

Article

Nickel-Based Catalysts for Hydrogen Production Through Partial Oxidation: The Role of KIT-6 and Promoter Effects

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Abstract

Partial oxidation of methane (POM) is a good way to make syngas because it uses exothermic reactions to keep itself going. This study made a series of Ni/KIT-6 catalyst precursors with Gd (0.5–2 wt.%) added to them and then carefully looked at how they changed into active catalysts. The first tests on the precursors using N₂ physisorption, XRD, and H₂-TPR showed that they had a high surface area and changed how they reduced. However, the high-temperature activation (700 °C) and reaction (682 °C) conditions caused thermal evolution and sintering. Tests of catalytic performance and RSM optimization found that the 5Ni + 1Gd/KIT-6 formulation was the best. Under the best conditions, it converted 89.0% of CH₄ and 87.4% of H₂. Using TEM and Raman spectroscopy to look at the used catalysts showed that 1 wt.% Gd was able to control the size distribution of the metallic particles and stop disordered carbon from forming, even after thermal recrystallisation. A 24 h stability test confirmed these findings, indicating a stable H₂ yield (85–87%) and minimal performance degradation, thereby demonstrating that Gd promotion maintains the stability of the active metallic phase under operational stress.

Keywords: green energy; hydrogen production; Gd-promoted Ni/KIT-6; numerical optimization; POM; syngas



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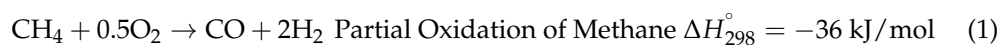
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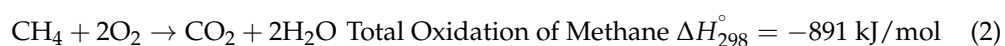
1. Introduction

The global need and the pursuit of cleaner energy and lower greenhouse gas emissions has intensified the search for efficient hydrogen production technologies [1]. The partial oxidation of methane (POM) is a promising approach due to its exothermic nature, which allows autothermal operation and direct synthesis gas (H₂ and CO) production without external heat input [1]. Compared to the common steam methane reforming (SMR), POM

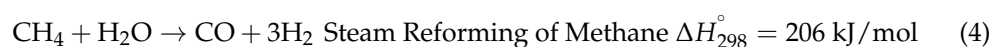
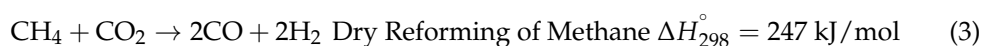
offers distinct advantages, including faster start-up [2], reduced reactor size [3], and lower water consumption [4], features that are highly attractive for modular and decentralized hydrogen generation systems [4,5]. POM proceeds via two primary mechanisms: the direct oxidation pathway [6], where methane converts directly to syngas:



or the indirect combustion-reforming mechanism [7], involving initial total oxidation to CO_2 and H_2O :



followed by reforming, as shown in the equations below [8].



Nickel-based catalysts are widely used in methane reforming due to their high performance and cost-effectiveness compared to noble metals [9]. However, their application in POM is limited by fast deactivation caused by carbon deposition and sintering [10,11], particularly under high-temperature and carbon-rich conditions [12]. To solve these limitations, recent efforts have focused on tailoring catalyst composition and structure through advanced supports and promoters [13]. Han [9] reported that adding ceria (CeO_2) to Ni@SiO_2 catalysts helped reduce carbon build-up and showed high stability during catalytic performance. Khani [14] synthesized a Ni-based catalyst with a mix of Ce, Zr, and Gd, and they found that Gd efficiently improves oxygen mobility and reduces coke formation. Al-Fatesh et al. [15] found that using Gd with $\text{Ni/Y}_2\text{O}_3$ increased H_2 production and improved the catalyst's CO_2 conversion efficiency. Mesoporous silica frameworks such as KIT-6, with their high surface area and interconnected pore networks, provide excellent platforms for dispersing Ni nanoparticles and enhancing active site accessibility [16,17]. Huang et al. [18] found that using KIT-6 as a support for NiO helped improve methane combustion. The KIT-6 structure provided good pore connection and large surface area, which allowed better oxygen flow and heat control [18]. This helped the catalyst stay active and stable during the reaction. Incorporating rare-earth elements like Gd as promoters has shown great promise in further enhancing catalyst stability [19]. Zhang et al. [20] reported that the incorporation of Gd into Ni-based catalysts improves the dispersion of Ni particles and enhances metal support interaction, which helps suppress Ni sintering during high-temperature reactions. They also observed that Gd increases oxygen mobility and thermal stability, contributing to better resistance against deactivation in methane reforming processes [21]. Da Costa et al. [21] found that yttrium-promoted catalysts supported on KIT-6 significantly enhanced excess-methane dry reforming. Compared to unpromoted catalysts, the addition of yttrium led to exceptionally stable syngas production and reduced deactivation, achieved by increasing basicity and lowering nickel reduction temperatures [22]. In the partial oxidation of methane (POM), two main mechanisms are involved: the Langmuir–Hinshelwood (LH) and the Mars–van Krevelen (MvK) [22,23]. In the LH mechanism, both methane and oxygen adsorb on the surface of the nickel catalyst and react to form hydrogen and carbon monoxide [24]. In the MvK mechanism, lattice oxygen from the support helps oxidize methane, and this oxygen is later restored from gas-phase O_2 [25]. When Gd is added as a promoter, it enhances the oxygen storage and release ability of the support, especially when incorporated into materials like KIT-6 [26]. This helps improve the lattice oxygen contribution in the MvK mechanism, which can

reduce carbon build-up and improve catalyst stability [27]. This work differs from prior Ni/KIT-6 and rare-earth-promoted Ni studies in two ways. First, it targets partial oxidation of methane with low Gd loadings (0.5–2.0 wt.%) on KIT-6, while much of the existing work centres on DRM or higher promoter levels. Second, it couples performance mapping with a response-surface design to define an operating window that meets the $H_2/CO \approx 2.4$ target for downstream use. Structure performance links are drawn using BET/XRD/TEM, H_2 -TPR, and Raman on spent catalysts.

2. Results

2.1. BET Analysis

The N_2 isotherms depicted in Figure 1A show type-IV behaviour with H_1 hysteresis ($p/p_0 \approx 0.5$ – 0.8) for all samples, consistent with capillary condensation in uniform, interconnected mesopores typical of KIT-6 [27]. The pore-size distributions from the desorption and adsorption branches (Figure 1B–C) are narrowly centred at 5.7–6.0 nm with only minor shifts across the series. The textural properties of the catalysts are summarized in Table 1. All samples exhibit a high surface area (509–529) m^2/g and consistent pore diameters 6.0 nm, confirming that the mesoporous KIT-6 framework remains structurally robust despite Gd promotion and metal impregnation. These modest variations indicate limited pore filling/surface coverage upon metal promoter addition and, importantly, preservation of the KIT-6 mesostructured after impregnation and calcination [28]. Figure 1B (Desorption Curve) and Figure 1C (Adsorption curve) display the pore size distribution curves, confirming the mesoporous nature of the KIT-6 support, displaying a sharp, uniform peak centred around 58 Å across all catalyst samples. The position of this primary pore width remains stable, indicating that structural integrity upon Gd addition remains intact. However, increasing the Gd loading slightly decreases the peak intensity ($dV/d\log(w)$), which is attributed to minor pore filling or narrowing caused by the deposition of the Ni and Gd precursor species onto the inner channel walls.

Table 1. Textural properties of catalyst samples and the support obtained from N_2 physisorption.

