

A novel Ni-doped γ -Al₂O₃ catalyst for low-temperature CO₂ methanation aided by frustrated Lewis pairs and spinel interlayers

Hubdar Ali Maitlo

Hanyang University

Ki-Hyun Kim

kkim61@hanyang.ac.kr

Hanyang University

Research Article

Keywords: NiO/ γ -Al₂O₃, synergistic acid-base pairs, strong metal-support interaction, CO₂ methanation reaction

Posted Date: August 11th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-9955515/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

A novel Ni-doped γ -Al₂O₃ catalyst for low-temperature CO₂ methanation aided by frustrated Lewis pairs and spinel interlayers

Hubdar Ali Maitlo, Ki-Hyun Kim *

Department of Civil and Environmental Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-Gu, Seoul, 04763, Republic of Korea

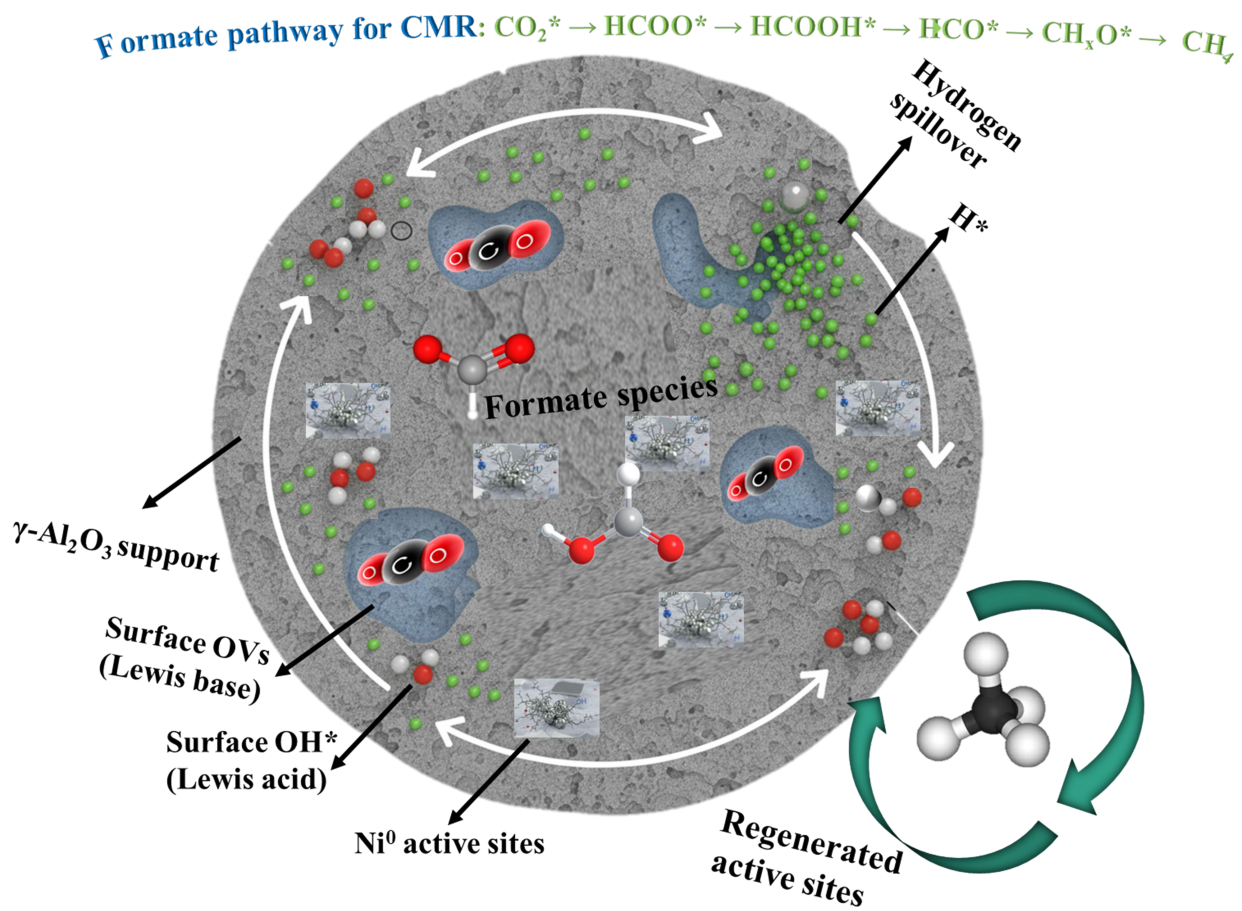
Abstract

This research introduces a novel, high-performance Ni-doped γ -Al₂O₃ multifunctional catalyst (MFC) for the CO₂ methanation reaction (CMR). The catalysts are designated as A_xN_y, where x and y are the mass ratios between the [NH₄]₂CO₃ additive for γ -Al₂O₃ (A) and Ni (N) precursor, respectively, used in the synthesis. This design integrates multiple distinct functions, including catalysis, adsorption, and stabilization, into a single nanomaterial. The A_xN_y features strong metal-support interaction (MSI) interlayers with a high density of both Lewis acid (surface hydroxyls: OH*) and Lewis base sites (oxygen vacancies: OVs). The optimized A₅₀N₂₀ composite catalyst exhibits the best CMR performance, achieving a 92.1% conversion of 1 vol% CO₂ with an 82.8% yield at 400°C. This corresponds to a high CH₄ formation rate of 19.9 mmol g⁻¹ h⁻¹ and a turnover frequency of 0.25 s⁻¹ at 400°C. The catalyst's irregular, defect-rich structural morphology provides evidence of synergistic acid-base pairs, originating from adjacent OH* groups and OVs on the γ -Al₂O₃ surface. The strong MSI stemming from the NiAl₂O₄ interface ensures the stabilization of ultra-fine Ni⁰ nanoparticles, preventing their sintering under reaction conditions. This enhancement in textural and electrical properties improves the accessibility of CO₂ to the exposed Ni active sites, promoting efficient reaction kinetics and CMR performance. This synergistic integration of multiple chemical and structural functions within a single material provides a compelling strategy to facilitate the development of sustainable, chemically tailored MFMs with high potential to surpass current industrial CMR benchmarks.

26 **Keywords:** Ni⁰/γ-Al₂O₃; synergistic acid-base pairs; strong metal-support interaction; CO₂ methanation
27 reaction.

28 ***Corresponding Author:** kkim61@hanyang.ac.kr

29



1. Introduction

The rise in atmospheric CO₂ emissions since the industrial revolution is primarily driven by anthropogenic sources, such as fossil-fuel consumption and large-scale deforestation (Maitlo et al., 2025b). The transition to green energy and the pursuit of comprehensive environmental remediation depend on the development of innovative, sustainable technologies. In response, the European Commission's Green Deal has set an ambitious roadmap for a low-carbon future, targeting an 80-95% reduction in CO₂ emissions by 2050. Likewise, carbon capture and utilization (CCU) has emerged as a promising strategy, with techniques developed for chemical fixation, hydrogenation, and catalytic reduction (Overa et al., 2022; Liu et al., 2026). However, the widespread deployment of these technologies is often hindered by significant operational challenges.

The CO₂ methanation reaction (CMR) has attracted a great deal of interest due to its simple experimental setup, relatively low energy demand, capacity to reduce carbon footprints, and potential to generate chemical building blocks essential for a sustainable society (Bueno-Ferrer et al., 2025; Ju et al., 2025). The primary challenge of CMR lies in the activation of the reactant (i.e., non-polar CO₂). Generally, CO₂ with a symmetrical linear structure and a high O=C=O bond dissociation energy (806 kJ mol⁻¹) is perceived as a chemically inert and thermodynamically stable gas. These properties make its adsorption and activation highly challenging (Kim et al., 2025; Lee et al., 2025). Additionally, the overall CMR is a thermodynamically exothermic reaction (i.e., Sabatier reaction = CO₂ + 4H₂ → CH₄ + 2H₂O, ΔH⁰_{298K} = -165 kJ mol⁻¹); thus, theoretically, it can be carried out at low temperature and high pressure (Zhang et al., 2024a). However, sluggish reaction kinetics, deactivation of catalysts, equilibrium limitations, and the competing reverse water gas shift (RWGS) (CO₂ + H₂ → CO + H₂O, ΔH⁰_{298K} = +41 kJ mol⁻¹) are pressing challenges, thereby hindering the feasibility of CMR for industrial-scale application under low temperature conditions (Celoria et al., 2025; Ullah et al., 2025).

In the pursuit of active and selective multifunctional catalysts capable of overcoming these limitations, supported metal catalysts have emerged as indispensable options. Specifically, noble (Pt, Ru, and Pd) and non-noble (Ni, Co, and Cu) metals supported on various metal oxides (e.g., SiO₂, MgO, ZrO₂, CeO₂, Y₂O₃, and Al₂O₃) have been actively investigated for high-performance CMR (Chen et al., 2024a; Wang et al., 2024; Bueno-Ferrer et al., 2025; Ju et al., 2025; Yin et al., 2025). However, industrial applications of noble metal-based catalysts are inadequate due to their high costs and limited availability. Recently, nickel-based catalysts have been recognized as an exceptional choice for CMR due to their superb product selectivity, low cost, and industrial-scale accessibility (Gao et al., 2024; Ma et al., 2024; Fan et al., 2025). However, the practical application of nickel-based catalysts still faces several unresolved challenges. A critical issue during CMR is the formation of volatile Ni carbonyl compounds (i.e., volatile organometallic compounds = $\text{Ni} + 4\text{CO} \rightarrow \text{Ni}(\text{CO})_4$) (Zhang et al., 2024b). These volatile organometallic compounds readily leave the catalyst surface, leading to Ni metal loss, reduced anti-coking properties, and subsequent catalyst deactivation (Onrubia-Calvo et al., 2024). Furthermore, catalytic performance is critically influenced by the size and dispersion of Ni nanoparticles, as the dispersion of Ni species is highly dependent on the physicochemical properties of the underlying metal oxide supports (Ye et al., 2024b; Guo et al., 2025). In this regard, selecting an appropriate metal oxide support is essential. An ideal support provides a high-surface-area scaffold for uniform metal particle dispersion and modulates their electronic properties via strong metal support interactions (MSI) overlayer (Ye et al., 2024b; Barreau et al., 2025). Additionally, metal oxide supports featuring surface hydroxyl species (OH*) and oxygen vacancies (OVs) play a crucial role in accelerating H₂ spillover effects and promoting the CO₂ adsorption/hydrogenation reaction (Wang et al., 2016; Cisneros et al., 2023; Wang et al., 2023). Generally, the OVs can be formed by removing oxygen atoms from interfacial sites with lower formation energies than those at other surface regions (Li et al., 2019).

This study advances the concept of multifunctional nanomaterials (MFMs) through the rational design of a novel Ni-doped γ -Al₂O₃ catalyst. By strategically engineering strong MSI interlayers, we construct a material with a high density of frustrated Lewis pairs (FLPs) comprising adjacent surface OH* (Lewis acid) and OVs (Lewis base). This unique architecture is expressly designed to achieve a highly uniform dispersion of ultra-fine Ni nanoparticles, enhance CO₂ activation, and ultimately boost CMR activity and stability. The *operando* experimental analyses were used to understand the multi-step CMR pathway on this tailored Ni/ γ -Al₂O₃ MFM. This all-embracing approach, which synergistically combines rational catalyst design with advanced mechanistic study, bridges the gap between fundamental research and industrial implementation. Thus, it is presumed that this approach will pave the way for the adaptation of high-performance and chemical-tailored MFMs that are sustainable and capable of surpassing the current state-of-the-art in CMR for the generation of industrial fuels.

2. Materials and methods

2.1. Chemicals and Materials

All chemicals used in this study were of analytical grade or higher and were purchased from Sigma-Aldrich (USA), including Ni(NO₃)₂·6H₂O (99.999%), Al₂O₃ (99.5%), [NH₄]₂CO₃ (99.8%), and C₂H₂O₄ (99.5%). All the chemicals were used without any further purification, unless otherwise specified. Standard gas cylinders (e.g., CO₂ (99.999%), N₂ (99.999%), and H₂ (99.999%)) were obtained from Union Gas Co., Ltd. (Yongin, Republic of Korea).

2.2. Synthesis of MFM Catalysts

2.2.1. Synthesis of γ -Al₂O₃ support.

The γ -Al₂O₃ support was synthesized via a modified precipitation method (Lim et al., 2026). Briefly, commercial Al₂O₃ powder was dispersed in DI water to form a suspension (Solution A). The separate aqueous solutions of C₂H₂O₄ (solution X1) and [NH₄]₂CO₃ (solution X2) were prepared separately into

500 mL Pyrex breakers (Corning Incorporated, NY, USA) and ultrasonicated for 10 minutes at room temperature. Subsequently, solution X1 was added dropwise into solution A, which was kept stirring at 100°C for 2 hrs. The resulting precipitate was collected, washed three times with DI water, and then re-dispersed in 100 mL of DI (solution A2). Next, solution X2 was added dropwise to solution A2 under continuous stirring for 1 hr at room temperature. The mixture was then aged for 48 hrs at 60°C. Finally, the resulting suspension was washed repeatedly three times with DI water, oven dried at 100°C, pulverized into powder, and calcinated at 400°C for 3 hrs. The obtained γ -Al₂O₃ support was labeled as A_x (where x represents the mass ratio of [NH₄]₂CO₃ to initial Al₂O₃), as summarized in **Table 1**.

