



© 2026. The Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution-ShareAlike 4.0 International Public License (CC BY SA 4.0, <https://creativecommons.org/licenses/by-sa/4.0/legalcode>), which permits use, distribution, and reproduction in any medium, provided that the article is properly cited.

Directional Regulation of Biomass Pyrolysis Gas Coupling for Hydrogen-Rich Fuel Gas Production over a Hydrophobic NiCo-CeO₂/F-Ti₃C₂ Catalyst

Chen Jihao^{1,2}, Miao Pengjie^{1,2*}

¹College of Energy and Chemical Engineering, Xinjiang Institute of Technology, Aksu 843100, China

²Xinjiang Key Laboratory of New Energy and Energy Storage Technology,
Xinjiang Institute of Technology, Aksu 843100, China

*Corresponding author's e-mails: 37743386@qq.com

Keywords: Ti₃C₂ MXene; CeO₂; Ni-Co alloy; biomass hydrogen production; hydrophobicity.

Abstract: A key challenge in hydrogen-rich fuel gas production via biomass pyrolysis gas coupling is catalyst hydrothermal deactivation. In this study, hydrophobic F-Ti₃C₂ MXene nanosheets are prepared by a combination of HF-HCl etching and perfluorooctanesulfonic acid (PFOS) modification. Using the nanosheets as the support, CeO₂ promoters and Ni-Co alloy active components are loaded via impregnation, nitrogen calcination and hydrogen reduction processes. Finally, a catalyst with high activity and high hydrophobicity is successfully prepared. The performance of the catalyst is tested in a fixed-bed reactor. The effects of total NiCo loading, Ni/Co molar ratio, and Ce loading on CO/CH₄ conversion and H₂ selectivity are systematically investigated. The catalyst is characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and contact angle measurements, and the mechanisms of underlying its activity and hydrophobicity enhancement are

Introduction

Driven by the dual goals of carbon peaking and carbon neutrality, as well as energy structure transformation, the high-efficiency resource utilization of renewable energy has become a global research hotspot (Gyimah et al. 2024). Biomass is a renewable carbon source that can be converted into solid, liquid and gaseous fuels. It has abundant reserves and remarkable carbon-neutrality characteristics. Its pyrolysis conversion technology is one of the important approaches to addressing fossil energy shortage and environmental problems (Wang et al. 2024). Therefore, developing efficient biomass pyrolysis gas conversion technologies is of great practical significance. It can upgrade biomass pyrolysis gas into high-value-added clean energy, thereby optimizing the energy structure and protecting ecological environment. The pyrolysis gas produced by biomass is mainly composed of CH₄, CO, CO₂, C₂/C₃ hydrocarbons, and H₂O. It has extremely high conversion potential. Hydrogen-rich fuel gas can be prepared through the coupled reforming of biomass pyrolysis gas. The key to this technology is the synergistic occurrence of multiple

reactions. These reactions include CH₄ reforming, CO water-gas shift reaction, and C₂/C₃ hydrocarbon cracking. They can achieve efficient enrichment of hydrogen (Wang et al. 2024). However, water is involved in the hydrogen production process from biomass pyrolysis gas, causing problems such as sintering of catalyst active components and hindrance of mass transfer (Guo et al. 2025). Thus, developing catalysts with both high activity and strong hydrophobicity is one of the keys to realizing the industrialization of hydrogen-rich fuel gas production via biomass pyrolysis gas coupling.

Chen et al. (2023) prepared a hydrophobic Fe₂O₃@SiO₂-xHDTMS catalyst via a room-temperature solid-phase method for light hydrocarbon synthesis. The hydrophobic long-chain alkyl groups of HDTMS can graft onto the SiO₂ surface, replacing polar hydroxyl groups. This treatment increased the maximum contact angle of the catalyst to 155.2°, achieving superhydrophobicity. Khojasteh et al. (2024) modified SiO₂ with perfluorooctyltriethoxysilane (PFOS) to prepare a superhydrophobic glass coating. PFOS provides low surface energy groups and increases surface

roughness. The water contact angle of the coating reached 144° . Ma et al. (2024) etched Cu/ZnO/Al₂O₃ with NaOH, and then prepared superhydrophobic catalysts via MTMS modification and PFOTES grafting, respectively, for syngas-to-methanol conversion. PFOTES exhibited better hydrophobic performance than MTMS. The contact angles of both catalysts exceeded 150° . These catalysts can rapidly remove surface water molecules and improve the hydrothermal stability of the catalysts. Bootpakdeetam et al. (2024) loaded cobalt and ruthenium onto a SiO₂ support. After calcination, the supported catalyst was treated with a PFOS-toluene solution to prepare a superhydrophobic Co-Ru/SiO₂ catalyst for Fischer-Tropsch synthesis. PFOS grafted onto the support surface via siloxane bonds. The catalyst showed a contact angle of over 150° and a sliding angle of less than 5° . It effectively repelled water generated during the reaction, thereby avoiding cobalt oxidation and deactivation. The CO conversion rate increased to 38%. Benkacher et al. (2025) modified Algerian palygorskite (A-Pal) with triethoxyoctylsilane (TEOS) to prepare a hydrophobic O-Pal material. Silane molecules replaced hydroxyl groups and introduced hydrophobic octyl groups. This effectively improved the dispersion and compatibility of the material in hydrophobic biopolymers. In summary, silane-based hydrophobic groups such as HDTMS, PFOS, MTMS, and TEOS can endow modified catalysts with excellent water resistance.

The support is a key factor governing catalyst stability and, in the present context, also provides the platform for hydrophobic-group grafting. Therefore, it directly determines the stability of the catalyst in the complex pyrolysis gas atmosphere. Conventional supports, including Al₂O₃, SiO₂, and ZrO₂, have been widely employed; however, each exhibits inherent limitations. γ -Al₂O₃ possesses strong hydrophilicity and a relatively limited specific surface area, whereas SiO₂ provides a high specific surface area but suffers from relatively poor mechanical strength and insufficient stability. ZrO₂ exhibits good thermal stability, but its relatively simple pore structure can restrict mass transfer. All these supports have certain defects. Two-dimensional nanomaterials can serve as ideal materials for catalyst preparation. They have the advantages of ultra-large specific surface area, abundant pore structures, and adjustable surface properties. Two-dimensional MoS₂ loaded with Ni has a specific surface area of up to 680 m²/g. Meanwhile, hydrophobic groups such as fluoro and alkyl groups can be grafted onto the MoS₂ surface. This improves water resistance. Moreover, the interlayer structure can inhibit carbon deposition and agglomeration (Wei et al. 2019). Two-dimensional Ti₃C₂ MXene constructs a porous structure through etching modification. Ti₃C₂ loaded with Ni-Ce has high conductivity. It can promote electron transfer and enhance catalytic activity. Meanwhile, its surface -OH and -F functional groups enable hydrophobic group grafting. In addition, the layered structure can enhance the stability of active components. It has great advantages in the application of hydrogen production from biomass pyrolysis gas (Reghunath et al. 2023). Therefore, two-dimensional nanomaterials not only have high-efficiency active component dispersion capacity and structural stability, But they can also meet modification requirements such as hydrophobic group grafting and active component/promoter loading. High activity

and strong hydrophobicity of the catalyst are achieved through multi-performance synergy.

Aiming at the drawbacks of existing hydrophobically modified catalysts, most of which are based on traditional supports such as silica and palygorskite, and adopt single-component metal active sites, these catalysts are prone to sintering of active components and failure of hydrophobic layers under high-temperature water vapor environments. Meanwhile, conventional supports, including Al₂O₃, SiO₂, and ZrO₂ have inherent deficiencies such as strong hydrophilicity, single pore structures, and poor metal dispersion. In this work, two-dimensional Ti₃C₂ MXene nanosheets are used as the support to construct a novel fluorinated hydrophobic NiCo-CeO₂/F-Ti₃C₂ catalyst for coupled hydrogen production from biomass pyrolysis gas. Compared with the reported silane-modified hydrophobic catalytic systems, this work has three prominent innovations and differentiated advantages.

First, layered F-Ti₃C₂ supports are fabricated via HF-HCl co-etching combined with PFOTS perfluorosilane fluorination modification. The two-dimensional layered MXene skeleton provides abundant anchoring sites for metal species, while covalently grafted perfluoroalkyl chains construct a stable hydrophobic interface with low surface energy, fundamentally inhibiting hydrothermal poisoning caused by water vapor adsorption. Second, CeO₂ promoters and Ni-Co bimetallic alloy active centers are simultaneously loaded on the hydrophobic support. Different from the existing single-Ni or single-Co catalytic systems, the synergistic effect of the bimetallic alloy and the reversible Ce³⁺/Ce⁴⁺ redox cycle of cerium-based oxides synergistically enhance the activities of CH₄ reforming, the water-gas shift reaction, and light hydrocarbon cracking. Third, hydrophobic interface regulation, bimetallic alloy catalysis, and rare-earth promoter modification are integrated into one system. Relying on the highly conductive layered structure of MXene to accelerate interfacial electron transfer, the catalyst achieves high CO and CH₄ conversion rates as well as high H₂ selectivity, and greatly improves the hydrothermal stability of the catalyst at high temperature. This study provides a new strategy for designing anti-deactivation catalysts for efficient hydrogen production from biomass pyrolysis gas.