Catalyst	BET Surface Area ($m^2 \cdot g^{-1}$)	Pore Volume ($cm^3 \cdot g^{-1}$)	Pore Width (Å)	NiO Crystalline Size (nm)
KIT-6-uncalcined	585	0.73	62.7	-
KIT-6 calcined	525	0.55	49.7	-
5Ni/KIT-6	515	0.66	61.0	16.1
5Ni + 0.5Gd/KIT-6	529	0.66	60.1	18.1
5Ni + 1Gd/KIT-6	517	0.65	60.5	20.1
5Ni + 2Gd/KIT-6	509	0.64	60.3	17.3

2.2. X-Ray Diffraction (XRD)

Powder XRD of Figure 2 was recorded for the calcined Ni/KIT-6 series to identify crystalline phases and check structure stability. The characteristic crystalline peaks for KIT-6 are observed below 10° Bragg's angle [29], whereas the broad signal in the 20 – 30° 2θ range corresponds to the amorphous nature of the KIT-6 silica structure. The crystalline silica peak of KIT-6 is preserved after calcination and it is shifted to the higher Bragg's angle after loading of Ni and Gd. The retention of crystalline framework of KIT-6 after doping (with Ni and Gd) and after calcination justify its stability against high temperature and dopant incorporation. For the unpromoted 5Ni/KIT-6, distinct reflections at 37.2° , 43.3° , 62.9° , 75.4° , and 79.4° 2θ are indexed to cubic NiO corresponding to the (111), (200), (220), (311), and (222) planes (JCPDS 47-1049). The crystalline size of NiO for 2θ (43.3°) over 5Ni/KIT-6 is 16.1 nm. Upon increasing loading of Gd, the crystalline size of cubic NiO does not fluctuate much; it remains between 17.3 and 20.1 nm.

2.3. TEM Analysis

To confirm the structure of the catalysts, TEM analysis was performed in Figure 3. Figure 3A displays the results of Ni/KIT-6 catalyst. The images reveal a well-ordered mesoporous structure with a clear honeycomb-like pattern, which is typical for KIT-6 [24]. This indicates that the KIT-6 framework remains intact after Ni loading. The results for the fresh Ni + 1Gd/KIT-6 catalyst is shown in Figure 3B. The TEM image verifies that the indicated highly dispersed NiO crystallites are uniformly distributed throughout the pores, exhibiting no substantial agglomerations. Furthermore, the average particle size distribution for the Ni + 1Gd/KIT-6 catalyst is depicted in Figure 3C. The Ni + 1 Gd /KIT-6 image shows particles distributed within the mesopores without large agglomerates; the corresponding histogram indicates a narrow size distribution, further validating the high dispersion of the metal phase.

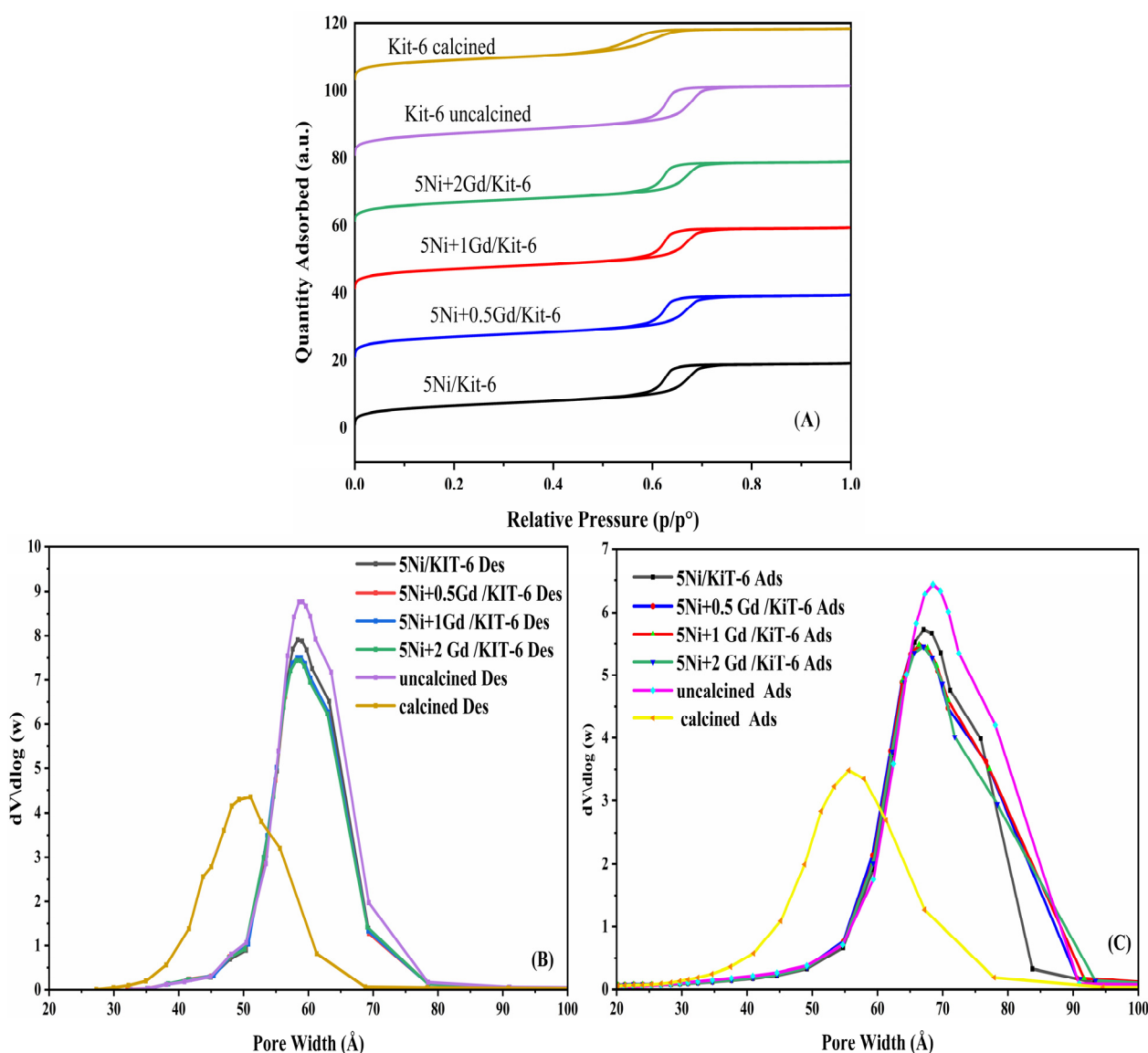


Figure 1. N₂ physisorption of Ni/Gd-KIT-6 catalysts. (A) Adsorption isotherms at 77 K in the capillary condensation region ($p/p_0 = 0.5-0.8$), showing type-IV behaviour with H1 hysteresis for all samples. (B) Pore-size distribution from the desorption branch. (C) Pore-size distribution from the adsorption branch.