2.2.2. *Synthesis of Ni-doped A_x catalyst (A_xN_y).*

The A_x support was dispersed in DI water (Solution A3). A separate aqueous solution of Ni(NO₃)₂·6H₂O was prepared (Solution Y). Both solutions were ultrasonicated for 10 min at room temperature, after which solution Y was added dropwise into solution A3 and kept for 2 hr stirring at 60°C. The resulting suspension was washed repeatedly three times with DI water, oven dried at 100°C, followed by reduction at 400°C for 1 h under a flowing H₂/N₂ mixture (e.g., 5% H₂/N₂) in a tube furnace. The final product, Ni-doped A_x, was labeled as A_xN_y (where y represents the weight ratio of Ni to A_x) as summarized in **Table 1**.

2.3. Characterization techniques

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE diffractometer (Bruker Corp., Billerica, USA) using Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$) over a 2θ range of 5-80° to identify the crystalline phases and structures of the catalysts. High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) were performed on a JEOL JEM-2100F microscope (Tokyo, Japan). Energy dispersive X-ray spectrometer (EDS) mapping was conducted on an FEI Nova Nano SEM 450 (FEI Co., Hillsboro, OR, USA). These techniques were used for

microstructural and crystallographic analysis (e.g., lattice fringes, particle size), surface morphology, and elemental compositions of the catalysts. The textural properties (e.g., surface area, pore volume, and pore size distribution) of the MFMs were analyzed by N₂ adsorption-desorption isotherms at 77 K using a Micromeritics ASAP 2010 analyzer (Micromeritics Instrument Corp., Norcross, GA, USA). The elemental composition and surface chemical states of the MFMs were examined by X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Fisher Scientific, Waltham, USA), with all binding energies calibrated against the C 1s peak at 285.0 eV. The surface basicity and reducibility of the MFMs were evaluated by CO₂ temperature-programmed desorption (CO₂-TPD) and H₂ temperature-programmed reduction (H₂-TPR) using a chemisorption analyzer (AMI, Altamira Instruments, USA). CO₂-TPD was conducted with 10% CO₂/He, whereas H₂-TPR was performed with 10% H₂/Ar at a flow rate of 30 mL min⁻¹ with TCD detection under a ramped heating program up to 900°C (heating rate of 10°C min⁻¹).

2.4. Data analysis

The CMR performance of A_xN_y, as MFM, was extensively evaluated by considering key metrics, such as CO₂ conversion efficiency (X_{CO2}: %, **Eq. 1**), product yield (Y_{CH4}: %, **Eq. 2**), product selectivity (S_{CH4}: %, **Eq. 3**), CH₄ formation rate (r_{CH4}: mmol g⁻¹ h⁻¹, **Eq. 4**), and turnover frequency (TOF: s⁻¹, **Eq. 5**). The S_{CH4} metric signifies the fraction of CH₄ in total hydrocarbon products (i.e., CH₄ and CO). Similarly, the r_{CH4} value represents the catalytic activity of the CMR system, signifying the CH₄ production rate normalized by the mass of the MFM and reaction time under different operating conditions.

$$X_{CO2} = \left(1 - \left(\frac{F_{CO2,out}}{F_{CO2,in}}\right)\right) \times 100 \quad (1)$$

$$Y_{CH4} = \left(\frac{F_{CH4,out}}{F_{CO2,in}}\right) \times 100 \quad (2)$$

$$S_{CH_4} = \left(\frac{F_{CH_4,out}}{F_{CO,out} + F_{CH_4,out}} \right) \times 100 \quad (3)$$

$$r_{CH_4} = Y_{CH_4} \times \left(\frac{F_{CH_4,out}}{Mass\ of\ MFM_{(g)}} \right) \quad (4)$$

$$TOF = \frac{X_{CO_2} \times F_{CO_2,in} \times S_{CH_4} \times M_{Ni}}{m_{CAT} \times W \times D_{Ni}} \quad (5)$$

$$D_{Ni} = \frac{6V_{Ni}}{A_{Ni}d_{i(Ni)}} = \frac{2r_{(Ni)}}{3d_{i(Ni)}} \quad (6)$$

Here, F_{in} and F_{out} (mol h^{-1}) denote the molar flow rate of carbonaceous compounds (i.e., CO_2 , CO , and CH_4) at the reactor inlet and outlet, respectively. The M_{Ni} (g mol^{-1}) is the atomic mass of the Ni active site, m_{CAT} (g) is the mass of the A_xN_y catalyst, W is the Ni content within the A_xN_y catalyst, and D_{Ni} (%) is the dispersion of the Ni catalyst estimated from TEM-based Ni particle size analysis (**Eq. 6**). Where, V_{Ni} and A_{Ni} refer to the atomic volume and surface area of Ni, respectively (Abdel-Mageed et al., 2020; Chen et al., 2024a).

3. Results and discussion

3.1. Characterization of materials

3.1.1. Crystallographic and surface textural characterization

The $A_{50}N_{20}$ composite catalyst, which exhibited the most promising performance in preliminary tests, has been examined, along with its reference materials (e.g., A_0N_{20} and $\gamma\text{-Al}_2\text{O}_3$), to analyze their crystalline patterns. Pristine $\gamma\text{-Al}_2\text{O}_3$ showed characteristic peaks at $2\theta = 37.5^\circ$ (311), 45.7° (400), and 67.2° (440), consistent with its metastable phase (PDF# 047-1308) (**Fig. 1a**) (Bravo et al., 2025). It is noteworthy that the $A_{50}N_{20}$ and A_0N_{20} composite catalysts exhibited comparable XRD patterns, sharing the characteristic diffraction peaks of $\gamma\text{-Al}_2\text{O}_3$ without a significant shift in their diffraction angles. Additionally, for metallic Ni^0 nanoparticles, the XRD pattern of $A_{50}N_{20}$ and A_0N_{20} composite catalysts displayed three

strong diffraction peaks at 2θ values of 44.5, 51.9, and 76.4, corresponding to the (111), (200), and (220) facets of the face-centered cubic structure of metallic Ni^0 crystals (PDF# 04-0850), respectively (Tian et al., 2023). The $\gamma\text{-Al}_2\text{O}_3$ structure remained intact after Ni incorporation, indicating no phase transformation. Besides, the crystallite size ($D_n = \text{nm}$) of the prepared catalysts (e.g., $\text{A}_{50}\text{N}_{20}$, and A_0N_{20} , and $\gamma\text{-Al}_2\text{O}_3$) was computed using Debye-Scherrer's equation (**Eq. 7**) (Ali Maitlo et al., 2025).

$$D = \frac{k \times \lambda}{\beta \times \cos \theta} \quad (7)$$

Where λ , β , k , and θ represent the X-ray wavelength (0.154 nm), angular line width at half-maximum of the crystal plane, shape factor (0.9), and Bragg angle in degree, respectively (Maitlo et al., 2025a). The crystallite sizes of $\gamma\text{-Al}_2\text{O}_{3(440)}/\text{Ni}^0_{(111)}$ were 4.9/2.6 nm for $\text{A}_{50}\text{N}_{20}$, 5.2/3.0 nm for A_0N_{20} , and 5.9/– nm for $\gamma\text{-Al}_2\text{O}_3$ (**Table S1**). The smaller Ni^0 crystallite size in $\text{A}_{50}\text{N}_{20}$ (2.6 nm) compared to A_0N_{20} (3.0 nm) indicates a higher dispersion of Ni nanoparticles. This high Ni^0 dispersion promotes the H_2 dissociation and spillover, which is expected to enhance reaction kinetics and product yield (Liu et al., 2025a).

Fig. 1(b-c) shows the N_2 adsorption-desorption isotherms and pore size distributions for $\text{A}_{50}\text{N}_{20}$ and reference materials (e.g., A_0N_{20} and $\gamma\text{-Al}_2\text{O}_3$). The N_2 adsorption isotherms of all catalysts showed a gradual uptake at low relative pressure ($P/P_0 < 0.5$), followed by a pronounced adsorption step in the range of $P/P_0 = 0.5\text{--}0.9$ (**Fig. 1b**). All isotherms are Type IV with H_3 hysteresis, confirming mesoporous structures from the stacking of plate-like particles as defined by International Union of Pure and Applied Chemistry (IUPAC) standards (Lin et al., 2024; Zhang et al., 2024b). Additionally, pore size distributions were centered around 4 nm, confirming uniform mesoporosity (**Fig. 1c**).

The mesoporous structure of $\text{A}_{50}\text{N}_{20}$ facilitates Ni nanoparticle dispersion and provides channels that can expedite the mass transfer process during the CMR process (Ye et al., 2024a). According to **Table**

S1, the BET surface area (BET_{SA} of $104.8 \text{ m}^2 \text{ g}^{-1}$), pore volume (P_v of $0.15 \text{ cm}^3 \text{ g}^{-1}$), and average pore diameter (P_d of 4.41 nm) values of $\text{A}_{50}\text{N}_{20}$ composite catalyst are higher than those of A_0N_{20} (BET_{SA} of $101.4 \text{ m}^2 \text{ g}^{-1}$, P_v : $0.15 \text{ cm}^3 \text{ g}^{-1}$, and P_d of 3.98 nm). The improved textural properties of the $\text{A}_{50}\text{N}_{20}$ catalyst enhance CO_2 access to Ni active sites, thereby promoting reaction kinetics and improving the catalytic performance of the CMR system.

3.1.2. Morphological and microstructural characterization

The Field-emission scanning electron microscopy with energy-dispersive X-ray spectroscopy (FE-SEM-EDS) was used to assess the surface morphology and elemental distribution. The surface morphologies of the catalysts are shown in **Fig. 2(a-c)**. The pristine $\gamma\text{-Al}_2\text{O}_3$ showcased a polycrystalline structure composed of numerous smaller, highly agglomerated angular crystallites with well-defined polyhedral facets and edges (**Fig. 2a**). In contrast, $\text{A}_{50}\text{N}_{20}$ exhibited a complex, porous microstructure due to Ni doping and strong MSI (**Fig. 2c**). Specifically, the highly porous and aggregated structure of $\text{A}_{50}\text{N}_{20}$ provides a high surface area for catalyst-support interactions (Liu et al., 2025a). Additionally, the ultra-fine metallic Ni^0 nanoparticles were highly dispersed and integrated into the $\gamma\text{-Al}_2\text{O}_3$ matrix.

The fine Ni^0 dispersion indicates strong MSI (Zhao et al., 2024; Choudhary et al., 2026). The NiAl_2O_4 interlayer electronically and structurally anchors Ni particles, inhibiting sintering and ensuring long-term stability (Huang et al., 2025). The high interface density creates nanoscale environments for synergistic acid-base catalysis (Chen et al., 2024a). FE-SEM-EDS mapping was used to visualize the distribution of the active phase and support material. The pristine $\gamma\text{-Al}_2\text{O}_3$ exhibits a uniform background of Al (wt.% of 49.86) and O (wt.% of 50.14) across the surface (**Fig. 2d** and **Table S1**). The EDS mapping $\text{A}_{50}\text{N}_{20}$ catalyst, however, explicitly illustrated the uniform distribution and strong integration of ultra-fine metallic Ni^0 nanoparticles within the $\gamma\text{-Al}_2\text{O}_3$ matrix (e.g., Al wt.% of 39.11, O wt.% of 38.34, and Ni wt.% of 22.56) (**Fig. 2(e-f)** and **Table S1**).

Fig. 3(a-f) shows HR-TEM images of A₅₀N₂₀, A₀N₂₀, and γ -Al₂O₃ at different magnifications (i.e., 20 nm and 5 nm) (**Fig. 3(a-f)**). The pristine γ -Al₂O₃ showed agglomerated, irregular crystallites forming a sponge-like morphology (**Fig. 3a**). A₅₀N₂₀ displayed a porous, platelet-like morphology with well-dispersed Ni⁰ nanocrystals (dark spots) within the γ -Al₂O₃ matrix (**Fig. 3c**). The defect-rich morphology provides a high density of Lewis acid (OH*) and base (OVs) sites on the γ -Al₂O₃ surface.

The A₅₀N₂₀ composite catalyst exhibited an average Ni⁰ particle size of 11.47 nm, significantly smaller than that of A₀N₂₀ (17.28 nm) (**Fig. 3(b-c)**). The crystallite size of the pristine γ -Al₂O₃ support was 19.51 nm (**Fig. 3a**). The smaller Ni size in A₅₀N₂₀ confirms that the [NH₄]₂CO₃ additive strengthens MSI and inhibits sintering (Chen et al., 2024a; Ma et al., 2024; Liu et al., 2025a). The d-spacings and lattice fringes in selected regions of A₅₀N₂₀ composite catalyst and its reference materials (e.g., A₀N₂₀ and γ -Al₂O₃) were confirmed by HR-TEM with inversed Fourier transformed (IFT) patterns and corresponding line histograms (d-spacing of various facets) (Lim et al., 2026). In the case of pristine γ -Al₂O₃, the crystal interplanar spacing of 0.14 nm matches the (440) plane of the metastable crystalline phases of aluminum oxide (**Fig. 3d**) (Zeng et al., 2021). A₀N₂₀ showed lattice fringes for γ -Al₂O₃(440) (at 0.41 nm) and Ni⁰(111) (at 0.201 nm) (**Fig. 3e**) (Ma et al., 2024). A₅₀N₂₀ exhibited fringes for Ni⁰(111) (at 0.207 nm) and Ni⁰(200) (at 0.176 nm) within the γ -Al₂O₃ matrix (**Fig. 3f**) (Chen et al., 2024a).