Experimental section

Experimental reagents

Ti₃AlC₂ powder (purity $\geq 98\%$, particle size 400 mesh) and perfluorooctyltriethoxysilane (PFOTS, purity $\geq 97\%$) were purchased from Aladdin Reagent Co., Ltd. Hydrogen fluoride (HF, mass fraction 40%), hydrochloric acid (HCl, mass fraction 37%), cerium nitrate (Ce(NO₃)₃·6H₂O, purity $\geq 99\%$), nickel nitrate (Ni(NO₃)₂·6H₂O, purity $\geq 99\%$), cobalt nitrate (Co(NO₃)₂·6H₂O, purity $\geq 99\%$), and absolute ethanol (C₂H₅OH, purity $\geq 99.7\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd.

The power density and rated power parameters of all experimental testing equipment are listed in Section 2.3.

Preparation of catalysts

Preparation of Ti₃C₂ MXene two-dimensional nanosheet support

A total of 100 mL of 10 mol/L HF solution is taken and slowly added to a polytetrafluoroethylene beaker containing 5

g of Ti_3AlC_2 powder. The mixture is stirred at room temperature for 24 h to etch and remove the Al layer in Ti_3AlC_2 . Then, 50 mL of 8 mol/L HCl solution is added, and stirring is continued for 6 h to enhance the etching effect. A crude Ti_3C_2 MXene product is obtained. The crude product is centrifuged and washed with deionized water. The washing process is repeated until the pH value of the supernatant reaches 6-7. The washed precipitate is dried in a vacuum oven at 60 °C for 12 h. The resulting Ti_3C_2 MXene two-dimensional nanosheet support is obtained and denoted as Ti_3C_2 .

Preparation of fluoro-group modified Ti_3C_2 MXene support

A total of 2 g of Ti_3C_2 MXene two-dimensional nanosheets is weighed and dispersed in 50 mL of absolute ethanol. The mixture is ultrasonically dispersed for 30 min to form a uniform suspension. Then, 0.4 g of PFOTS is added, and the mixture is stirred at room temperature for 6 h for hydrophobic group grafting. The product is vacuum-dried at 120 °C for 8 h. The fluoro-group-modified Ti_3C_2 MXene support is obtained and denoted as F- Ti_3C_2 .

Preparation of $\text{CeO}_2/\text{F-Ti}_3\text{C}_2$ support

The corresponding mass of cerium nitrate is calculated and weighed according to the designed Ce loading. A homogeneous cerium nitrate solution is prepared. A total of 2.0 g of F- Ti_3C_2 support is weighed and placed in a beaker. The cerium nitrate solution is slowly added dropwise onto the F- Ti_3C_2 support. The mixture is stirred at room temperature for 4 h. The mixture is then vacuum-dried at 120 °C for 12 h. The dried sample is transferred into a muffle furnace and calcined at 290 °C for 2 h under nitrogen atmosphere. The calcination is performed to ensure the complete decomposition of cerium nitrate into CeO_2 . The $\text{CeO}_2/\text{F-Ti}_3\text{C}_2$ support is obtained.

Preparation of $\text{NiCo-CeO}_2/\text{F-Ti}_3\text{C}_2$ catalyst

The corresponding masses of nickel nitrate and cobalt nitrate are calculated and weighed according to the total NiCo loading and molar ratio. A homogeneous solution is prepared with the weighed nickel nitrate and cobalt nitrate. $\text{CeO}_2/\text{F-Ti}_3\text{C}_2$ support is weighed. The prepared solution is slowly added dropwise onto the $\text{CeO}_2/\text{F-Ti}_3\text{C}_2$ support. The mixture is stirred at room temperature for 6 h. The mixture is then vacuum-dried at 120 °C for 12 h. The dried sample is placed into a muffle furnace and calcined at 260 °C for 1.5 h under nitrogen atmosphere. After calcination, the sample is reduced at 290 °C for 2 h under hydrogen atmosphere. The $\text{NiCo-CeO}_2/\text{F-Ti}_3\text{C}_2$ catalyst is obtained.

Activity evaluation of catalysts

Figure 1 shows the process flow diagram of catalyst activity evaluation. The fixed-bed reactor is a quartz tube with inner diameter 10 mm and a length of 500 mm. The programmed heating furnace is equipped with a heating tube with a rated power density of 12 W/cm², a maximum heating power of 1.8 kW, and a temperature control accuracy is $\pm 1^\circ\text{C}$. The gas chromatograph is equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID), with a rated power of 60 W and 120 W, respectively, ensuring stable and continuous online detection of gas components. The gas chromatograph is equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID), and The gas products are analyzed using a GC-2014c gas chromatograph, and the detailed testing conditions are listed in the table 1. It can simultaneously detect components such as H_2 , CO, CO_2 , CH_4 and C_2/C_3 hydrocarbons. A total of 0.5 g of catalyst (40-60 mesh) is weighed and uniformly loaded in the middle part of the quartz tube of the fixed-bed reactor. The upper and lower ends of the catalyst are filled with quartz wool to prevent catalyst particles from being blown away by the gas flow. The nitrogen cylinder is opened, and the flow rate is adjusted to 50 mL·min⁻¹. The reactor is purged for 30 min to remove air inside the reactor. Then, the temperature of the reactor is raised to 600 °C. The nitrogen cylinder is closed, and the simulated biomass pyrolysis gas cylinder is opened. The flow rate is adjusted to 25 mL·min⁻¹. The pyrolysis gas contacts the catalyst for the coupling hydrogen production reaction. The product components are determined by gas chromatography.

Calculation of evaluation indexes

CH_4 conversion rate, CO conversion rate, and H_2 yield are used as the indexes for evaluating catalyst performance. The calculation formulas are as follows:

$$\text{CO conversion: } X_{\text{CO}} = \frac{n_{\text{CO}, \text{in}} - n_{\text{CO}, \text{out}}}{n_{\text{CO}, \text{in}}} \times 100\%$$

$$\text{CH}_4 \text{ conversion: } X_{\text{CH}_4} = \frac{n_{\text{CH}_4, \text{in}} - n_{\text{CH}_4, \text{out}}}{n_{\text{CH}_4, \text{in}}} \times 100\%$$

$$\text{H}_2 \text{ yield: } Y_{\text{H}_2} = \frac{n_{\text{H}_2, \text{out}}}{(n_{\text{CO}, \text{in}} - n_{\text{CO}, \text{out}}) + 2(n_{\text{CH}_4, \text{in}} - n_{\text{CH}_4, \text{out}})} \times 100\%$$

Catalyst characterization tests

(1) X-ray diffraction (XRD) test: XRD is used to analyze the phase composition, existing forms of metals, and crystallinity. Cu target $\text{K}\alpha$ radiation is adopted. The tube voltage is set at 40 kV, and the tube current is set at 40 mA. The scanning range is $2\theta = 5^\circ - 80^\circ$. The scanning rate is 5°·min⁻¹. The step size is 0.02°.

Table 1: Operating conditions of GC

Detector	TCD	FID
Chromatographic column	Chromosorb 101, 3 m×1/8 inch stainless steel packed column	Porapak Q, 3 m×1/8 inch stainless steel packed column
Gasification chamber temperature (°C)	360	360
Column box temperature (°C)	80	80
Detector temperature (°C)	100	150
Determination of gases	CO_2 , H_2 , CO	CH_4 , C_2/C_3

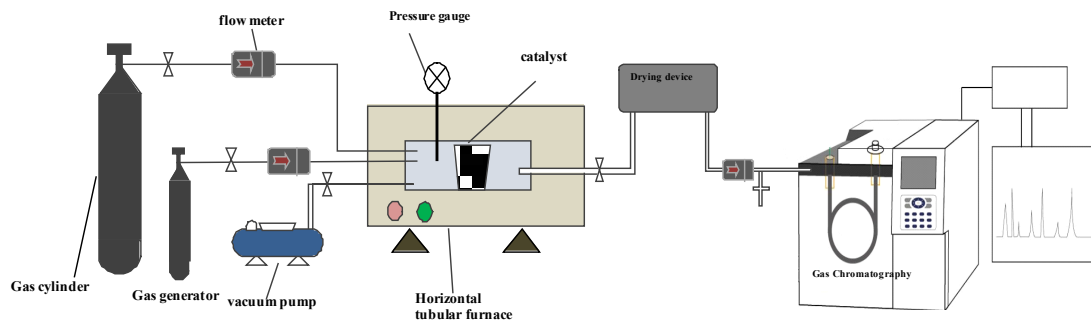


Fig. 1. Process flow diagram of catalyst activity evaluation

(2) Scanning electron microscopy (SEM) test: SEM is used to observe the microscopic morphology. The accelerating voltage is 10 kV, and the magnification is 5000-50000 times. The secondary electron imaging mode is employed. The samples are subjected to gold-spraying treatment before the test. The gold-spraying thickness is 5-10 nm.