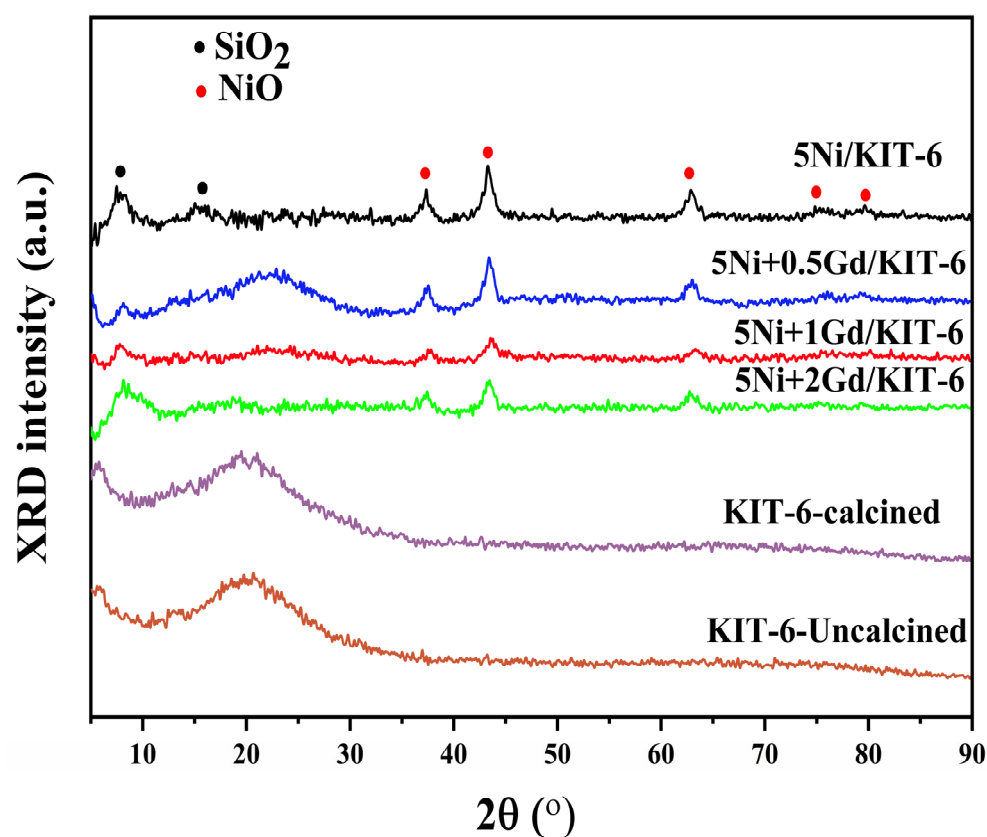


Figure 2. XRD patterns of as-prepared KIT-6 and calcined KIT-6, Ni/KIT-6 and Gd-promoted Ni/KIT-6 catalysts.

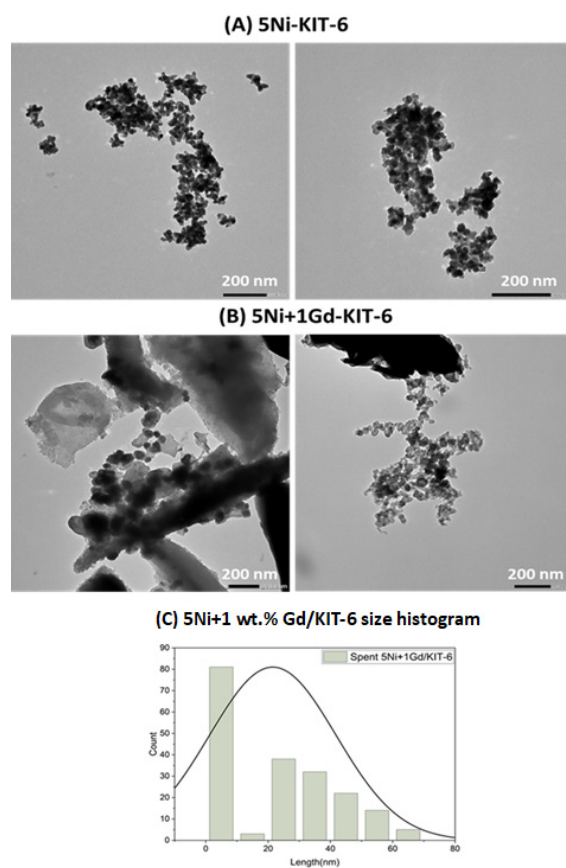


Figure 3. TEM images (A) for 5Ni/KIT-6, (B) for 5Ni + 1Gd/KIT-6 catalyst, and (C) the average particle size for 5Ni + 1Gd/KIT-6 catalyst.

2.4. Raman and UV–Vis Spectroscopy

Figure 4A illustrates the Raman spectra of fresh 5Ni/KIT-6 promoted with 0–2 wt.% Gd. The primary bands at about 500 cm^{-1} and 700 cm^{-1} are due to the stretching modes of Ni–O in cubic NiO and surface nickel silicates, respectively. As the loading of Gd increases from 0.5 to 2 wt.%, the NiO bands exhibit slight shifts and sharpening, indicating that Gd modulates the size and dispersion of the nickel oxide crystallites. The broad features between 1800 cm^{-1} and 2800 cm^{-1} in the unpromoted 5Ni/KIT-6 sample, attributed to nickel oxide overtones or surface defects, significantly diminish in the Gd-modified samples. This quenching effect suggests a strong interaction between Gd and Ni, facilitating a more ordered surface structure. At higher concentrations of Gd, new, subtle peaks appear at 1450 cm^{-1} , which suggests that Gd-associated surface complexes are forming. These complexes may help keep the nickel active sites from sintering. Figure 4B of UV–Vis absorbance spectra show the oxidation states and electronic environment of the metal species in the KIT-6 framework. All samples display broad UV absorption with similar onsets, and no systematic edge shift, which implies that the optical band gap remains relatively stable as observed with Gd loading [26]. The strong absorption bands in the ultraviolet range (200–350 nm) are due to ligand-to-metal charge transfer transitions, specifically from O_2^- to Ni_2^+ and from O_2^- to Gd_3^+ . This shows that these metal ions have been successfully added to the silica matrix. The wide peaks between 600 and 800 nm in the visible range are typical of d–d transitions for octahedral Ni_2^+ ions in a NiO lattice. As the amount of Gd increases, the absorbance across the whole spectrum becomes stronger. This suggests that there are more surface-active species and more electronic states that can be excited. This trend suggests that Gd is a good structural promoter that makes the Ni species and the support interact better. This could lead to a stronger electronic structure that is better for catalytic processes like DRM.

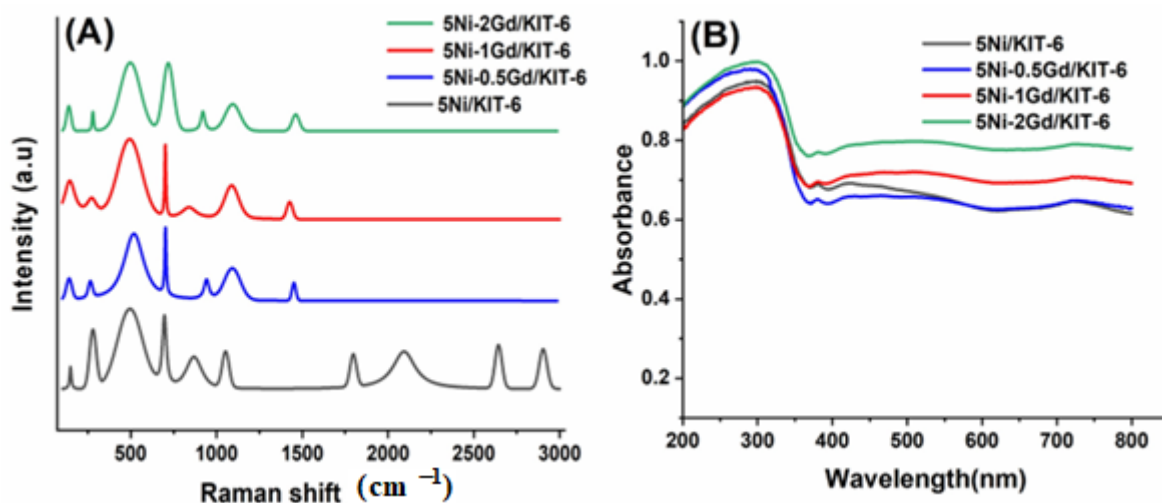


Figure 4. (A) Raman spectra of fresh catalysts. (B) UV–Vis diffuse reflectance spectra of fresh catalysts.