The selected area electron diffraction (SAED) analysis was used as a complementary technique in conjunction with HR-TEM to analyze the structural features of a specific nanoparticle, grain, or region (Liu et al., 2025b; Zhang et al., 2025). This technique successfully endorsed the existence of specific crystalline phases. The SAED pattern of the γ -Al₂O₃, A₀N₂₀, and A₅₀N₂₀ displays several bright circular rings that are assigned to the (311)/(400)/(440) planes of γ -Al₂O₃ and the (111) plane of Ni⁰ crystal (**Fig. 3(g-i)**), which are in good agreement with the HR-TEM and XRD analyses. The combined HR-TEM, IFT,

and SAED analyses confirm the co-existence of highly crystalline γ -Al₂O₃ and metallic Ni⁰ phases, consistent with a strong MSI.

3.1.3. Surface composition and chemical state analysis

The XPS was used to investigate the surface composition and electronic states of the A₅₀N₂₀ and its counterpart (i.e., A₀N₂₀). The Al 2p peak at ~74.2 eV confirmed Al³⁺ in γ -Al₂O₃, with no metallic Al⁰ detected (**Fig. 4a**). **Fig. 4b** displays the Ni 2p spectra of A₅₀N₂₀ catalysts along with A₀N₂₀. The deconvolution of the Ni 2p core region of A₀N₂₀ displays prominent peaks at 852.0 eV (Ni⁰), 855.1 eV (Ni²⁺ in NiO), and 873.3 eV (Ni²⁺ in NiAl₂O₄) with a distinct satellite peak at 861.5-873.2 eV (Ni²⁺ in NiO) (Tian et al., 2023). In the case of the A₅₀N₂₀, the Ni 2p peaks for both Ni⁰ (from 852.0 eV to 852.2 eV) and Ni²⁺ (from 855.6/873.3 eV to 855.7/873.4 eV for Ni²⁺) species exhibit a small positive shift of approximately +0.2 eV (**Fig. 4b**). This positive shift indicates decreased Ni electron density, signifying strong MSI with the modified A₅₀ support. The surface concentration of Ni⁰ also increases slightly from 2.4% to 2.5% (**Table S3**), suggesting the A₅₀ support promotes the stabilization of a dispersed Ni⁰ phase (Liu et al., 2025a). These electronic modifications and the high Ni dispersion contribute to a more active Ni⁰ phase in the A₅₀N₂₀ catalyst.

As shown in **Fig. 4c**, the O 1s spectra can be deconvoluted into three main components. The first peak at 529.6-529.7 eV is ascribed to the lattice oxygen (O_L) in Ni-Al-O mixed oxide phase, while the components at 531.1 eV and 532.1-532.2 eV are attributed to OV_s and OH* group, respectively. The relative concentrations of OV_s and OH* groups were determined from the peak area ratios (**Table S3**). A₅₀N₂₀ had significantly higher relative concentrations of OV_s (90.2% vs. 82.2%) and OH* groups (86.5% vs. 56.4%) than A₀N₂₀ (**Table S3**). The higher OV_s contents imply the presence of a superior density of electron-rich low-coordination oxygen defect sites, which would promote the activation of adsorbed CO₂, provide lattice sites for oxygen migration, and facilitate electron transfer (Liu et al., 2009;

Zhang et al., 2022). The OH* groups anchor Ni nanoparticles and can participate directly in CO₂ hydrogenation through the addition of an H atom of the OH* group into CO₂ (Liu et al., 2025a). Therefore, the combined high density of OV/OH* and modified Ni electronic state creates a superior surface environment for CO₂ activation and methanation on A₅₀N₂₀.

3.1.4. Optical, redox, and surface acid-base properties characterization

The solid-state UV–vis spectroscopy provided insights into the electronic structure and coordination environment of nickel ions (Ni²⁺) in A₅₀N₂₀ composite catalyst and its counterpart (A₀N₂₀). The strong and broad peak at 292 nm is associated with ligand-to-metal charge transfer from the 2p orbital of O²⁻ ligand to the 3d orbital of Ni²⁺ metal (**Fig. 5a**) (He et al., 2024). The bands in the 600-700 nm region are assigned to the ³A₂(F)→³T₁(P) d-d transition, characteristic of tetrahedrally coordinated Ni²⁺ in the NiAl₂O₄ spinel structure (**Fig. 5a**) (Kim et al., 2004; Pham-Ngoc et al., 2025). In contrast, the bands at 387 nm and 728 nm are attributed to the ³A_{2g}(F)→³T_{1g}(P) and ³A_{2g}(F)→³T_{1g}(F) transitions, respectively, of octahedrally coordinated Ni²⁺ species in the NiO-like environments (**Fig. 5a**) (Kim et al., 2004; Pham-Ngoc et al., 2025). Thus, the presence of tetrahedrally coordinated Ni²⁺ confirms the formation of NiAl₂O₄ spinel, where Ni²⁺ ions incorporate into the Al₂O₃ lattice, indicating a strong MSI. This interaction provides a clear explanation for the high dispersion of small metallic Ni⁰ particles after reduction. This strong interaction is key to generating and stabilizing the highly dispersed metallic Ni⁰ particles, which are responsible for the high CMR activity and stability.

The reducibility and the extent of MSI of the prepared catalysts were investigated by H₂-TPR. The H₂-TPR analysis revealed that the A₅₀N₂₀ catalyst exhibits significantly enhanced reducibility compared to the reference A₀N₂₀, a finding evidenced by the substantial low-temperature shift of the primary reduction (α) peak from 182°C (A₀N₂₀) to 168°C (A₅₀N₂₀) (**Fig. 5b**). This 14°C shift is a direct indicator of stronger MSI between the Ni active sites and the γ-Al₂O₃ support. The enhanced MSI facilitates the

reduction process, which is further promoted by the hydrogen spillover phenomenon occurring at the Ni/ γ -Al₂O₃ interface (Chen et al., 2024a; Lin et al., 2024). Specifically, H atoms adsorbed on the Ni metal spill over to attack the Al-O bonds of the support, ultimately leading to the formation of OV_s and surface OH* groups (Chen et al., 2024a). This restructuring of the interface is highly advantageous as it creates the necessary conditions for the construction of an FLP structure, which is crucial for improving the catalyst's CMR performance. In addition, the β reduction peak, which is generally assigned to the reduction of larger or less-dispersed NiO nanoparticles, provides further insight into the structural quality of the catalysts. The A₅₀N₂₀ catalyst displayed its β peak at 247°C, representing a 5°C negative shift compared to the 252°C peak observed for the A₀N₂₀ catalyst (**Fig. 5b**). This shift to a lower reduction temperature strongly suggests that the Ni nanoparticles in the A₅₀N₂₀ catalyst have an intrinsically smaller cluster size and superior dispersion across the support surface (Chen et al., 2024a; Lin et al., 2024). These characteristics are highly beneficial, as smaller, well-dispersed metal clusters maximize the available catalytic surface area. Consequently, this improved morphology is predicted to favor higher activity, specifically yielding higher CMR performance. The final component of the H₂-TPR profile, the γ reduction peak, provides crucial information about the most stable Ni species, which is typically the NiAl₂O₃ phase. The A₅₀N₂₀ catalyst displayed its γ peak at a significantly higher temperature of 545°C, a substantial positive shift compared to the 488°C peak seen in A₀N₂₀ (**Fig. 5b**). This suggests a greater extent of stability of the NiAl₂O₄ spinel formation (Chen et al., 2024b). Thus, the A₅₀N₂₀ catalyst presents a trade-off: superior low-temperature activation via FLP formation and dispersion, balanced against a higher loss of active Ni to the spinel phase.

The CO₂-TPD analysis was employed to assess the surface basicity of the catalysts, a property critically linked to CO₂ activation and overall catalytic performance, particularly at low temperatures (Tian et al., 2023). CO₂ desorption peaks typically fall into three temperature regions: weak basic sites (50-200°C,

related to $\text{CO}_{2\text{ads}}$), medium basic sites (200-450°C, associated with bicarbonate “ CO_3H^* ” and bidentate carbonate “ b-CO_3^* ”), and strong basic sites (450-800°C, related to monodentate carbonates “ m-CO_3^* ”) (Chen et al., 2024b). Catalytic performance is highly dependent on CO_2 adsorption on the weak and medium sites, which facilitate the formation of crucial reaction intermediates (e.g., CO_3^* and b-CO_3^*) (Ye et al., 2024a; Zhang et al., 2024c). The CO_2 -TPD results confirmed the superior potential of the $\text{A}_{50}\text{N}_{20}$ catalyst for CO_2 activation. While the A_0N_{20} catalyst showed two key peaks at 137°C and 280°C, the $\text{A}_{50}\text{N}_{20}$ profile was notably improved: it featured a $\text{CO}_{2\text{ads}}$ peak at a lower temperature (128°C), indicating more readily reversible adsorption on weak sites. It also showed an increased population of medium basic sites, evidenced by two well-defined peaks at 273°C and 430°C (**Fig. 5c**). This rich basicity profile suggests that CO_2 is not only more easily adsorbed and activated into the required carbonate species on $\text{A}_{50}\text{N}_{20}$, but the catalyst also possesses a greater number and wider distribution of medium-strength basic sites that are vital for sustaining a favorable reaction pathway, strongly suggesting enhanced CMR performance.

3.2. CO_2 methanation reaction

3.2.1. Effect of weight ratios on A_xN_y composites

The CMR performance of the A_xN_y catalysts is strongly influenced by both the $\gamma\text{-Al}_2\text{O}_3$ support modification and the Ni loading level. The CMR performance of the A_xN_y catalysts and a reference catalysts was evaluated with 1 vol% CO_2 in a H_2/CO_2 ratio of 4 over a temperature range of 200 to 400°C. The corresponding key performance metrics (e.g., X_{CO_2} (%), Y_{CH_4} (%), S_{CH_4} (%), and r_{CH_4} ($\text{mmol g}^{-1} \text{h}^{-1}$) of the CMR process are summarized in **Table 2**. The pristine $\gamma\text{-Al}_2\text{O}_3$ support showed negligible activity (X_{CO_2} of < 3%), consistent with physisorption of CO_2 without catalytic methanation (**Fig. 6a** and **Table 2**). In contrast, the A_xN_y composite catalysts exhibited drastically improved CMR performance, with maximum X_{CO_2} values at 400°C of 41.1, 41.7, 41.8, 45.8, 58.8, 67.1, and 68.3% for A_{50}N_5 , $\text{A}_{50}\text{N}_{30}$,

A₀N₂₀, A₅₀N₁₀, A₁₀N₂₀, A₅₀N₂₀, and A₂₀N₂₀, respectively (**Fig. 6a** and **Table 2**). The S_{CH₄} (%) and r_{CH₄} (mmol g⁻¹ h⁻¹) followed a similar trend, with A₂₀N₂₀ (98.6%, 20 mmol g⁻¹ h⁻¹) and A₅₀N₂₀ (95.2%, 16.2 mmol g⁻¹ h⁻¹) exhibiting the highest values (**Table 2**). The superior CMR performance of A₅₀N₂₀ is attributed to its higher contents of OV_s and OH* species (refer to *Section 3.1*), which facilitate CO₂ adsorption and activation. Moreover, the electronically modified and accessible N⁰ sites (refer to *Section 3.1*) enhance H₂ dissociation and hydrogen spillover to the activated CO₂. These synergistic effects collectively create an optimized surface environment for the sequential hydrogenation of CO₂ to CH₄.

3.2.2. Effects of process variables

The CMR performance of the A₅₀N₂₀ catalyst was optimized by evaluating the effect of the H₂/CO₂ ratio (4 to 10) over a temperature range of 250-400°C (**Fig. 6b**). It was observed that the X_{CO₂} value for A₅₀N₂₀ increased substantially from 67.1% to 92.1% at 400°C as the H₂/CO₂ ratio in the feed gas increased from 4 to 10, while maintaining the inlet CO₂ concentration of 1 vol% (**Fig. 6b** and **Table 2**). At 400°C and an H₂/CO₂ ratio of 10, the A₅₀N₂₀ catalyst achieved its maximum S_{CH₄} of 98.5% (**Table 2**). Similarly, the r_{CH₄} value increased from 16.3 to 19.9 mmol g⁻¹ h⁻¹ as the H₂/CO₂ ratio increased from 4 to 10 (**Table 2**).

The enhanced performance at a higher H₂/CO₂ ratio is attributed to the higher H₂ partial pressure, which drives the hydrogenation of surface intermediates, reduces poisoning by carbonaceous species, and facilitates CH₄ desorption. The higher H₂/CO₂ ratio thermodynamically favors methanation over the RWGS reaction, thereby suppressing CO formation and maximizing CH₄ selectivity. The abundant H₂ also helps to maintain an active catalyst surface by preventing carbon deposition (coking) and ensuring sufficient surface hydrogen coverage for successive hydrogenation steps in the CMR process.