(3) X-ray photoelectron spectroscopy (XPS) test: XPS is used to analyze the surface chemical composition and element valence states. Al target K α radiation ($h\nu=1486.6$ eV) is used. The vacuum degree is $\leq 1 \times 10^{-9}$ Pa. The binding energy is calibrated using C 1s (284.8 eV). The full-spectrum scanning range is 0-1200 eV. The high-resolution scanning range is adjusted according to target elements.

(4) Contact angle test: The contact angle test is used to evaluate the hydrophobicity. The sessile drop method is adopted. The test temperature is 25 °C, and the humidity is 50%. The volume of deionized water droplets is 5 μ L. Each sample is tested 3 times, and the average value is taken as the final contact angle.

Results and discussion

Characterization analysis of Ti_3C_2 and F- Ti_3C_2 supports

XRD analysis

Figure 2 shows the XRD patterns of Ti_3AlC_2 , Ti_3C_2 , and F- Ti_3C_2 . The pristine Ti_3AlC_2 phase exhibits strong diffraction peaks at $2\theta=9.5^\circ$, 19.0° , and 39° . These peaks correspond to its (002), (004), and (104) crystal planes, respectively. The Ti-C layers and Al layers in Ti_3AlC_2 stack alternately. This is a typical characteristic of the MAX phase (Guénolé et al. 2022). For the Ti_3C_2 two-dimensional nanosheets obtained by HF-HCl etching, the strong peaks of the original Ti_3AlC_2 basically disappear. A distinct characteristic peak of Ti_3C_2 appears near $2\theta=6.5^\circ$. This indicates that the Al atomic layer is effectively stripped and the structure of Ti_3AlC_2 is disassembled. Two-dimensional sheet-dispersed Ti_3C_2 is successfully obtained. The diffraction peaks of fluorine-modified F- Ti_3C_2 shift to lower angles at small 2θ values, and the peak heights also decrease. According to the Bragg equation ($2d\sin\theta=n\lambda$), this indicates that the interlayer spacing d increases (Guan et al. 2020). This suggests that fluorine groups intercalate between the layers and widen the interlayer distance. The decrease in peak height reflects a reduction in the crystal domain size of Ti_3C_2 and a slight decrease in layered order. These two phenomena together confirm the successful fluoro-group modification.

SEM analysis

Figure 3 shows the SEM images of Ti_3AlC_2 , Ti_3C_2 , and F- Ti_3C_2 . Figure 3(a) corresponds to Ti_3AlC_2 powder. It presents a bulk aggregation morphology, with fine particles attached to its surface. It is a typical dense bulk structure of the MAX phase. Figure 3(b) corresponds to Ti_3C_2 MXene two-dimensional nanosheets obtained by HF-HCl etching. Clear and uniformly dispersed two-dimensional layered structures are observed, with gaps between the layers. Meanwhile, the surface of the nanosheets is relatively smooth without obvious impurities. This indicates that the etching process is relatively complete and that the two-dimensional layered structure is successfully exfoliated (Hasan et al. 2025). Figure 3(c) shows F- Ti_3C_2 obtained by PFOTS modification. It still maintains a complete two-dimensional layered structure, with only a slightly rough surface. This is attributed to the hydrophobic film formed by PFOTS grafting via siloxane bonds. The film has no obvious particles and uniformly covers the surface. The comparison shows that HF-HCl etching of Ti_3AlC_2 can successfully obtain a layered structure with clear two-dimensional morphology. Subsequent PFOTS modification can uniformly form a hydrophobic film while maintaining its two-dimensional layered structure (Zhou et al. 2022).

XPS analysis

Figure 4 shows the XPS spectra of Ti_3C_2 and F- Ti_3C_2 . Characteristic peaks of F 1s, O 1s, C 1s, and Ti 2p are observed in the survey spectrum of pristine Ti_3C_2 in Figure 4(a). This

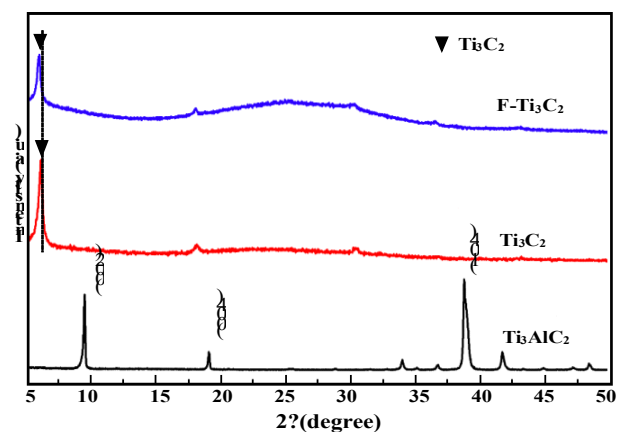


Fig. 2. XRD patterns of Ti_3AlC_2 , Ti_3C_2 and F- Ti_3C_2

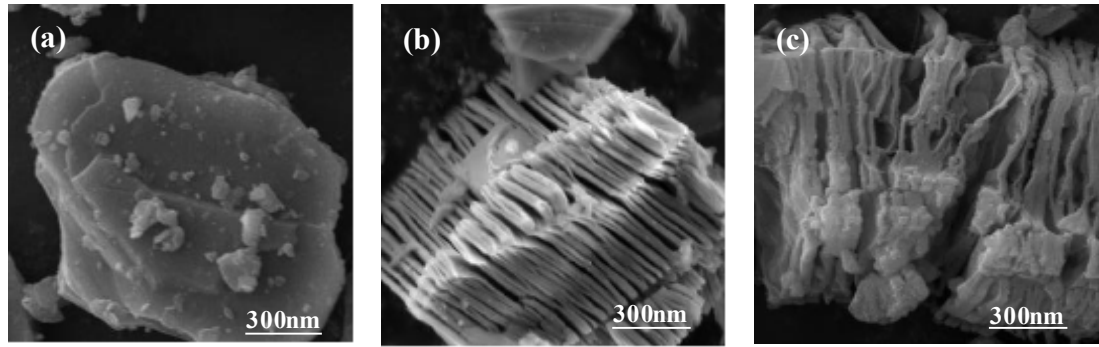


Fig. 3. SEM of Ti_3AlC_2 , Ti_3C_2 and $\text{F-Ti}_3\text{C}_2$

confirms the formation of typical MXene surface functional groups such as Ti-F and Ti-O/Ti-OH on Ti_3C_2 after HF-HCl etching. It provides direct evidence that the Al layer is effectively etched. Characteristic peaks of Ti^{2+} (Ti-C, 454.8 eV/460.5 eV), Ti^{3+} (Ti-O/Ti-X, 456.2 eV/462.0 eV), and Ti^{4+} (TiO_2 , 458.6 eV/464.3 eV) are obtained by peak fitting of the high-resolution Ti 2p spectrum in Figure 4(b). The appearance of the Ti^{4+} peak is attributed to slight oxidation on the Ti_3C_2 surface. The fitted peak of the Ti-X (X=F/O) bond reflects the diversity of surface functional groups after etching (Li et al. 2020). The C 1s spectrum in Figure 4(c) can be deconvoluted into C-C (284.8 eV), C-O (286.0 eV), and Ti-C (281.6 eV) peaks. As the characteristic skeleton bond of Ti_3C_2 , the Ti-C bond shows a sharp peak and a significant proportion. This indicates that the layered structure of MXene is not destroyed (Zeng et al. 2024). The O 1s spectrum in Figure 4(d) is further fitted into Ti-O-Ti (529.8 eV), Ti-OH (531.2 eV), and surface-

adsorbed oxygen (532.5 eV) peaks. It shows that the surface of pristine Ti_3C_2 is dominated by hydrophilic functional groups such as hydroxyl and oxy groups as active sites (Huang et al. 2020).

