



Sustainable hydrogen production via methane decomposition using Fe—Ni bimetallic catalysts

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ABSTRACT

Catalytic decomposition of methane (CDM) is emerging as an efficient, greenhouse gas emission-free path for hydrogen production. This study demonstrates the notable performance of bimetallic Fe—Ni catalysts in CDM. Incorporating nickel into an iron-based catalyst significantly enhances methane conversion and hydrogen yield, with the benefit of producing valuable carbon nanotubes (CNT) as a byproduct. The 40Fe—5Ni catalyst exhibits remarkable performance with 86 % methane conversion. A kinetic model is proposed; the removal of the first hydrogen atom from methane is the rate-determining step following its molecular adsorption on the catalyst surface. Additionally, catalyst deactivation is observed to follow first-order kinetics, with progressive accumulation of carbon deposits leading to a decline in catalytic activity over time. Furthermore, systematic DFT calculations reveal that Fe—Ni alloying shifts the d-band center, strengthening intermediate adsorption and enhancing methane decomposition for efficient hydrogen production. Overall, Fe—Ni bimetallic catalysts emerge as a cost-effective, scalable solution for sustainable hydrogen production, enabling carbon-neutral energy from methane.

1. Introduction

The global push toward carbon neutrality has evolved the search for clean and sustainable energy sources [1,2]. Among these, hydrogen has emerged as a pivotal player due to its versatility and environmental benefits [3–8]. Producing pure hydrogen from hydrocarbons, particularly methane, holds significant practical importance given global abundance and low cost, and serves as a highly attractive feedstock [9–12]. Simultaneous hydrogen and CNT production enhances the economic viability of this process, as CNT possess exceptional electrical, mechanical, and thermal properties that find applications in diverse industries [13–16].

Conventional hydrogen production methods, such as dry reforming (using CO₂), steam reforming (using H₂O), and partial oxidation of methane, yield synthesis gas that requires additional processing to produce relatively pure hydrogen [17,18]. Compared to these hydrogen production methods, CMD offers a significant environmental advantage

due to its near-zero direct CO₂ emissions. Steam methane reforming (SMR) produces 9–12 kgCO₂ per kgH₂ where as dry reforming, a relatively cleaner alternative, results in 2–3 kgCO₂ per kgH₂ [19]. In contrast, CMD provides a low-carbon pathway, producing hydrogen without direct CO₂ emissions, provided that the valuable CNT is a byproduct. This highlights CMD as a promising route for cleaner hydrogen production, offering a balance between energy efficiency and environmental sustainability.

Transition metals such as Fe, Co, and Ni are highly effective catalysts for CMD due to their partially filled 3d orbitals, which facilitate methane activation [17,20–22]. Although Ni catalyst has shown prominent activity, Fe stands out for industrial scale applications due to its cost-effectiveness, environmental sustainability, and high resistance to deactivation at elevated temperatures [23–30]. Operating in the 700–950 °C range, iron-based catalysts achieve excellent thermodynamic conversions while offering stability against carbon coking and poisoning [31,32]. This property enables iron catalysts to achieve a

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balanced rate of hydrogen production and carbon deposition, extending their longevity and effectiveness. Additionally, carbon produced using iron-based catalysts is free from hazardous metals, making it safe for commercial applications and long-term storage [33–36]. However, monometallic iron catalysts encounter limitations in methane conversion and CNT graphitization [20,37]. To overcome these challenges, bimetallic Fe–Ni catalysts have been identified as a promising alternative, using the ability of Ni to enhance the conversion and CNT quality while maintaining cost-effectiveness [38]. Recent studies have emphasised the significant potential of bimetallic Fe–Ni catalysts in enhancing methane decomposition and CNT synthesis. Wang et al. reported that Fe–Ni alloys significantly improve catalytic lifespan and carbon yield, positioning them as a promising approach for optimizing methane decomposition [39]. Similarly, Zhang et al. observed that Ni–Fe/AC catalysts, compared to Ni–Co/AC catalysts, exhibited lower surface area and pore volume but demonstrated greater mesoporosity at identical metal loadings. This increased mesoporosity, combined with the incorporation of iron, significantly enhanced catalytic stability. The addition of Fe not only improved the stability of Ni/AC catalysts more effectively than Co but also altered the morphology of carbon deposits, promoting the formation of carbon fibers on Ni–Fe/AC instead of the encapsulated carbon seen on Ni/AC and Ni–Co/AC catalysts [40]. Huang et al. found the superior catalytic performance of alloy catalysts in carbon yield, with the trend $\text{Ni}_{2.7}\text{Fe}_{0.3}\text{Al} > \text{Ni}_{2.7}\text{Co}_{0.3}\text{Al} > \text{Ni}_3\text{Al}$. This finding emphasizes the advantages of alloying Fe or Co with Ni–Al, which not only increases carbon yield but also extends catalytic lifespan, underscoring the synergistic effects of these metals [41]. Further, Liu et al. observed that Ni–Fe catalysts achieved the highest carbon nanomaterial (CNMs) yield of 44.4 wt%, outperforming monometallic Fe (30.0 wt%) and Ni (18.2 wt%) [42]. This superior performance was ascribed to metal-support interaction and synergistic effects between Ni and Fe, which promoted CNM production. Collectively, these findings highlight the remarkable potential of bimetallic Fe–Ni catalysts in optimizing methane decomposition processes, improving hydrogen production, and enhancing the yield and quality of carbon nanomaterials.

While significant progress has been made in CMD, several gaps persist, particularly in the development and application of Fe–Ni bimetallic catalysts. Most studies on CMD have predominantly focused on Ni-based bimetallic catalysts, offering limited insight into the synergistic effects within bimetallic systems like Fe–Ni. The role of Ni incorporation in enhancing methane conversion, hydrogen yield, and CNT graphitization on Fe-based catalysts remains limited. Further, investigating its kinetic parameters becomes fundamentally important to propose a mechanism involving the stepwise dehydrogenation of surface species after the direct dissociative adsorption of methane. [43,44]. The Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetic modelling, combined with deactivation analysis, provides deeper insights into the reaction mechanisms, with particular emphasis on the influence of nickel loading on hydrogen production and the quality of the resulting CNT. Further, the DFT analysis of the Fe-based bimetallic system provides deeper insights into the role of Ni incorporation and its impact on the behaviour and performance of Fe-based catalysts. This study aims to describe the synergistic effects of Fe–Ni catalysts, paving the way for more efficient, cost-effective, and sustainable technologies for large-scale methane decomposition.

2. Methodology

2.1. Catalyst preparation

The catalysts were synthesized using the wet impregnation method, a process that ensures uniform dispersion of metal salts onto the support material. Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were purchased from Merck, Germany. The spherical alumina support (100–150 mesh size) was provided by

Sasol, Germany. These metal salts and alumina were mixed in distilled water and stirred for 2 h to ensure thorough mixing. After stirring, the slurry was dried in an oven at 120 °C for 12 h. The calcination process was conducted at 750 °C, with a temperature ramp rate of 3 °C per minute for 5 h. The calcination process plays a crucial role in stabilizing the catalyst structure and improving its catalytic properties. Once calcined, the catalyst was reduced in situ before each catalytic reaction. The catalyst was initially reduced by heating the reactor to 600 °C and maintaining it at that temperature for 5 h under a hydrogen-nitrogen mixture (1:1 by volume) with a total flow rate of 40 mL/min. This treatment ensures the complete reduction of the catalyst. This reduction process transformed the metal oxides into their active metallic forms, which are essential for promoting the catalytic reaction. All the catalysts were prepared for the experiments, along with their compositions in weight percentage, are summarized in Table 1.

2.2. Catalyst characterization

A variety of advanced characterization techniques were employed to analyse the catalysts and the produced CNT. X-ray diffraction (XRD) patterns were obtained using a Rigaku MiniFlex 600 diffractometer at 40 kV and 15 mA, scanning over a 2θ range of 10° to 80° at 4° per minute to examine the crystalline phases of the catalysts and CNT. The external morphologies of the catalysts and CNT were analysed using a JEOL JSM-7800F Prime field-emission scanning electron microscope (FESEM), which offers a spatial resolution of up to 0.5 nm and is equipped with an energy-dispersive X-ray (EDS) mapping capability. Transmission electron microscopy (TEM) provided atomic-level resolution, enabling detailed observation of the metal catalyst structures and CNT growth, shedding light on the metal-carbon interactions and CNT formation mechanisms. Raman spectroscopy, with a 532 nm laser using a Renishaw inVia Qontor microscope, was employed to assess the vibrational modes of the carbon atoms, determining the crystallinity and defect density of the CNT. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 to evaluate the thermal stability of the CNT in an air atmosphere, providing insights into their degradation and structural integrity at elevated temperatures. Temperature-programmed reduction (TPR) was conducted on the calcined catalysts to assess their reducibility. The analysis was carried out using a Micromeritics Chemisorb 2720 (USA). The setup involved heating from room temperature to 900 °C at a rate of 10 °C/min under a 10 % H_2/Ar gas flow (30 mL/min), while monitoring voltage changes at a 1 Hz sampling rate using a thermal conductivity detector.