The effect of relative humidity (RH: 0-30%) on the CMR performance of A₅₀N₂₀ was also investigated (**Fig. 6c**). The best performance metrics for A₅₀N₂₀ at 0% RH included S_{CH₄} (98.5%) and r_{CH₄} (19.9 mmol g⁻¹ h⁻¹), which were 1.2- and 1.7-fold, respectively, higher than those obtained at 30% RH (**Fig. 6c** and **Table 2**). The presence of water vapor significantly inhibited the CMR performance, primarily due to the competitive adsorption of H₂O on the active sites. Water vapor also acts as a diluent, reducing the partial pressures of H₂ and CO₂ and thus suppressing the reaction rate. Furthermore, H₂O can react with surface OV_s and OH* groups, altering the catalyst's surface basicity and redox properties and thereby diminishing its activity.

3.3. CMR mechanism and pathway

3.3.1. DRIFT analysis

In-situ DRIFTS analysis was conducted to probe the mechanism of CO₂ adsorption and activation on the A₅₀N₂₀ catalyst under a gas mixture of 1% CO₂ and 10% H₂ at ambient temperature (25°C) and high (400°C) operating temperatures (**Fig. 7(a-b)**). In **Fig. 7a**, a series of vibration bands gradually appeared and intensified with increasing CO₂ adsorption time from 0 to 60 min at ambient conditions, reflecting the successive accumulation and surface interaction of CO₂-derived species on the A₅₀N₂₀ catalyst surface. Specifically, observed peaks were assigned to bicarbonate (HCO₃* at 1630 cm⁻¹ and 1227 cm⁻¹), monodentate carbonate (m-CO₃* at 1392 cm⁻¹), and bidentate carbonate (b-CO₃* at 1338 cm⁻¹) (Ma et al., 2024). The carbonate-based intermediate species are derived from the reaction of CO₂ with terminal hydroxyls (OHT*: 3740 cm⁻¹) and bridging hydroxyls (OHB*: 3676 cm⁻¹) groups of A₅₀N₂₀ catalyst (Liu et al., 2025a). The additional bidentate carbonate can also be derived from CO₂ adsorbed on OV_s of the A₅₀N₂₀ catalyst. A weak but observable signal at 1004 cm⁻¹, attributed to methoxy groups (OCH₃), further implies that some of the surface intermediates undergo additional transformation toward hydrogenated products (Li et al., 2022). The absence of CH₄ and CO peaks at 25°C confirms that hydrogenation does

not occur at ambient temperature. The rapid formation of carbonate and bicarbonate species instead demonstrates the strong CO₂ adsorption capacity of A₅₀N₂₀, facilitated by its high density of OV_s and OH* groups.

As the reaction temperature increased to 400°C, the *in-situ* DRIFTS spectra displayed significant changes associated with the enhanced hydrogenation of surface-bound carbonate-type intermediates to methane (**Fig. 7b**). The characteristic bands of bicarbonate, monodentate carbonate, and bidentate carbonate gradually diminished with increasing temperature, indicating their conversion into formate and carbonyl species. The newly formed bands emerged at 1575, 1455, and 1227 cm⁻¹, attributed to surface formate species (Ma et al., 2024). These formate intermediates subsequently decompose into formyl (CHO, 1755 cm⁻¹) and are then hydrogenated to methoxy species (OCH₃, 962 cm⁻¹) (Chen et al., 2025). As a result, the appearance of a peak at 3013 cm⁻¹, corresponding to the C-H stretching vibration of CH₄, confirms methane generation during thermal treatment (Liu et al., 2025a). The absence of detectable CO-related species indicates that the formate pathway (CO₂→carbonates→formate→CH₄) dominates over the CO-based pathway. These findings highlight the central role of carbonate and formate species in the CMR process and demonstrate that CH₄ formation proceeds through stepwise hydrogenation facilitated by strong Ni-Al₂O₃ interactions that promote CO₂ activation and intermediate stabilization. Collectively, these results demonstrate the high activity of the A₅₀N₂₀ catalyst in adsorbing, activating, and converting CO₂, underscoring its potential for efficient CO₂ methanation.

3.3.2. CMR pathway on A_xN_y

The CO₂ methanation is a key strategy for mitigating greenhouse gas emissions while producing sustainable fuels and chemical feedstocks (Razavi et al., 2025). The possible reaction pathways for CMR mainly include the formate route: CO₂*→HCOO*→HCOOH*→HCO*→CH_xO*→CH₄, and the CO route: CO₂*→CO*→HCO*→CH_xO*→CH₄ (Li et al., 2025a). Among the various reaction pathways,

the formate route is widely recognized as dominant on Ni-doped metal-oxide catalysts due to its relatively low activation barriers and the effective stabilization of intermediates on the catalyst surface (Chen et al., 2025; Qiang et al., 2025). The DRIFTS analysis (Section 3.3.1) confirms that the formate pathway dominates on the A₅₀N₂₀ catalyst, facilitated by a synergistic network of metallic Ni⁰ sites, OV_s, and OH* groups.

The reaction initiates with CO₂ chemisorption at Lewis acid-base pairs, where OV_s (Lewis base) and adjacent OH* groups (Lewis acid) cooperatively polarize the CO₂ molecule. Simultaneously, H₂ molecules dissociate on exposed Ni⁰ sites, generating highly reactive hydrogen atoms (H*) that migrate across the catalyst surface via hydrogen spillover. These activated hydrogen atoms react with the adsorbed CO₂ to form surface-bound formate species (HCOO* and HCOOH*), the key intermediate driving the reaction along the low-energy formate pathway. Stepwise hydrogenation then produces formyl (CHO) and methoxy (OCH₃) intermediates, which are stabilized by interactions with the oxide support. Stepwise hydrogenation of the adsorbed formate produces formyl (CHO*) and methoxy (OCH₃*) as intermediate species, which are stabilized through interactions with OH* groups and adjacent OV_s. Finally, hydrogenation and C-O bond cleavage of the methoxy species (OCH₃*) releases CH₄, regenerating the active sites.

The cooperative interplay between Ni⁰ nanoparticles, the NiAl₂O₄ interface, OV_s, and OH* groups is critical for the high activity and selectivity. Ni provides active sites for H₂ dissociation, the NiAl₂O₄ interlayer stabilizes Ni nanoparticles and promotes hydrogen spillover, while OV_s and OH* enhance CO₂ adsorption and intermediate stabilization. Collectively, this multi-component system establishes a low-energy, selective pathway for CMR, minimizing side reactions and highlighting the mechanistic dominance of the formate route.

4. Performance comparison of A_xN_y with literature reports

The catalytic performance of the optimized $A_{50}N_{20}$ catalyst was benchmarked against state-of-the-art Ni-based systems reported in recent literature to evaluate its advancement. The comparison clearly demonstrates that $A_{50}N_{20}$ delivers cutting-edge performance in terms of X_{CO_2} , S_{CH_4} , and TOF (**Table 3**). Under industrially relevant higher temperatures (400°C , $H_2/CO_2 = 4$), $A_{50}N_{20}$ achieves an X_{CO_2} of 67.1% with an S_{CH_4} of 95.2% and a TOF of 0.18 s^{-1} . A detailed analysis of **Table 3** reveals the critical impact of support and promoter selection. For example, the modification of a simple Ni/ Al_2O_3 catalyst (X_{CO_2} : 25.5% at 275°C) with a Eu promoter in 5Eu-Ni/ Al_2O_3 dramatically improves X_{CO_2} to 80.8% under identical conditions, highlighting the efficacy of rare-earth promotion in enhancing Ni reducibility and CO_2 activation (Wang et al., 2025). Similarly, the choice of support composition is paramount, as seen in the 25Ni/ ZrO_2 -based series. Replacing part of the ZrO_2 with CeO_2 (i.e., 25Ni/20 CeO_2 -55 ZrO_2) yields an X_{CO_2} of 72.53% at 250°C , significantly higher than with Y_2O_3 (45.55%) or without a promoter (27.97%), underscoring CeO_2 's role in providing oxygen storage capacity and promoting metal dispersion (Italiano et al., 2025).

A key advantage of $A_{50}N_{20}$ is revealed under reactant-rich conditions ($H_2/CO_2 = 10$), where its performance surges to an X_{CO_2} of 92.1% and a TOF of 0.25 s^{-1} . Although a direct comparison is challenging due to differing temperatures, this TOF under high-conversion conditions is highly competitive. For instance, it surpasses the TOF of catalysts like 25Ni/20 CeO_2 -55 ZrO_2 (0.09 s^{-1} at 250°C) and Ni- La_2O_3/Na^+ -BEA (0.12 s^{-1} at 250°C), despite $A_{50}N_{20}$ operating at a significantly higher temperature where thermodynamics are less favorable for CO_2 conversion, underscoring its superior intrinsic kinetics and active site efficiency (Italiano et al., 2025; Kizil et al., 2025) (**Table 3**). The intrinsic activity, measured by TOF, further distinguishes $A_{50}N_{20}$. Its TOF of 0.25 s^{-1} (H_2/CO_2 of 10) is notably higher than that of many promoted and structured catalysts in **Table 3**, including 15Ni/ CeO_2 -U (0.06 s^{-1}

at 200°C) and the Ni-CeCr_{0.1}/Sepiolite system (0.0055 s⁻¹ at 150°C) (Han et al., 2025; Li et al., 2025b). This high TOF, achieved at a high space velocity (GHSV = 60 L g⁻¹ h⁻¹), indicates exceptionally efficient use of Ni active sites. Furthermore, while many entries in **Table 3** report performance under mild conditions (< 300°C) to avoid Ni sintering, A₅₀N₂₀ maintains high activity and stability at 400°C. This demonstrates the success of its design principle: the strong MSI via the NiAl₂O₄ interface and the high defect density (OVs, OH*) collectively stabilize the active phase under demanding conditions where other Ni catalysts typically deactivate.

5. Conclusions

This study successfully developed a high-performance Ni-doped γ -Al₂O₃ multifunctional catalyst (A₅₀N₂₀) for low-temperature CO₂ methanation. The strategic use of [NH₄]₂CO₃ as an additive engineered a catalyst with a unique synergistic structure, featuring a high density of frustrated Lewis pairs (surface OH* and OVs) and a strong NiAl₂O₄ metal-support interaction interface. This design resulted in superior CO₂ adsorption, activation, and exceptional stabilization of ultra-fine Ni⁰ nanoparticles. The optimized A₅₀N₂₀ catalyst demonstrated outstanding catalytic performance, achieving 92.1% CO₂ conversion with 98.5% CH₄ selectivity at 400°C under a H₂/CO₂ ratio of 10, corresponding to a high turnover frequency of 0.25 s⁻¹. This performance surpasses many state-of-the-art Ni-based catalysts, highlighting its remarkable intrinsic activity and stability at industrially relevant temperatures. The *operando* DRIFTS analysis confirmed that the reaction proceeds dominantly via the low-energy formate pathway, facilitated by the synergistic acid-base sites. In summary, the rational integration of multiple chemical functions, adsorption, activation, and catalysis within a single nanomaterial provides a compelling strategy. The A₅₀N₂₀ catalyst represents a significant advancement, demonstrating high potential to bridge the gap between fundamental research and the industrial implementation of efficient CO₂ methanation technology for sustainable fuel production.

6. Acknowledgement

This work was supported by a grant from the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (MSIT) of the Korean government (Grant No: 2021R1A3B1068304). This research was also supported by the Center for Polymers and Composite Materials (CPCM), Hanyang University, Korea, through Korea Basic Science Institute (National Research Facilities and Equipment Center) grant funded by the Ministry of Education (2022R1A6C101A779).