Figure 4(e) shows the survey spectrum of $\text{F-Ti}_3\text{C}_2$ after PFOTS modification. The intensity of the F 1s peak is significantly enhanced compared with that of pristine Ti_3C_2 . A characteristic Si-O peak appears in the O 1s spectrum. This provides evidence that PFOTS molecules are successfully grafted onto the surface of Ti_3C_2 . Two characteristic peaks of C-F (688.0 eV) and C-Ti-F_x (685.5 eV) are fitted from the high-resolution F 1s spectrum in Figure 4(k). The C-F bond is the typical bonding form of perfluoroalkyl groups in PFOTS molecules. The C-Ti-F_x peak indicates that PFOTS forms chemical bonding with Ti sites on the Ti_3C_2 surface, which supports the formation of chemical bonding rather than simple physical adsorption. New characteristic peaks of -CF₂-

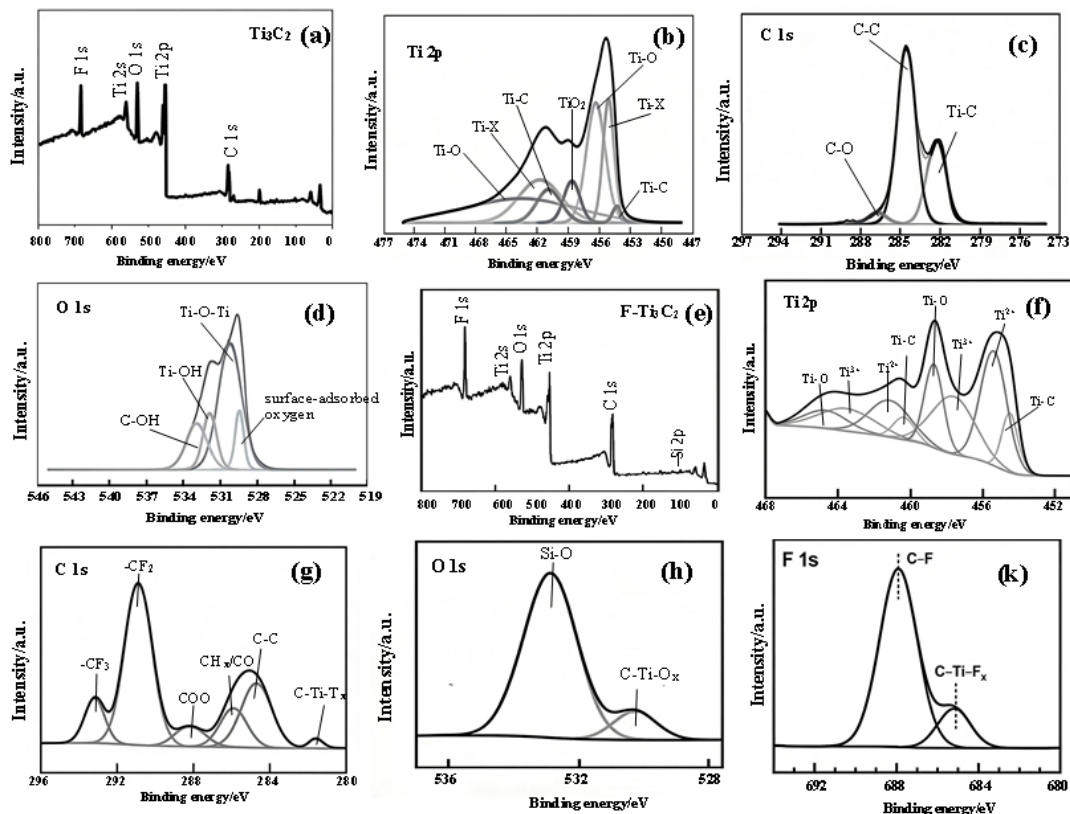


Fig. 4. XPS spectra of Ti_3C_2 and $\text{F-Ti}_3\text{C}_2$: (a)-(d) correspond to the survey spectrum and high-resolution spectra of Ti, C and O for Ti_3C_2 ; (e)-(k) correspond to the survey spectrum and high-resolution spectra of Ti, C, O and F for PFOTS-modified $\text{F-Ti}_3\text{C}_2$.

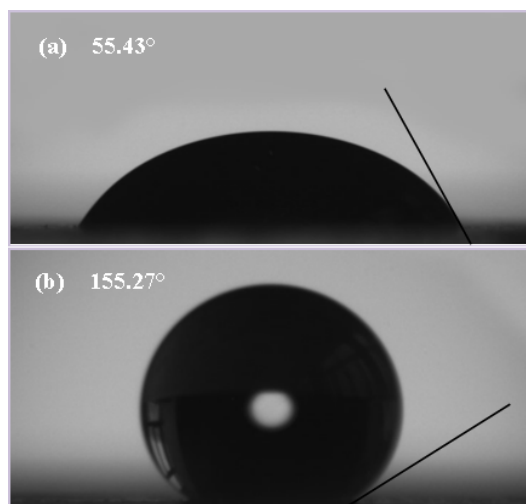


Fig. 5. The contact angle test results of Ti_3C_2 and $\text{F-Ti}_3\text{C}_2$

(291.0 eV) and $-\text{CF}_3$ (293.5 eV) appear in the C 1s spectrum deconvolution in Figure 4(g). These are characteristic carbon peaks of the perfluorooctyl chain in PFOTS. Meanwhile, the appearance of CH_x/CO (285.5 eV) and COO (288.0 eV) peaks corresponds to the alkyl and ester groups in PFOTS molecules. The retention of the Ti-C (281.6 eV) peak indicates that the main framework of Ti_3C_2 is not destroyed. The Si-O (532.0 eV) peak becomes the main peak in the O 1s spectrum deconvolution in Figure 4(h). It replaces the dominant position of Ti-OH in pristine Ti_3C_2 . This indicates that PFOTS is covalently bonded to the hydroxyl groups on the Ti_3C_2 surface through a Si-O-Ti condensation reaction. The grafting of hydrophobic functional groups is thus achieved. The proportion of Ti^{4+} in the Ti 2p spectrum deconvolution of $\text{F-Ti}_3\text{C}_2$ in Figure 4(f) increases slightly. This is speculated to be caused by slight oxidation on the surface. However, the strong signal of the Ti-C main peak still indicates the structural integrity of MXene.

In summary, the XPS characterization results show that PFOTS modification introduces hydrophobic functional groups onto the Ti_3C_2 surface via Si-O-Ti bonds without destroying

the main layered structure of Ti_3C_2 . Meanwhile, it promotes the transformation of Ti_3C_2 surface functional groups from hydrophilic groups ($-\text{OH}$, $-\text{O}-$) to hydrophobic ones. Thus, the hydrophobicity of the Ti_3C_2 interface is achieved.

Contact angle analysis

Figure 5 shows the contact angle test results of Ti_3C_2 and $\text{F-Ti}_3\text{C}_2$. The contact angle of Ti_3C_2 is only 55.43° , indicating that pristine Ti_3C_2 has strong hydrophilicity. This is because a large number of hydroxyl groups exist on its surface. These groups are prone to adsorb water vapor. The contact angle of $\text{F-Ti}_3\text{C}_2$ support modified by PFOTS increases significantly to 155.27° . This demonstrates that the hydrophobicity of Ti_3C_2 is greatly improved after fluoro-group modification. It meets the standard of strong hydrophobicity. A hydrophobic film forms on the surface of modified $\text{F-Ti}_3\text{C}_2$. Combined with the determination results in Figure 4(g), the $-\text{CF}_3$ and $-\text{CF}_2-$ groups have extremely strong hydrophobicity and can effectively repel water molecules. They can inhibit water vapor adsorption and condensation on the support surface. Meanwhile, combined with the SEM image in Figure 3(c), the formation of the hydrophobic film does not block the interlayer gaps of Ti_3C_2 . It does not affect the subsequent loading of promoters and active components. The above results confirm that fluoro-group modification can significantly enhance the hydrophobicity of Ti_3C_2 support (Yang et al. 2025).

Optimization of catalyst preparation parameters and activity evaluation

Coupling evaluation experiments for hydrogen-rich fuel are conducted at 600°C . CO conversion, CH_4 conversion, and H_2 selectivity are used as the evaluation indicators. The optimal preparation parameters of the $\text{NiCo-CeO}_2/\text{F-Ti}_3\text{C}_2$ catalyst are screened. These parameters include NiCo metal loading, Ni/Co molar ratio, and Ce loading. The stability of the optimal catalyst is then evaluated.