2.3. Experiment setup

Catalyst evaluation was conducted in a fluidized bed reactor made from Incoloy HT800, selected for its excellent high-temperature properties. The schematic representation of the CMD experimental setup is shown in Fig. 1. The reactor used in this study was made of a nickel, iron, and chromium alloy. This material was selected specifically for its mechanical stability and corrosion resistance at the reaction temperature of 700 °C. The reactor featured an inner diameter of 12.7 mm and a length of 80 cm, designed to ensure optimal gas-solid interactions during the

Table 1
Composition of Fe–Ni bimetallic catalysts supported on Al_2O_3 . The metal loadings (Fe and Ni) are expressed in weight percent (wt%) relative to the total catalyst mass, with the balance being Al_2O_3 .

S.No	Catalyst	Fe (wt%)	Ni (wt%)
1	30Fe–5Ni/ Al_2O_3	30	5
2	30Fe–10Ni/ Al_2O_3	30	10
3	40Fe–5Ni/ Al_2O_3	40	5
4	40Fe–10Ni/ Al_2O_3	40	10
5	50Fe–5Ni/ Al_2O_3	50	5
6	50Fe–10Ni/ Al_2O_3	50	10

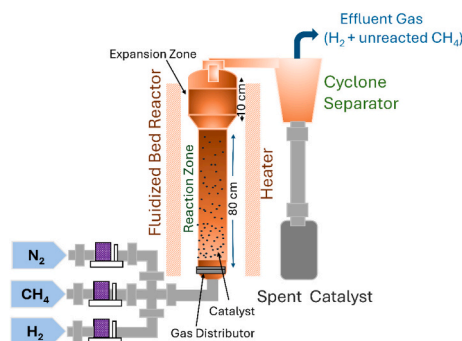


Fig. 1. Schematic representation of the CMD experimental setup. The system comprises a vertical fluidized-bed reactor and a downstream gas-solid separator. The gaseous products are directed to a gas analysis unit (not shown in the schematic), while the solid carbon product is collected at the bottom. This setup allows for the continuous evaluation of catalyst performance and hydrogen production.

reaction. To maintain a stable reaction environment, the reactor was equipped with a 10 cm expansion zone, which had an inner diameter of 25.4 mm. This expansion zone allowed for the return of entrained particles to the main reaction zone, preventing catalyst losses and ensuring a consistent flow of material. The reactor was heated by a PID-controlled, electrically heated 3-zone furnace (ATS, USA), which provided precise and uniform temperature control, which is crucial for the catalytic reactions. Temperature monitoring was facilitated by K-type thermocouples placed within thermo-wells in each heating zone, both inside and outside the reactor. These thermocouples ensured accurate temperature readings at various points within the system, which were critical for maintaining the desired reaction conditions and for observing any temperature gradients across the reactor. During the reaction temperature was kept at the desired reaction temperature of 700 °C. To maintain the reaction flow and ensure consistent catalyst performance, a total gas flow rate of 200 mL/min at NTP was maintained. Each experimental run utilized 10 g of catalyst, ensuring an appropriate catalyst-to-gas ratio for optimal reaction kinetics with a gas hourly space velocity (GHSV) of 1200 mL/gcat·h. The product gases were continuously monitored during the reaction using an Agilent 7820 Gas Chromatograph (USA) with a thermal conductivity detector. In this experiment, high-purity argon (Ar) was used as the carrier gas for the GC. This setup provided real-time analysis of the gas composition, allowing for precise tracking of the reaction progress and product yields. The product stream did not contain any detectable CO or CO₂, as confirmed by GC measurements within its detection threshold.

The kinetic parameters were estimated using the Levenberg-Marquardt optimization algorithm [45], as implemented in `scipy.optimize.minimize` [46]. The residuals from the fit were analysed to assess the predictive accuracy of the model. The model achieved a residual sum of squares (RSS) value, indicating a strong agreement between the observed and predicted reaction rates. Further statistical analysis showed that the residuals followed an approximately normal distribution, reinforcing the model's validity. Additionally, the kinetics of deactivation were determined through a linearization method to estimate the deactivation rate (k'_d).

2.4. Computational method

With a periodic slab model, spin-polarized DFT computations were carried out using the Vienna Ab initio Simulation Package (VASP) [47,48]. Kohn-Sham theory was used to account for exchange and correlation using the BEEF-vdW functional [49], while the projector-augmented wave (PAW) method was utilized to describe the interactions between valence electrons and ion cores [50]. The computations used an energy cutoff of 400 eV for the plane waves. With an

energy smearing of 0.2 eV, the Methfessel-Paxton scheme was used to calculate the partial electronic occupancies [51]. A Monkhorst-Pack grid was used to sample the slab model's first Brillouin zone [52].

In this study, slab models were constructed for transition metals, including Fe, Ni, and Fe₃Ni, with the (111) surfaces representing the terrace of the surface. A four-layer slab with a $p(2 \times 2)$ supercell was used to represent the (111) surfaces. The top two metal layers were allowed to relax while the bottom two were fixed throughout geometry optimisation. A vacuum layer of 15 Å was included to prevent periodic interactions between adjacent slabs. The first Brillouin zone of the two slabs was sampled using a $5 \times 5 \times 1$ Monkhorst-Pack grid.

CH₄ conversion and absorption energy are determined using the following equations:

$$CH_4 \text{ Conversion (\%)} = \frac{(CH_{4in} - CH_{4out})}{CH_{4in}} \times 100 \quad (1)$$

Here, CH_{4in} and CH_{4out} represent the moles of methane at the reactor inlet and outlet, respectively.

$$\Delta E^{ad} = \Delta E_{adsorbate+surface} - \Delta E_{surface} - \Delta E_{adsorbate} \quad (2)$$

The first term on the right-hand side ($\Delta E_{adsorbate+surface}$) represents the total energy of the bimetallic Fe—Ni surface with the adsorbate attached, the second term ($\Delta E_{surface}$) corresponds to the total energy of the bare bimetallic Fe—Ni surface, and the final term ($\Delta E_{adsorbate}$) denotes the total energy of the adsorbate in its isolated state.

3. Results and discussion

3.1. Structural characterization

The XRD patterns of all Fe—Ni catalysts (30Fe—5Ni, 30Fe—10Ni, 40Fe—5Ni, 40Fe—10Ni, 50Fe—5Ni, and 50Fe—10Ni) are shown in Fig. 2(a). It is confirmed that hematite (α -Fe₂O₃) is the dominant phase. The diffraction peaks observed at $2\theta = 24.4^\circ, 33.5^\circ, 35.9^\circ, 41.2^\circ, 49.8^\circ, 54.5^\circ, 62.8^\circ, 64.3^\circ$, and 66.8° , correspond to the (012), (104), (110), (113), (204), (116), (214), (300), and (125) planes of Fe₂O₃, consistent with the reference pattern (JCPDS card no. 33-0664). The slight peak shifts upon Ni incorporation can be attributed to substitutional replacement of Fe by Ni in the Fe₂O₃ lattice. Since Ni has a smaller ionic radius than Fe, its incorporation induces lattice contraction, which shifts certain reflections to higher 2θ values (smaller d-spacing) in accordance with Bragg's law [53].

The XRD patterns of the catalysts after the reaction are shown in Fig. 2(b). Notably, a peak at $2\theta = 26.2^\circ$ is observed, corresponding to a graphitic structure, along with a peak at $2\theta = 45^\circ$, indicating deposited carbon [31,54]. The intensity of the graphitic peak at 26.2° is highest for the 40Fe—5Ni catalyst, followed by the 40Fe—10Ni, 30Ni—5Ni, 30Fe—10Ni, 50Fe—5Ni, and 50Fe—10Ni catalysts. This suggests that the degree of graphitization is most noticeable in the 40Fe—5Ni catalyst, implying a more ordered carbon structure with higher crystallinity, which is generally associated with improved material properties. Additionally, weak peaks between $2\theta = 35^\circ$ and 40° are observed, corresponding to the formation of Fe₃C (cementite), a phase frequently detected in Fe-based catalysts during carbon deposition processes. Fe-based catalysts are well-known for their dual role in facilitating the formation of both graphitic carbon and Fe₃C. It is proposed that Fe₃C and α -Fe act as catalytically active species in the methane decomposition process. The subsequent decomposition of Fe₃C into α -Fe and carbon is hypothesized to enhance the production of filamentous carbon, consistent with findings from previous studies [14].

