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PHYSICOCHEMICAL PROPERTIES AND CATALYTIC ACTIVITY OF A 0.5% RH/13X CATALYST IN THE CO₂ HYDROGENATION REACTION

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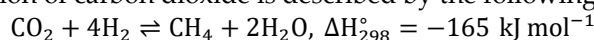
ABSTRACT

A 0.5% Rh/13X catalyst was synthesized by incipient wetness impregnation, and its structural, physicochemical, and catalytic properties were investigated in the carbon dioxide hydrogenation reaction. The morphology, elemental composition, and phase composition of the catalyst were characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction analysis. The surface adsorption properties were studied using CO₂ temperature-programmed desorption (CO₂-TPD), while the reduction behavior was examined by H₂ temperature-programmed reduction (H₂-TPR). Catalytic activity was evaluated in a fixed-bed flow reactor over the temperature range of 180–700 °C. It was established that rhodium deposition did not disrupt the crystalline structure of the 13X zeolite, while the active phase was characterized by high dispersion and the presence of readily reducible surface species. The catalyst was shown to contain basic sites of different strengths that facilitate carbon dioxide adsorption. Catalytic tests demonstrated that CO₂ conversion increased with temperature, reaching a maximum value of 93.5%. The obtained results confirm the potential of the 0.5% Rh/13X catalyst for CO₂ hydrogenation to methane.

INTRODUCTION

The continuous increase in anthropogenic carbon dioxide emissions caused by the extensive use of fossil fuels and the development of energy-intensive industries has become one of the major environmental challenges of modern society^{1,2}. Consequently, the development of efficient technologies for CO₂ capture and its subsequent chemical utilization has attracted considerable attention. Among the available approaches, catalytic CO₂ hydrogenation to methane (the Sabatier reaction) is considered one of the most promising because it simultaneously reduces greenhouse gas emissions and enables the conversion of renewable hydrogen into synthetic natural gas, providing an effective pathway for hydrogen storage and transportation^{3,4}.

The hydrogenation of carbon dioxide is described by the following reaction⁵:



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The highly exothermic nature of the reaction thermodynamically favors methane formation at relatively low temperatures. However, the high chemical stability of the CO₂ molecule results in slow activation kinetics, necessitating the use of highly active catalysts ^{1,2}. At elevated temperatures, the contribution of the reverse water–gas shift (RWGS) reaction increases, leading to CO formation and a decrease in methane selectivity. Therefore, the development of catalysts exhibiting high activity at moderate temperatures together with high methane selectivity remains one of the key challenges in CO₂ methanation research ^{3,6}.

Among platinum-group metals, rhodium has attracted considerable attention owing to its excellent ability to dissociatively adsorb hydrogen and efficiently activate CO₂-derived surface intermediates ^{7,8}. Rh-supported catalysts exhibit high catalytic activity in CO₂ hydrogenation; however, their performance strongly depends on the dispersion of the active metal phase, the oxidation state of rhodium, and the nature of the metal–support interaction. Nevertheless, the high cost of rhodium necessitates the development of low-loaded Rh catalysts capable of maintaining high catalytic performance while minimizing noble metal consumption ^{7,9–11}.

Zeolite 13X is considered a promising support because of its well-developed microporous structure, high specific surface area, and excellent adsorption capacity toward both CO₂ and H₂O ^{12,13}. Its crystalline framework promotes the formation of highly dispersed rhodium particles while suppressing metal agglomeration. In addition, the ability of zeolite 13X to adsorb the water produced during the reaction may shift the reaction equilibrium toward methane formation according to Le Chatelier's principle.

Despite extensive research on Rh-containing catalysts, most published studies have focused on multicomponent catalytic systems or catalysts with relatively high noble metal loadings¹⁴. Furthermore, many synthesis methods involve multistep procedures and exhibit limited scalability for practical applications ^{9,15–21}. Consequently, the physicochemical properties and catalytic performance of a low-loaded 0.5 wt.% Rh/13X catalyst prepared by the incipient wetness impregnation method remain insufficiently investigated, particularly over a wide temperature range of CO₂ hydrogenation ^{12,21}.

Therefore, the aim of the present study was to synthesize a 0.5 wt.% Rh/13X catalyst by the incipient wetness impregnation method and to comprehensively investigate its structural, physicochemical, and reduction properties, as well as its catalytic performance in CO₂ hydrogenation over the temperature range of 180–700 °C, with particular emphasis on the effect of reaction temperature on CO₂ conversion and the composition of gaseous reaction products.

MATERIALS AND METHODS

Catalyst Preparation

Commercial granular 13X zeolite (particle size 1.6–2.5 mm, China) was used as the catalyst support. Prior to impregnation, the zeolite was dried at 110 °C for 1 h to remove physically adsorbed moisture.

The pore volume of the zeolite, determined by the incipient wetness method, was 0.35 mL g⁻¹ and was used to calculate the volume of the impregnation solution.

