

IRSTI: 31.21.01

## METHANE SYNTHESIS VIA CARBON DIOXIDE HYDROGENATION OVER OXIDE CATALYSTS

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### ABSTRACT

Currently, the increasing amount of carbon dioxide (CO<sub>2</sub>) in the atmosphere has become one of the environmental problems. This situation has a negative impact on climate change. Therefore, recycling CO<sub>2</sub> and converting it into useful products is an important scientific direction. Methane production through the reduction of carbon dioxide over oxide catalysts is one of the effective methods. The aim of the study: To prepare highly efficient oxide catalysts for the conversion of carbon dioxide into methane. The catalysts were prepared using conventional impregnation and solution combustion methods, and their structures were investigated using modern methods such as scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and gas chromatography. Scientific novelty and practical significance: As a result of the research, methane was obtained in the presence of Ni-Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> oxide catalysts. In addition, the main parameters determining the productivity of the carbon dioxide-to-methane conversion process were classified, and the indicators related to the stability and efficiency of the catalysts were compared. Results and conclusions: The catalytic activity and stability of the catalysts were investigated in the laboratory using an AKQ setup by feeding gases into the reactor at a flow rate of 100  $\mu$ L/min within a temperature range of 200–400 °C in 50 °C increments. The temperature range of 300–450 °C was found to be the optimal region for catalyst activity in the reaction of methane production through carbon dioxide reduction, with the methane yield reaching a maximum value of 97–99%.

**Keywords:** CO<sub>2</sub> hydrogenation; Ni-Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts; Traditional impregnation method; Catalytic activity; Methane.

### 1 INTRODUCTION

The prolonged persistence of carbon dioxide (CO<sub>2</sub>) in the atmosphere, global warming, and rising global temperatures are directly associated with its ability to absorb infrared radiation. According to the International Energy Agency (IEA) 2025 report, global CO<sub>2</sub> emissions increased by 0.8% compared with 2024, reaching 37.8 Gt CO<sub>2</sub>, while the atmospheric CO<sub>2</sub> concentration reached 422.5 ppm. These continuously increasing CO<sub>2</sub> levels demonstrate that reducing emissions and developing efficient CO<sub>2</sub> utilization technologies are not only environmental priorities but also critical technological and energy-related challenges [1]. The principal approaches to reducing atmospheric CO<sub>2</sub> emissions include improving energy efficiency, expanding the use of renewable energy sources, producing decarbonized hydrogen, and implementing industrial gas purification technologies. The Sixth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) emphasizes that deep, rapid, and sustained reductions in CO<sub>2</sub> emissions are essential to limit global warming to 1.5–2.0 °C [2]. The continuous accumulation of atmospheric carbon dioxide has therefore become one of the most complex and multidimensional challenges in contemporary environmental science. According to the latest IPCC assessment, the global average surface temperature during 2011–2020 was approximately 1.1 °C higher than the pre-industrial level as a consequence of anthropogenic activities [3].

Lee et al. reported in their review of low-temperature thermocatalytic CO<sub>2</sub> methanation that current research is primarily focused on improving reaction thermodynamics and kinetics, optimizing catalyst composition, and achieving high methane selectivity under low-temperature conditions [4].

During catalyst pretreatment under a hydrogen atmosphere, oxide species such as NiO are partially reduced to metallic Ni<sup>0</sup>. Subsequently, hydrogen dissociation, CO<sub>2</sub> adsorption, and the hydrogenation of surface intermediates to methane occur on the catalyst surface [5].

The catalytic performance depends strongly on several factors, including the specific surface area of the support, pore structure, acid–base properties, redox characteristics, and the interactions between the active metal and the oxide support [6]. Oxide catalysts are generally classified into three groups. The first group consists of oxides that provide a high specific surface area and excellent structural stability. The second group includes oxides possessing basic active sites that facilitate CO<sub>2</sub> adsorption. The third group comprises oxides with superior redox properties and a high capacity to generate oxygen vacancies, which play an important role in catalytic reactions [7].