2.5. H_2 -TPR

Figure 5 shows the H_2 -TPR profiles of 5Ni + xGd/KIT-6 ($x = 0, 0.5, 1.0, 2.0$ wt.%). All samples exhibit a main reduction feature between 300 and 700°C , assigned to the reduction of NiO to Ni on silica. With Gd, the main peak shifts slightly and broadens, indicating a modified Ni–support interaction [19]. The H_2/Ni molar ratios for the Gd-promoted and 5Ni/KIT-6 samples are presented in Table 2. The unpromoted catalyst has an H_2/Ni ratio that is just above the stoichiometric 1:1 requirement for turning NiO into Ni0. This is probably because there are bulk-like NiO species that can be easily reduced. Adding Gd brings the ratio closer to one, which means that the reduction process is more controlled.

This decrease means that promoting Gd improves the interaction between the metal and the support, which successfully traps Ni species in the KIT-6 framework. This slightly lowers the total amount of H₂ used while greatly increasing the thermal stability of the active sites by stopping the formation of large, easily reducible Ni clusters that can easily sinter. Among the promoted catalysts, 1 wt.% Gd shows the lowest T_{max} and a more symmetric low-temperature contribution, suggesting a more accessible distribution of Ni, whereas at 2 wt.% Gd the peak area/uptake drops further, consistent with partial site blocking (over-promotion). Gd₂O₃ is not reduced in this range; the measured uptake therefore reflects NiO reduction.

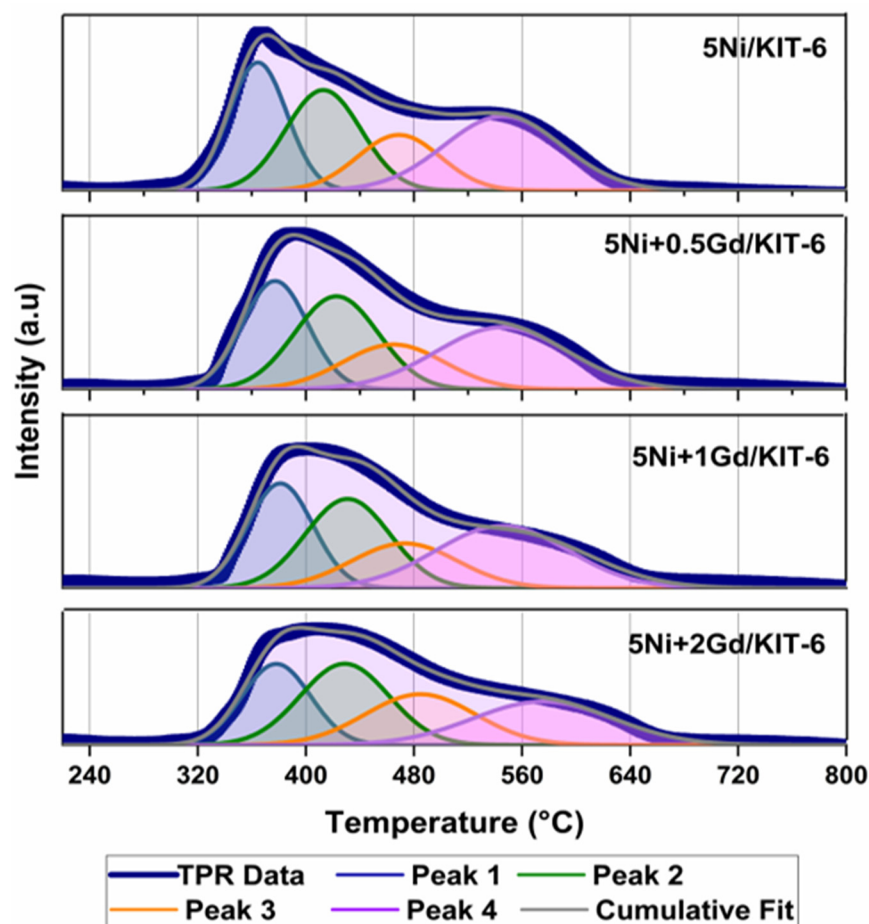


Figure 5. H₂-TPR profiles of Ni + xGd/KIT-6 (x = 0.0, 0.5, 1, 2) catalysts.

Table 2. Measurement of hydrogen consumption and H₂/Ni molar ratio.

Catalyst	T _{max} (°C)	H ₂ Consumption (cm ³ /g)	H ₂ /Ni Molar Ratios
5Ni/KIT-6	392	22.13	1.16
5Ni + 0.5Gd/KIT-6	415	18.89	0.99
5Ni + 1Gd/KIT-6	438	19.10	1.00
5Ni + 2Gd/KIT-6	442	18.92	0.99

2.6. Catalytic Performance

The catalytic performance of Ni + xGd/KIT-6 (x = 0.0, 0.5, 1, 2) catalysts was evaluated at 650 °C for the POM, as shown in Figure 6. The unpromoted 5Ni/KIT-6 catalyst exhibited the lowest activity, with a CH₄ conversion of 62.8%, an H₂ yield of 62%, and a CO yield of 49%. The resulting H₂/CO ratio was 2.5, indicating limited syngas quality and optimization. Introducing 0.5 wt.% Gd led to a mild improvement, increasing CH₄ conversion to 73.8%,

with corresponding H₂ and CO yields of 72.6% and 59.4%, respectively. The H₂/CO ratio decreased slightly to 2.45. It is noted that H₂/CO ratios > 2.0, exceeding the stoichiometry of direct POM (Equation (1)), suggest the occurrence of concurrent steam reforming or water–gas shift reactions (WGSR) utilizing H₂O produced from combustion pathways. The best performance was observed with 1 wt.% Gd, achieving 77.9% CH₄ conversion, a 75.6% H₂ yield, and a 61% CO yield. The H₂/CO ratio was 2.4, indicating better syngas selectivity and suppressed CO₂ formation. These improvements are consistent with stronger metal–support interactions and literature-reported basicity effects for rare-earth promotion [30]. However, at 2 wt.% Gd, the catalytic performance slightly declined, with CH₄ conversion dropping to 75.4%, H₂ yield to 73.8%, and CO yield to 60%. This decrease may result from excessive Gd loading, which could block active sites or lead to the formation of inactive Gd-containing phases. When the amount of Gd increases, Gd₂O₃ can fill the pores of the catalyst. This reduces Ni dispersion, which lowers the density of available active sites. As a result, the catalyst becomes less effective. Table S3 presents the activity performance in tabular form. Sápi et al. [31] establish a crucial benchmark for the efficacy of mesoporous materials in dry reforming (DRM) and CO₂ hydrogenation. This study investigates the POM using Gd-promoted Ni/KIT-6 catalysts. It asserts that secondary reactions such as DRM and steam reforming are crucial for elevating the H₂/CO ratio to 2.4–2.5. Sápi et al. demonstrate that mesoporous NiO exhibits significant activity independently of noble metal promotion due to its intrinsic formation of metallic Ni/NiO_x sites. Both findings demonstrate that ordered mesoporous frameworks, particularly those employing supports such as KIT-6 or SBA-15, are superior in maintaining uniform metal distribution and mitigating sintering in Ni-based catalysts. Sápi has observed that the H₂/CO ratios in DRM can exceed unity at elevated temperatures (973 K). This aligns with the primary study's conclusions that intricate side reactions significantly influence final hydrogen yields, underscoring the critical role of structural engineering in optimizing syngas production.