7. References

- Abdel-Mageed, A.M., Wiese, K., Parlinska-Wojtan, M., Rabeah, J., Brückner, A., Behm, R.J., 2020. Encapsulation of Ru nanoparticles: Modifying the reactivity toward CO and CO₂ methanation on highly active Ru/TiO₂ catalysts. *Applied Catalysis B: Environmental* 270, 118846.
- Ali Maitlo, H., Younis, S.A., Kim, K.-H., 2025. Understanding oxidation potential and degradation mechanism of acid-treated TiO₂ coupled g-C₃N₄ S-scheme heterojunction photocatalyst for the removal of gaseous formaldehyde. *Sep. Purif. Technol.* 356, 129862.
- Barreau, M., Salusso, D., Zhang, J., Haevecker, M., Teschner, D., Efimenko, A., Borfecchia, E., Sobczak, K., Zafeirotos, S., 2025. Thermal Activation and Deactivation of Ni-Doped Ceria Catalysts in CO₂ Methanation. *Small Science* 5, 2400540.
- Bravo, L.M., Meunier, F.C., Kopyscinski, J., 2025. Rare earth oxide promoted Ru/Al₂O₃ dual function materials for CO₂ capture and methanation: An operando DRIFTS and TGA study. *Applied Catalysis B: Environment and Energy* 361, 124591.
- Bueno-Ferrer, J., López-Rodríguez, S., Martínez-López, I., Martín-García, I., Guillén-Bas, E., Dieste, V.P., Davó-Quñonero, A., Lozano-Castelló, D., Bueno-López, A., 2025. Highly active, selective and stable Ru/NiO-CeO₂ catalyst for low-temperature CO₂ methanation. *Chem. Eng. J.* 522, 167951.
- Celoria, F., Salomone, F., Tauro, A., Gandiglio, M., Ferrero, D., Champon, I., Geffraye, G., Pirone, R., Bensaid, S., 2025. Kinetic study and deactivation phenomena for the methanation of CO₂ and CO mixed syngas on a Ni/Al₂O₃ catalyst. *Chem. Eng. J.* 512, 162113.
- Chen, S., Costley-Wood, L., Lezcano-Gonzalez, I., Campbell, E., Weng, Z., Asunción Molina, M., Wu, Y., Beale, A.M., 2025. Understanding defect generation on CeO₂ and its utilization for enhanced metal-support interactions in Ni/CeO₂ catalysts for improved CO₂ methanation performance. *Applied Catalysis B: Environment and Energy* 366, 125029.
- Chen, X., Ye, R., Sun, C., Jin, C., Wang, Y., Arandiyán, H., Lim, K.H., Song, G., Hu, F., Li, C., Lu, Z.-H., Feng, G., Zhang, R., Kawi, S., 2024a. Optimizing low-temperature CO₂ methanation through frustrated Lewis pairs on Ni/CeO₂ catalysts. *Chem. Eng. J.* 484, 149471.
- Chen, Y., Zhu, S., Zhou, J., Wang, Y., Zhang, Z., Liu, N., Meng, R., He, S., 2024b. Synthesis of a Ni/Al₂O₃ catalyst for hydrogen production via bioethanol steam reforming: Role of the preparation method. *Int. J. Hydrogen Energy* 96, 309-320.
- Choudhary, N., Srivastava, N., Annadata, H.V., Ghosh, B., Da Costa, P., 2026. Strategic integration of yttrium single atoms on CeO₂ supported nickel catalysts for enhanced CO₂ methanation catalysis. *Applied Catalysis B: Environment and Energy* 382, 125918.

Cisneros, S., Santa-Taborda, L., Martínez Quintana, L., Rabee, A.I.M., Abed, H., Rockstroh, N., Bartling, S.,
 Romero-Sáez, M., Atia, H., Belén Dongil, A., Brückner, A., Rabeah, J., 2023. The effect of O-vacancies on
 intermediates stability and electron delocalization over MgO modified Ru/ZrO₂: Spectroscopic insights
 during CO₂ methanation. *Chem. Eng. J.* 474, 145646.
 Fan, H., Xu, D., Liu, K., Hou, G., Li, Y., Huang, S., Wu, K., Xu, Y., Shan, R., Zhang, Z., Ding, M., 2025.
 Enhanced low-temperature CO₂ methanation performance over mesoporous Y₂O₃ confined Ni
 catalysts. *Chem. Eng. J.* 503, 158545.
 Gao, P., Tang, S., Han, X., Hao, Z., Chen, J., Pan, Y., Zhang, Z., Zhang, H., Zi, X., Chen, L., Li, M., Ma, X.,
 2024. Boosting CO₂ methanation via tuning metal-support interaction over hollow Ni/CeO₂. *Chem. Eng.*
J. 498, 155784.
 Guo, J., Yang, J., Song, Y., Yan, W., Liu, S., Luo, J., Zhao, N., Xiao, F., 2025. The impact of surface species
 migration on low-temperature CO₂ methanation over CeZrO_x/Ni catalysts. *Chem. Eng. J.* 522, 167588.
 Han, F., Liu, Q., Kou, B., Ouyang, J., 2025. A novel and facile Cr³⁺-doping strategy remarkably boosting
 low-temperature CO₂ methanation on Ni/sepiolite: Unravelling the nature of the promotional effect.
Int. J. Hydrogen Energy 136, 186-201.
 He, D., Wu, S., Cao, X., Chen, D., Zhang, L., Zhang, Y., Luo, Y., 2024. Dynamic trap of Ni at elevated
 temperature for yielding high-efficiency methane dry reforming catalyst. *Applied Catalysis B:*
Environment and Energy 346, 123728.
 Huang, H., Liu, W., Chen, H., Dang, C., Cai, W., 2025. Dry reforming of methane over Ni/Al₂O₃ catalyst
 derived from partially reduced dendritic layered NiAl₂O₄. *Fuel* 394, 135175.
 Italiano, C., Pino, L., Maccarrone, D., Vita, A., 2025. Enhanced low-temperature activity of CO₂
 methanation: Effect of metal oxide support on the performance of Ni-based catalysts. *Applied Catalysis*
A: General 707, 120529.
 Ju, Y., Bae, D., Park, J., Choi, H.W., Kang, J., Ryu, K.-H., Kim, Y.J., Kim, M., Kang, S.B., 2025. Role of
 electronic modulation of Ni-Pr bimetallic catalyst for low-temperature CO₂ methanation. *Applied*
Catalysis B: Environment and Energy 379, 125675.
 Kim, H.-J., Mori, K., Ichikawa, S., Nakano, T., Yamashita, H., 2025. Layered Na₂Ti₃O₇-supported Ru
 catalyst for ambient CO₂ methanation. *Nature Communications* 16, 2697.
 Kim, P., Kim, Y., Kim, H., Song, I.K., Yi, J., 2004. Synthesis and characterization of mesoporous alumina
 with nickel incorporated for use in the partial oxidation of methane into synthesis gas. *Applied Catalysis*
A: General 272, 157-166.
 Kizil, A., Osmanaga, S., Onal, I., Ipek, B., 2025. Effect of La₂O₃ and CeO₂ promoters on the CO₂
 methanation activity of mesoporous Ni/BEA, Ni/ZSM-5 and Ni/US-Y and optimum hydrophobicity for Ni-
 CeO₂/BEA. *Microporous Mesoporous Mater.* 396, 113737.
 Lee, J., Waterhouse, G.I.N., Mao, Y., Wang, Z., Zhu, E., Low, J., Chai, S.-P., Tan, L.-L., 2025. Lead-free
 halide perovskites and Bi-BTC frameworks: Engineering S-scheme heterojunctions for photocatalytic
 CO₂ conversion. *Applied Catalysis B: Environment and Energy* 365, 124942.
 Li, L., Wu, X., Cai, H., Yang, J., Zhu, J., Li, G., Hu, C., 2025a. Enhanced CO₂ methanation performance of
 Ni-ZrO₂ catalysts: A comparative study of phase-dependent activity and mechanism. *Chem. Eng. J.* 519,
 165036.
 Li, Y., Yang, Y., Huang, Z., Zhou, H., Zeng, R., Lin, X., Ma, X., Wang, L., Xiang, S., Zhang, Z., 2025b. Oxygen-
 vacancy-rich Ni/CeO₂: UiO-66-derived high-efficiency catalyst for low-temperature CO₂ methanation.
Chem. Eng. J. 511, 162073.
 Li, Z., He, Z., He, Y., Lai, H., Qi, X., Zhao, Z., Jin, T., 2022. ZnSe/Ta₂O₅ heterojunction with high carrier
 separation efficiency: Experimental and theoretical calculations. *Applied Surface Science* 593, 153456.
 Li, Z., Liu, Y., Zhang, A., Liu, Q., Shen, C., Wu, F., Xu, C., Chen, M., Fu, H., Zhou, C., 2019. Quasi-two-
 dimensional β-Ga₂O₃ field effect transistors with large drain current density and low contact resistance
 via controlled formation of interfacial oxygen vacancies. *Nano Res.* 12, 143-148.

546 Lim, D.-H., Maitlo, H.A., Younis, S.A., Boukhvalov, D.W., Kim, K.-H., Lee, J., 2026. Platinum/nitrogen-co-
 547 doped TiO₂ as photocatalyst and light-free catalytic adsorbent for gaseous formaldehyde. *J. Colloid*
 548 *Interface Sci.* 702, 138895.
 549 Lin, S., Gong, L., Zhao, N., Zhao, H., Zhao, F., Bai, Y., Li, Z., Liu, W., 2024. Tailoring metal-support
 550 interactions via spatial confinement of Ni/CeO₂ interfaces on h-BN for efficient CO₂ methanation.
 551 *Chem. Eng. J.* 494, 152937.
 552 Liu, L., Ahmadi, Y., Kim, Y.-H., Kim, K.-H., 2026. Advances in morphological and interfacial tuning of metal
 553 oxides for electrochemical CO₂ conversion. *Prog. Mater. Sci.* 155, 101522.
 554 Liu, M., Zou, R., Liu, C.-j., 2025a. Improvement in the activity of Ru/ZrO₂ for CO₂ methanation by the
 555 enhanced hydrophilicity of zirconia. *Applied Catalysis B: Environment and Energy* 360, 124549.
 556 Liu, N., Peng, Z., Sun, J., Tian, Y., Mei, L., Lv, G., He, R., Cabot, A., Zhang, J., 2025b. Enhanced
 557 Performance and Durability of Zinc–Air Batteries Utilizing W-Doped Cobalt Pentlandite Catalysts. *Adv.*
 558 *Funct. Mater.* 35, 2419515.
 559 Liu, X., Zhou, K., Wang, L., Wang, B., Li, Y., 2009. Oxygen Vacancy Clusters Promoting Reducibility and
 560 Activity of Ceria Nanorods. *J. Am. Chem. Soc.* 131, 3140-3141.
 561 Ma, J., Jiang, Q., Li, S., Chu, W., Qian, H., Perathoner, S., Centi, G., Liu, Y., 2024. High-dispersed CeO_x
 562 species on mesopores silica to accelerate Ni-catalysed CO₂ methanation at low temperatures. *Chem.*
 563 *Eng. J.* 479, 147453.
 564 Maitlo, H.A., Younis, S.A., Kim, K.-H., Yue, W., Lu, Z., Lim, D.-H., 2025a. Mechanism, Performance, and
 565 Application of g-C₃N₅-Coupled TiO₂ as an S-Scheme Heterojunction Photocatalyst for the Abatement of
 566 Gaseous Benzene. *ACS Appl. Mater. Interfaces* 17, 4711-4727.
 567 Maitlo, H.A., Younis, S.A., Lee, C.S., Kim, K.-H., 2025b. Progress in heterostructures for
 568 photoelectrocatalytic reduction of carbon dioxide into fuels and value-added products. *Adv. Colloid*
 569 *Interface Sci.* 341, 103483.
 570 Onrubia-Calvo, J.A., López-Rodríguez, S., Villar-García, I.J., Pérez-Dieste, V., Bueno-López, A., González-
 571 Velasco, J.R., 2024. Molecular elucidation of CO₂ methanation over a highly active, selective and stable
 572 LaNiO₃/CeO₂-derived catalyst by in situ FTIR and NAP-XPS. *Appl. Catal. B: Environ.* 342, 123367.
 573 Overa, S., Ko, B.H., Zhao, Y., Jiao, F., 2022. Electrochemical Approaches for CO₂ Conversion to Chemicals:
 574 A Journey toward Practical Applications. *Acc. Chem. Res.* 55, 638-648.
 575 Pham-Ngoc, N., Jamsaz, A., Lee, Y., Oh, E.-S., Shin, E.W., 2025. Homogeneous formation of a disordered
 576 NiAl₂O₄ structure in three-dimensional macroporous Ni/Al₂O₃ catalysts for dry reforming of methane
 577 and coke-resistant catalytic behavior on its Ni-oxygen vacancy interface. *Chem. Eng. J.* 510, 161545.
 578 Qiang, D., Mei, T., Liu, Y., Jin, H., Ye, Z., Li, Z., Zhao, S., 2025. Enhanced low-temperature activity for CO₂
 579 methanation over N-doped NiMn-LDO. *Chem. Eng. J.* 507, 160839.
 580 Razavi, S.A., Fargas, G., Serrano, I., Laguna-Bercero, M.Á., Vilella, T., Llanes, L., Rodríguez, D., Ginebra,
 581 M.-P., Llorca, J., Morales, M., 2025. 3D-printed Ni/γ-Al₂O₃ catalysts for CO₂ methanation: Effect of Ni
 582 loading and sintering temperature. *Chem. Eng. J.* 523, 168665.
 583 Tian, J., Zheng, P., Zhang, T., Han, Z., Xu, W., Gu, F., Wang, F., Zhang, Z., Zhong, Z., Su, F., Xu, G., 2023.
 584 CO₂ methanation over Ni nanoparticles inversely loaded with CeO₂ and Cr₂O₃: Catalytic functions of
 585 metal oxide/Ni interfaces. *Appl. Catal. B: Environ.* 339, 123121.
 586 Ullah, S., Ahmed, S.M., Huang, T., Pan, Y., Yu, Z., Xue, Q., Ye, R., Wang, Z., Kawi, S., Wang, Y., Luo, G.,
 587 2025. Tailoring Ni/CeO₂ oxygen vacancies and metal dispersion via microfluidic synthesis techniques for
 588 enhanced low-temperature CO₂ methanation. *Chem. Eng. J.* 515, 163859.
 589 Wang, C., Lu, Y., Zhang, Y., Fu, H., Sun, S., Li, F., Duan, Z., Liu, Z., Wu, C., Wang, Y., Sun, H., Yan, Z., 2023.
 590 Ru-based catalysts for efficient CO₂ methanation: Synergistic catalysis between oxygen vacancies and
 591 basic sites. *Nano Res.* 16, 12153-12164.

