

Binder-mediated regulation of coating structure over monolithic catalyst and its performance in CH₄-CO₂ reforming

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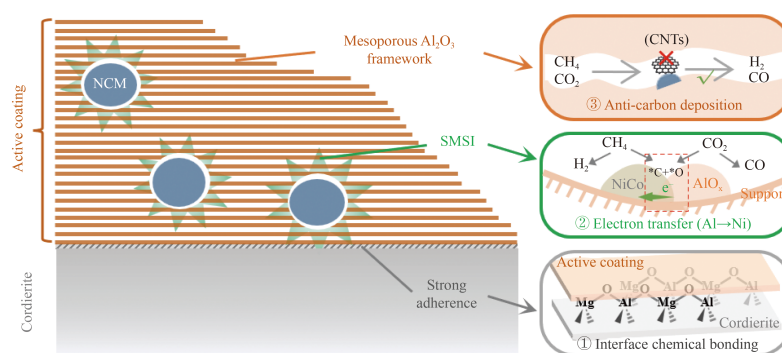
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Abstract: The CO₂ dry reforming of methane (DRM) reaction represents a pivotal technology for CO₂ utilization technology within the dual-carbon framework, offering significant advantages in carbon reduction, emission mitigation, and the production of value-added chemicals. However, research reports on shaped catalysts suitable for industrial-scale DRM processes remain limited. In

this work, a monolithic catalyst was constructed using honeycomb cordierite as the structural support, and the effects of organic and inorganic binders on the coating structure and catalytic performance were systematically investigated. Comparative studies revealed that the active coating fabricated with an inorganic aluminum sol exhibited a continuous uniform morphology and demonstrated excellent adhesion strength. Simultaneously during high-temperature calcination, elemental diffusion within the Al₂O₃ networks bridged the cordierite surface with active catalyst particles, forming a (Ni-Mg)Al_xO₄ composite structure. This created robust “metal-support” interactions between active sites and the residual alumina matrix. The interconnected mesoporous framework provided superior pore confinement, which ultimately contributed to strong coating adhesion, enhanced activity and improved resistance to carbon deposition in the monolithic *m*-NCM-Al-sol catalyst. In contrast, mesoporous network coatings derived from inorganic silica sol suffered from coating detachment and catalytic activity loss due to heterogeneous surface structures and poor adhesion. Organic binders demonstrated inferior performance compared to inorganic binders in macroscopic coating uniformity, adhesion strength, mesoporous confinement capability and localized electronic effects, resulting in the poorest catalytic performance among modified samples. Furthermore, by optimizing the aluminum sol coating process parameters such as binder content, active component dosage, and coating cycles, a synergistic balance between coating thickness and mass transfer performance was achieved. The optimized integrated catalyst demonstrated excellent performance in DRM reactions. This work provides valuable insights for controlling and constructing high-performance shaped catalysts with cordierite coatings.

Key words: dry reforming of methane; monolithic catalyst; aluminum sol; mesoporous framework coating; dual diffusion mechanism



Received: 2026-04-16; Revised: 2026-05-09

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Foundation items: Supported by the National Natural Science Foundation of China (22578255, 22178202), the Central Government Guidance Fund for Local Science and Technology Development (YDZJSX2024D004) and the Key Research and Development Special Program of Shanxi Province (202402090301006, 202302090301004).

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DOI: 10.1016/S1872-5813(26)60762-1 CSTR: 32157.14.2097-213X.2026.JFCT.0122 Associated Data DOI: 10.57760/sciencedb.j00124.00501