Effects of NiCo metal loading on CO/ CH_4 conversion and H_2 selectivity

Catalysts of $\text{NiCo}/\text{F-Ti}_3\text{C}_2$ are prepared. The total loadings of NiCo are set at 5%, 8%, 13%, and 17%. The Ni/Co molar

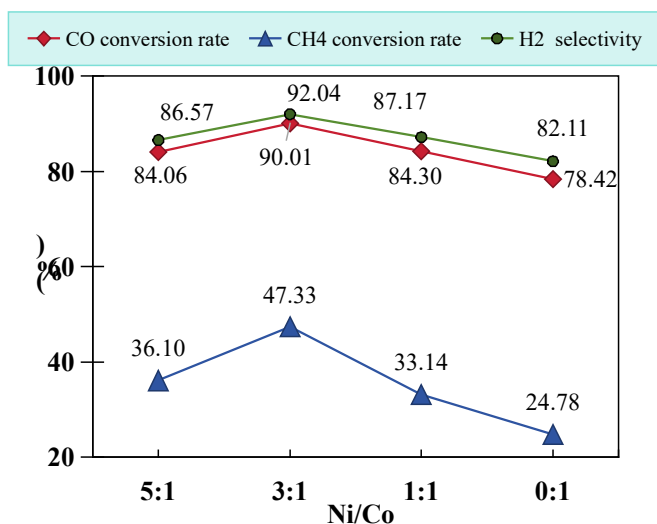


Fig. 6. Effects of NiCo loading on CO/ CH_4 conversion and H_2 selectivity

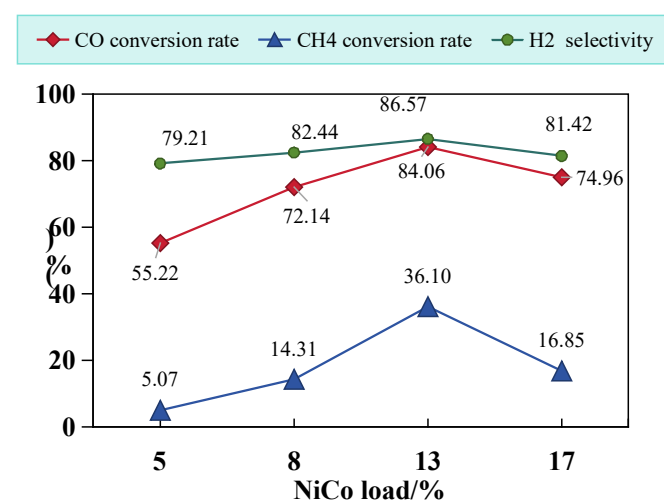


Fig. 7. Effects of Ni/Co molar ratio on CO/ CH_4 conversion and H_2 selectivity

ratio is controlled at 3:1. The results of the activity evaluation are shown in Figure 6. It can be seen from Figure 6 that CO conversion, CH₄ conversion, and H₂ selectivity all show a trend of first increasing and then decreasing with the increase in NiCo loading. The CO conversion, CH₄ conversion, and H₂ selectivity reach their peak values when the NiCo loading is 13%. The peak values are 79.21%, 36.10%, and 84.06%, respectively. The main reason is that a 13% NiCo loading can form a large number of Ni-Co alloy active sites. The interaction between the active sites and the support can efficiently activate the C–O bonds of CO and C–H bonds of CH₄. This improves the conversion efficiency and H₂ selectivity. When the loading increases to 17%, excessive NiCo metals agglomerate. This leads to a decrease in the exposure of active sites (Masoudpanah et al. 2025). It also blocks the pores of the support, hindering the contact between reactants and active sites as well as the desorption of H₂. Finally, all performance indicators decrease. Therefore, 13% is determined as the optimal NiCo loading.

Effects of Ni/Co molar ratio on CO/CH₄ conversion and H₂ selectivity

NiCo/F-Ti₃C₂ catalysts are prepared. The Ni/Co molar ratios are set at 5:1, 3:1, 1:1 and 0:1. The total NiCo loading is controlled at 13%. The results of the activity evaluation are shown in Figure 7. It can be observed from Figure 7 that, with the Ni/Co molar ratio changing from 5:1 to 0:1, both CO conversion and CH₄ conversion show a trend of first increasing and then decreasing. H₂ selectivity also first increases to a peak and then decreases continuously. When the Ni/Co molar ratio is 3:1, the CO conversion, CH₄ conversion, and H₂ selectivity reach 90.01%, 47.33%, and 92.04%, respectively. These values are the maximum within the entire ratio adjustment range. From the perspective of active sites and the alloy formation mechanism, when the Ni/Co molar ratio is 3:1, the proportion of nickel-dispersed active sites and the formation of nickel-cobalt alloys in the system reach a balance. The synergistic effect of the two types of sites maximizes the adsorption and activation efficiency of CO and CH₄ as well as the selectivity of H₂ generation. Thus, the catalytic performance reaches its peak. When the Ni/Co molar ratio is higher than 3:1 (e.g.,

5:1), the formation of nickel-cobalt alloys is limited, and the proportion of nickel active components is relatively high. Nickel is prone to agglomeration, leading to a reduction in the number of effective active sites. Therefore, the conversion effect and selectivity are poor. When the Ni/Co molar ratio is lower than 3:1 (e.g., 1:1), the increase in Co content promotes the formation of more nickel-cobalt alloys. The proportion of nickel-dispersed active sites decreases accordingly, and the total number of active sites is reduced. The catalytic performance further declines. When the ratio continues to decrease to 0:1, only cobalt active sites remain in the system. Cobalt is not only prone to self-agglomeration but also cannot achieve high-efficiency catalysis like nickel or nickel-cobalt alloys. Finally, the CO conversion, CH₄ conversion, and H₂ selectivity all remain at the lowest level. In summary, the optimal Ni/Co molar ratio is 3:1.

Effects of Ce loading on CO/CH₄ conversion and H₂ selectivity

Ce is first loaded onto the F-Ti₃C₂ support. The Ce loadings are set at 3%, 5%, 8%, and 11%. Then, NiCo metals are loaded onto the support. The total NiCo loading is controlled at 13%, and the Ni/Co molar ratio is fixed at 3:1. The NiCo-CeO₂/F-Ti₃C₂ catalysts are prepared via calcination under a nitrogen atmosphere followed by reduction under a hydrogen atmosphere. The results of the activity evaluation are shown in Figure 8.

It can be observed from Figure 8 that, with the Ce loading increasing from 2% to 11%, CO conversion, CH₄ conversion, and H₂ selectivity all show a trend of increasing significantly to a peak and then decreasing continuously. When the Ce loading is 5%, all catalytic performance indicators reach their maximum within the entire adjustment range. It achieves the optimal preparation effect of hydrogen-rich fuel gas. From the perspective of the catalytic mechanism, the core function of CeO₂ is to regulate the dispersion of Ni-Co alloy active metals. It improves the effective utilization and catalytic activity of active sites. When the Ce loading is lower than 5%, the content of CeO₂ is insufficient, and its regulating effect on the dispersion of Ni-Co alloys is limited. Some Ni-Co metals are

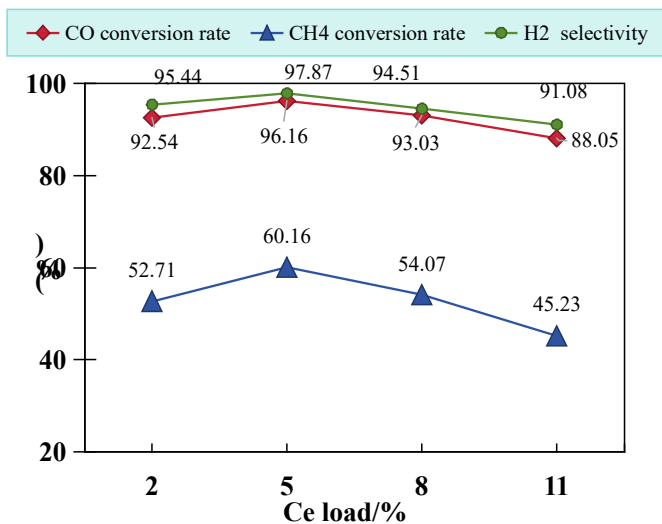


Fig. 8. Effects of Ce loading on CO/CH₄ conversion and H₂ selectivity

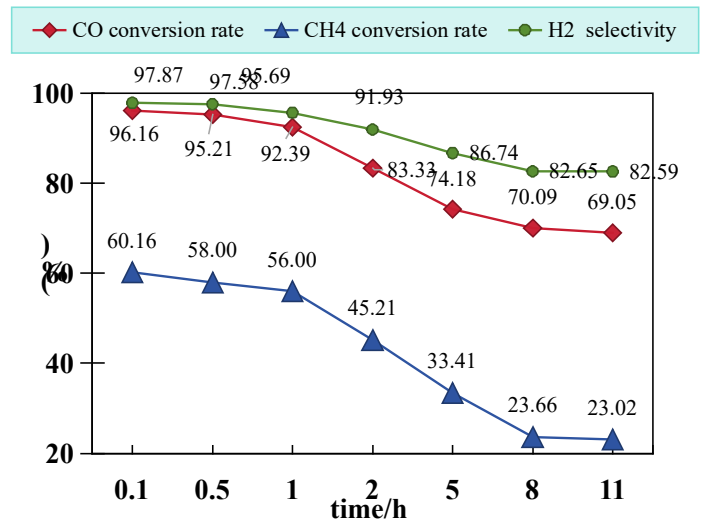


Fig. 9. Evaluation of the optimal NiCo-CeO₂/F-Ti₃C₂ catalyst

prone to agglomeration, leading to a reduction in the number of effective active sites. The catalytic performance cannot be fully exerted. When the Ce loading is higher than 5%, excessive CeO_2 cannot further optimize the dispersion of Ni-Co alloys. Instead, it aggregates on the support surface and blocks the pores. This hinders the mass transfer process of reactants and products, and the catalytic efficiency of active components decreases significantly. The catalytic performance continues to decrease with the increase in Ce loading. In summary, the optimal Ce loading is 5%.