2.7. TEM Analysis of the Spent Catalysts

TEM of the spent catalysts in Figure 7 shows pronounced aggregation and sintering for 5Ni/KIT-6, with agglomerate sizes on the order of ~150–300 nm in the micrographs of panel A. In contrast, the 1 wt.% Gd sample (panel B) displays smaller, more finely dispersed particles and reduced coalescence. The corresponding particle-size distribution (panel C) yields a mean size of 21.5 ± 20.3 nm, indicating that the majority of particles remain below 30 nm after reaction. These morphological features are consistent with suppressed sintering and the improved stability/activity observed for the Gd-promoted catalyst.

2.8. Raman Analysis

Figure 8 displays the Raman spectra of the spent catalyst, where spectra ($D \approx 1350$ cm^{−1}, $G \approx 1580$ – 1590 cm^{−1}, weak $2D \approx 2700$ cm^{−1}) were collected on spent samples under the base condition (650 °C, CH₄:O₂:N₂ = 2:1:1, 3 h). After baseline correction and Lorentzian fitting ($n \geq 3$ spots per sample), the I_D/I_G ratios were: 0.94 ± 0.03 (5Ni/KIT-6), 1.34 ± 0.05 (5Ni + 0.5 Gd/KIT-6), 0.85 ± 0.02 (5Ni + 1 Gd/KIT-6), and 0.86 ± 0.03 (5Ni + 2 Gd/KIT-6). Lower I_D/I_G indicates more ordered (less defective) carbon; thus, 1 wt.% Gd shows the least disordered coke, while 0.5 wt.% shows the most. The weak 2D band across the series points to mainly turbostratic/poorly stacked carbon rather than well-graphitized layers. The lower I_D/I_G at 1 wt.% Gd aligns with its steadier H₂/CO and higher conversion under the same conditions.

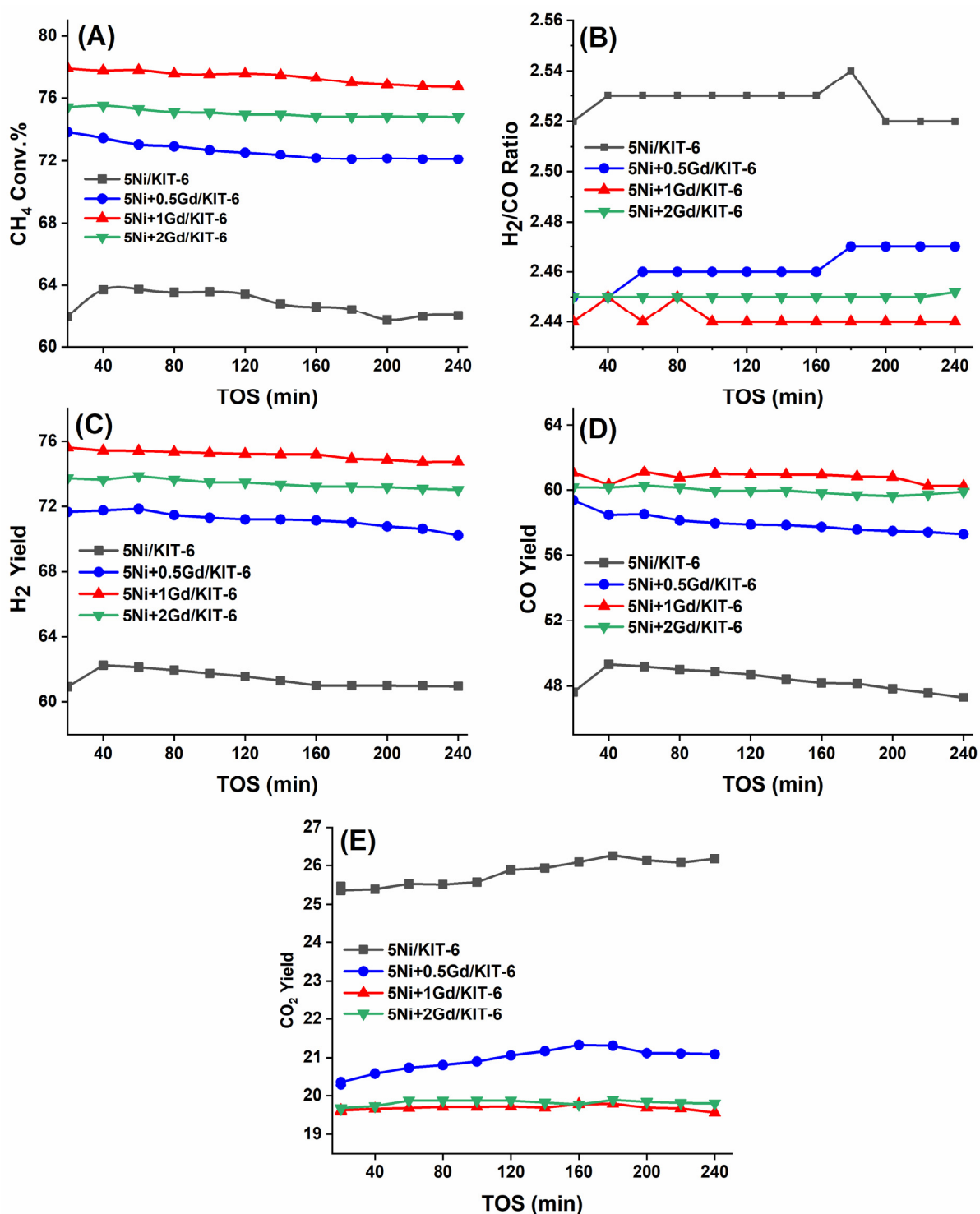


Figure 6. Catalytic performance at 650 °C of Ni/KIT-6 catalysts with varying Gd loadings (0.0, 0.5, 1, and 2 wt.%) for the partial oxidation of methane (POM). The evaluation was conducted at 650 °C over a time on stream (TOS) of 240 min. (A) CH_4 conv., (B) H_2/CO ratio, (C) yield of H_2 , (D) yield of CO, and (E) yield of CO_2 .