Raman spectroscopy was further performed to assess the structural quality of the CNT synthesized, focusing on key parameters such as the I_D/I_G and I_{2D}/I_G intensity ratios. This spectroscopy effectively studies the vibrational modes of carbon atoms in CNT, influenced by strain due to π -bond misalignment between adjacent carbon atoms. In the high-

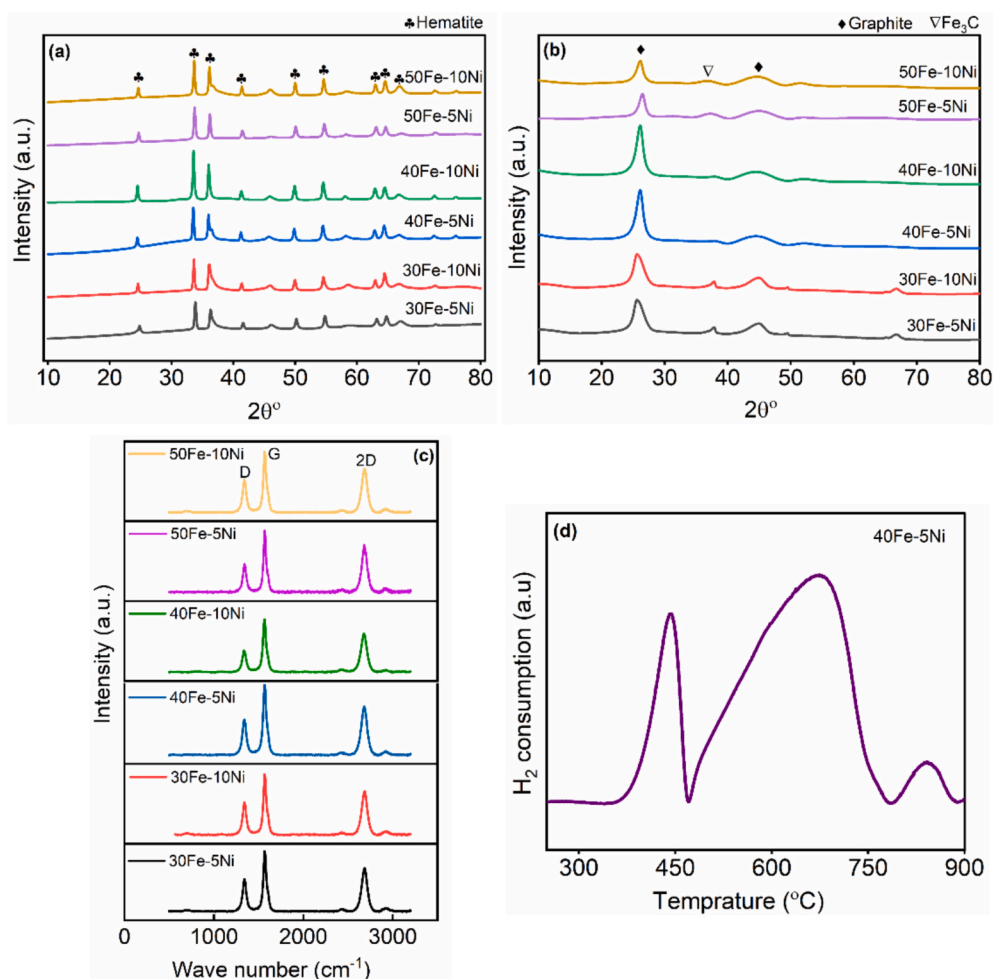


Fig. 2. (a) XRD patterns of fresh Fe-based bimetallic catalysts showing crystalline phases; (b) XRD patterns of spent catalysts after methane decomposition, indicating structural changes and carbon deposition; (c) Raman spectra of spent catalysts, highlighting the nature and degree of carbon species formed during the reaction; (d) H₂-TPR profiles of fresh catalysts, illustrating the reduction behaviour.

frequency region, CNT typically exhibits three characteristic peaks: the G-band, D-band, and 2D-band. The G-band, near 1565 cm^{-1} , corresponds to the in-plane stretching of C—C bonds and signifies ordered, graphitic sp^2 carbon. The D-band, around 1352 cm^{-1} , is associated with lattice defects and structural disorder, arising from disruptions in the sp^2 network. The 2D-band, observed near 2700 cm^{-1} , is the overtone of the D-band and provides insights into the number of graphene layers and stacking order within the CNT [23,55–57]. In this study, the 40Fe–5Ni catalyst demonstrated the best structural quality, with an $I_{\text{D}}/I_{\text{G}}$ ratio of 0.37, as mentioned in Table 2. This was followed by the 40Fe–10Ni catalyst, which exhibited an $I_{\text{D}}/I_{\text{G}}$ ratio of 0.51, while both 50Fe–5Ni and 30Fe–5Ni catalysts showed slightly higher values of 0.52. The 50Fe–10Ni and 30Fe–10Ni catalysts exhibited $I_{\text{D}}/I_{\text{G}}$ ratios of 0.53 and 0.56, respectively. This indicates an overall lower defect density and improved crystallinity in the graphitic domains produced from all

Table 2

Raman intensity ratios ($I_{\text{D}}/I_{\text{G}}$, $I_{2\text{D}}/I_{\text{G}}$) and carbon yield of the catalysts after the complete deactivation of the catalysts.

Catalyst	$I_{\text{D}}/I_{\text{G}}$	$I_{2\text{D}}/I_{\text{G}}$	Carbon Yield (gC/gMetal)
30Fe-5Ni	0.52	0.72	1.47
30Fe-10Ni	0.56	0.75	1.36
40Fe-5Ni	0.37	0.69	5.80
40Fe-10Ni	0.51	0.71	2.70
50Fe-5Ni	0.52	0.71	1.56
50Fe-10Ni	0.53	0.72	1.44

catalysts, as reported in Table 2 and illustrated in Fig. 2(c). Furthermore, the $I_{2\text{D}}/I_{\text{G}}$ ratio, which reflects the number of graphitic layers, indicated superior structural quality for the 40Fe–5Ni catalyst, with a value of 0.69 (Table 2), followed by 40Fe–10Ni, 50Fe–5Ni, 30Fe–5Ni, 50Fe–10Ni, and 30Fe–10Ni, suggesting the formation of multi-layered CNT [58].

The CNT yield, presented in Table 2, shows that the 40Fe–5Ni catalyst achieved the highest yield of 5.80 gC/gMetal which is significantly higher than the other catalysts. This enhanced performance may be correlated with its improved reducibility characteristics. The H₂-TPR profile of 40Fe-5Ni/Al₂O₃ (Fig. 2d) exhibited a prominent reduction peak at 677 °C, which is notably lower than that of the monometallic Fe catalyst (typically between 700 and 850 °C for FeO → Fe reduction). This shift indicates that the presence of Ni facilitates the reduction process by promoting Fe–Ni interactions, which likely help in metal-support reduction and alloy formation. Consequently, the bimetallic system demonstrates superior reducibility and activation at lower temperatures, thereby contributing to its higher catalytic activity and CNT yield compared to the monometallic counterpart [59,60].

To complement the structural insights obtained from XRD and Raman spectroscopy, thermogravimetric analysis (TGA), along with derivative thermogravimetry (DTG), was used in an air environment to evaluate the yield and thermal stability of carbon deposits on the spent catalysts. The TGA and DTG results for each catalyst are shown in Fig. 3 (a–f) and provide detailed information about the quality and purity of the synthesized CNT. The weight loss observed during TGA directly