The 0.5 wt.% Rh/13X catalyst was prepared by the incipient wetness impregnation method. An aqueous RhCl₃·xH₂O solution (39 wt.% Rh, Aldrich) was used as the rhodium precursor. The amount of precursor was calculated stoichiometrically to obtain the desired rhodium loading in the final catalyst.

The impregnation solution was added dropwise under continuous stirring until complete absorption by the zeolite granules. After impregnation, the samples were aged at room temperature for 12 h and subsequently subjected to thermal treatment in air. To prevent rapid thermal decomposition of the rhodium precursor, the samples were first heated at 250 °C for 40 min, followed by calcination at 500 °C for 3 h.

Catalytic Activity Measurements

The catalytic performance of the 0.5 wt.% Rh/13X catalyst in CO₂ hydrogenation was evaluated using a laboratory-scale fixed-bed continuous-flow reactor.

A catalyst bed containing 2 mL of catalyst (1.24 g) was loaded into a quartz tubular reactor. The reaction temperature was monitored using a chromel–alumel thermocouple positioned directly inside the catalyst bed.

Prior to catalytic testing, the catalyst was reduced in a H₂/Ar mixture (1:5, v/v) at 250 °C for 3 h with a total gas flow rate of 20 mL min⁻¹.

After reduction, the catalyst was exposed to a reactant gas mixture with a CO₂:H₂ molar ratio of 1:4 at a total flow rate of 33.3 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) of 1000 h⁻¹. Catalytic experiments were carried out under atmospheric pressure over the temperature range of 180–700 °C.

The inlet and outlet gas compositions were analyzed using a CHROMOS-1000 gas chromatograph equipped with a thermal conductivity detector (TCD). Gas samples were collected after steady-state conditions had been established at each reaction temperature. The concentrations of CO₂, CO, and CH₄ were determined from the chromatographic data.

The CO₂ conversion was calculated according to Equation (2):

$$X_{CO_2} = \frac{n_{CO_2,in} - n_{CO_2,out}}{n_{CO_2,in}} \quad (2)$$

The methane selectivity was calculated using Equation (3):

$$S_{CH_4} = \frac{n_{CH_4,out}}{n_{CO_2,in} - n_{CO_2,out}} \quad (3)$$

where $n_{CO_2,in}$ and $n_{CO_2,out}$ are the molar flow rates of CO₂ at the reactor inlet and outlet, respectively, and $n_{CH_4,out}$ is the molar flow rate of methane at the reactor outlet.

Catalyst Characterization

The surface morphology and microstructure of the catalyst were examined using scanning electron microscopy (SEM, SEM5000Pro) equipped with an Oxford Instruments X-Plore 30 energy-dispersive X-ray spectrometer. The elemental composition, elemental distribution, and elemental mapping were analyzed by energy-dispersive X-ray spectroscopy (EDS).

The crystalline phases of the catalyst were identified by X-ray diffraction (XRD) using a Tongda TD-3700 diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å). Diffraction patterns were collected over a 2θ range of 5–80°.

The reduction behavior of the 0.5 wt.% Rh/13X catalyst was investigated by hydrogen temperature-programmed reduction (H₂-TPR) using a USGA-101 analyzer equipped with a quartz flow reactor and a thermal conductivity detector. Approximately 100 mg of catalyst (particle size 0.30–0.50 mm) was used for each experiment. Prior to the measurements, the sample was pretreated in flowing argon at 480 °C for 40 min to remove adsorbed moisture and surface contaminants. After cooling to 50 °C, the sample was heated to 950 °C at a rate of 10 °C min⁻¹ under a gas mixture containing 10 vol.% H₂ in argon at a total flow rate of 30 mL min⁻¹. Hydrogen consumption was continuously monitored using a thermal conductivity detector, allowing the determination of the reduction temperature ranges of Rh-containing surface species.

The surface basicity of the catalyst was investigated by CO₂ temperature-programmed desorption (CO₂-TPD) using a TBD-CO₂ analyzer. Approximately 0.06 g of catalyst was used for each experiment. Before analysis, the samples were activated in flowing helium at 500 °C for 2 h. After cooling to room temperature, the catalyst was saturated with CO₂ at a flow rate of 20 mL min⁻¹ for 30 min. Subsequently, physically adsorbed CO₂ was removed by helium purging. CO₂ desorption was recorded during heating to 800 °C at a rate of 10 °C min⁻¹ under a helium flow of 20 mL min⁻¹.

RESULTS AND DISCUSSION

Morphology and Microstructure of the 0.5 wt.% Rh/13X Catalyst

The surface morphology of the 0.5 wt.% Rh/13X catalyst was investigated by scanning electron microscopy (SEM). The obtained SEM images are presented in Figure 1.