Stability evaluation of the optimal $\text{NiCo-CeO}_2/\text{F-Ti}_3\text{C}_2$ catalyst

The optimal catalyst is prepared with a Ce loading of 5%, a NiCo loading of 13% and a Ni/Co molar ratio of 3:1. A stability test is conducted on this catalyst. CO conversion, CH_4 conversion, and H_2 selectivity are measured at different time intervals. The measurement results are shown in Figure 9.

Figure 9 shows that, for the optimal catalyst, CO/ CH_4 conversion and H_2 selectivity decrease only slightly within 0-1 h, maintaining a stable trend. The performance indicators drop rapidly with a significant decrease within 1-8 h. The performance stabilizes without obvious fluctuations within 8-11 h. At the initial 6 minutes of the reaction, CO conversion reaches 96.16%, CH_4 conversion reaches 60.16%, and H_2 selectivity reaches 97.87%. After 11 h, CO conversion maintains at 69.05%, CH_4 conversion remains at 23.02%, and H_2 selectivity remains at 82.59%. Within 0-1 h, the catalytic performance attenuates slightly. The hydrophobic surface structure is assumed to remain relatively intact during this stage. The overall structure of the catalyst and the catalytic efficiency of active centers do not undergo substantial changes. The performance decline is therefore extremely small. Within 1-8 h, the high-temperature reaction environment causes thermal decomposition of fluoro-based hydrophobic groups on the Ti_3C_2 surface. The hydrophobic properties of the support are thereby weakened, which may lead to aqueous-phase poisoning of the catalyst. This results in a rapid decline of conversion and selectivity. Within 8-11 h, the support structure and hydrophobic groups of the catalyst undergo irreversible structural changes. A dynamic balance is achieved between slight carbon deposition and water vapor poisoning. The catalytic function of the active components is not completely lost, and they can still participate in the hydrogen production reaction. Therefore, all catalytic performance indicators tend to stabilize without significant fluctuations. In summary, the optimal catalyst exhibits stage-specific catalytic stability during the 11 h stability test. Performance attenuation is slight in the early stage, with good structural integrity. Performance drops sharply in the middle stage, which may be attributed to structural damage and poisoning effects. Performance

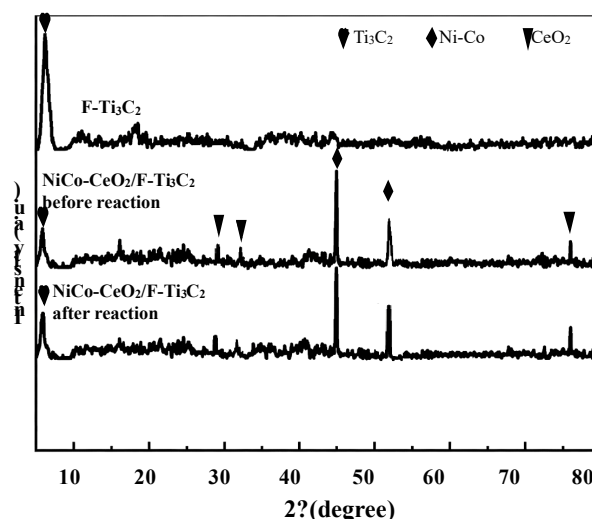


Fig. 10. XRD patterns of $\text{F-Ti}_3\text{C}_2$, the optimal $\text{NiCo-CeO}_2/\text{F-Ti}_3\text{C}_2$ before reaction and after 0.1 h of

stabilizes in the later stage after a balance between poisoning and catalytic processes is achieved. Overall, it has certain potential for long-term catalytic applications.

Catalyst characterization analysis

XRD analysis

It can be seen from Figure 10 that, in the XRD patterns of the optimal $\text{NiCo-CeO}_2/\text{F-Ti}_3\text{C}_2$ catalyst before and after the reaction, besides the characteristic diffraction peaks of Ti_3C_2 , there are obvious characteristic diffraction peaks of CeO_2 (Kanmaz et al. 2025). The peaks are located at $2\theta=28.6^\circ$, 33.1° , and 76.7° . This indicates that the successfully loaded Ce forms a stable oxide phase. The characteristic diffraction peaks of the Ni-Co alloy appear in the patterns (Rai & Hegde 2024). The peaks are located at $2\theta=44.5^\circ$ and 51.7° . This demonstrates that the oxides of Ni and Co are successfully reduced to the Ni-Co alloy. In addition, the characteristic diffraction peaks of the Ni-Co alloy have high intensity, indicating that the Ni-Co alloy has good crystallinity. The characteristic diffraction peaks of CeO_2 have low intensity, suggesting that CeO_2 is uniformly dispersed without obvious agglomeration. The characteristic peaks of the optimal catalyst show little change before and after the reaction. This indicates that the catalyst has good structural stability.

SEM analysis

Figures 11(a)-(c) show the SEM characterization results of the optimal $\text{NiCo-CeO}_2/\text{F-Ti}_3\text{C}_2$ catalyst. The results are obtained under the hydrogen-rich atmosphere of biomass pyrolysis gas at 600°C . The three states are the unreacted

Table 2: XPS analysis of Ni, Co, O and Co for the optimal catalyst

optimal catalyst	$\text{Ni}^0/\text{Ni}^{2+}$	$\text{Co}^0/\text{Co}^{2+}$	$\text{O}_{\text{ads}}/\text{O}_{\text{total}}$	$\text{Ce}^{3+}/\text{Ce}^{4+}$
	molar ratio	molar ratio	(at.%)	molar ratio
unreaction	1.55	1.17	26.1	0.28
after 8h reaction	2.06	1.49	18.6	0.17

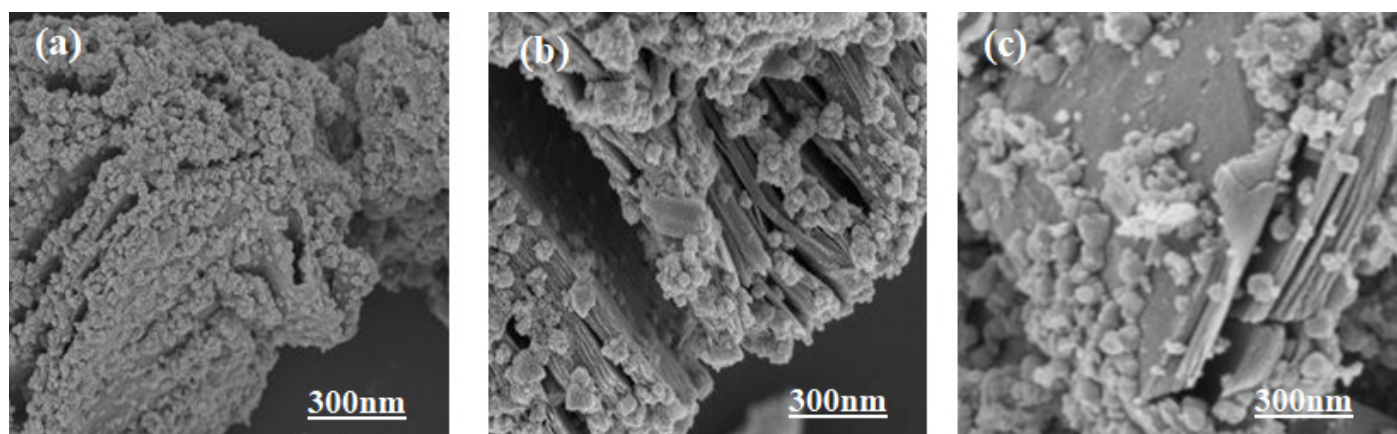


Fig. 11. SEM images of the optimal NiCo-CeO₂/F-Ti₃C₂ catalyst

catalyst, the catalyst reacted for 1 h, and the catalyst reacted for 8 h. For the unreacted catalyst (Figure 11 (a)), the active metal particles are uniformly dispersed on the support surface at the nanoscale. No obvious agglomeration is observed. The hydrophobicity imparted by fluoro-group modification endows the catalyst surface with a rough micromorphology, which provides highly dispersed active sites. After 1 h of reaction (Figure 11 (b)), the active particles show slight agglomeration, and some small particles fuse together. The catalyst structure remains intact. The catalyst surface still presents a fuzzy and rough state, indicating that the fluoro-based hydrophobic groups are not largely destroyed and the hydrophobicity is retained. When the reaction time is extended to 8 h (Figure 11 (c)), the agglomeration degree of active particles increases significantly. Large particle aggregates form on the support surface. Meanwhile, the support surface changes from rough to smooth and flat. This may be because the fluoro-based hydrophobic groups undergo thermal decomposition and are removed at 600 °C. The long-term thermal effect promotes further migration and fusion of active particles, eventually leading to significant changes in the surface morphology and active particle distribution of the catalyst (Liu et al. 2022). The changes in catalyst morphology further support the stability evaluation results in Figure 9.