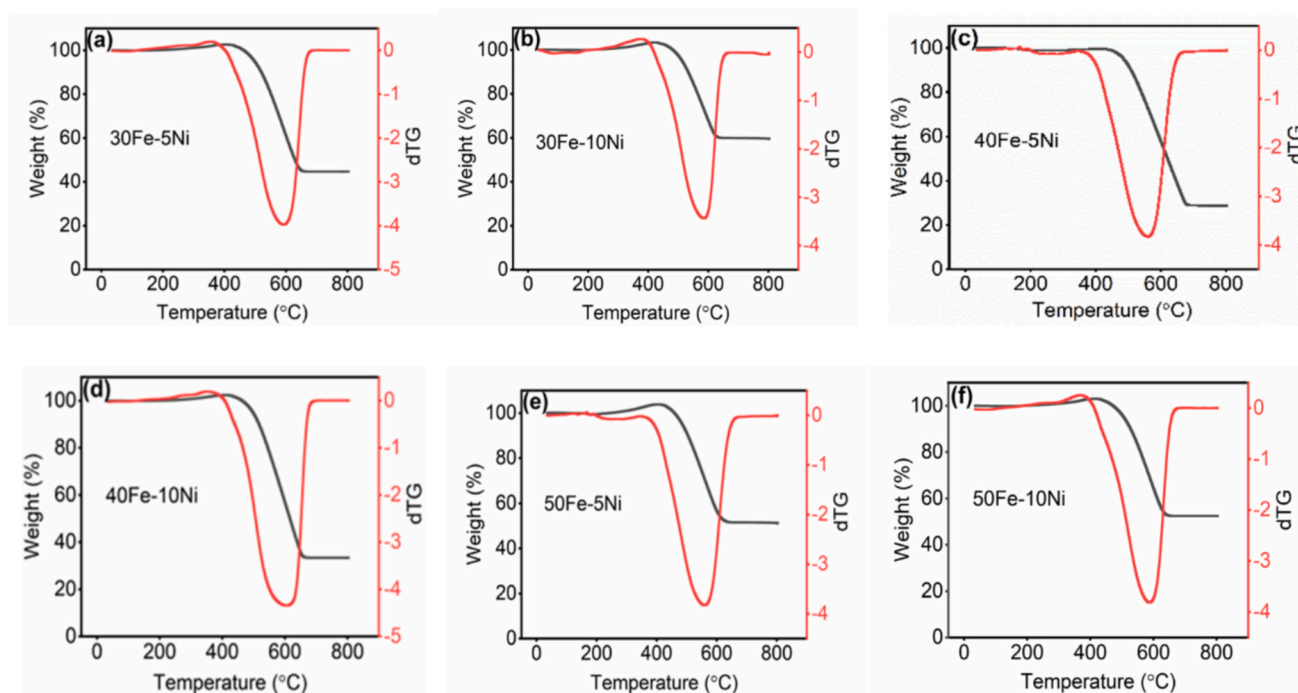


Fig. 3. TGA and DTG curves (a–f) for all catalytic samples, highlighting weight loss patterns and decomposition rates, offering insights into thermal stability and decomposition behaviour.

corresponds to the carbon accumulated during methane decomposition. All catalysts exhibited a similar single-step degradation pattern, confirming the absence of amorphous carbon and the successful synthesis of high-purity multi-wall CNT. The thermal stability of the CNT, as indicated by the degradation temperature, further supports the high crystallinity and graphitic nature of the synthesized materials. For all six catalysts, degradation was initiated at approximately 550 °C, emphasising the significant thermal stability of the CNT. Notably, the absence of weight loss in the 200 °C to 350 °C range confirms the lack of amorphous carbon, reinforcing the high degree of graphitization and purity of the CNT. Additionally, the DTG curves showed a peak maximum at 604.70 °C, further supporting the presence of highly crystalline and well-structured CNT. The DTG values of all catalysts have been included in Table S.3 in the SI.

3.2. Morphological characterization

The SEM and HR-TEM analyses of the spent Fe–Ni catalysts provided comprehensive insights into the structural characteristics of the carbon materials formed during methane decomposition. SEM imaging revealed a well-defined tubular morphology, with filament diameters ranging from 20 to 120 nm, as depicted in Fig. 4(a–f). Among the catalysts, the 40Fe–5Ni sample exhibited the most uniform diameter distribution between 80 and 120 nm illustrated in Fig. 4(c), while other compositions, such as 40Fe–10Ni, 50Fe–5Ni, 50Fe–10Ni, 30Fe–5Ni, and 30Fe–10Ni, demonstrated greater variations in diameter. The larger diameters observed in these CNT structures highlight their potential for applications in high-strength composites and microelectronics.

HR-TEM analysis further revealed the formation of filamentous carbons with various structural features over the catalysts. These structures were categorized into two distinct types based on morphology. The first type consisted of multi-walled CNT with characteristic concentric graphene layers, indicating well-defined structural integrity as illustrated in Fig. 4(g). The second type comprised filamentous carbons with chain-like morphologies exhibiting a “fishbone” or “herringbone” pattern within the CNT walls, characterized by

graphene layers oriented obliquely to the nanotube axis, depicted in Fig. 4(h). This unique arrangement introduces controlled defects and edge-plane sites, enhancing the electronic, mechanical, and chemical properties of the CNT [61,62]. The interplanar distances observed in these carbon filaments show a spacing of approximately 0.35 ± 0.02 nm, matching the d-spacing of graphite C (002), as shown in Fig. 4(i, j). This alignment is influenced by the epitaxial effect of the metal surface on graphite layer formation, contributing to the growth of structurally robust and well-defined carbon filaments. The advanced features of these CNT, including high crystalline integrity, suggest enhanced performance potential for electronic, mechanical, and catalytic applications [63,64]. Additionally, the average crystal size, calculated using the Scherrer equation, was 5.5 nm, which is smaller than the 10 nm particle size observed by HR-TEM, indicating polycrystalline nanoparticles. Given that the CNT wall thickness (10–20 nm) is larger than the particle size, the nanoparticles are likely encapsulated within the CNT-wall interface, emphasising the critical role of catalyst size and structure in CNT growth.

3.3. Catalyst performance

The CH₄ conversion as a function of time on stream (TOS) for six bimetallic catalyst compositions, 30Fe–5Ni, 30Fe–10Ni, 40Fe–5Ni, 40Fe–10Ni, 50Fe–5Ni, and 50Fe–10Ni, were evaluated in a fluidized bed reactor, as shown in Fig. 5(a). The reaction was conducted at 700 °C with a methane flow rate of 200 mL/min under atmospheric pressure using pure methane as the feed at a steady state with a GHSV of 1200 mL/gcat.h. These catalysts demonstrated excellent activity and stability for producing only hydrogen and CNT. The initial conversion rates for these catalysts were measured at 73 %, 78 %, 86 %, 86 %, 87 %, and 88 %, respectively. Initially, all catalysts achieved high methane conversions, but a steady decline in performance was observed over time, as illustrated in Fig. 5(a), due to the deposition of CNT.

Among the tested catalysts, the 40Fe–5Ni catalyst showed the best performance, achieving an 86 % methane conversion in the first 50 min with a hydrogen yield of 4.42 mmol/gcat.h as shown in Fig. 5(b). However, its activity declined gradually, with conversion decreasing to