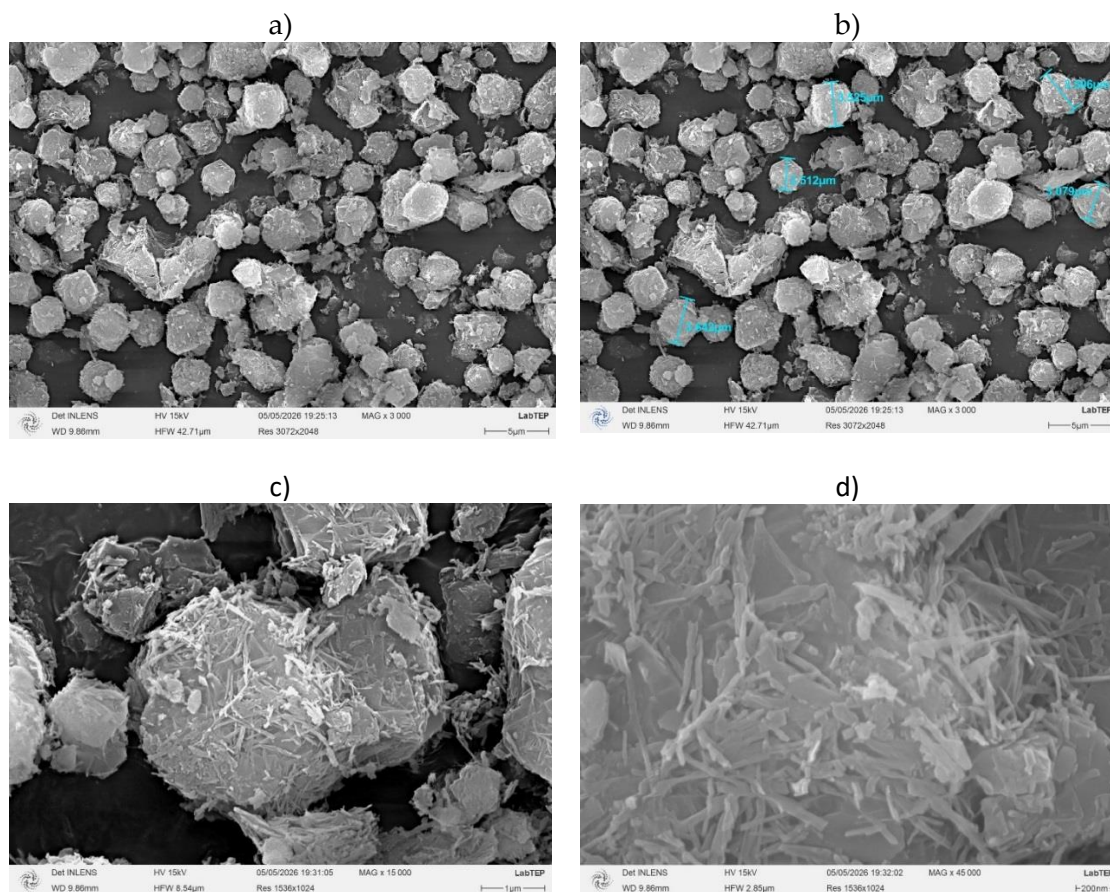


Figure 1. SEM images of the 0.5 wt.% Rh/13X catalyst at different magnifications: (a) general view of the catalyst particles ($\times 3000$); (b) particle size measurement; (c) surface morphology of individual particles ($\times 15000$); (d) high-magnification view of the surface microstructure ($\times 45000$)

At low magnification (Figure 1a), the catalyst was observed to consist of irregularly shaped polyhedral particles uniformly distributed over the examined surface. Although partial agglomeration was observed, the preservation of distinct particle boundaries and interparticle voids suggests that extensive particle coalescence and densification were not evident within the examined regions ²².

Measurements of several representative particles (Figure 1b) showed that their sizes ranged from 2.5 to 3.6 μm . In addition to these particles, smaller fragments with irregular morphology were also observed.

At a magnification of $\times 15,000$ (Figure 1c), the particles exhibited a well-developed surface relief. The catalyst surface was characterized by pronounced roughness and numerous plate-like and elongated crystalline features uniformly distributed over the particle surface. Such a developed and heterogeneous surface morphology may promote the exposure and accessibility of surface sites ²³.

At the highest magnification (Figure 1d), the surface microstructure became more clearly distinguishable. The particle surface consisted of uniformly distributed plate-like and elongated

crystalline features. No evidence of significant morphological heterogeneity, particle melting, structural degradation, or the formation of large surface agglomerates was detected, indicating that the morphology of the 13X zeolite support was preserved after rhodium deposition and subsequent thermal treatment. However, SEM analysis did not allow the direct visualization of rhodium particles because of their low loading and the expected nanoscale dimensions of the active phase. Therefore, conclusions regarding the presence and physicochemical state of rhodium were drawn based on the combined results of complementary physicochemical characterization techniques.