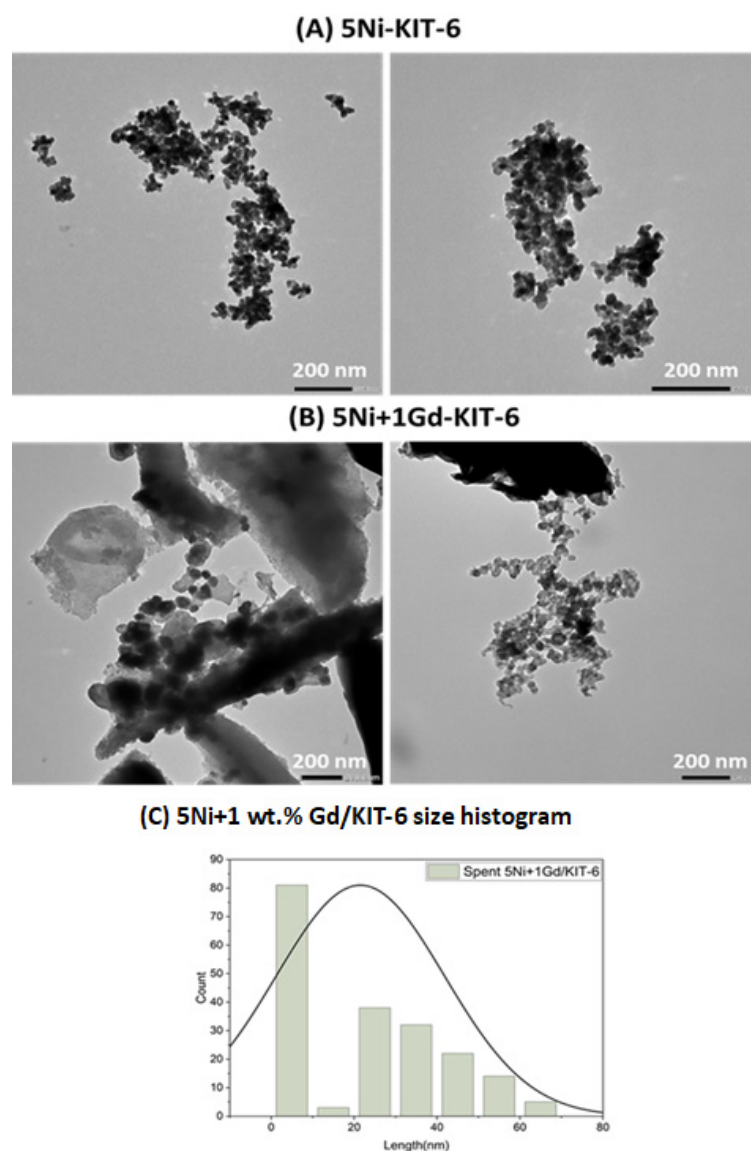


Figure 7. TEM of spent catalysts: (A) 5Ni/KIT-6; (B) 5Ni + 1 wt.% Gd/KIT-6; (C) 5Ni + 1 wt.% Gd/KIT-6 size histogram.

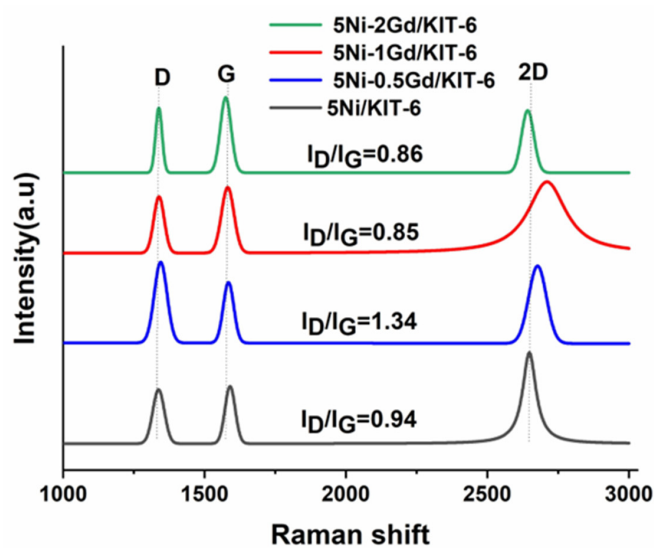


Figure 8. Raman spectra for spent catalysts.

2.9. RSM Analysis

The RSM analysis is provided in the Support Information as: RSM Analysis of Partial Oxidation of Methane S1.

2.10. Prediction and Process Optimization

2.10.1. Model Accuracy and Predictive Performance

The statistical evaluation of the model predicting hydrogen yield (YH_2) reveals a high degree of accuracy and reliability. As shown in Table S1, the closeness between the actual and predicted values demonstrates the robustness of the fitted model. The mean absolute percentage error (MAPE) was found to be 1.62%, indicating that, on average, the model's predictions deviate by only 1.62% from the experimental values. This low error percentage supports the model's suitability for predictive analysis and process optimization.

Furthermore, the ANOVA results indicate an R^2 value of 0.9917, meaning that approximately 99.17% of the variance in hydrogen yield is explained by the model. The strong predictive capability is further supported by the adjusted R^2 , which accounts for the number of terms in the model and remains high, ensuring that overfitting is minimal. The predicted R^2 also remains above 0.99 (as visualized in Figure 9), reinforcing that the model maintains high accuracy when used to predict new data points.

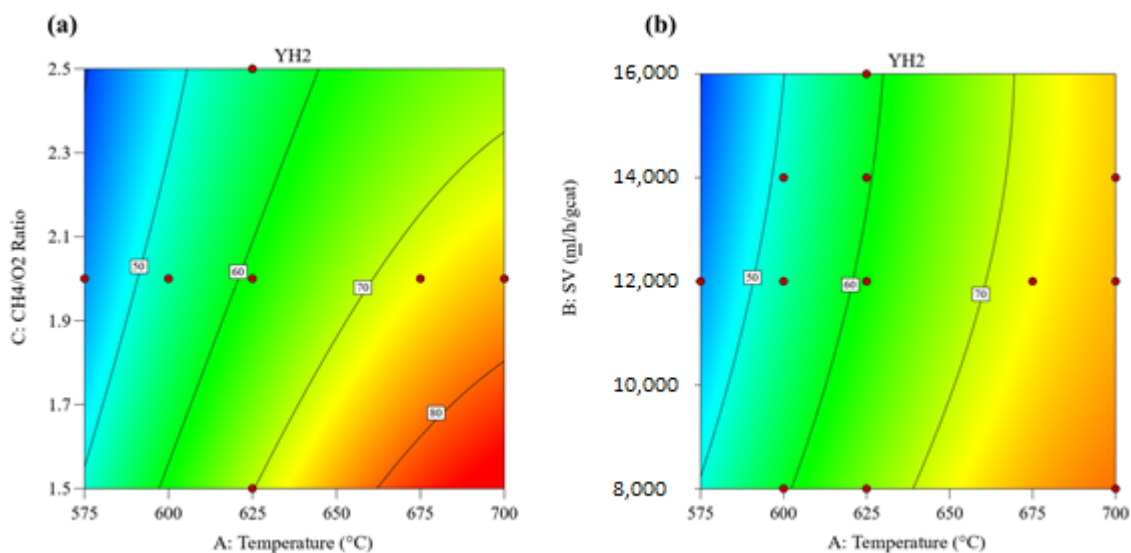


Figure 9. Contour plots for (a) relationship between the temperature, ratio, and H_2 yield at $\text{SV} = 12,000$ and (b) relationship between the temperature, SV , and H_2 yield at a ratio = 2.00.

2.10.2. Factor Significance and Interaction Analysis (ANOVA)

Analysis of Variance (ANOVA), shown in Table S2, was used to assess the statistical significance of the developed quadratic models and the individual factors influencing each response. Results were considered statistically significant if the p -value was less than 0.05. As can be seen from Table S1, the model for methane conversion was highly significant, with an F -value of 164.44 and a p -value of < 0.0001 . There is only a 0.01% chance that such a large F -value could occur due to noise. The main effects of temperature (A), SV (B), and CH_4/O_2 ratio (C), the two-way interactions between temperature and SV (AB) and temperature and ratio (AC), and the quadratic effect of temperature (A^2) were all found to be significant model terms ($p < 0.05$). On the other hand, the interaction between SV and ratio (BC), and the quadratic terms for SV (B^2) and ratio (C^2) were not significant. The largest F -value of 1041.53 for temperature indicates that this factor is the most influential one affecting methane conversion. The model for the H_2/CO ratio was also statistically significant, with an F -value of 254.02 and a p -value < 0.0001 . All model terms were found

to be significant except for the main and quadratic effects of SV (B and B²). The significant terms are A, C, AB, AC, BC, A², and C². Again, the temperature was the most dominant factor with an F-value of 1380.43, followed by the quadratic effect of temperature (A²) and the interaction between temperature and the CH₄/O₂ ratio (AC). For hydrogen yield, the model was determined to be significant, with an F-value of 186.60 and a *p*-value < 0.0001. Similarly to methane conversion, the significant model terms were the main effects A, B, and C, the interactions AB and AC, and the quadratic term A². The BC interaction and the quadratic terms B² and C² were insignificant. Also, the temperature had the most profound impact on hydrogen yield, evidenced by its F-value of 1188.81. The model for CO yield was significant with an F-value of 102.25 and a *p*-value < 0.0001. The significant model terms were temperature (A), SV (B), the interaction between them (AB), and the quadratic term for temperature (A²). The main effect of the CH₄/O₂ ratio (C) and its interaction with temperature (AC) were marginally significant (slightly higher than the *p* < 0.05 threshold), with *p*-values of 0.0654 and 0.0725, respectively. The remaining terms (BC, B², C²) were not significant. The temperature was again the most dominant factor with an F-value of 814.14. The adequacy and accuracy of the models were validated by comparing the predicted values with the experimental (actual) values. As shown in Figure S1, the data points for all four responses are tightly clustered around the 45-degree line, indicating a strong correlation between the experimental results and the values predicted by the models.