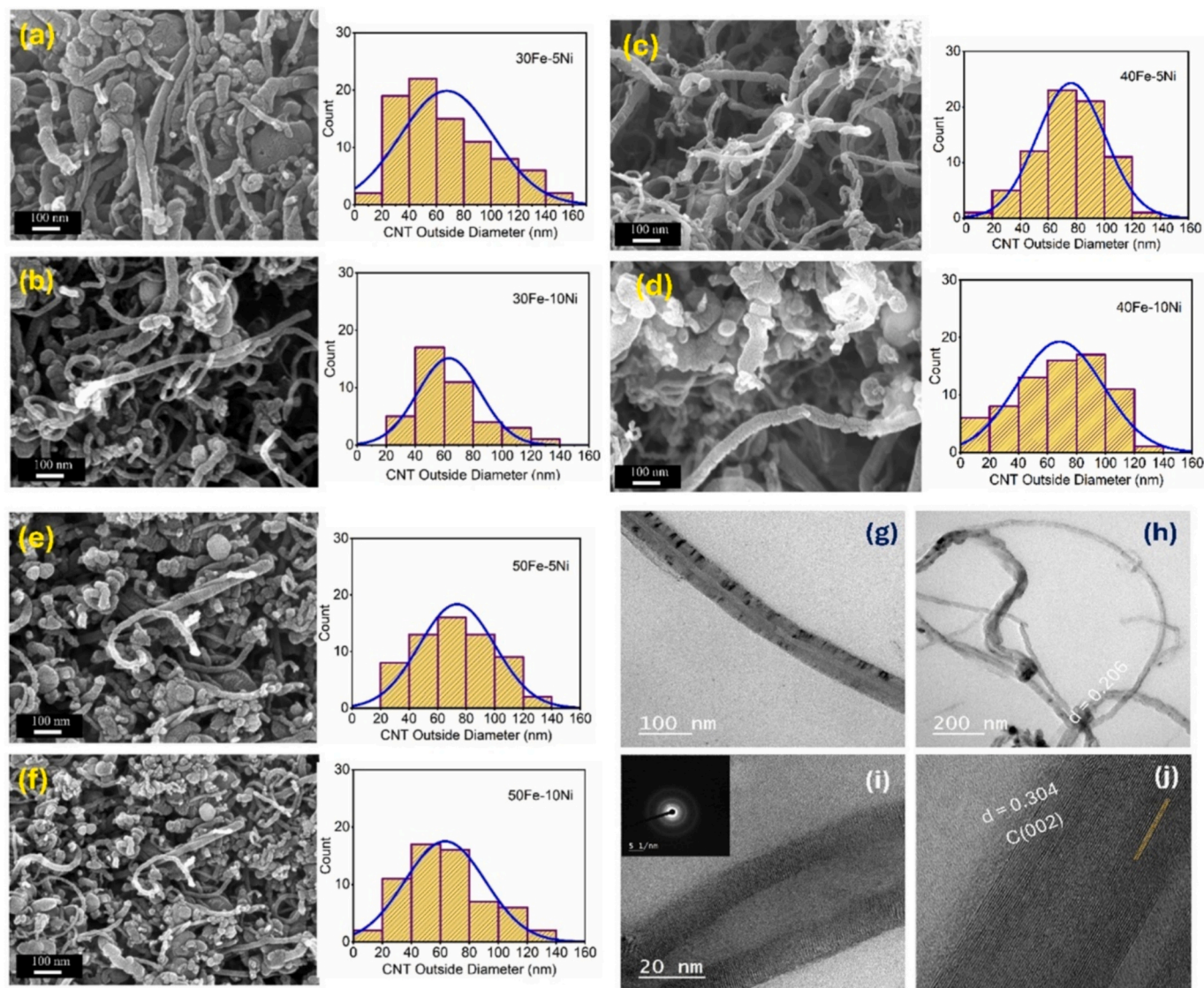


Fig. 4. SEM and HR-TEM analyses of spent Fe–Ni catalysts showing the structural characteristics of carbon materials formed during methane decomposition. (a–f) SEM image depicting tubular morphologies with filament diameters ranging from 20 to 120 nm, highlighting uniform diameter distribution in the catalysts; (g–j) HR-TEM image illustrating multi-wall CNT with concentric graphene layers and filamentous carbons with chain-like morphology exhibiting a “fishbone” or “herringbone” pattern within CNT walls.

46 % at the 300-min mark. In comparison, the 40Fe–10Ni catalyst exhibited an initial conversion of 86 % during the first 30 min of reaction. Its performance declined steadily, reaching 33 % by 200 min with the 4.14 mmol/gcat.h hydrogen yield. This faster deactivation of the 40Fe–10Ni catalyst is likely due to its higher nickel content, which accelerates deactivation compared to the 40Fe–5Ni catalyst [65]. Further, the carbon deposition was calculated, and detailed information depicted in Fig. S.2 in section S.1 in Supplementary Information (SI) shows that the 40Fe–5Ni catalyst accumulates 26 g of carbon, compared to 13.5 g for the 40Fe–10Ni catalyst. In the case of 50Fe–5Ni and 50Fe–10Ni, catalysts displayed similar initial performance, achieving nearly 87–88 % conversion within the first 10 min of the reaction, respectively. However, these catalysts deactivated more rapidly than the 40 % metal-loaded catalysts due to their higher overall metal content. Their activity declined steadily, reaching approximately 44 % conversion by 90 min and a hydrogen yield of 4.0 and 3.74 mmol/gcat.h, respectively, as shown in Fig. 5(a, b). Carbon deposition measurements showed 8.58 g of carbon for the 50Fe–5Ni catalyst and 8.64 g for the 50Fe–10Ni catalyst. In addition, the 30Fe–5Ni and 30Fe–10Ni catalysts exhibited lower initial conversions compared to the higher

metal-loaded catalysts, with a maximum conversion of 73 % and 78 % respectively, within 20 min of reaction. Their activity declined gradually, reaching approximately 44 % by 100 min. The carbon accumulated on these catalysts is 5.2 g and 5.44 g of carbon, and with a hydrogen yield of nearly 3.53 mmol/gcat.h and 3.41 mmol/gcat.h, respectively.

The better performance of Ni incorporated Fe catalyst may be due to the strong Fe–Ni synergy, enhancing reducibility, as confirmed by H₂-TPR. Further, the DFT results (Section 3.6) show that due to the influence of Ni on Fe, modifies the electronic environment through mutual interactions, leading to d-band center shifts (downward for Ni, upward for Fe). These electronic changes, in line with the d-band theory, strengthen adsorbate binding, enhancing catalytic performance. Further, the adsorption studies show that atomic carbon binds more strongly to Fe₃Ni than to Fe, indicating Ni role in reinforcing metal-carbon interactions. This synergistic effect improves CH₄ cracking and H₂ desorption, enhancing the overall CMD process. In addition, catalysts with higher metal loadings (e.g., 40Fe–10Ni, 50Fe-xNi) showed higher initial CH₄ conversion due to more active sites but suffered faster deactivation from Ni-induced agglomeration, which reduced metal dispersion and hydrogen yield.

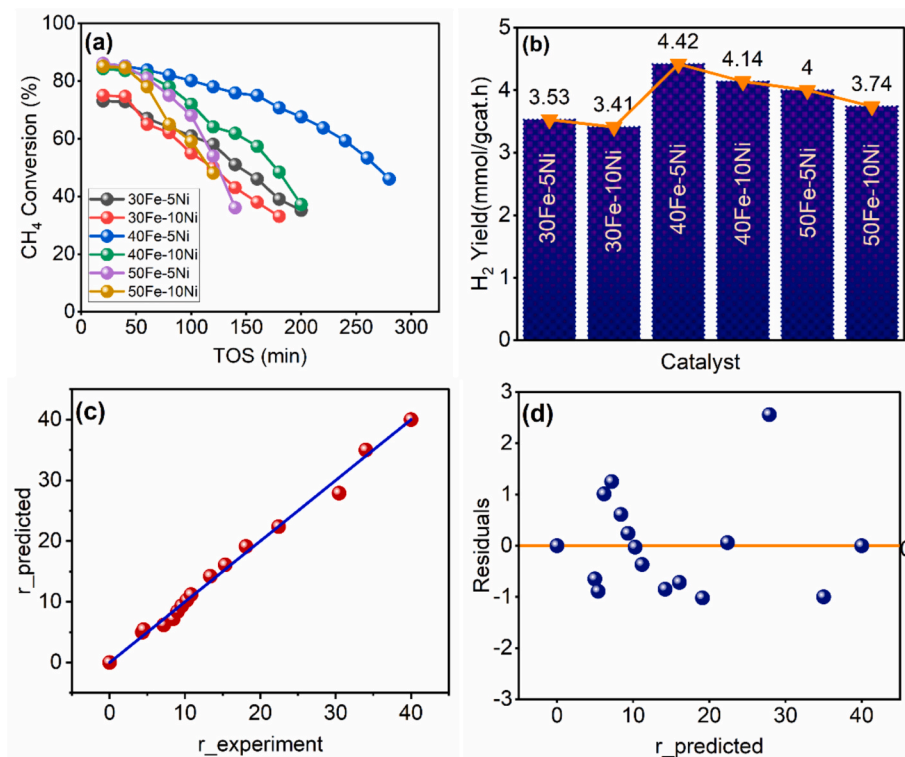


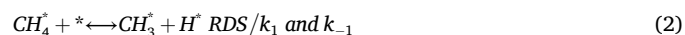
Fig. 5. (a) CH₄ conversion as a function of time with a GHSV of 1200 mL/gcat.h at 700 °C, (b) hydrogen production in mmol/gcat.h, (c) parity plot comparing experimental and predicted values for the LHHW kinetic model, and (d) residuals plot for the kinetic model, highlighting the distribution of errors and model accuracy.

Compared with the Fe-only catalyst, Lijun Jin et.al studied with 40 % loading of Fe, and the conversion achieved is 39 % [21]. Whereas the Lu Zhou. et.al reported nearly 80 % conversion with a Fe-catalyst prepared from the fusion method on the alumina support [66]. While Ni-only catalysts are known for their high activity in CMD, they typically exhibit faster deactivation due to excessive filamentous carbon formation. In comparison, optimized Fe–Ni bimetallic systems offer improved stability by reducing the carbon buildup [59,67–69]. With references to Wang et al., evaluated catalysts with compositions 2Ni–1Fe–1Al (Ni: 41.9 wt%, Fe: 19.9 wt%, Al: balance) and 1Ni–2Fe–1Al (Ni: 20.6 wt%, Fe: 39.1 wt%, Al: balance). In a fixed-bed reactor at a reaction temperature of 700 °C, these catalysts achieved initial methane conversions of 70 % and 60 %, respectively [70]. Similarly, Fakeeha et al. presented methane conversion for Ni–Fe/Al₂O₃ catalysts at 700 °C, which included compositions such as 30 %Ni–30 %Fe/Al₂O₃, 6 %Ni–30 %Fe/Al₂O₃, and 15 %Ni–30 %Fe/Al₂O₃. Each of these catalysts achieved a conversion of approximately 65 % [71]. Fatesh et al. investigated methane conversion over time for Ni-promoted Fe/Al₂O₃ catalysts. The optimized catalyst achieved a methane conversion of approximately 65 % [72]. In another study, Pudukudy et al. observed that the Ni–Fe/SBA-15 catalyst initially achieved a methane conversion of 51 % during the first 30 min of the reaction. However, after 60 min, the activity dropped to around 44 % and continued to decrease gradually, with a final hydrogen yield of about 33 % after 300 min [73]. In addition, Shah et al. investigated the decomposition of undiluted methane over alumina-supported Fe-based bimetallic catalysts with Pd, Mo, and Ni. These catalysts produced gaseous products with more than 80 % hydrogen yield when tested at temperatures between 700 and 800 °C [74].