The nature of the catalyst plays a decisive role in the CO<sub>2</sub> methanation reaction. Because the CO<sub>2</sub> molecule is thermodynamically stable, its hydrogenation to CH<sub>4</sub> cannot proceed efficiently in the absence of an appropriate catalyst. Consequently, both noble metal catalysts, such as Ru, Rh, and Pd, and non-noble metal catalysts, including Ni, Co, and Fe, have been extensively investigated for CO<sub>2</sub> methanation. Ruthenium-based catalysts exhibit excellent catalytic activity at relatively low temperatures; however, their widespread application is limited by their high cost. In contrast, nickel-based catalysts have attracted considerable attention because they provide an economically viable alternative while maintaining high catalytic performance [8].

Nickel-based catalysts are among the most widely used catalytic systems for methane production from carbon dioxide. They are commonly supported on high-surface-area materials such as alumina (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>), and zeolites. Nickel catalysts are well known for their high catalytic activity and excellent selectivity toward methane formation. Their outstanding CH<sub>4</sub> selectivity, combined with relatively high catalytic activity, has made Ni-based catalysts one of the primary research focuses in recent years. Together with their satisfactory stability under relatively low-temperature conditions, these characteristics make nickel catalysts highly promising for industrial CO<sub>2</sub> methanation processes [9].

Nickel is an effective catalyst because of its strong ability to dissociate molecular hydrogen. The active hydrogen species generated on the Ni surface subsequently participate in the hydrogenation of reaction intermediates formed during CO<sub>2</sub> adsorption, ultimately leading to methane formation. In addition, nickel is an abundant, readily available, and economically attractive metal. Wang *et al.* systematically reviewed the development of Ni-based catalysts over the past 25 years, analyzing the effects of different catalyst supports, promoters, synthesis methods, and reaction mechanisms on catalytic performance. Their findings demonstrate that Ni-based catalytic systems should not be regarded simply as metallic nickel but rather as complex catalytic materials whose performance is governed by the synergistic interactions among the active metal, the support, and promoter components [10].

## 2 MATERIALS AND METHODS

### 2.1 Preparation of catalysts by the conventional incipient wetness impregnation method

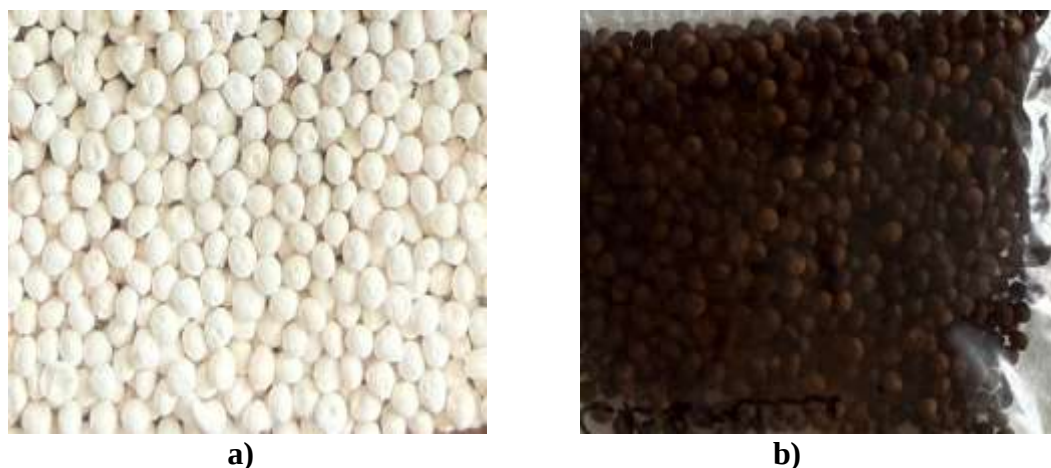
All chemicals used for catalyst preparation were employed as received without any additional purification. A series of catalysts with different metal-to-support ratios was prepared using the conventional incipient wetness impregnation method. Granular  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was used as the catalyst support, while aqueous solutions of iron(III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), and cobalt(II) nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) served as metal precursors.

Prior to impregnation, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was dried in a drying oven at 200 °C for 2 h, followed by calcination at 500 °C for 2 h. After cooling to room temperature, the water absorption capacity of the support was determined. A 1 g sample of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was found to absorb 0.76 mL of water, which was subsequently used to calculate the volume of precursor solution required for incipient wetness impregnation.