592 Wang, F., He, S., Chen, H., Wang, B., Zheng, L., Wei, M., Evans, D.G., Duan, X., 2016. Active Site
 593 Dependent Reaction Mechanism over Ru/CeO₂ Catalyst toward CO₂ Methanation. *J. Am. Chem. Soc.*
 594 138, 6298-6305.
 595 Wang, K., He, X., Liang, X., 2024. Ni–MgO catalyst prepared by a sol-gel method for low temperature
 596 CO₂ methanation. *Int. J. Hydrogen Energy* 66, 195-207.
 597 Wang, Y., Zhang, Y., Guo, X., Meng, T., Guo, Q., 2025. CO₂ methanation over Eu₂O₃ promoted Ni/ γ -
 598 Al₂O₃ catalyst: The role of Eu₂O₃ and the reaction pathway. *Chem. Eng. J.* 525, 169874.
 599 Ye, Q., Li, S., Liao, Y., Wang, Y., He, Y., Chen, J., Xu, J., Su, Q., Cui, X., 2024a. Ce enhanced RuNi alloy
 600 multi-metal synergic hydrotalcite oxide derived catalyst for high performance CO₂ methanation. *Chem.*
 601 *Eng. J.* 486, 150426.
 602 Ye, R., Ma, L., Hong, X., Reina, T.R., Luo, W., Kang, L., Feng, G., Zhang, R., Fan, M., Zhang, R., Liu, J.,
 603 2024b. Boosting Low-Temperature CO₂ Hydrogenation over Ni-based Catalysts by Tuning Strong Metal-
 604 Support Interactions. *Angew. Chem. Int. Ed.* 63, e202317669.
 605 Yin, S.-n., Zhao, J., Wu, S., Han, X., Ren, J., 2025. Fabrication of highly efficient Ni/Al₂O₃ catalysts for the
 606 CO₂ methanation reaction using atomic layer deposition technology. *Chem. Eng. J.* 504, 158723.
 607 Zeng, L., Liu, F., Zhao, T., Cao, J., 2021. Superior ZSM-5/ γ -Al₂O₃ Composite Catalyst for Methanol and
 608 Ethanol Coconversion to Light Olefins. *ACS Omega* 6, 19067-19075.
 609 Zhang, M., Lu, X., Qu, Y., He, C., Dong, J., Luo, K., Ye, J., Lu, N., Niu, Q., Zhang, P., Dai, S., 2024a. Ba²⁺
 610 doping into Ni/Al₂O₃ nanofibers promotes CO₂ methanation via alkaline modulation. *Chem. Eng. J.* 497,
 611 154872.
 612 Zhang, M., Ye, J., Qu, Y., Lu, X., Luo, K., Dong, J., Lu, N., Niu, Q., Zhang, P., Dai, S., 2024b. Highly Stable
 613 and Selective Ni/ZrO₂ Nanofiber Catalysts for Efficient CO₂ Methanation. *ACS Appl. Mater. Interfaces*
 614 16, 34936-34946.
 615 Zhang, T., Zheng, P., Gao, J., Han, Z., Gu, F., Xu, W., Wang, F., Zhu, T., Xu, G., Zhong, Z., Su, F., 2024c. Self-
 616 dispersed bimetallic NiRu nanoparticles on CeO₂ for CO₂ methanation. *Chem. Eng. J.* 481, 148548.
 617 Zhang, Y., Lu, J., Zhang, L., Fu, T., Zhang, J., Zhu, X., Gao, X., He, D., Luo, Y., Dionysiou, D.D., Zhu, W.,
 618 2022. Investigation into the catalytic roles of oxygen vacancies during gaseous styrene degradation
 619 process via CeO₂ catalysts with four different morphologies. *Appl. Catal. B: Environ.* 309, 121249.
 620 Zhang, Y., Si, J., Chen, Z., Zhao, L., Qiu, F., Li, W., Zhang, W., Miao, S., 2025. High Crystalline MxSby
 621 (M=Fe, Co, and Ni) Nanocrystals Tuned by Antimony for Boosting Overall Water Splitting Catalysis.
 622 *Advanced Energy Materials* 15, 2405275.
 623 Zhao, Y., Zhan, J., Hu, R., Luo, G., Fan, J., Clark, J.H., Zhang, S., 2024. Water-assisted catalytic transfer
 624 hydrogenation of guaiacol to cyclohexanol over Ru/NiAl₂O₄. *Chem. Eng. J.* 485, 149934.

625 **Tables**

626 **Table 1.** Detailed mass composition and sample codes for Ni-doped γ -Al₂O₃ composite catalysts (A_xN_y) prepared for CO₂ methanation
627 reaction^{A]}.

Order	Sample code	Mass (mg)					M/A mass ratio	N/A mass ratio
		Metal oxide	Dopant		Treatment			
		γ -Al ₂ O ₃ [A]	Ni(NO ₃) ₂ ·6H ₂ O as a Ni precursor	Ni (N)	C ₂ H ₂ O ₄ (first) ^{B]}	(NH ₄) ₂ CO ₃ (second) ^{C]}	%	%
1	A	1000	0	0	0	0	0	0
[II] 20% Ni-Doped γ -Al ₂ O ₃ composites synthesized with varying (NH ₄) ₂ CO ₃ concentrations								
2	A ₀ N ₂₀	1000	975	200.42	0	0	0	20
3	A ₁₀ N ₂₀	1000	975	200.42	89	100	10	20
4	A ₂₀ N ₂₀	1000	975	200.42	89	200	20	20
5	A ₅₀ N ₂₀	1000	975	200.42	89	500	50	20
[III] γ -Al ₂ O ₃ composites with varying Ni doping levels (treated with 50% (NH ₄) ₂ CO ₃ template)								
6	A ₅₀ N ₅	1000	244	50.16	89	500	50	5
7	A ₅₀ N ₁₀	1000	488	100.31	89	500	50	10
8	A ₅₀ N ₂₀	1000	975	200.42	89	500	50	20
9	A ₅₀ N ₃₀	1000	1460	300.12	89	500	50	30

628 **A]** The final product is named as A_xN_y, where x = level of second (ammonium carbonate) treatment and y = level of Ni doping.

629 **B]** The γ -Al₂O₃ is treated first by C₂H₂O₄ to increase dispersion (peptization) and enhance the reactivity of the alumina for the subsequent treatment.

630 **C]** It is then treated by (NH₄)₂CO₃ to create oxygen vacancies (OVs) and enhance the surface basicity of the product to help doping.

631

632 **Table 2.** Summary of CRM performance of prepared catalysts under diverse operating reaction conditions.

633

S. No	Materials	CO ₂ C _{in} (%)	H ₂ /CO ₂ ratio	RH (%)	WHSV (L g ⁻¹ h ⁻¹)	Temp (C)	X _{CO2} (%)	Y _{CH4} (%)	S _{CH4} (%)	r _{CH4} (mmol g ⁻¹ h ⁻¹)
Catalysts										
1	Al ₂ O ₃	1	4	0	60	400	2.4	0.0	0.0	0.0
2	A ₀ N ₂₀						41.8	48.8	87.1	12.6
3	A ₁₀ N ₂₀						58.8	62.2	93.2	15.3
4	A ₂₀ N ₂₀						68.3	77.9	98.6	20.0
5	A ₅₀ N ₅						41.1	41.6	73.7	11.2
6	A ₅₀ N ₁₀						45.8	51.0	85.7	13.8
7	A ₅₀ N ₂₀						67.1	65.7	95.2	16.2
8	A ₅₀ N ₃₀						41.7	46.0	87.0	11.1
Effects of H ₂										
9	A ₅₀ N ₂₀	1	4	0	60	400	67.1	65.9	95.2	16.3
10			6				68.7	34.0	88.8	8.1
11			8				75.1	67.2	94.4	17.0
12			10				92.1	82.8	98.5	19.9
Effects of RH										
13	A ₅₀ N ₂₀	1	10	0	60	400	92.1	82.8	98.5	19.9
14				10			79.9	26.7	92.3	6.7
15				20			57.1	22.2	79.3	5.1
16				30			53.4	43.5	84.8	11.4

634

635 **Table 3.** Performance comparison between A₅₀N₂₀ and other catalysts employed for CMR.

Order	Catalysts	Cat. mass	GHSV	H ₂ /CO ₂	Temp	X _{CO2}	S _{CH4}	TOF	References
		(mg)	(L g ⁻¹ h ⁻¹)	(%)	(°C)	(%)	(%)	(s ⁻¹)	
1	Ni/Al ₂ O ₃	150	24	4	275	25.5	-	~0.015	(Wang et al., 2025)
2	5Eu-Ni/Al ₂ O ₃	150	24	4	275	80.8	-	~0.05	(Wang et al., 2025)
3	25Ni/20CeO ₂ -55ZrO ₂	100	30	4	250	72.53	-	0.09	(Italiano et al., 2025)
4	25Ni/20Y ₂ O ₃ -55ZrO ₂	100	30	4	250	45.55	-	0.06	(Italiano et al., 2025)
5	25Ni/20CeO ₂ -55Y ₂ O ₃	100	30	4	250	37.66	-	0.07	(Italiano et al., 2025)
6	25Ni/20ZrO ₂ -55Y ₂ O ₃	100	30	4	250	27.97	-	0.05	(Italiano et al., 2025)
7	15Ni/CeO ₂ -U	100	30	4	200	77.1	98.7	0.06	(Li et al., 2025b)
8	Ni/Na ⁺ -BEA	100	12.5	4	250	3	94	0.005	(Kizil et al., 2025)
9	Ni-La ₂ O ₃ /Na ⁺ -BEA	100	12.5	4	250	30	99	0.12	(Kizil et al., 2025)
10	Ni-CeO ₂ /Na ⁺ -BEA	100	12.5	4	250	30	99	0.09	(Kizil et al., 2025)
11	Ni/Sep	100	30	4	400	75.3	97.6	0.0013*	(Han et al., 2025)
12	Ni-Ce/Sep	100	30	4	350	84.6	99.5	0.0035*	(Han et al., 2025)
13	Ni-CeCr _{0.1} /Sep	100	30	4	350	89.8	99.9	0.0055*	(Han et al., 2025)
14	A ₅₀ N ₂₀	50	60	4	400	67.1	95.2	0.18	This work
15	A ₅₀ N ₂₀	50	60	10	400	92.1	98.5	0.25	

636 *TOF values computed based on the X_{CO2} at 150°C.

637

638

Figures

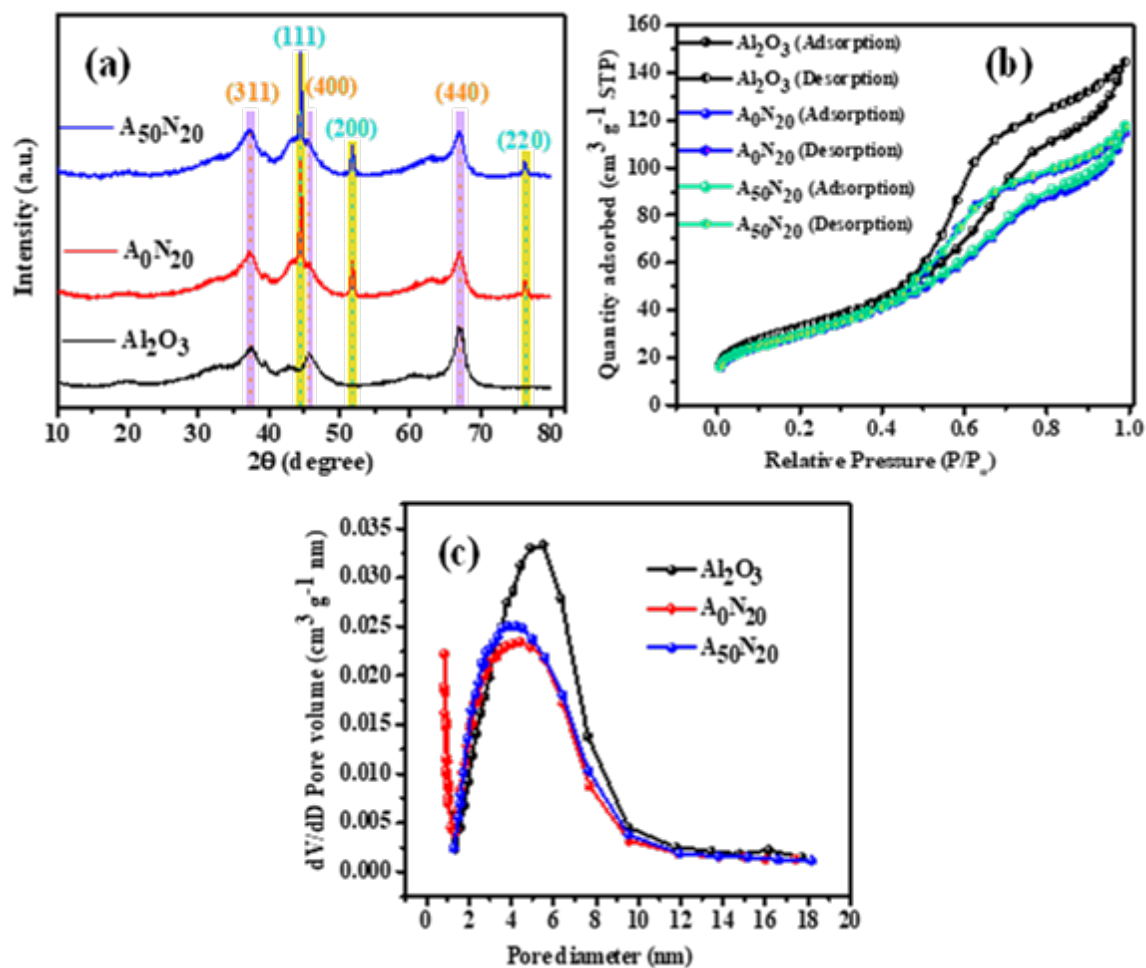


Figure 1. Crystalline and surface textural properties of $A_{50}N_{20}$ composite catalyst and its reference catalysts (i.e., A_0N_{20} and $\gamma-Al_2O_3$): (a) XRD patterns, (b) N_2 adsorption-desorption isotherms, and (c) pore size distributions.