3.4. Kinetic study

Based on the best catalyst, the kinetic of methane decomposition was analysed to explain the reaction $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ mechanism and identify the rate-controlling steps using the LHHW model. This approach as-

sumes that the rate-controlling step is the slowest, with all other steps being in equilibrium as mentioned in reactions 1–6. The widely accepted mechanism for methane decomposition involves the following steps: 1. Adsorption of Methane: Methane molecules adsorb onto the active sites of the catalyst surface. This step initiates the reaction by providing a surface for methane activation. 2. Stepwise Dehydrogenation: Adsorbed methane undergoes successive bond scission events, breaking C–H bonds to release hydrogen atoms. 3. Associative Desorption of Hydrogen: The hydrogen atoms formed during dehydrogenation combine to form hydrogen, which desorbs from the catalyst surface, contributing to the hydrogen yield. 4. Carbon Nucleation and Growth: The residual carbon atoms aggregate and reorganize on the catalyst surface, forming CNT [75,76].



The symbol * represents an unoccupied active site on the catalyst surface, while the adsorbed species, including CH₃*, CH₂*, CH*, C*, and H*, correspond to intermediates derived from methane and hydrogen, all of which are attached to the surface. The reaction rate is expressed in the following parameter model that includes the rate constant (k_1) and the adsorption equilibrium constants for the metal surface (refer to S.2 in SI). These factors collectively promote the hydrogen production and growth of well-defined carbon filaments [63,64].

The effect of diffusional resistance on the reaction regime was studied using the Weisz-Prater criterion [77,78].

$$C_{wp} = \frac{r' \rho_p R_p^2}{C_s D_e} \quad (3)$$

where r' is the observed reaction rate per unit mass of catalyst (mol/gcat h), ρ_p is the apparent particle density (g/cm³), R_p is the radius of the catalyst particle (cm), C_s is the concentration of the reactant gas (mol/cm³), and D_e is the effective diffusivity of the reactant within the catalyst pores (cm²/s). When $C_{wp} < 0.3$, diffusion effects are negligible. The calculated value of the Weisz-Prater criterion C_{wp} is 0.27, which is less than 0.3, indicating that diffusional resistance is negligible. This suggests that the observed reaction rate is primarily governed by the surface kinetics rather than being limited by diffusion.

Thus, assuming the reaction is governed by surface kinetics, step (1) of the dissociative adsorption pathway is considered the rate-limiting step, and the corresponding rate law is formulated as follows: (The kinetic equations employed herein are adapted from the work of J.W. Snoeck, G.F. Froment, and M. Fowles in Ref. [79].)

$$r = k_1 p_{CH_4} \theta_*^2 - k_{-1} \theta_{CH_3} \theta_H \quad (4)$$

Here, k_1 and k_{-1} represent the rate constants for the forward and reverse reactions of step (1), respectively. θ_* , θ_{CH_3} , and θ_H denote the fractions of active sites that are vacant and occupied by CH₃ and H, respectively. Here, p_{CH_4} represents the partial pressures of methane. With step (1) identified as the rate-controlling step, all other steps are assumed to be in equilibrium. When the surface concentrations H*, CH*, and CH₂* are negligible, the rate equation is written as

$$r = \frac{k_1 K_{CH_4} \left(p_{CH_4} - \frac{1}{K_1} p_{H_2}^2 \right)}{\left(1 + p_{H_2}^{3/2} \frac{1}{K_{eq}} + K_{CH_4} p_{CH_4} \right)^2} \quad (5)$$

A detailed derivation is presented in Section S.2 of the SI.

Nonlinear regression was employed to fit the model to experimental data, minimizing the residual sum of squares between observed and predicted reaction rates. The key parameters, such as the reaction rate constant (k_1), the adsorption equilibrium constants K_{CH_4} , and the pseudo-equilibrium constant (K_{eq}) were determined from the fitting process. The kinetic model, developed through parameter estimation and model testing, suggests that methane breaks down gradually by losing hydrogen atoms one by one. The slowest and most crucial step in this process is removing the first hydrogen atom from the methane molecule when it is adsorbed on the surface. The parity plot confirms the optimal fit between $r_{predicted}$ and $r_{observed}$, depicted in Fig. 5(c), which is further supported by the residuals plot in Fig. 5(d), demonstrating the best fit between the two. The fitted parameter values, which are summarized in Table. 3, indicate that the methane reaction constant (k_1) and the equilibrium constant K_{CH_4} . This strong agreement validates the competitive adsorption behaviour of methane and hydrogen on the catalyst surface. The correlation between experimental data and the

LHHW model confirms that the reaction mechanism is effectively described by the dissociative adsorption of methane onto the catalyst surface, followed by the desorption of hydrogen (refer to Table. S1 in the SI).

3.5. Deactivation rate and mechanism

To further advance the study, the activity rate and its underlying mechanism were investigated. The activity of the catalyst, denoted as $a(t)$ given in Eq. (6), is typically expressed as a function of time and relates to the catalytic efficiency or performance over a specific period [78].

$$a(t) = r_c(t)/r_{co} \quad (6)$$

The catalyst deactivation rate can be represented as a function of the deactivation rate constant (k_d), the residence time (t_R) in minutes, and the catalyst activity ($a(t)$). Furthermore, it can be expressed using the Arrhenius equation as follows:

$$-\frac{da}{dt} = k_d t_R^m a^d = k_{d0} e^{-E_a/RT} t_R^m a^d \quad (7)$$

Here, m represents the exponent associated, and d denotes the deactivation order. The term k_{d0} is the pre-exponential factor, E_a (in J/mol) is the activation energy for the deactivation reaction, R is the gas constant (8.3143 J/mol K), and T is the temperature in K. When k_d and t_R are constants, the integral of Eq. (7) can be simplified and evaluated as follows:

$$-\ln a = k'_d t \quad d = 1 \quad (8)$$

$$\text{where } k'_d = k_d t_R^m$$

$$a^{1-d} = 1^{1-d} - (1-d)k'_d t \quad d \neq 1 \quad (9)$$

The activity (a) of the catalyst with $d = 1$ was analysed by fitting the experimental data to the linearized form of the kinetic model, where the relationship between $\ln a$ and time (t) was established in Eq. (8). The results showed a clear linear correlation, confirming that the catalyst follows first-order deactivation behaviour illustrated in Fig. 6(a). This suggests that the rate of deactivation is directly proportional to the reaction time, consistent with the assumption of a constant deactivation rate constant k'_d . Further, the activity equation (Eq. (10)) is derived considering the first order deactivation reaction shown in Fig. 6(b).

$$a = \exp^{-k'_d t} \quad (10)$$

To investigate the deactivation mechanism, HR-TEM analysis was conducted. As depicted in Fig. 6(c-f), the images revealed two distinct types of carbon deposits: filamentous carbon with metal particles attached to their tips, as depicted in Fig. 6(c), and large carbon lumps encapsulating the metal particles, as shown in Fig. 6(d, e). During methane decomposition, as illustrated in Fig. 6(d), metal particles fragmented into smaller pieces and became encapsulated within graphite layers. Additionally, filamentous carbon structures comprising spherical carbon units, many of which contain metal particles highlighted in Fig. 6(e). These spherical units are surrounded by concentric graphite layers originating from the central metal particles, confirming the encapsulation process [80]. Additionally, scanning transmission electron microscopy (STEM) and energy-dispersive spectroscopy (EDS) enabled high-contrast imaging and elemental mapping, providing further insights into the spatial distribution of active metals. The STEM image as shown in Fig. 6(f) reveals a 0.205 nm distance between the corresponding lattice fringes, which matches the lattice spacing of a Ni-Fe bimetallic, thus confirming the encapsulation of metal particles and contributing to catalyst deactivation [81].

To complement further, EDS was employed to investigate the

Table 3
Kinetic parameters calculated from the LHHW model.