The required amount of the pretreated support was weighed, and predetermined volumes of the metal precursor solutions with the desired concentrations were gradually introduced onto the support

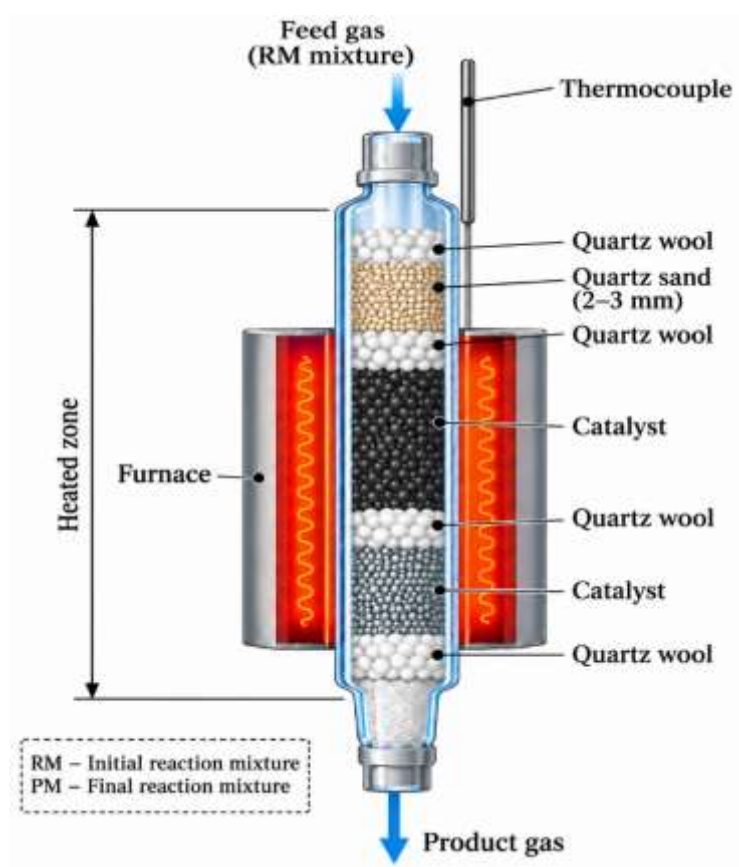
by sequential impregnation until complete absorption was achieved. After impregnation, the obtained samples were dried and thermally treated in a muffle furnace at 250 °C for 1 h, followed by calcination at 500 °C for 2 h. After thermal treatment, the catalysts were allowed to cool to room temperature, weighed, and stored in sealed sample containers.

Figure 1 presents photographs of the catalyst prepared by the conventional incipient wetness impregnation method, showing (a) the initial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support and (b) the final calcined catalyst.



**Figure 1** - Initial support (a) and the final catalyst prepared by the conventional incipient wetness impregnation method (b)

The catalytic performance of the oxide catalysts for the reduction of carbon dioxide to methane was evaluated using a continuous-flow catalytic reactor system.



**Figure 2** - Schematic diagram of quartz tubular reactor

The experimental setup consists of three main components: (i) a gas supply and feed preparation system, (ii) a continuous-flow quartz tubular catalytic reactor, and (iii) a gas chromatograph for analyzing the reaction products. During catalytic activity measurements, the reactor temperature was gradually increased from 200 to 400 °C in 50 °C intervals. Since the reaction temperature significantly influences the reaction rate, CO<sub>2</sub> conversion, and CH<sub>4</sub> selectivity, the composition of the reaction products was analyzed separately at each temperature. Approximately 2 mL of catalyst was loaded into the quartz tubular reactor, through which the reactant gas mixture was continuously supplied.

Figure 2 shows a schematic representation of the catalytic reactor. A 2 mL portion of the catalyst was placed in a quartz reactor with a diameter of 20 mm and a length of 410 mm. The catalyst, with a particle size of 0.21-0.42 mm, was used without dilution and placed on a layer of quartz wool. The height of the catalytic bed was 5 mm.

The reactor system was operated using the dedicated LABkat software, while chromatographic data acquisition and processing were performed using the CHROMOS software.

Catalytic activity is one of the most important characteristics for evaluating catalyst performance in the CO<sub>2</sub> methanation reaction. The activity of the synthesized catalysts was investigated in the catalytic hydrogenation of carbon dioxide to methane. During the experiments, the CO<sub>2</sub> conversion was calculated according to the following equation 1:

$$X_{\text{CO}_2} = \frac{[F_{\text{CO}_2}]_{\text{in}} - [F_{\text{CO}_2}]_{\text{out}}}{[F_{\text{CO}_2}]_{\text{in}}} \times 100\% \quad (1)$$

Where:  $X_{\text{CO}_2}$  - CO<sub>2</sub> conversion, %;  $[F_{\text{CO}_2}]_{\text{in}}$  - molar flow rate of CO<sub>2</sub> at the reactor inlet;  $[F_{\text{CO}_2}]_{\text{out}}$  - molar flow rate of CO<sub>2</sub> at the reactor outlet.