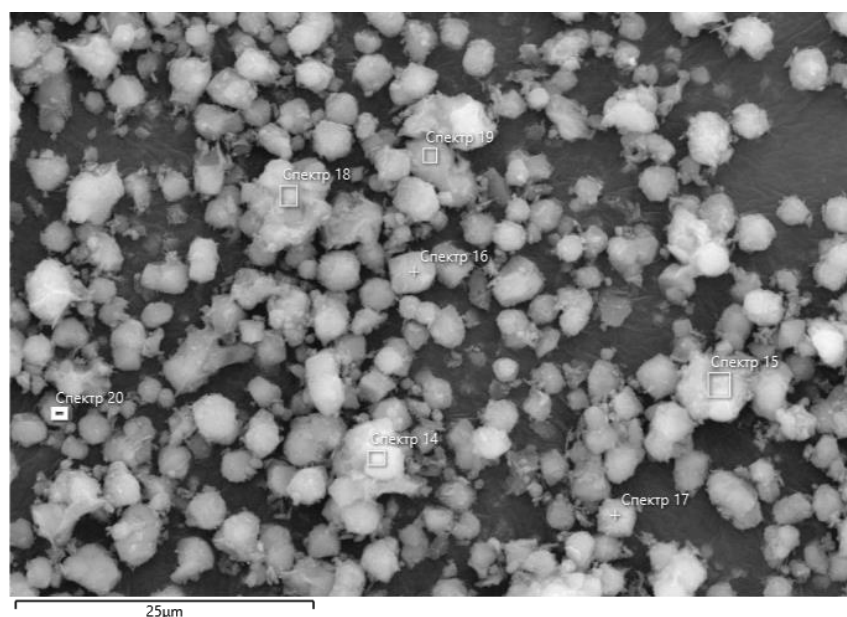


Figure 2. SEM image of the 0.5 wt.% Rh/13X catalyst indicating the regions selected for local energy-dispersive X-ray spectroscopy (EDS) analysis

Table 1. Average elemental composition of selected local surface regions of the 0.5 wt.% Rh/13X catalyst, as determined by point EDS analysis (wt.%)

Element	Average composition $\pm$ SD (wt.%)
O	48.23 ± 2.35
Na	12.38 ± 0.94
Mg	1.36 ± 0.41
Al	15.52 ± 1.14
Si	22.23 ± 1.89
Ca	0.31 ± 0.17
Fe	0.41 ± 0.16

EDS analysis revealed a similar elemental composition across the investigated surface regions. Oxygen, silicon, and aluminum were identified as the predominant framework elements, while sodium was present as the principal charge-compensating cation, consistent with the composition of Na-form 13X zeolite. Minor amounts of magnesium, calcium, and iron were also detected and are attributed to trace impurities present in the original support material. Rhodium was not reliably detected by local SEM–EDS analysis, most likely because its nominal loading was close to the practical detection limit of the technique and its signal was diluted within the analyzed interaction volume ²⁴.

Phase Composition of the 0.5 wt.% Rh/13X Catalyst (XRD)

The phase composition of the 0.5 wt.% Rh/13X catalyst was investigated by X-ray diffraction (XRD). The corresponding XRD pattern is presented in Figure 3.

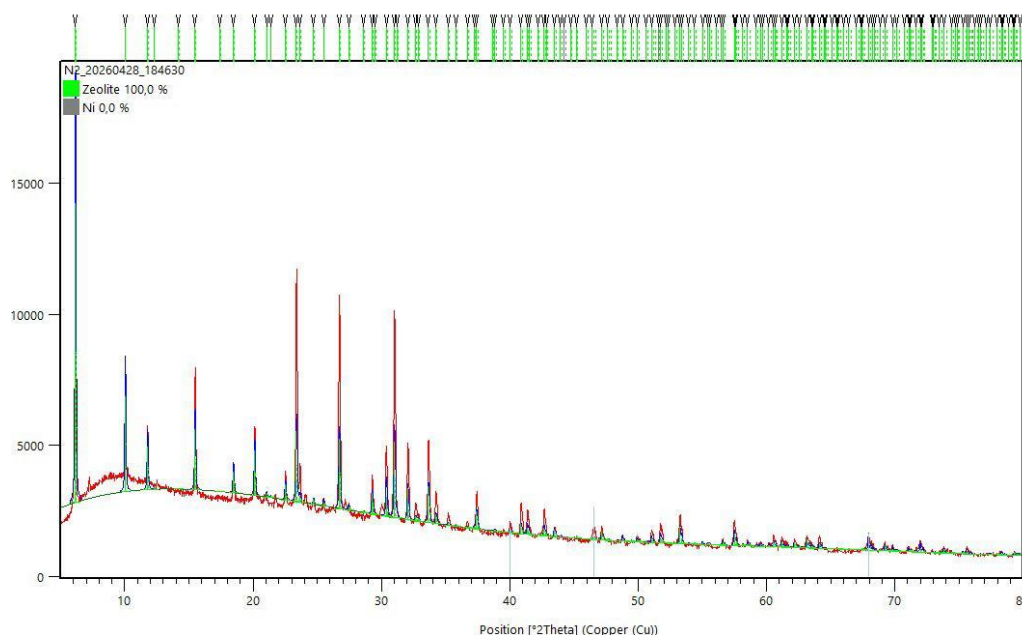


Figure 3. XRD pattern of the 0.5 wt.% Rh/13X catalyst and the corresponding phase identification

The major diffraction peaks observed in the experimental XRD pattern are in good agreement with the reference diffraction pattern of 13X zeolite, indicating that the crystalline framework of the zeolite support was preserved after rhodium deposition and subsequent thermal treatment. No noticeable shifts in the positions of the characteristic diffraction peaks were observed relative to the reference pattern, suggesting that the aluminosilicate framework of the zeolite remained structurally unchanged during catalyst preparation.