Parameters	Value
Optimized k_1	0.74
Optimized K_{CH_4}	0.28
Optimized K_{eq}	2.18
Optimized k'_d	0.24
Residual Sum of Squares (RSS)	1.49e-05
Root Mean Squared Error (RMSE)	0.0010
Mean Absolute Error (MAE)	0.00082
R-squared (R^2)	0.98

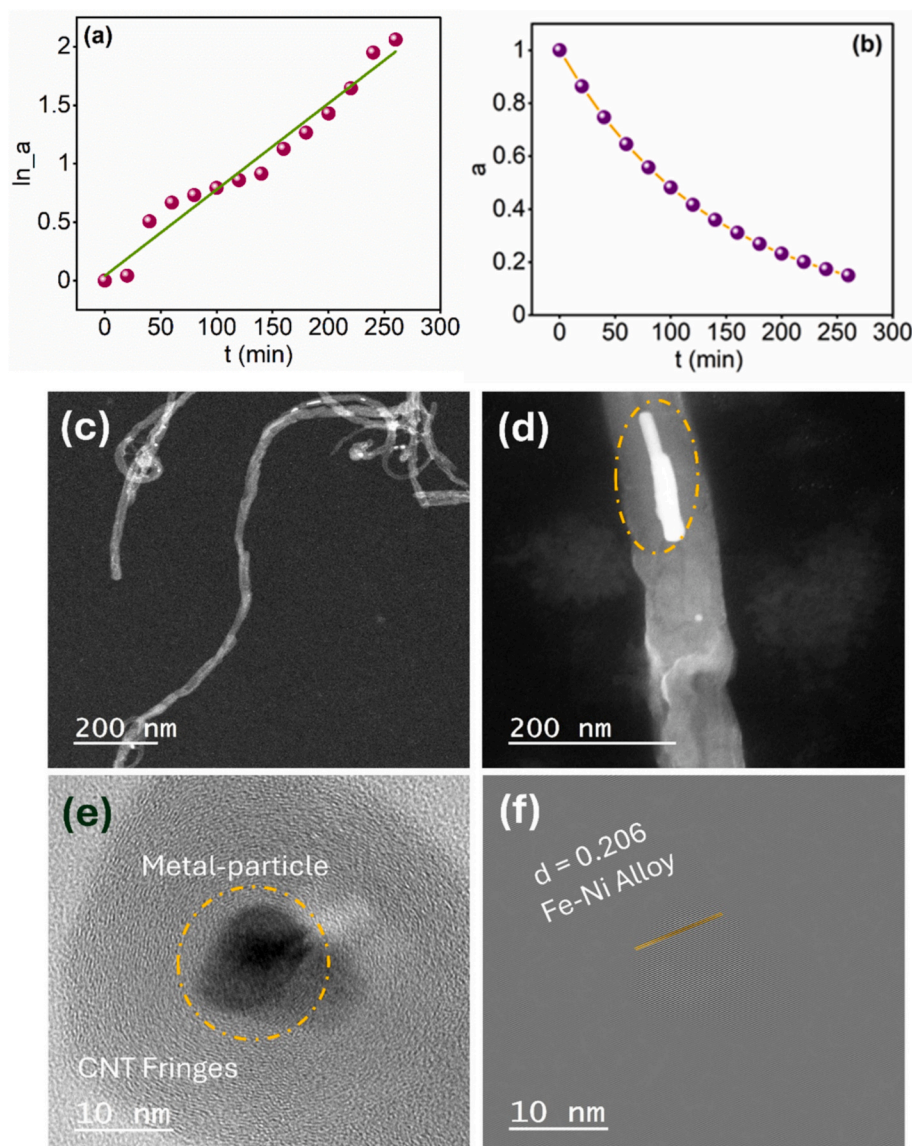


Fig. 6. (a) Linear plot representing the first-order deactivation kinetics of the catalyst, indicating a constant deactivation rate over time. (b) Non-linear curve illustrating the actual deactivation behaviour of the catalyst under reaction conditions, reflecting changes in activity due to factors such as carbon deposition or sintering. HR-TEM images of carbon nanostructures formed during methane decomposition: (c) filamentous carbon with metal particles located at the tips, (d) fragmented metal particles encapsulated within graphite layers, (e) spherical carbon units with metal particles surrounded by concentric graphite shells, and (f) STEM image displaying a lattice spacing of 0.205 nm corresponding to the Ni–Fe alloy, confirming encapsulation of metal nanoparticles within graphitic layers.

elemental composition of the spent catalysts. EDS analysis confirmed the presence of Fe and Ni as the primary active metals and identified significant carbon deposits resulting from methane decomposition, shown in Fig. S.3. in section S.3 of the SI. Localized carbon accumulation near metallic particles, as observed through EDS mapping, highlighted the deactivation of the catalysts due to carbon buildup at active sites. This fragmentation and encapsulation of metal particles likely hindered their ability to interact effectively with methane molecules, which ultimately led to the deactivation of the catalyst. These findings provide valuable insights into the deactivation pathways and suggest potential strategies for designing more stable and efficient catalysts by addressing issues such as carbon deposition, particle agglomeration, and weakened metal-support interactions. Moreover, EDS analysis revealed the distribution of Ni throughout the Fe domain, indicating that Ni and Fe are homogeneously distributed along the bimetallic catalyst [82].

3.6. DFT study

To provide deeper insights into the experimental findings, DFT calculations were performed. These calculations offered a detailed theoretical perspective on the electronic changes at the surfaces, the interactions between adsorbates and catalyst surfaces, and the overall stability of the systems.

3.6.1. Electronic properties

When a bimetallic is formed, the atomic spacing undergoes expansion or compression due to the differing lattice parameters of the constituent metal atoms. For example, combining a metal with a large atomic radius, such as Fe, with a smaller-radius metal like Ni to form a surface alloy or overlayer causes significant changes in the electronic structure. These changes are apparent as a broadening of the d-band and a shift in its center toward lower energy, moving further away from the Fermi level. The projected density of states (PDOS) for the d orbitals of Ni and Fe on three surfaces, Ni(111), Fe(111), and the Fe₃Ni(111) as

illustrated in Fig. 7. The incorporation of Ni atoms into the Fe surface results in broader PDOS curves and a distinct shift of the d-band center farther from the Fermi level compared to the pure Ni(111) surface, emphasising the electronic interactions.

Likewise, from the d-band center, values for Ni(111) and Fe(111) are found at -1.49 eV and -2.27 eV, respectively. In the Fe_3Ni bimetallic, the d-band center shift to -2.05 eV for Ni and -2.00 eV for Fe, as illustrated in Fig. 7 (the d-band center values for surfaces are provided in Table S.2 of the S-I). This downward shift for Ni and a reasonable upward shift for Fe demonstrates a redistribution of electronic states due to the mutual interaction of both elements. These electronic interactions between Fe and Ni lead to the observed PDOS broadening and shifts in the d-band center. According to the d-band model, such shifts make the Fe_3Ni bimetallic form have stronger bonds compared to monometallic Fe with adsorbates, which could influence its catalytic performance by providing the optimum bonding strength with adsorbates [83]. Thus, the changes in the electronic structure by incorporating Ni in the Fe system enhance the catalyst activity as well as stability.

3.6.2. Adsorption energy

The adsorption energy of the adsorbate was calculated on the bimetallic Fe_3Ni and monometallic Fe and Ni surfaces along the (111) plane. As depicted in Fig. 8 (The upper panel shows the top view, whereas the lower panel presents the side view of the surfaces), which shows the adsorption of C on the surface of Fe_3Ni (Fig. 8(a)), Fe (Fig. 8(b)), and Ni (Fig. 8(c)). In the CDM reaction, the adsorption energy of adsorbed C serves as a descriptor for characterizing the adsorption energies of other adsorbates on the metal surface [84–86]. The bare surfaces of the above catalyst are mentioned in Fig. S.4 in the SI.

3.6.3. Scaling relation

Previous studies by Nørskov et al. demonstrated a linear correlation

between the adsorption energies of CH , CH_2 , and CH_3 and the adsorption energy of C across various transition metals [87,88]. In this study, the scaling relations between the adsorption energies of CH_x and C on the catalytic surface are considered, with slopes approximately corresponding to the ratio of the number of dangling bonds in CH_x to the total number of C – H bonds, consistent with the findings of Abild-Pedersen et al. [89]. As expected, a plot of the adsorption energies of CH_x against the adsorption energy of C yields straight lines, as mentioned in detail in section S.4.2, eqs. 12–14, and Fig. S.5 in the SI.

Based on the scaling relation, the adsorption energies of all intermediates were calculated, as mentioned in the Table 4. Atomic C shows the interaction, with adsorption energies of -6.488 eV for Fe (111), -7.992 eV for Ni(111), and -7.225 eV for Fe_3Ni (111). The adsorption energy data reveal that the Fe_3Ni (111) catalyst surface exhibits the strongest interactions with all species (CH_3 , CH_2 , CH , and C) compared to monometallic Fe(111), as mentioned in Table.4. Thus, these results indicate that the presence of Ni in the Fe substantially improves the adsorption energy of the catalyst toward key reaction intermediates.

To further explain the effect of Ni incorporation in Fe-based catalysts, Bader charge analysis was performed. The resulting values show that the C accumulates different electron charges across the systems -0.32 e in Fe, -0.50 e in Fe_3Ni , and -0.92 e in Ni, which indicates a redistribution of electronic charge on the carbon adsorption site. A more negative charge signifies stronger electron donation from the metal to C. As compared with pure Fe, the highly negative charge, -0.50 e, indicates strong electron transfer, leading to strong metal-carbon bonding compared with Fe_3Ni . Thus, Fe_3Ni bimetallic, with a charge of -0.50 e, is a more favourable surface than monometallic Fe.