The experiments were carried out using a CO<sub>2</sub>/H<sub>2</sub> gas mixture with a molar ratio of 1:4. The catalytic reactions were performed at different temperatures, and the composition of the reaction products was determined by gas chromatography (GC).

### 3 RESULTS AND DISCUSSION

The catalytic activity of the prepared catalysts was investigated over the temperature range of 200-400 °C, with temperature increments of 50 °C. At each reaction temperature, the catalyst was exposed to the reactant gas mixture for 10 min to ensure steady-state conditions before the reaction products were analyzed by gas chromatography. The reaction temperature was then increased stepwise, and the same experimental procedure was repeated at each temperature.

**Table 1.** Comparative catalytic performance of the prepared catalysts in the CO<sub>2</sub> methanation reaction

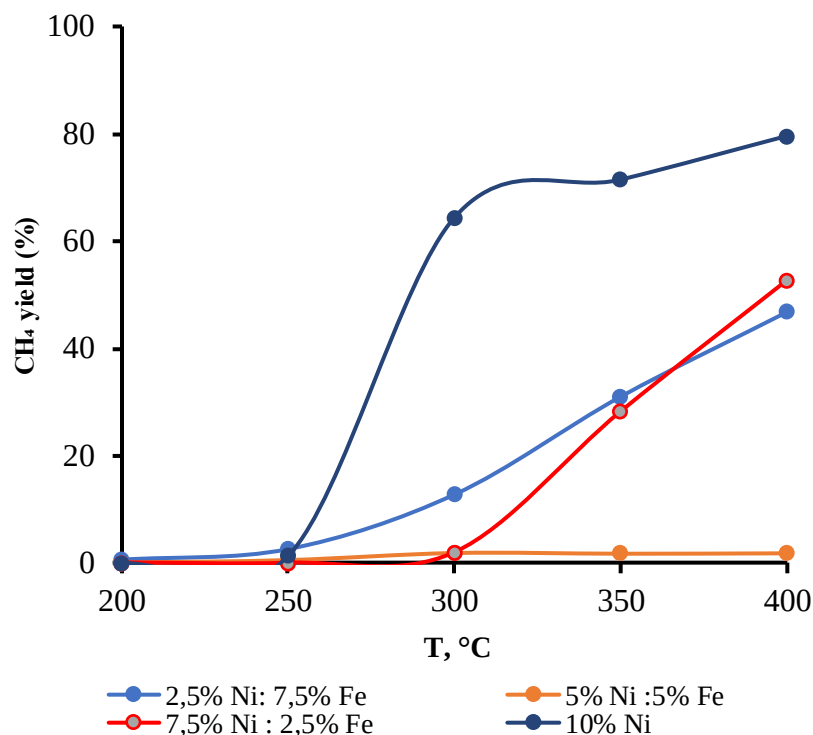
| Nº | Catalyst composition                            | Optimum reaction temperature ( °C) | CH <sub>4</sub> yield (%) |
|----|-------------------------------------------------|------------------------------------|---------------------------|
| 1  | 2,5%Ni+7,5%Fe/ γ-Al <sub>2</sub> O <sub>3</sub> | 400°C                              | 95%                       |
| 2  | 5%Ni+5%Fe/ γ-Al <sub>2</sub> O <sub>3</sub>     | 400°C                              | 94%                       |
| 3  | 7,5%Ni+2,5%Fe/ γ-Al <sub>2</sub> O <sub>3</sub> | 400°C                              | 99,7%                     |
| 4  | 10% Ni/ γ-Al <sub>2</sub> O <sub>3</sub>        | 400°C                              | 99,99%                    |

The design and operating principle of the continuous-flow catalytic reactor provide suitable conditions for investigating the CO<sub>2</sub> methanation process. The system enables experimental observation of the key reaction stages, including the adsorption of carbon dioxide on the catalyst surface, its reaction with hydrogen, and the subsequent formation of methane. Furthermore, the reactor allows the influence of reaction temperature on catalytic activity to be evaluated and facilitates a comparative assessment of oxide catalysts with different compositions.

