promoter used, the more CH_4 is produced. This is because the addition of Zn can enhance the catalytic activity in the methanation of CO_2. The activation and regeneration of the Ni/Al_2O_3 catalyst are crucial for ensuring that the catalyst functions effectively in converting CO_2 into CH_4 gas.

This finding opens up opportunities for further exploration with variations in promoters and reaction conditions that can enhance the efficiency of CO_2 conversion. Additionally, the results of this research can serve as a foundation for the development of better energy policies, encouraging investment in clean energy technologies and supporting efforts to reduce greenhouse gas emissions, thereby contributing to sustainability and energy resilience.

References

[1] Zhang, C., Liu, H., & Sun, X. (2018). The promoting effect of Fe and La on Ni/Al2O3 catalysts for CO2 methanation. Journal of CO2 Utilization, 26, 1-9. doi:10.1016/j.jcou.2018.01.006

[2] Sutardi, T., & Budiman, A. H. (2020). Potensi Pemanfaatan Co2 Dan Hidrogen Sebagai Bahan Bakar Alternatif Di Indonesia. *Jurnal Energi dan Lingkungan (Enerlink)*, *16*(1), 31-38.

[3] Hermawan, P., & Nugroho, A. R. (2021). Studi Pemanfaatan Gas CO2 (Karbon Dioksida) Sebagai Sumber Asam Alternatif Untuk Pikling Pada Pengolahan Kulit Kambing. *Berkala Penelitian Teknologi Kulit, Sepatu, dan Produk Kulit*, *20*(2), 148-160.

[4] Aliev, F., Mirzaev, O., Kholmurodov, T., Slavkina, O., & Vakhin, A. (2022). Utilization of Carbon Dioxide via Catalytic Hydrogenation Processes during Steam-Based Enhanced Oil Recovery. *Processes*, *10*(11), 2306.

[5] Aditya, A. R. (2023). Metanasi CO_2 Menggunakan Katalis Ni/Al_2O_3 Dengan Variasi Temperature dan Zn Sebagai Promotor.

[6] Ridzuan, N. H. A. M., Marwan, N. F., Khalid, N., Ali, M. H., & Tseng, M. L. (2020). Effects of agriculture, renewable energy, and economic

growth on carbon dioxide emissions: Evidence of the environmental Kuznets curve. *Resources, Conservation and Recycling*, *160*, 104879.

[7] Zhong, H., Yao, G., Cui, X., Yan, P., Wang, X., & Jin, F. (2019). Selective conversion of carbon dioxide into methane with a 98% yield on an in situ formed Ni nanoparticle catalyst in water. *Chemical Engineering Journal*, *357(April 2018),421–427.*

[8] Krisnandi, Y. K., Abdullah, I., Prabawanta, I. B. G., & Handayani, M. (2020). In-situ hydrothermal synthesis of nickel nanoparticle/reduced graphene oxides as catalyst on CO2 methanation. *AIP Conference Proceedings, 2242(June)*Wang, D., Huang, J., Liu, F., Xu, X., Fang, X., Liu, J., Xie, Y., & Wang, X. (2020). Rutile RuO2 dispersion on rutile and anatase TiO2 supports: The effects of support crystalline phase structure on the dispersion behaviors of the supported metal oxides. *Catalysis Today, 339(January2019),220–232*.

[9] Wang, D., Huang, J., Liu, F., Xu, X., Fang, X., Liu, J., Xie, Y., & Wang, X. (2020). Rutile RuO2 dispersion on rutile and anatase TiO2 supports: The effects of support crystalline phase structure on the dispersion behaviors.

[10] Liza, Yurika Dewi Safitri. (2022). Optimasi Proses Metanasi CO_2 Menggunakan Katalis Ni-Fe/Al_2O_3 pada Suhu Rendah. *Tugas Akhir*. Palembang: Politeknik Negeri Sriwijaya.

[11] Chein, R. Y., & Wang, C. C. (2020). Experimental Study on CO2 Methanation over Ni/Al2O3, Ru/Al2O3, and Ru-Ni/Al2O3 Catalysts. *Catalysts*, *10*(10), 1112.

[12] Stangeland, K., Kalai, D., Li, H., & Yu, Z. (2017). CO2 Methanation: The Effect of Catalysts and Reaction Conditions. *Energy Procedia*, 105, 2022-2027

[13] Türks D, Mena H, Armbruster U, Martin A. Methanation of CO_2 on Ni/Al_2O_3 in a Structured Fixed-Bed Reactor—A Scale-Up Study. *Catalysts*. 2017; 7(5):152.

[14] Putri, T. M., Junaidi, R., & Meidinariasty, A. (2023). Pembuatan Gas Metana Dari Gas Karbon Dioksida (CO2) Menggunakan Katalis Ni/Al2O3 Dengan Promotor Logam Fe. *Jurnal Serambi Engineering*, *8*(4).

[15] Yuliani, Tasya Dwi. (2023). Making methane gas from CO_2 using Ni/Al_2O_3 catalyst in a fixed bed reactor. Konversi 12(2) 66-69.