No additional diffraction peaks attributable to crystalline Rh or rhodium oxide phases were detected. Considering the low nominal Rh loading, this may be associated with a low concentration and/or high dispersion of the Rh-containing species. Consequently, any crystalline Rh-containing domains, if present, were likely too small or insufficiently abundant to be detected by conventional XRD ¹⁴.

It should be noted that the absence of diffraction peaks corresponding to metallic Rh or rhodium oxides does not indicate the absence of rhodium in the catalyst. This behavior has been widely reported for supported noble-metal catalysts ¹² and is generally attributed to the low loading of the active component, its high dispersion, or the combined effect of both factors.

Overall, the XRD results demonstrate that incipient wetness impregnation followed by calcination did not cause detectable changes in the crystalline structure of the 13X zeolite support. The absence of diffraction peaks attributable to crystalline Rh-containing phases suggests that their concentration and/or coherent crystallite size was below the detection capability of conventional XRD ¹⁴.

Adsorption Properties of the 0.5 wt.% Rh/13X Catalyst (CO₂-TPD)

The adsorption properties of the 0.5 wt.% Rh/13X catalyst were investigated by CO₂ temperature-programmed desorption (CO₂-TPD). The resulting CO₂-TPD profile is shown in Figure 4.

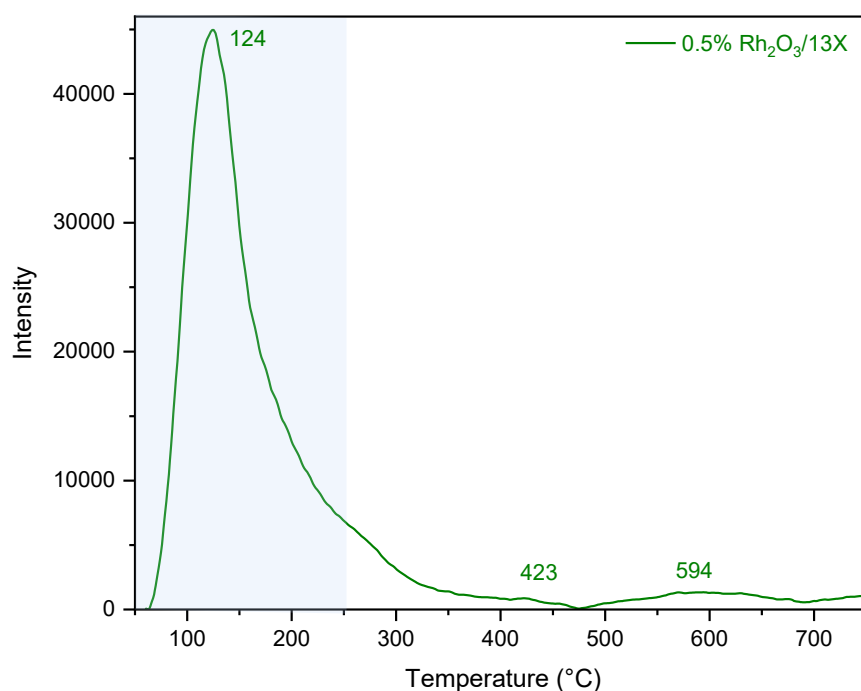


Figure 4. CO₂ temperature-programmed desorption (CO₂-TPD) profile of the 0.5 wt.% Rh/13X catalyst

The CO₂-TPD profile exhibited an intense low-temperature desorption peak centered at 124 °C and two less intense peaks at 423 and 594 °C. The presence of several desorption maxima reflects a heterogeneous distribution of CO₂ adsorption sites with different interaction strengths, with higher desorption temperatures generally corresponding to more strongly bound CO₂ species ²⁵.

The dominant contribution to the desorption profile originates from the low-temperature peak at 124 °C, which is attributed to the desorption of weakly adsorbed CO₂ from weak basic sites. The desorption peaks observed at 423 °C and 594 °C indicate stronger interactions between adsorbed CO₂ molecules and the catalyst surface and can therefore be assigned to medium-strength and strong basic sites, respectively ²⁶.

Compared with the low-temperature desorption peak, the high-temperature peaks exhibit significantly lower intensities, indicating that weak basic sites predominate, whereas medium- and strong-strength basic sites are present in considerably smaller amounts.