XPS analysis

Table 2 presents the XPS analysis results of the optimal catalyst before the reaction and after 8 h of reaction. The changes in the valence states of various elements and adsorbed oxygen clearly reflect the structural evolution and activity decay mechanism of the catalyst under the hydrogen-rich atmosphere of biomass pyrolysis gas at 600 °C. In the unreacted catalyst, the molar ratios of Ni⁰/Ni²⁺ and Co⁰/Co²⁺ are 1.55 and 1.17, respectively. After 8 h of reaction, these two ratios increase to 2.06 and 1.49, respectively. This indicates that Ni and Co elements are reduced to their metallic states during the high-temperature reaction process (Zhang et al. 2024). Although metallic Ni and Co are the active centers of the catalytic reaction, combined with the particle agglomeration observed in the SEM characterization, the aggregation of metallic species leads to a decrease in the effective exposure of active sites.

The proportion of adsorbed oxygen (O_{ads}) in the total oxygen decreases from 26.1% to 18.6%. As a key active

oxygen species in the catalytic reaction, the sharp reduction in its content significantly weakens the adsorption and activation ability of the catalyst for the reactants of biomass pyrolysis gas. The molar ratio of Ce³⁺/Ce⁴⁺ decreases from 0.28 to 0.17, indicating an increase in the proportion of Ce⁴⁺. The Ce³⁺/Ce⁴⁺ redox cycle is the core of the cocatalytic effect of cerium dioxide promoter (Gong et al. 2025). The reduction in the efficiency of this cycle further weakens the promoting effect of the promoter on the main catalytic reaction (Mathew & Devi 2024). The comprehensive changes in the valence states of the above elements and oxygen species, together with the agglomeration of catalyst morphology and the decomposition of hydrophobic groups, constitute the internal reasons for the catalytic activity first decreasing sharply and then stabilizing during the reaction process.

Contact angle analysis

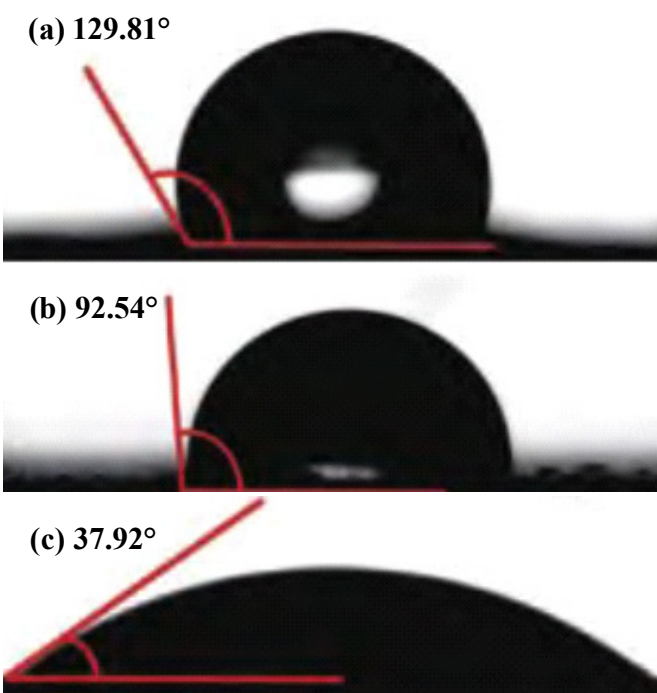


Fig. 12. S. Contact angle measurement results of the optimal catalyst in unreacted state, after 1 h of reaction and after 8 h of reaction

Figures 12(a)-(c) show the contact angle measurement results of the optimal catalyst in the unreacted state, after 1 h of reaction, and after 8 h of reaction. The contact angle values decrease from 129.81° to 92.54° and then to 37.92° . This trend is highly correlated with the catalytic activity evolution of the hydrogen production reaction in the aqueous phase of biomass pyrolysis gas. The contact angle of the unreacted catalyst is much larger than 90° . The strong hydrophobic surface constructed by fluoro-group modification and the uniformly dispersed active particles can resist the adsorption and agglomeration of water vapor in the reaction system (Zhang et al. 2025). This avoids the coverage of active sites by water film and ensures sufficient contact between CO, CH₄, and active centers. Thus, the catalyst exhibits excellent initial activity. After 1 h of reaction, the contact angle is slightly larger than 90° . The hydrophobicity decreases significantly. This is because some fluoro-based hydrophobic groups decompose under high temperature. Meanwhile, the slight agglomeration of active particles reduces the surface roughness (Chen 2026). A small amount of water vapor begins to adsorb and occupy the active sites. The catalytic activity shows an initial sharp decline. After 8 h of reaction, the contact angle drops sharply to 37.92° . The catalyst surface becomes hydrophilic (Chen & Wang 2026). The fluoro-based groups may have substantially decomposed under the synergistic effect of high temperature and water vapor. Severe particle agglomeration makes the surface tend to become smooth. A large amount of water vapor adsorbs to form a water film. It not only blocks the active sites but also hinders the diffusion of reactants. It also inhibits the hydrogen production reaction. As a result, the catalytic activity drops continuously and sharply during 1-8 h. The subsequent stable activity is related to the substantial decomposition of hydrophobic groups and the dynamic equilibrium of water vapor adsorption.

Conclusions

This study prepares hydrophobic F-Ti₃C₂ MXene two-dimensional nanosheets. The preparation involves HF-HCl solution etching and perfluorooctyltriethoxysilane (PFO TS) modification. The F-Ti₃C₂ MXene serves as the catalyst support. CeO₂ promoters and Ni-Co alloy active components are loaded onto the support. The loading process adopts the impregnation method combined with nitrogen calcination and hydrogen reduction. A catalyst with both high activity and strong hydrophobicity is obtained. A fixed-bed reactor is used to evaluate the catalyst performance for hydrogen-rich gas production. The effects of total NiCo loading, Ni/Co molar ratio, and Ce loading on CO/CH₄ conversion and H₂ selectivity are investigated. Characterization techniques including XRD, SEM, XPS, and contact angle measurement are applied to analyze the catalytic mechanism. The main conclusions are as follows:

(1) The NiCo-CeO₂/F-Ti₃C₂ catalyst exhibits optimal performance under the following parameters: the total NiCo loading is 13%, the Ni/Co molar ratio is 3:1, and the Ce loading is 5%. In the initial reaction stage, the catalyst achieves a CO conversion rate of 96.16%, a CH₄ conversion of 60.16%, and an H₂ selectivity of 97.87%. The catalyst shows excellent performance in hydrogen production from biomass pyrolysis gas.

(2) The optimal catalyst has a contact angle of 129.81° , showing strong hydrophobicity. XRD characterization confirms the presence of characteristic peaks of the Ni-Co alloy and CeO₂ after nitrogen calcination and hydrogen reduction. SEM characterization reveals an intact two-dimensional layered structure of the catalyst and uniform dispersion of the active components. XPS analysis before and after the reaction indicates changes in the valence states of the elements. The Ce³⁺/Ce⁴⁺ redox cycle efficiency decreases, which impairs the catalyst performance. The catalyst maintains high and stable catalytic activity within 0-1 h, during which the hydrophobic groups remain relatively intact.

(3) The hydrophobic interface constructed by fluoro-group modification effectively resists the hydrothermal deactivation of the catalyst and improves the efficiency of biomass pyrolysis gas conversion. Future work will focus on preparing protective carbon films to protect the hydrophobic groups and prevent them from being damaged during the reaction. This strategy will extend the stable reaction time of the catalyst.