As shown in Table 1, the catalytic activity of the prepared catalysts was found to depend directly on the nature of the active metal species as well as the ratio between the active metal and the promoter.

Nickel serves as the primary active component in the methanation reaction because it facilitates the dissociative adsorption of hydrogen and promotes the hydrogenation of carbon-containing intermediate species. Iron and cobalt act as promoters, enhancing the activation and transformation of CO<sub>2</sub> molecules during the reaction.

A comparison of the catalytic performances presented in Table 1 indicates that the 7.5 wt.% Ni-2.5 wt.% Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 10 wt.% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts exhibited the highest catalytic activities among the prepared samples.



**Figure 3** - Comparative catalytic activity of the prepared catalysts in the CO<sub>2</sub> methanation reaction

As shown in Figure 3, increasing the nickel content enhances the number of active sites available for methane formation, while the addition of 2.5 wt.% Fe may improve the adsorption and activation of CO<sub>2</sub> molecules. Owing to these synergistic effects, the 7.5 wt.% Ni-2.5 wt.% Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst exhibited higher CO<sub>2</sub> conversion and methane production than the other catalyst samples investigated.

Reaction temperature also had a significant influence on catalytic performance. At lower temperatures, the methanation reaction proceeded slowly, resulting in limited methane formation. As the reaction temperature increased, both the reaction rate and the CO<sub>2</sub> conversion improved, leading to a corresponding increase in CH<sub>4</sub> production. In particular, at 400 °C, the 7.5 wt.% Ni-2.5 wt.% Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 10 wt.% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts demonstrated the highest catalytic activity, indicating that these catalysts are the most promising candidates for efficient CO<sub>2</sub> methanation.

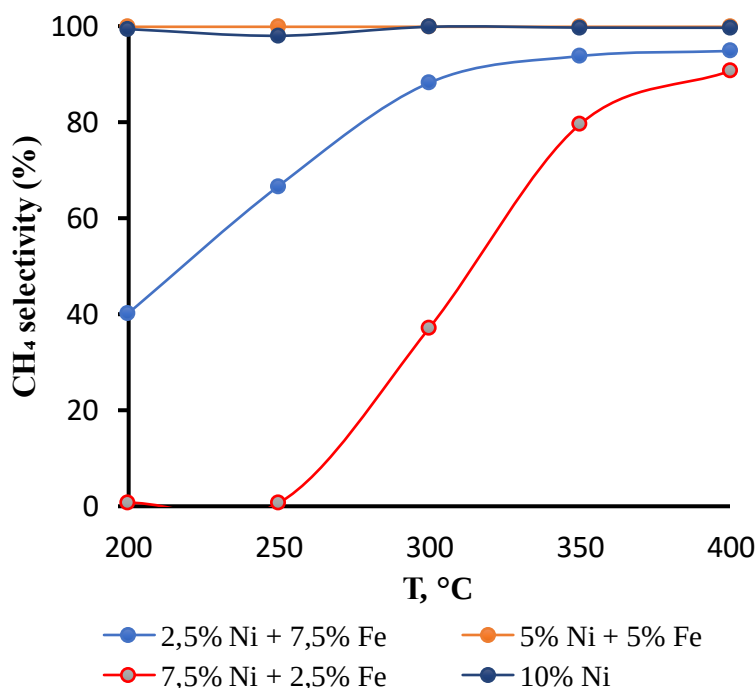
### 3.1 Calculation of methane selectivity

The performance of the catalyst in the hydrogenation of carbon dioxide to methane is commonly evaluated by methane selectivity. Methane selectivity represents the fraction of methane among all reaction products formed during the catalytic process and reflects the extent to which the reaction proceeds toward the desired product, CH<sub>4</sub>.

Figure 4 shows the effect of reaction temperature on CH<sub>4</sub> selectivity for catalysts with different Ni/Fe compositions. A strong dependence of methane selectivity on catalyst composition is observed, particularly at temperatures below 300 °C. The 2.5% Ni + 7.5% Fe catalyst exhibits a relatively low

CH<sub>4</sub> selectivity of 40% at 200 °C, which progressively increases to approximately 95% at 400 °C. Similarly, the 7.5% Ni + 2.5% Fe catalyst shows negligible CH<sub>4</sub> selectivity at 200–250 °C but undergoes a sharp increase to 37%, 80%, and 90% at 300, 350, and 400 °C, respectively.