These results demonstrate that the surface of the 0.5 wt.% Rh/13X catalyst contains a heterogeneous distribution of basic sites. The predominance of weak basic sites together with the presence of a limited number of medium- and strong-strength basic sites suggests the existence of several types of adsorption sites differing in their interaction strength with CO₂ molecules.

Reduction Behavior of the 0.5 wt.% Rh/13X Catalyst (H₂-TPR)

The reduction behavior of the 0.5 wt.% Rh/13X catalyst was investigated by hydrogen temperature-programmed reduction (H₂-TPR). The experimental H₂-TPR profile together with the deconvoluted reduction peaks is presented in Figure 5.

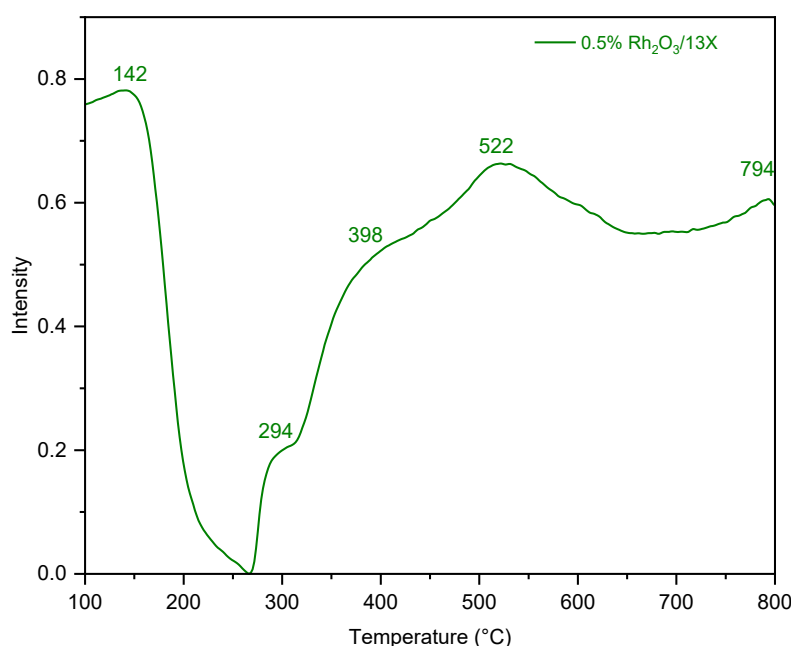


Figure 5. H₂-TPR profile of the 0.5 wt.% Rh/13X catalyst showing the identified reduction temperature regions

The H₂-TPR profile exhibits several reduction regions with maxima at 142, 294, 398, 522, and 794 °C, indicating heterogeneous reduction behavior of the catalyst. The intense low-temperature peak centered at 142 °C can be tentatively assigned to the reduction of readily reducible RhO_x species weakly interacting with the zeolite support ²⁷. The higher-temperature signals may originate from Rh-containing species interacting more strongly with the support and/or reducible impurities and binder components present in the commercial 13X material.

The additional peaks at 294, 398, and 522 °C are considerably less intense and can be attributed to species requiring higher reduction energies. This indicates the presence of several types of surface compounds differing in the strength of their interaction with the zeolite support.

A weakly pronounced peak is detected in the high-temperature region at 794 °C, and its intensity is significantly lower than that of the main low-temperature peak. This indicates that only a small fraction of the surface species is highly resistant to reduction. However, the exact nature of these species cannot be unambiguously determined solely from the H₂-TPR results.

Overall, the H₂-TPR results demonstrate that the major fraction of the surface species is reduced in the low-temperature region, whereas only a minor fraction exhibits higher thermal stability and undergoes reduction at elevated temperatures.

These findings are consistent with the XRD results, which showed no distinct diffraction peaks attributable to crystalline rhodium phases, a feature commonly observed for highly dispersed Rh catalysts ¹². The combined XRD and H₂-TPR data therefore support the assumption that the active phase is present in a highly dispersed state, in which individual crystalline rhodium phases remain below the detection limit of X-ray diffraction.

Catalytic Activity of the 0.5 wt.% Rh/13X Catalyst

The catalytic activity of the 0.5 wt.% Rh/13X catalyst was investigated in the CO₂ hydrogenation reaction over the temperature range of 180–700 °C. The experiments were conducted at a CO₂:H₂ volumetric ratio of 1:4, a gas hourly space velocity of 1000 h⁻¹, and atmospheric pressure. Prior to catalytic testing, the catalyst was reduced in a H₂/Ar mixture (1:5) at 250 °C for 3 h.

The results of the catalytic tests are presented in Table 2 and Figure 6.