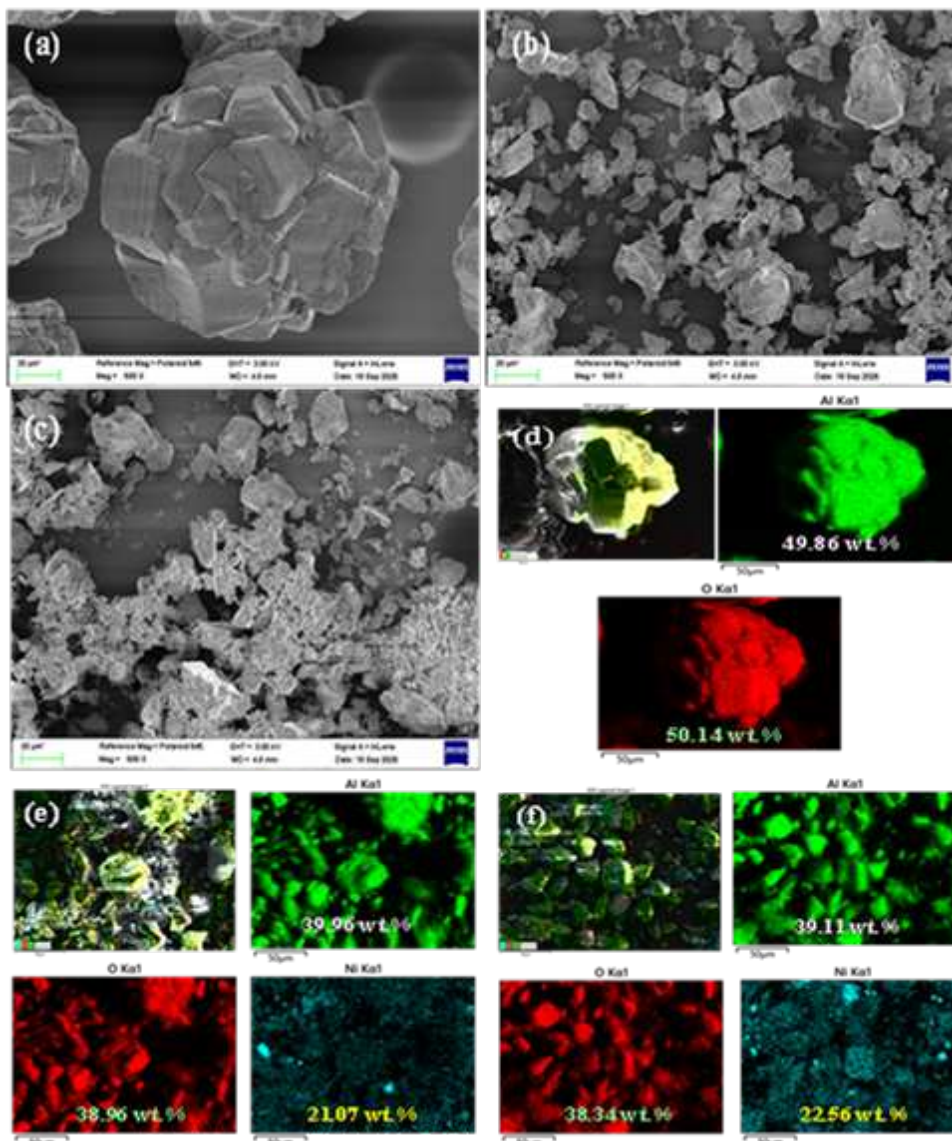
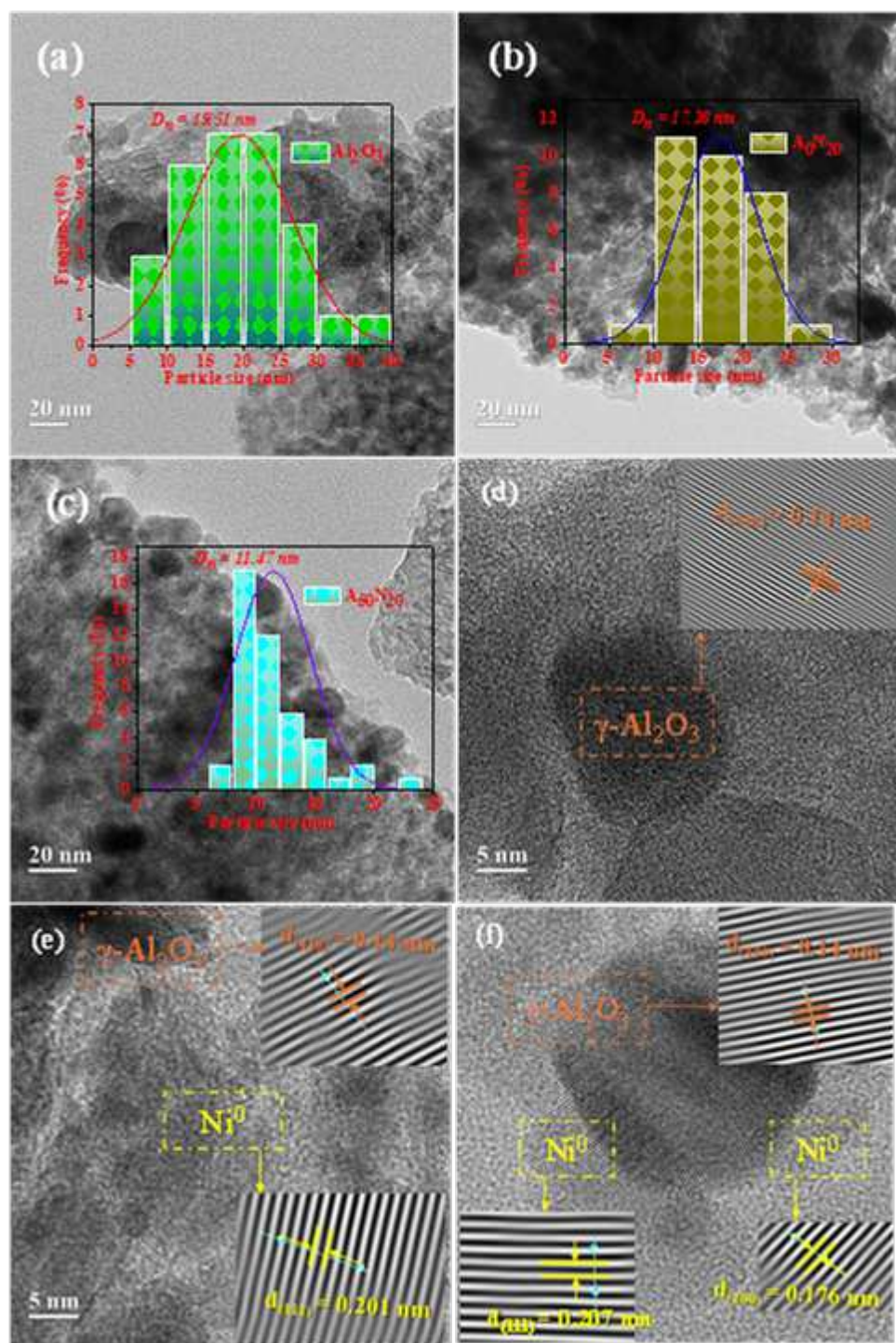


Figure 2. Surface morphology and elemental mapping of $A_{50}N_{20}$ composite catalyst and its reference catalysts (i.e., A_0N_{20} and $\gamma\text{-Al}_2\text{O}_3$): (a and d) SEM and EDS mapping of $\gamma\text{-Al}_2\text{O}_3$, (b and e) SEM and EDS mapping of A_0N_{20} , and (c and f) SEM and EDS mapping of $A_{50}N_{20}$.



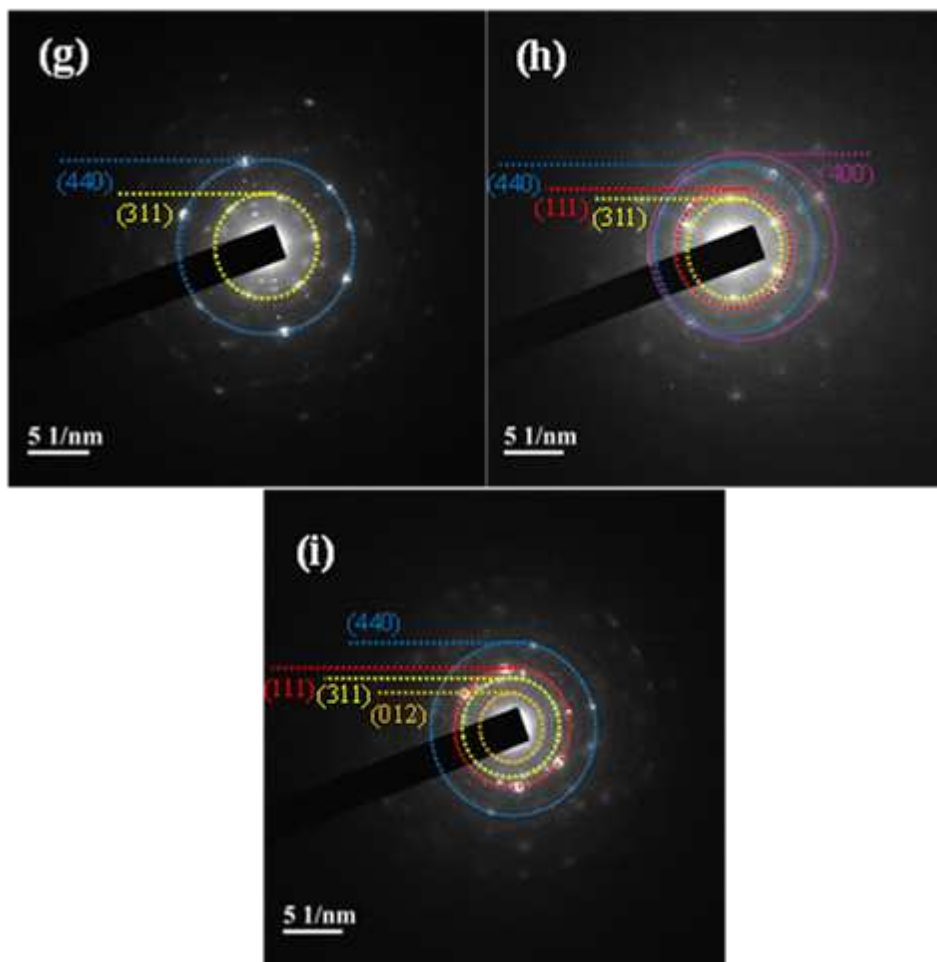


Figure 3. Crystallographic structure and particle dispersion of A₅₀N₂₀ composite catalyst and its reference catalysts (i.e., A₀N₂₀ and γ -Al₂O₃): (a, d, and g) TEM, RH-TEM with IFT, and SAED of γ -Al₂O₃, (b, e, and h) TEM, RH-TEM with IFT, and SAED of A₀N₂₀, and (c, f, and i) TEM, RH-TEM with IFT, and SAED of A₅₀N₂₀.