In contrast, the 5% Ni + 5% Fe and 10% Ni catalysts maintain nearly complete CH<sub>4</sub> selectivity (~98–100%) over the entire temperature range. Thus, higher Ni incorporation appears to favor methane formation and significantly decreases the temperature dependence of CH<sub>4</sub> selectivity.



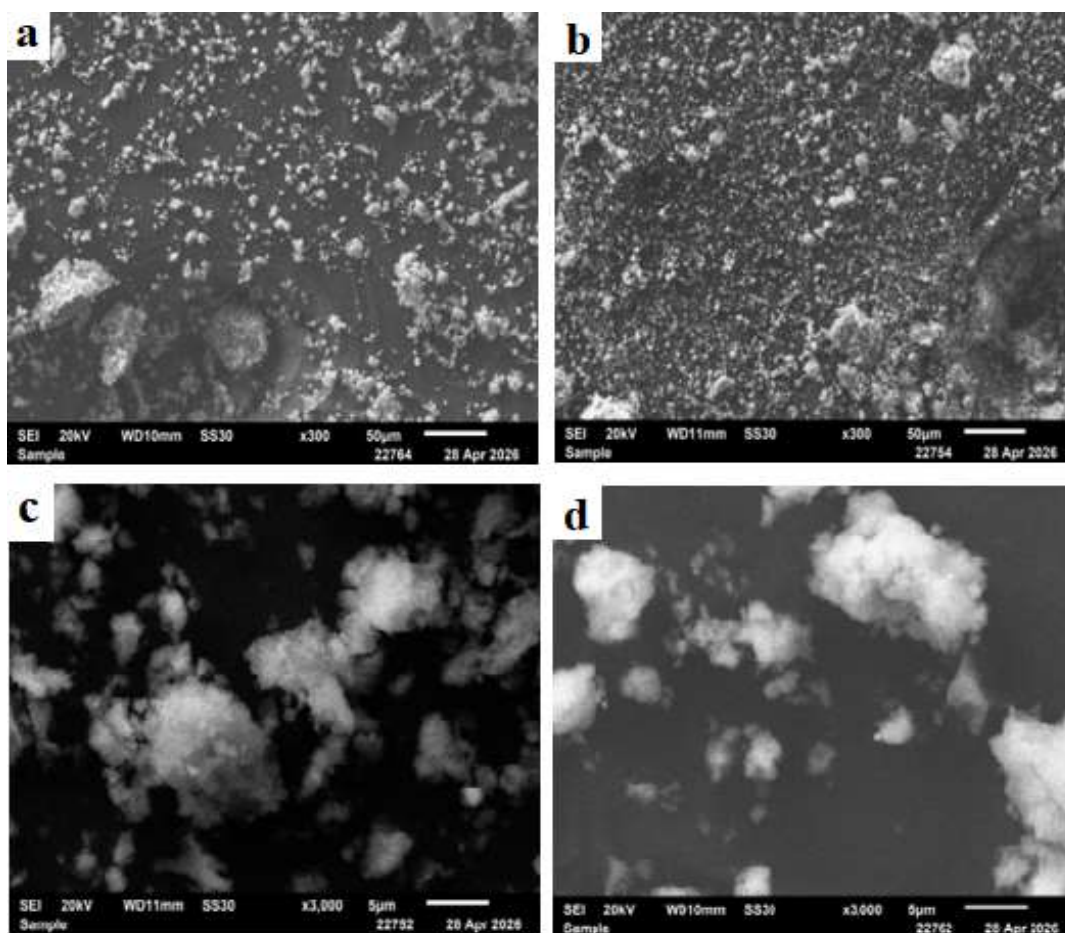
**Figure 4** - Effect of temperature on the methane selectivity of Ni–Fe and Ni catalysts with different compositions during the CO<sub>2</sub> methanation reaction

### 3.2 Scanning electron microscope (SEM) measurements

The morphological characteristics and surface structure of the synthesized Ni–Fe/Al<sub>2</sub>O<sub>3</sub> catalyst were investigated using a JSM-6610 (JEOL) scanning electron microscope (SEM). The JEOL JSM-6610LV instrument operates at an accelerating voltage of up to 30 kV and provides a high resolution of up to 2.5 nm. The microscope is equipped with a versatile analytical system incorporating an Oxford X-Max 50 mm<sup>2</sup> SDD X-ray detector. This system is suitable for determining the elemental composition of samples using energy-dispersive X-ray spectroscopy (EDS). The instrument is also equipped with a medium-sized chamber, an EDS system, and additional stages for sample heating and cooling.