Table 2. Catalytic performance of the 0.5 wt.% Rh/13X catalyst in the CO₂ hydrogenation reaction

Temperature (°C)	X _{CO₂} (%)	S _{CH₄} , %	CH ₄ (vol.%)	CO (vol.%)
180	55.0	2.91	0.015	0.5
200	57.5	1.64	0.03	1.8
220	61.5	2.91	0.06	2.0
240	63.0	4.06	0.11	2.6
300	65.0	26.32	1.0	2.8
350	76.0	73.45	8.3	3.0
400	87.5	75.18	10.6	3.5
450	89.0	75.38	14.7	4.8
500	93.0	70.29	12.3	5.2
550	93.5	67.07	11.2	5.5
600	86.0	61.04	9.4	6.0
650	85.0	49.18	6.0	6.2
700	83.5	37.38	5.6	6.7

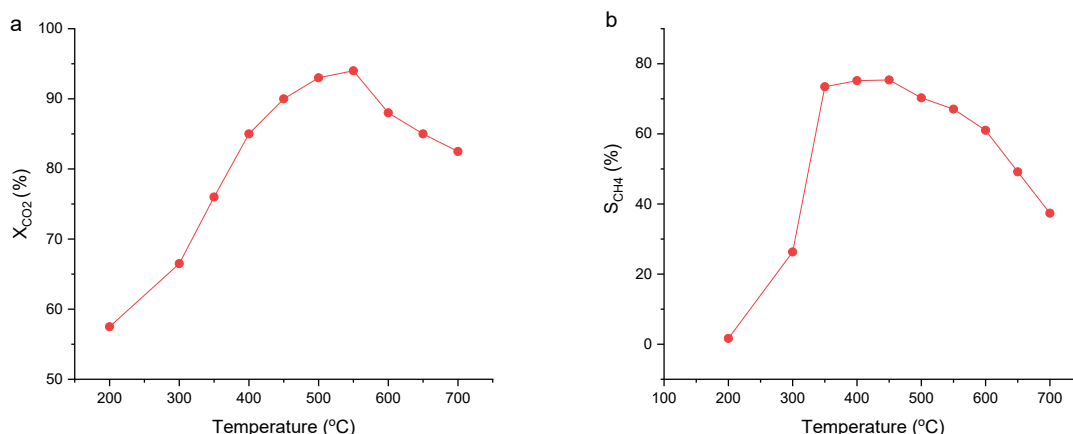


Figure 6. Effect of reaction temperature on the catalytic performance of the 0.5 wt.% Rh/13X catalyst: (a) CO₂ conversion; (b) CH₄ selectivity

According to the data presented in Table 2 and Figure 6a, increasing the reaction temperature from 180 to 550 °C resulted in a gradual increase in CO₂ conversion from 55.0% to 93.5%. The most pronounced increase was observed in the temperature range of 300–400 °C, where the conversion rose from 65.0% to 87.5%, indicating more efficient CO₂ hydrogenation within this interval.

The maximum CO₂ conversion of 93.5% was achieved at 550 °C. A further increase in temperature led to a gradual decline in conversion, which decreased to 83.5% at 700 °C.

The variation in methane content in the reaction products (Figure 6b) followed a different trend. In the temperature range of 180–300 °C, methane formation was limited, and its concentration did not exceed 1.0 vol.%. With a further increase in temperature, the CH₄ concentration increased sharply and reached a maximum value of 14.7 vol.% at 450 °C. Above this temperature, the methane concentration gradually decreased, reaching 5.6 vol.% at 700 °C.

The difference between the temperatures corresponding to the maximum CO₂ conversion and the maximum CH₄ concentration can be explained by the occurrence of two competing CO₂ hydrogenation pathways. The measured CO₂ conversion includes its transformation through both methanation and the RWGS reaction. Increasing the temperature up to 550 °C promotes the overall conversion of CO₂; however, above 450 °C, the product distribution progressively shifts from CH₄ toward CO. This behavior results from the thermodynamic suppression of the exothermic methanation reaction and the increasing contribution of the endothermic RWGS reaction at elevated temperatures ^{11,21}.

At 450 °C, the catalyst provided a favorable combination of CO₂ conversion (89.0%), CH₄ selectivity (75.38%), and the maximum CH₄ concentration (14.7 vol.%). Increasing the temperature to 500 °C raised the CO₂ conversion to 93.0%, while the CH₄ selectivity and concentration decreased moderately to 70.29% and 12.3 vol.%, respectively. At 550 °C, only a marginal additional increase in CO₂ conversion was obtained, whereas methane formation declined further. Therefore, 450–500 °C can be considered the optimal operating range for achieving a balance between high CO₂ conversion and methane formation, with approximately 450 °C being preferable when maximizing CH₄ production is the primary objective ²¹.