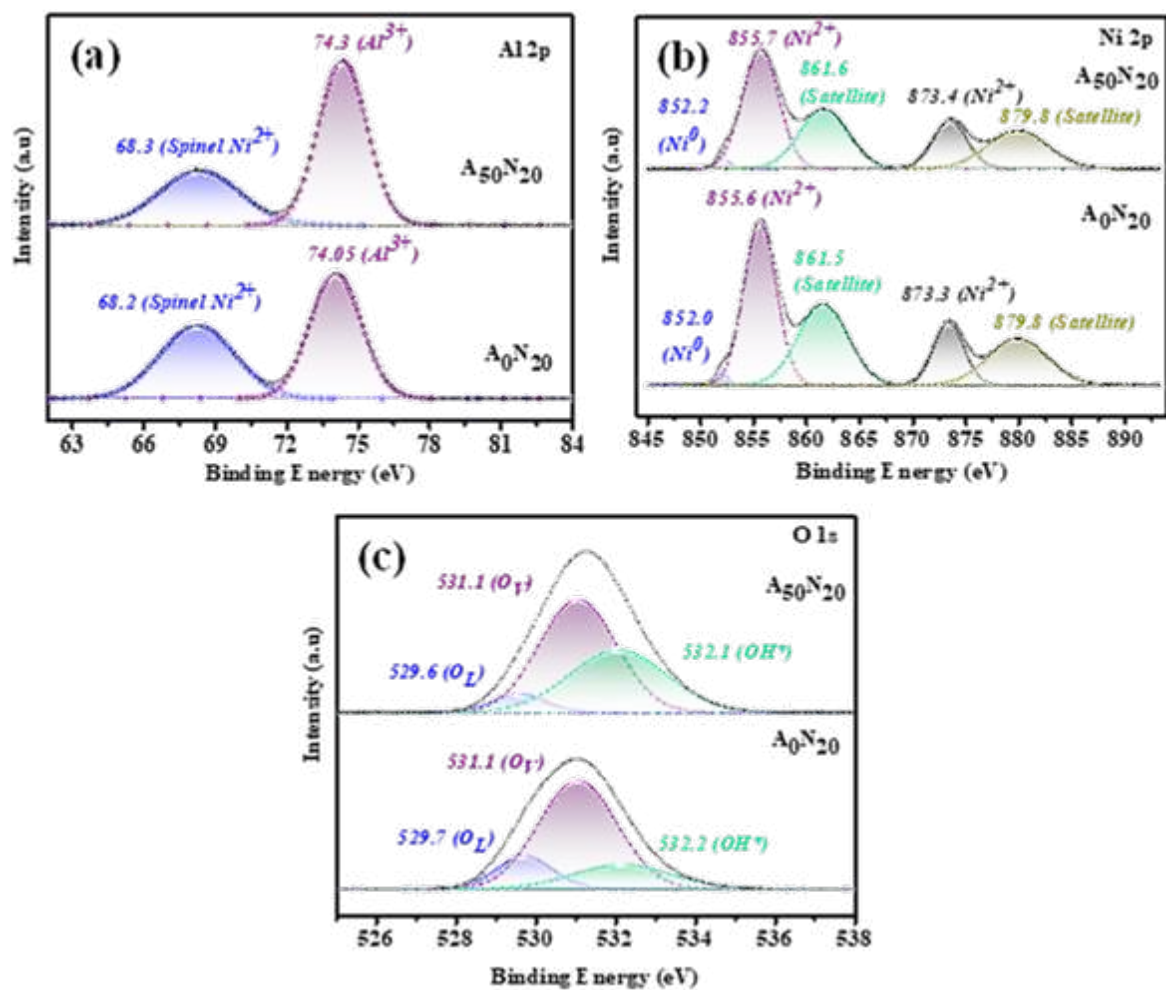


Figure 4. Chemical bonding states of $A_{50}N_{20}$ composite catalyst and its reference catalyst (i.e., A_0N_{20}): (a) Al 2p, (b) Ni 2p, and (c) O 1s spectra.

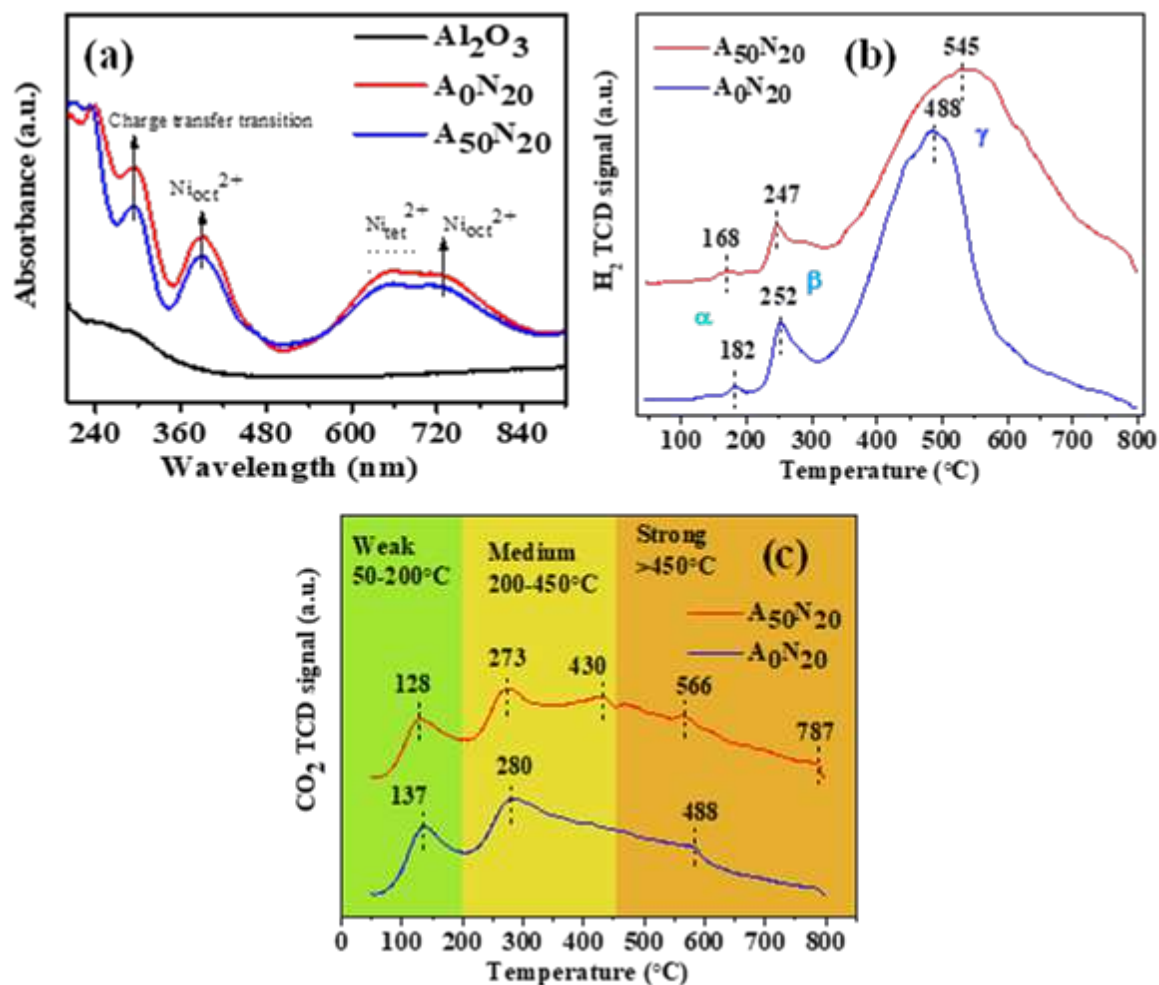


Figure 5. Optical and surface acid-base properties of $A_{50}N_{20}$ composite catalyst and its reference catalyst (i.e., A_0N_{20}): (a) UV-vis DRS spectra, (b) H_2 -TPR, and (c) CO_2 -TPD.

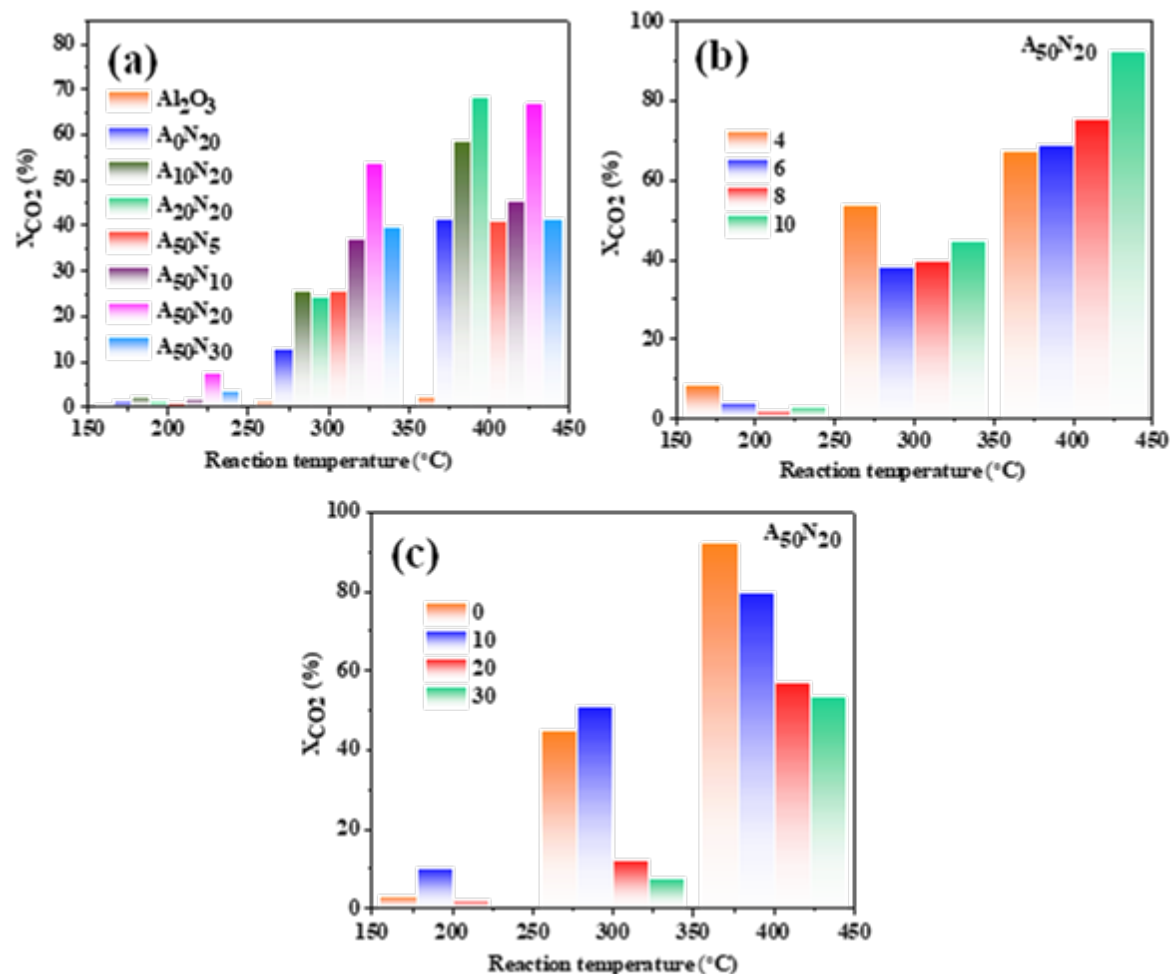


Figure 6. The effects of process variables on CO₂ methanation performance of prepared catalysts across a multi-isothermal temperature ramp from 250°C to 400°C at WHSV of 60 L g⁻¹ h⁻¹: (a) A₅₀N₂₀ and its reference, (b) A₅₀N₂₀ with different H₂/CO₂ ratio, and (c) A₅₀N₂₀ with different RH levels.

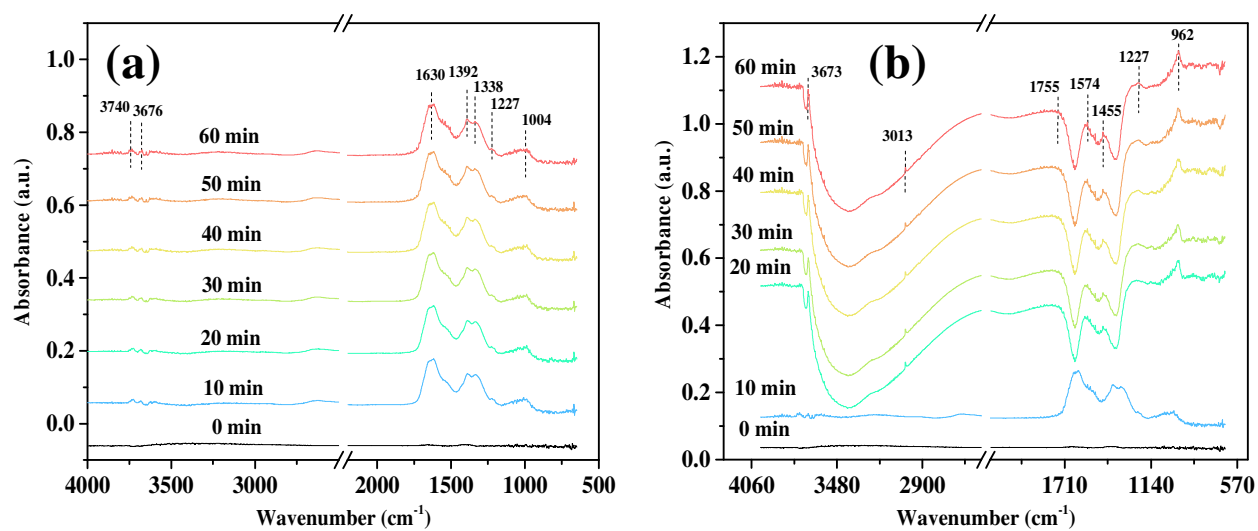


Figure 7. In-situ DRIFTS spectra of A₅₀N₂₀ catalyst for CMR: (a) CO₂ adsorption at 25°C and (b) CO₂ methanation at 400°C.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [260607SupplementaryInformation.docx](#)