The high predictive capability of the models is further confirmed by the low average error percentages between the actual and predicted values, shown in Table S1 of the Supporting Information. The average error percentages for XCH₄, H/CO ratio, YH₂, and YCO are 1.67, 0.89, 1.62, and 3.49, respectively. These low error margins underscore the robustness and reliability of the developed regression models for predicting the system's behaviour within the studied range. The 3D surface and contour plots are instrumental in visualizing the interactive effects of the independent variables on the responses. The contour plots and 3D surface plots for hydrogen yield (YH₂) are presented in Figures 9 and 10, respectively. The interaction between temperature (A) and the CH₄/O₂ ratio (C), Figure 9a, demonstrates that the highest hydrogen yields are achieved at high temperatures and low CH₄/O₂ ratios. As the ratio decreases from 2.5 to 1.5, YH₂ increases substantially, particularly at temperatures above 650 °C. This highlights a strong synergistic effect between these two factors, which was also confirmed by the significance of the AC interaction term in the ANOVA. Similarly, for interaction between temperature (A) and SV (B), Figure 9b, the highest hydrogen yields are also found to be achieved at high temperatures and low SV values. Furthermore, the 3D surface plot, Figure 10, shows that YH₂ increases significantly as the reaction temperature is raised from 575 °C to 700 °C. Conversely, an increase in space velocity from 8000 to 16,000 mL/h/gcat leads to a decrease in YH₂. This suggests that lower space velocity provides longer residence time for more hydrogen production.

2.11. Raman Analysis

Figure 8 displays the Raman spectra of the spent catalyst, where spectra (D ≈ 1350 cm⁻¹, G ≈ 1580–1590 cm⁻¹, weak 2D ≈ 2700 cm⁻¹) were collected on spent samples under the base condition (650 °C, CH₄: O₂: N₂ = 2:1:1, 3 h). After baseline correction and Lorentzian fitting (*n* ≥ 3 spots per sample), the I_D/I_G ratios were: 0.94 ± 0.03 (5Ni/KIT-6), 1.34 ± 0.05 (5Ni + 0.5 Gd/KIT-6), 0.85 ± 0.02 (5Ni + 1 Gd/KIT-6), and 0.86 ± 0.03 (5Ni + 2 Gd/KIT-6). Lower I_D/I_G indicates more ordered (less defective) carbon; thus, 1 wt.% Gd shows the least disordered coke, while 0.5 wt.% shows the most. The weak 2D band across the series points to mainly turbostratic/poorly stacked carbon rather than well-graphitized layers. The lower I_D/I_G at 1 wt.% Gd aligns with its steadier H₂/CO and higher conversion under the same conditions.

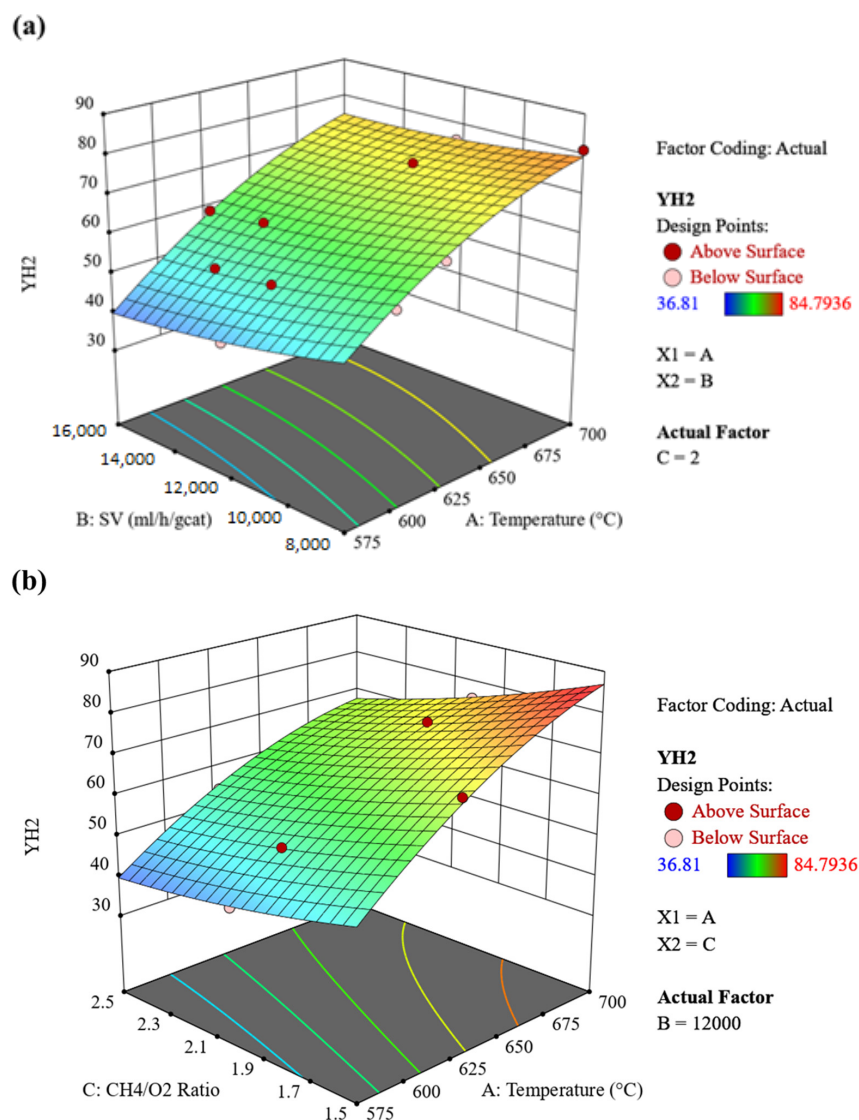


Figure 10. (a) Relationship between the temperature, SV, and H₂ yield at a ratio = 2.00. (b) Relationship between the temperature, ratio, and H₂ yield at SV = 12,000.

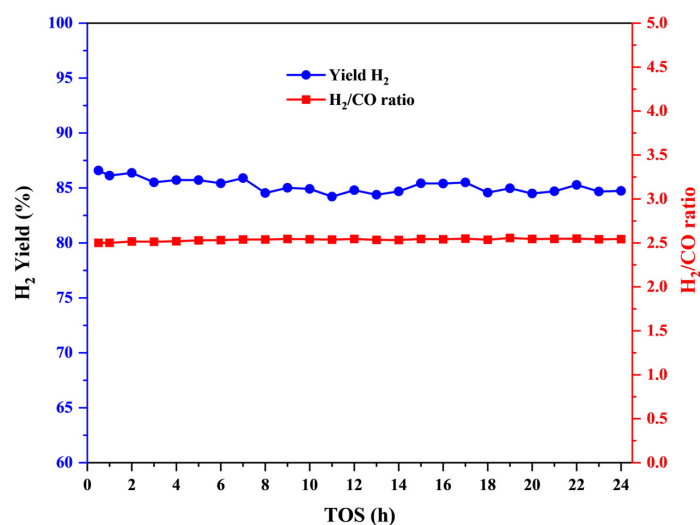


Figure 11. Time on stream (TOS) of the 5Ni + 1Gd/KIT-6 catalyst for long time test in hours under optimized conditions: T = 682 °C, GHSV = 8155 mL h⁻¹g-cat⁻¹, and CH₄/O₂ = 1.52.