Table 3. Catalytic performance of representative zeolite-supported catalysts for CO₂ methanation

Catalyst	Metal loading, wt. %	Conditions	Temperature, °C	XCO ₂ , %	SCH ₄ , %	Ref.
Rh/13X	0.5 Rh	1 atm; GHSV 1000 h ⁻¹ ; H ₂ /CO ₂ = 4	450	89.0	75.4	this work
Rh/13X	0.5 Rh	1 atm; GHSV 1000 h ⁻¹ ; H ₂ /CO ₂ = 4	550	93.5	67.1	this work
Ni/ITQ-2	5 Ni	1 atm; GHSV 3500 h ⁻¹ ; H ₂ /CO ₂ = 4	400	82	99	28
Ni–Ru/ZSM-5	10 Ni + 5 Ru	GHSV 30 000 mL gcat ⁻¹ h ⁻¹	400	82	100	29
Ru/modified silicalite-1	1 Ru	1 atm; H ₂ /CO ₂ = 4	250–450	—*	>90	30

Note – The conversion is not presented as a single tabular value in the study; therefore, it is best not to specify an approximate figure read from the graph.

A comparison with representative zeolite-supported methanation catalysts (Table 3) shows that the catalytic performance strongly depends not only on the active-metal loading but also on the reaction temperature, pressure, and space velocity. For example, a 5 wt.% Ni/ITQ-2 catalyst provided 82% CO₂ conversion and 99% CH₄ selectivity at 400 °C and a GHSV of 3500 h⁻¹ ²⁸, whereas a bimetallic 10 wt.% Ni–5 wt.% Ru/ZSM-5 catalyst reached approximately 82% conversion with 100% CH₄ selectivity at 400 °C and a considerably higher space velocity of 30,000 mL gcat⁻¹ h⁻¹ ²⁹. A catalyst containing 1 wt.% Ru supported on alkali-modified silicalite-1 also exhibited CH₄ selectivity above 90% in the temperature range of 250–450 °C ³⁰. In comparison, the 0.5 wt.% Rh/13X catalyst investigated in the present study achieved 89.0% CO₂ conversion and 75.4% CH₄ selectivity at 450 °C. The maximum conversion of 93.5% was obtained at 550 °C, although the CH₄ selectivity decreased to 67.1% because of the enhanced contribution of the RWGS reaction. Thus, the present catalyst provides high overall CO₂ conversion at a substantially lower noble-metal loading, but its methane selectivity is lower and its optimum operating temperature is higher than those of optimized Ni- and Ru-containing zeolite catalysts. It should also be noted that the relatively low GHSV employed in the present work favors high conversion; therefore, the comparison should be regarded as qualitative rather than as a direct assessment of intrinsic catalytic activity.

It should be noted that the present study was focused on the temperature-dependent catalytic performance of the 0.5 wt.% Rh/13X catalyst, whereas its long-term stability was not evaluated. Although the catalyst exhibited high CO₂ conversion within the investigated temperature range, these results alone are insufficient to assess its resistance to deactivation under prolonged operation. Therefore, future studies should include extended time-on-stream testing under the identified optimal conditions, accompanied by post-reaction characterization to evaluate possible Rh particle sintering, carbon deposition, and changes in the structure and surface properties of the zeolite support.

CONCLUSIONS

The 0.5 wt.% Rh/13X catalyst prepared by incipient wetness impregnation retained the crystalline structure and characteristic morphology of the 13X zeolite support after Rh deposition and calcination. No distinct diffraction peaks attributable to crystalline Rh or Rh oxide phases were detected, indicating that the concentration and/or coherent crystallite size of the Rh-containing species was below the detection capability of conventional XRD.

CO₂-TPD revealed a heterogeneous distribution of surface basic sites. The dominant low-temperature desorption peak at 124 °C was associated with weak CO₂ adsorption sites, whereas the less intense peaks at 423 and 594 °C indicated the presence of smaller amounts of medium- and strong-strength sites. The H₂-TPR profile was dominated by a reduction peak at 142 °C, tentatively assigned to readily reducible RhO_x species weakly interacting with the zeolite support. The additional higher-temperature peaks indicated minor contributions from more strongly interacting Rh-containing species and/or reducible components of the commercial support.

CO₂ conversion increased from 55.0% at 180 °C to a maximum of 93.5% at 550 °C, whereas the maximum CH₄ concentration of 14.7 vol.% was obtained at 450 °C. Above 450 °C, methane formation gradually decreased while CO production increased, reflecting the growing contribution of the RWGS reaction. Consequently, 450–500 °C was identified as the optimal operating range providing a favorable balance between CO₂ conversion and methane formation. A temperature of approximately 450 °C is preferable when maximizing methane production is the primary objective, while operation at 500 °C provides higher CO₂ conversion with a moderate decrease in CH₄ selectivity.

Nevertheless, long-term time-on-stream experiments and post-reaction characterization are required to assess catalyst stability and possible deactivation before its practical applicability can be established.

CONFLICT OF INTEREST: The authors declare no conflict of interest.

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INFORMED CONSENT STATEMENT: Not applicable. This study did not involve human participants.

DATA AVAILABILITY STATEMENT: The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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OpenAI. (2026, August 3). *Language editing and improvement of the manuscript* [Large language model]. ChatGPT (GPT-5.5). <https://chatgpt.com>

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