Acknowledgments: This work was financially supported by the Key Industrial Talent Support Project of Xinjiang Uygur Autonomous Region (No. XJRC-2025-GX-ZDCY-04), the Regional Collaborative Innovation Program (Science and Technology Aid to Xinjiang) of Xinjiang Uygur Autonomous Region (No. 2025E02036), and the Xinjiang Uygur Autonomous Region Natural Science Foundation (Youth Fund, Southern Xinjiang United Fund) (Grant No. 20271161766).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Benkacher, N., Iggui, K., Mekhania, Z. A., Benhamida, A., Djermoune, A., Merzeg, F. A., Satha, H. & Layachi, A. (2025). Influence of surface modification of Algerian palygorskite with triethoxyoctylsilane as a hydrophobic agent for enhanced performance, *Journal of Coatings Technology and Research*, 22, 6, pp.2105–2118. DOI:10.1007/s11998-025-01102-x.
- Bootpakdeetam, P., Igboenyasi, O. V., Dennis, B. H. & MacDonnell, F. M. (2024). Superhydrophobic Surface Modification of a Co-Ru/SiO₂ Catalyst for Enhanced Fischer-Tropsch Synthesis, *Catalysts*, 14, 9, pp.638. DOI:10.3390/catal14090638.
- Chen, J. (2026). Preparation of NiFe-CeLaOx/HAP catalyst and its performance and mechanism for high-efficiency methanation of coal pyrolysis gas, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 48, 1, 2595287. DOI:10.1080/15567036.2025.2595287.
- Chen, J. & Wang, J. (2026). Research Progress in Photocatalytic Degradation of Cyclic Pollutants by Electrospun Black TiO₂ / Ag@SiO₂ Nanofiber Membranes, *Inorganics*, 14, 5, 131. DOI:10.3390/inorganics14050131.
- Chen, Z., Meng, Y., Lu, J., Zhou, W., Yang, Z. & Zhou, A. (2023). The Effect of Hydrophobically Modified Iron Catalysts with Hexadecyltrimethoxysilane on Fischer-Tropsch Synthesis, *Chemistry Select*, 8, e202202903. DOI:10.1002/slct.202202903.
- Gong, Y., Qi, W., Lu, W., Chang, Q., Xie, Y., Wang, J. & Deng, X. (2025). Construction of CeO₂/Ti₃C₂Tx heterojunction with antibacterial and antioxidant capabilities for diabetic wound healing, *Journal of Colloid and Interface Science*, 689, 137247. DOI:10.1016/j.jcis.2025.03.036.
- Guan, Y., Zhang, M., Qin, J., Ma, X., Li, C. & Tang, J. (2020).

- Hydrophilicity-Dependent Distinct Frictional Behaviors of Different Modified MXene Nanosheets, *The Journal of Physical Chemistry C*, 124, 25, pp.13664–13671. DOI:10.1021/acs.jpcc.0c01551.
- Guénolé, J., Taupin, V., Vallet, M., Yu, W. & Guitton, A. (2022). Features of a nano-twist phase in the nanolayered Ti₃AlC₂ MAX phase, *Scripta Materialia*, 210. DOI:10.1016/j.scriptamat.2021.114425.
- Guo, H., Wang, Z., Kang, K. & Li, D. (2025). Production of Hydrogen-Rich Syngas via Biomass-Methane Co-Pyrolysis: Thermodynamic Analysis, *Polymers*, 17, 19, pp.2695. DOI:10.3390/polym17192695.
- Gyimah, J., Nyantakyi, G. & Isaac, S. H. (2024). The effect of renewable energy on carbon emissions through globalization, *Heliyon*, 10, e26894. DOI:10.1016/j.heliyon.2024.e26894.
- Hasan, M. Z., Haque, M. H., Ali, M. A., Hossain, M. M. & Uddin, M. M. (2025). Structural, optical, and photocatalytic efficacy of Ti₃C₂ and M₂C (M=Ti, V, Cr, Nb) MXene materials synthesized by etching technique, *AIP Advances*, 15, 3. DOI:10.1063/5.0251436.
- Huang, K., Li, C., Li, H., Ren, G., Wang, L., Wang, W. & Meng, X. (2020). Photocatalytic Applications of Two-Dimensional Ti₃C₂ MXenes: A Review, *ACS Applied Nano Materials*, 3, 10, pp.9581 – 9603. DOI:10.1021/acsanm.0c02481.
- Kanmaz, , Köksal, O. K., Apaydin, G., Tomakin, M. & Cengiz, E. (2025). Investigation of radiation shielding properties of CeO₂ thin films prepared at different molarities, *Physica Scripta*, 100, pp.035945. DOI:10.1088/1402-4896/adb349.
- Khojasteh, H., Mazhari, M.-P., Heydaryan, K., Aspoukeh, P., Ahmadiazar, S., Hamad, S. M. & Shaikhah, D. (2024). Enhancing glass surface hydrophobicity: the role of Perfluorooctyltriethoxysilane in advanced surface modification, *Journal of Sol-Gel Science and Technology*, 112, pp.857–869. DOI:10.1007/s10971-024-06593-5.
- Li, Q., Zhou, J., Li, F. & Sun, Z. (2020). Novel MXene-Based Hierarchically Porous Composite as Superior Electrodes for Li-Ion Storage, *Applied Surface Science*, 530, 147214. DOI:10.1016/j.apsusc.2020.147214.
- Liu, Z., Zhao, Y., Li, S., Sun, T., Liu, H., Wang, K. & Chen, X. (2022). CeO₂/Ti₃C₂T_x MXene Nanostructures for Microwave Absorption, *ACS Applied Nano Materials*, 5, 4, pp.5764–5775. DOI:10.1021/acsanm.2c00829.
- Ma, F., Liu, J., Chen, K. & Cheng, Z. (2024). Thermal Stability Improvement of Cu-Based Catalyst by Hydrophobic Modification in Methanol Synthesis, *Processes*, 12, 9, pp.2008. DOI:10.3390/pr12092008.
- Masoudpanah, S. M., Koohdar, H. R., Derakhshani, M., Ranjbar, K., Sarkar, T. & Aslibeiki, B. (2025). Enhancement of microwave absorption performance of MOF-derived NiCo₂O₄ by adding Ti₃C₂T_x MXene, *Journal of Materials Science: Materials in Electronics*, 36, 1184. DOI:10.1007/s10854-025-15264-2.
- Mathew, S. & Devi, S. K. R. (2024). Rationally designed CeO₂ decorated Ti₃C₂ MXene interface for efficient water splitting and enhanced supercapacitor performance, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 684, 133170. DOI:10.1016/j.colsurfa.2024.133170.
- Rai T., Y. & Hegde, A. C. (2024). Electrodeposition and Electrocatalytic Study of Ni–Co Alloy Coatings, *Protection of Metals and Physical Chemistry of Surfaces*, 60, 6, pp.1084–1093. DOI:10.1134/S2070205124702514.
- Reghunath, B. S., Rajasekaran, S., Mathew, S., Pinheiro, D., Devi, S. K. R., Jung, S., Jayaraman, T. & Choi, M. Y. (2023). Two-dimensional Ti₃C₂ MXene for photocatalytic hydrogen production: A review, *Bulletin of the Korean Chemical Society*, 44, pp.969–988. DOI:10.1002/bkcs.12783.
- Wang, T., Zhou, T., Li, C., Song, Q., Zhang, M. & Yang, H. (2024). Development Status and Prospects of Biomass Energy in China, *Energies*, 17, 17, pp.4484. DOI:10.3390/en17174484.
- Wang, Y., Shen, G., Wang, C., Gao, F., Wang, J. & Shen, M. (2024). Mechanistic insights into the deactivation of Pd/BEA methane combustion catalysts by hydrothermal aging, *Molecular Catalysis*, 558, pp.114027. DOI:10.1016/j.mcat.2024.114027.
- Wei, C., Liu, C., Gao, L., Sun, Y., Liu, Q., Zhang, X. & Guo, J. (2019). MoS₂ nanosheets decorated Ni (OH)₂ nanorod array for active overall water splitting, *Journal of Alloys and Compounds*. DOI:10.1016/j.jallcom.2019.05.071.
- Yang, P., Wang, J., Ning, F., Qi, L., Chen, J. & Zhang, X. (2025). The electrowetting-on-dielectric and photothermal performance of the porous Ti₃C₂@PVDF composite and dehumidification application, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 714, pp.136556. DOI:10.1016/j.colsurfa.2025.136556.
- Zhang, H., Bao, L., Pan, Y., Du, J. & Wang, W. (2024). Interface reconstruction of MXene-Ti₃C₂ doped CeO₂ nanorods for remarked photocatalytic ammonia synthesis, *Journal of Colloid and Interface Science*, 675, pp.130–138. DOI:10.1016/j.jcis.2024.07.008.
- Zhang, W., Wang, Y., Jiao, Z., Wang, W., Ge, Y., Wang, C., Sun, L. & Zhou, C. (2025). Rapid detection and anti-humidity NO₂ sensor at room temperature based on CeO₂/few-layer Ti₃C₂ MXene composite, *Microchemical Journal*, 216, 114742.
- Zeng, F., Chen, H., Mei, Y., Ye, L., Zhuang, S., Pu, N. & Wang, L. (2024). Performance and mechanism of sulfonamide-antibiotic adsorption by Ti₃C₂ MXene, *New Journal of Chemistry*, 48, 38, pp.16742–16752. DOI:10.1039/d4nj03341h.
- Zhou, L., Qi, H., Lei, Y., Yu, J., Guo, B. & Zhang, D. (2022). Ti₃C₂ MXene induced high tribological performance of polyimide/polyurea copolymer at a wide temperature range, *Applied Surface Science*, 608, 155157. DOI:10.1016/j.apsusc.2022.155157.