3. Materials and Methods

3.1. Materials

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (purity 98%, Alfa Aesar, Waltham, MA, USA), $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (purity 99.9%, Thermo Scientific, Waltham, MA, USA), KIT-6 mesoporous silica (ACS Material, Pasadena, CA, USA, SKU: MSKI6020). As per the specification of KIT-6 (from ACS Material), it possesses a 3D discontinuous cubic Ia3d structure with a BET surface area exceeding $600 \text{ m}^2/\text{g}$ and well-ordered mesopores. Methane, oxygen, and nitrogen (purity $\geq 99.99\%$, certified gas supplier) were used as feed gases. Distilled water was used as the solvent for catalyst preparation.

3.2. Catalyst Preparation

The catalysts were prepared via the conventional wet-chemical method. A fixed nickel loading of 5 wt.% was achieved using nickel (II) nitrate hexahydrate (0.371 g), while gadolinium (III) nitrate hexahydrate was introduced as a promoter at three levels: 0.5 wt.% (0.0215 g), 1 wt.% (0.0430 g), and 2 wt.% (0.0861 g). Nickel (II) nitrate hexahydrate and gadolinium (III) nitrate hexahydrate were dissolved in 20 mL of deionized water. Commercial KIT-6 was added, and the suspension was stirred at 80°C while the solvent was evaporated to dryness; the solids became free-flowing. The resulting solid was dried at 110°C for 24 h and calcined in air at 600°C for 3 h (ramp 5°C min^{-1}). The catalysts were denoted as 5Ni/KIT-6 (unpromoted) and, for the promoted samples, as 5Ni + xGd/KIT-6, where x = 0.5, 1.0, and 2.0 wt.%, corresponding to the respective Gd loading levels.

3.3. Catalyst Characterization

Nitrogen physisorption. Nitrogen adsorption/desorption measurements were carried out at 77 K on a Micromeritics TriStar II 3020 (Micromeritics Instrument Corporation, Norcross, GA, USA). All samples were degassed identically (150°C , 12 h, high vacuum) to remove physisorbed water without risking mesostructured softening or collapse of silica at higher temperatures. Degas conditions and analysis settings were kept constant across the series. Specific surface area was calculated by the BET method, and pore volume and pore-size distribution were obtained using the BJH model. **X-ray diffraction.** Powder XRD patterns were recorded on a Rigaku MiniFlex 600 (Rigaku Corporation, Tokyo, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) over $2\theta = 10\text{--}80^\circ$. **H_2 -TPR.** Temperature-programmed reduction was performed on a Micromeritics AutoChem II 2920. Approximately 70 mg of the sample was pre-treated in helium at 200°C , cooled, and then heated to 900°C in 10% H_2/Ar to assess reducible species. In H_2 -TPR, the sample was heated in an automated furnace (10°C/min up to 1000°C) at atmospheric pressure in a gas flow rate (40 mL/min) of H_2/Ar mixture. **Transmission electron microscopy.** Morphology and metal dispersion were examined on a JEOL JEM-2100 (JEOL Ltd., Tokyo, Japan). Powders were ultrasonically dispersed in ethanol and drop-cast onto carbon-coated copper grids. **Raman spectroscopy.** Spent catalysts were analyzed on a JASCO Raman instrument (JASCO, Tokyo, Japan) with a 532 nm laser to characterize carbon deposits. For the RSM optimization study described in Section 2.9, the Space Velocity (SV) was varied between 8000 and 16,000 $\text{mL g}^{-1} \text{ h}^{-1}$ by adjusting the total inlet flow rate while maintaining the feed ratio constant.

3.4. Catalyst Activity Test

Tests were carried out for POM in a fixed-bed tubular reactor (PID Eng. & Tech., Madrid, Spain, i.d. 9.1 mm, length 300 mm). A K-type thermocouple monitored the bed centre temperature. For each run, 0.10 g catalyst was reduced in situ in 10% H_2/N_2 (30 mL min^{-1}) at 700°C for 1 h, purged with N_2 , then held at 650°C . Feed: CH_4 12 mL min^{-1} , O_2 6 mL min^{-1} , N_2 6 mL min^{-1} ($\text{CH}_4\text{O}_2\text{N}_2 = 2:1:1$). Flows were controlled by calibrated MFCs. Effluent

gases (CH_4 , H_2 , CO , CO_2 , N_2) was analyzed online by GC-TCD (Shimadzu GC-2014, Shimadzu, Kyoto, Japan).

Conversion and yields of H_2 , CO , and CO_2 were calculated by the standard relations given in the equations section [32,33]:

$$X_{\text{CH}_4} (\%) = \frac{\text{mol CH}_{4,\text{in}} - \text{mol CH}_{4,\text{out}}}{\text{mol CH}_{4,\text{in}}} \times 100 \quad (5)$$

$$Y_{\text{H}_2} (\%) = \frac{\text{mol H}_{2,\text{out}}}{2 \times \text{mol CH}_{4,\text{in}}} \times 100 \quad (6)$$

$$Y_{\text{CO}} (\%) = \frac{\text{mol CO}_{\text{out}}}{\text{mol CH}_{4,\text{in}}} \times 100 \quad (7)$$

$$Y_{\text{CO}_2} (\%) = \frac{\text{mol CO}_{2,\text{out}}}{\text{mol CH}_{4,\text{in}}} \times 100 \quad (8)$$

Across all runs, carbon balances closed within 97–103% at the base condition and within the optimized window, taking C-in from CH_4 feed and C-out from GC-measured CO , CO_2 , and CH_4 slip; the small residual is attributed to deposited carbon measured post-run.

4. Conclusions

This study shows that the performance of Ni/KIT-6 catalysts in the partial oxidation of methane is mostly determined by how the catalyst precursors change shape as they become active. The first characterization of the precursors set a baseline for a high-surface-area, but the high-temperature activation (700 °C) and reaction (682 °C) conditions caused the metallic phase to sinter and recrystallize. 1 wt.% Gd-promoted catalyst turned out to be the best formulation. Instead of stopping sintering completely, adding 1 wt.% Gd optimized the distribution of Ni particle sizes during the operational phase, keeping active crystallites at a stable mean size of about 21.5 nm. The promoter's ability to change the surface environment of the active metallic sites is what makes the catalyst more stable and gives it a higher hydrogen yield (85–87%). This is because it greatly reduced the formation of disordered carbon, as shown by the lower I_D/I_G ratios in the spent catalyst Raman analysis. In the end, this work shows that the structural integrity of the active catalyst under operational stress, not the initial precursor state, is what makes syngas production efficient and long-lasting.

Supplementary Materials: The following supporting information is quoted: <https://www.mdpi.com/article/10.3390/catal16020201/s1>, RSM Analysis of Partial Oxidation of Methane S1; Figure S1. Experimental and model-predicted data for (a) CH_4 conversion, (b) H_2/CO ratio, (c) H_2 yield, and (d) CO yield; Table S1. Analysis of Variance for the Various Components of the Quadratic Model; Table S2. The average error percentages for X_{CH_4} , H_2/CO ratio, Y_{H_2} and Y_{CO} ; Table S3. Catalytic performance comparison at 600 °C; Table S4. Justification of Final Conclusions.

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