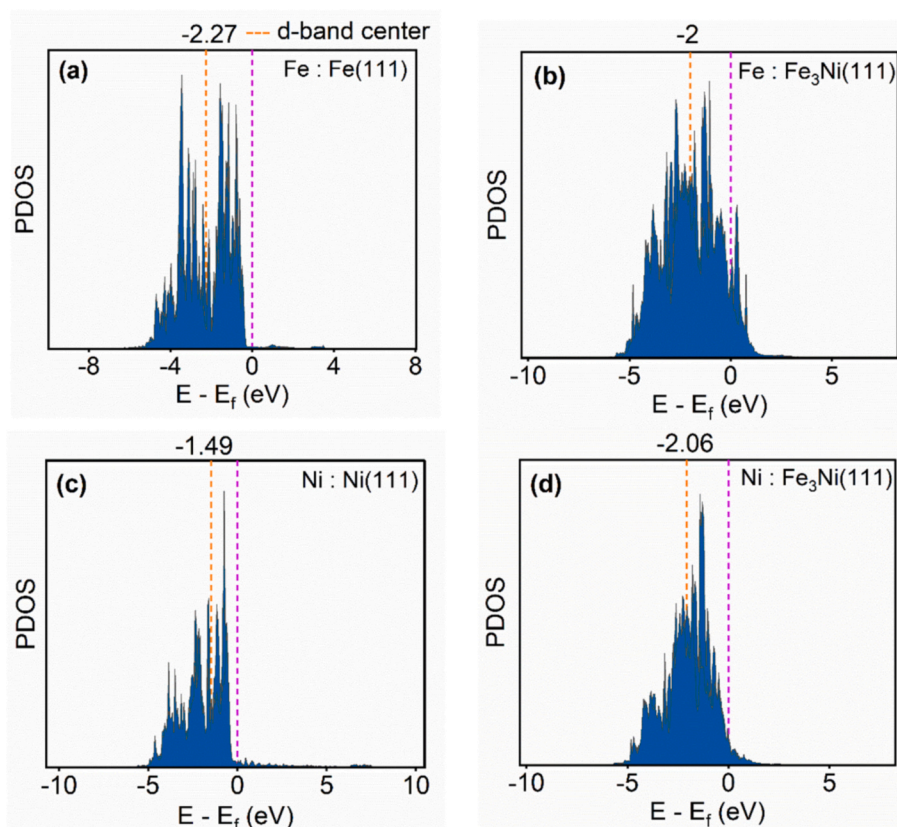


Fig. 7. PDOS for surface Fe and Ni atoms on Fe(111), Ni(111), and Fe_3Ni (111). The d-band center of pure (a) Fe(111) and (b) Ni(111) are -2.27 eV and -1.49 eV, respectively. In (c,d) Fe_3Ni (111), the center shift to -2.05 eV for Ni and -2.00 eV for Fe, which leads to the favouring optimized catalytic performance.

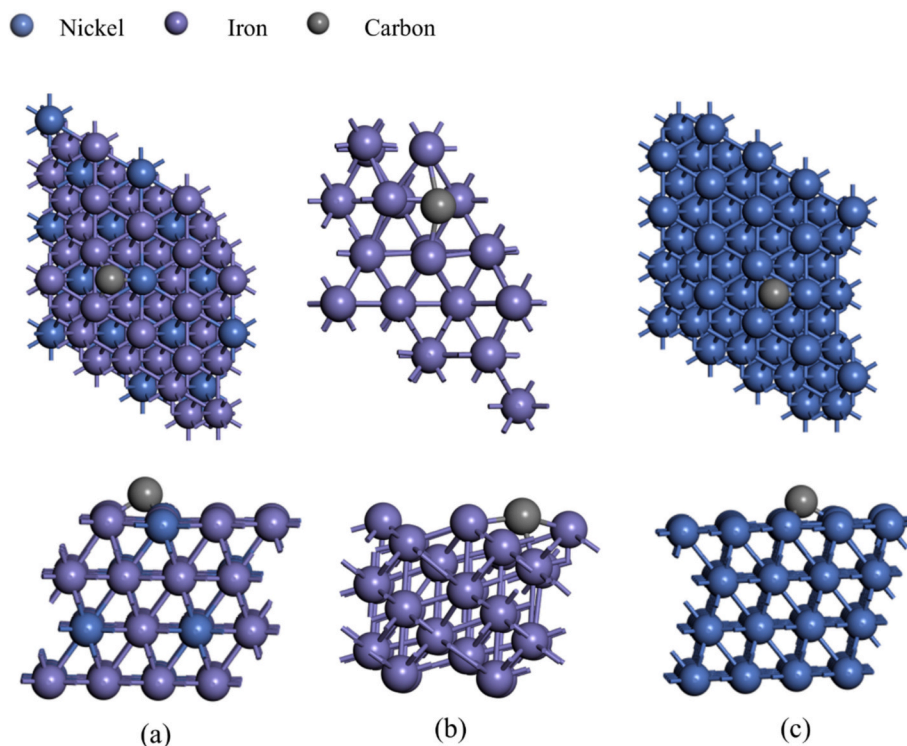


Fig. 8. Preferred carbon adsorption configurations and surface interactions on (a) Fe₃Ni(111), (b) Fe(111), and (c) Ni(111) surfaces, illustrated with both top and side views (top panel shows the top views, while bottom panel depicts side views of the optimized surface slabs).

Table 4

Adsorption energies of reaction intermediates on Fe(111), Ni(111), and Fe₃Ni(111) surfaces (in eV).

Catalyst	$E_{\text{CH}_3}^{\text{ad}}$	$E_{\text{CH}_2}^{\text{ad}}$	$E_{\text{CH}}^{\text{ad}}$	E_{C}^{ad}
Fe (111)	−1.487	−3.189	−5.256	−6.488
Ni (111)	−1.848	−3.956	−6.414	−7.992
Fe ₃ Ni (111)	−1.664	−3.567	−5.823	−7.225

4. Conclusion

This study demonstrates the remarkable potential of bimetallic Fe—Ni catalysts for CMD. Incorporating Ni into the Fe-based catalyst system notably enhanced methane conversion, facilitated hydrogen production, and improved CNT quality. Among the tested catalysts, the 40Fe—5Ni composition exhibited the highest performance, achieving 86 % methane conversion and producing 4.42 mmol/gcat.h of hydrogen at 700 °C. The CNT formed exhibited minimal defects, uniform diameters (80–120 nm), and high crystalline quality, as confirmed by Raman spectroscopy ($I_D/I_G = 0.37$), SEM, and HR-TEM, while TGA revealed a high degradation temperature of 550 °C. In addition to the catalytic performance, kinetic studies were conducted to explain the reaction behaviour and deactivation mechanism. The CMD reaction kinetics with a rate constant k_1 of 0.74 reflects the efficient catalytic activity under the given reaction conditions, whereas catalyst deactivation was also observed to follow first-order kinetics, with a deactivation constant k'_d of 0.24. These kinetic parameters highlight the catalyst high activity while also highlighting the need to address deactivation issues to further improve long-term stability and overall performance.

In addition, DFT calculations reveal that incorporation of Ni with Fe enhances the catalyst adsorption strength and electronic properties, leading to superior catalytic performance. From the d-band center, the electronic interaction between Fe and Ni leads to a downward shift in the d-band center of Ni and an upward shift in that of Fe. This shifting of the electronic structure enhances the catalytic performance and stability

of the bimetallic system. Moreover, the Fe₃Ni(111) surface shows the strongest interactions with the reaction descriptor of atomic carbon than monometallic Fe(111), with adsorption energies of −7.225 eV. Bader charge analysis further confirms that Fe₃Ni achieves an optimal balance of electron transfer. These effects result in an improved CMD process, making Fe₃Ni an efficient catalyst for carbon-based reactions.

Fe—Ni catalysts demonstrate considerable potential for sustainable hydrogen and CNT production via CMD. This study primarily focused on the relationship between catalyst design, structure, and performance under fixed operational conditions (700 °C, 200 mL/min), enabling consistent and comparative evaluation. To fully assess the scalability and industrial relevance of these catalysts, future investigations should explore their long-term stability, regeneration strategies, and conduct techno-economic analyses under a broader range of reaction conditions.

CRediT authorship contribution statement

Shashank Shekhar: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Komal Tripathi:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Amir Kartton:** Writing – review & editing, Software, Resources, Methodology, Formal analysis. **Shantanu Roy:** Writing – review & editing, Resources. **Rakesh Joshi:** Writing – review & editing, Visualization, Validation, Supervision, Investigation, Formal analysis. **Kamal Kishore Pant:** Writing – review & editing, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2025.168485>.

Data availability

Data will be made available on request.

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