Prior to analysis, the samples were mounted on cylindrical aluminum stubs using carbon adhesive tape. To improve the electrical conductivity of the samples and minimize charging effects during electron microscopy, their surfaces were coated with an ultrathin layer of gold. Gold coating was performed under vacuum using a Polaron 5100 sputter coater. The sputtering process was carried out at a voltage of 2.6 kV and a current of 25 mA for 45 s. As a result, a thin gold layer approximately 5–10 nm thick was deposited on the sample surface.

During the analysis, an accelerating voltage of 20 kV and a working distance (WD) of 10–11 mm were employed. The SEM images were acquired in the secondary electron imaging (SEI) mode, which provides high-resolution visualization of surface topography. The catalyst morphology was comprehensively examined at magnifications of ×300 and ×3,000 enabling detailed observation of structural features from the macro- to the nanoscale.



**Figure 5** - SEM images of (a, c) Ni-Fe/Al<sub>2</sub>O<sub>3</sub> and (b, d) Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at ×300 magnification (scale bar: 50 μm). ×3,000 magnification (scale bar: 5 μm)

As shown in Figure 5 a,b, the overall surface morphology of the catalyst samples can be clearly observed. At this magnification, the well-developed surface architecture and pronounced porous structure formed by the Al<sub>2</sub>O<sub>3</sub> support particles are evident. At intermediate magnification (Figure 5 c, d), the interaction between the active metal phases and the support matrix can be clearly observed. The SEM micrographs show that the nickel and iron clusters are firmly anchored to the surface of the Al<sub>2</sub>O<sub>3</sub> support. The strong adhesion between the metal particles and the support indicates good mechanical integrity and high thermal stability of the catalyst, both of which are essential characteristics for catalytic applications.

#### 4 CONCLUSION

In this study, the catalytic performance of Ni-Fe/γ-Al<sub>2</sub>O<sub>3</sub> catalysts for the hydrogenation of carbon dioxide to methane was systematically investigated. The environmental and energy-related significance of CO<sub>2</sub> utilization was examined, demonstrating that its catalytic conversion into methane represents an effective and sustainable approach for carbon recycling.

The catalytic activity and stability of the synthesized catalysts were evaluated in a continuous-flow reactor over a temperature range of 200-400 °C with 50 °C intervals, using a total gas flow rate of 100 mL min<sup>-1</sup>. The experimental results showed that the methane yield reached its maximum value at 350-400 °C, achieving 97-99%.

The obtained results demonstrate that the 7.5 wt.% Ni-2.5 wt.% Fe/γ-Al<sub>2</sub>O<sub>3</sub> and 10 wt.% Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalyst systems exhibit excellent catalytic performance for the conversion of carbon dioxide into methane. Their superior activity is attributed to the synergistic interaction between the Ni and Fe active species and the favorable structural characteristics of the γ-Al<sub>2</sub>O<sub>3</sub> support.

Overall, this study confirms the environmental and energy-related potential of catalytic CO<sub>2</sub> methanation. Further optimization and development of Ni-Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst systems could contribute to advancing CO<sub>2</sub> utilization technologies and support the implementation of Power-to-Gas (PtG) technologies for sustainable energy storage and carbon-neutral energy systems.

### Acknowledgments

The research undertaken was made possible by the equal scientific involvement of all the authors concerned.

**Author Contributions:** Conceptualization, Galina Xanthopoulou; Formal analysis, Rabiga Sarsenova; Investigation, Rabiga Sarsenova; Methodology and Supervision, Galina Xanthopoulou; Writing – original draft, Zauresh Zheksenbaeva; Writing – review & editing, Zauresh Zheksenbaeva.

**Funding:** Not applicable.

**Conflict of interest:** The authors declare no conflict of interest.

**Data availability statement:** The data presented in this study may be obtained on request from the corresponding author.

**Disclosure of the use of Generative AI:** OpenAI ChatGPT was used for language editing, structural review, and arithmetic checks. It was not used to generate experimental data. The authors verified the source data, calculations, interpretations, and bibliographic references and accept full responsibility for the manuscript.

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