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Against the backdrop of global warming and the accelerating shift towards green, low-carbon energy, the synergistic conversion of CO_2 and CH_4 has attracted considerable attention for its potential to mitigate greenhouse gas emissions. The dry reforming of methane (DRM) enables the direct conversion of CO_2 and CH_4 into syngas ($\text{H}_2/\text{CO} = 1$), which is highly valuable for downstream industrial processes such as Fischer-Tropsch synthesis and methanol production^[1–6]. However, DRM is a highly endothermic reaction that typically operates at 700–900 °C. Under these severe conditions, metal sintering and carbon deposition can readily occur, resulting in rapid catalyst deactivation^[7–10]. Among various catalyst systems, Ni-based catalysts are regarded as the most promising candidates for industrial DRM applications owing to their high activity in CH_4 activation and relatively low cost^[11–12]. Nevertheless, the strong C–H bond cleavage capability of Ni tends to accelerate deep dehydrogenation and coke formation, while high-temperature conditions further exacerbate metal sintering^[13–14]. In this context, layered double hydroxide (LDH)-derived mixed metal oxides have shown remarkable advantages in suppressing both sintering and coke deposition owing to their high metal dispersion, excellent thermal stability, and tunable basic sites^[15–17]. Despite these advances, current studies mainly focus on powder catalysts, which suffer from high pressure drop, limited mass transfer, and poor mechanical stability in practical applications^[18–19]. In contrast, monolithic catalysts featuring ordered honeycomb channels offer superior heat and mass transfer characteristics, lower pressure drop, and enhanced structural stability. In particular, cordierite-based monoliths have been widely applied in industrial catalytic processes. Nevertheless, the effective fabrication of monolithic DRM catalysts still faces critical challenges, especially regarding the insufficient adhesion strength between active coatings and substrates under high-temperature conditions. Moreover, the role of binders in regulating coating morphology, pore architecture, and metal-support interactions remains inadequately understood. Therefore, in this work, monolithic Ni-Co-based DRM catalysts were fabricated using a LDH-derived Ni-Co/Mg(Al)O as the active coating. The effects of inorganic and organic binders on the coating structure and catalytic performance were systematically investigated, along with the optimization of cordierite pretreatment and coating process parameters. This study aims to provide theoretical guidance for the design and engineering application of highly efficient monolithic DRM catalysts.

1 Experimental

1.1 Cordierite pretreatment

Cordierite honeycomb monoliths with a cell density of 400 cpsi were selected as the support and cut into cuboids with dimensions of 0.5 cm × 0.5 cm × 2 cm. The monoliths

were first rinsed with deionized water and subsequently ultrasonically cleaned in deionized water for 20 min to remove residual dust inside the channels. After drying, the cordierite monoliths were immersed in 28% nitric acid solution for acid etching for 12 h. The treated samples were then repeatedly washed with deionized water until neutral pH was reached, followed by drying. Finally, the samples were calcined in air at 500 °C for 5 h and naturally cooled to room temperature before use.

1.2 Preparation of the pristine NCM catalyst

A metal salt solution A was prepared by dissolving measured amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 150 mL of deionized water. Separately, 200 mL NaOH solution (1.0 mol/L) and Na_2CO_3 solution (0.5 mol/L) were prepared. The Na_2CO_3 solution was placed in a beaker and heated to 65 °C under magnetic stirring. Subsequently, solution A and the NaOH solution were simultaneously added dropwise while maintaining the pH value of the system within the range of 9.5–10.0. After complete addition, the resulting suspension was continuously stirred and aged for 24 h. The obtained precipitate was collected by filtration, dried at 80 °C for 12 h, and calcined in air at 800 °C for 5 h, ultimately yielding the pristine NCM catalyst derived from the topotactic transformation of the LDH precursor.

1.3 Preparation of monolithic *m*-NCM-*X* catalysts

Different binders, including hydroxyethyl cellulose (HEC), silica sol (Si-sol), and alumina sol (Al-sol), were employed for the preparation of monolithic *m*-NCM-*X* catalysts (*X* = HEC, Al-sol, and Si-sol). Typically, 2.5 g of the pristine NCM catalyst was placed in a beaker, followed by the addition of an appropriate amount of deionized water and binder (the binder content accounted for 3% of the total slurry). The mixture was then transferred into a ball mill and milled for 1 h to obtain a homogeneous and stable coating slurry. The pretreated cordierite monolith was immersed into the prepared slurry for several minutes to ensure sufficient penetration of the slurry into the honeycomb channels. Subsequently, the monolith was removed, and excess slurry inside the channels was removed by air blowing. The coated monolith was then dried at 80 °C for 1 h, which was defined as one coating cycle. The immersion-drying procedure was repeated and the coating loading was controlled by a weight-gain method based on the mass change of the cordierite monolith before and after coating, until the desired final specific loading (0.1 g catalyst/0.8 g cordierite support) was achieved. The coated samples were finally calcined in air at 700 °C to obtain the monolithic Ni-Co/Mg(Al)O catalysts, denoted as *m*-NCM-*X*. In addition, the residual slurry after coating was dried and calcined in air at 700 °C to obtain the corresponding active coating reference samples, denoted as NCM-*X*.

The preparation procedure of *m*-NCM-Al-sol catalysts with different Al-sol contents was similar to that described above, except that the Al-sol content was adjusted to 1%, 3%, 5% and 7%, respectively. Similarly, catalysts with different active component loadings were prepared by varying the amount of pristine NCM catalyst in the slurry (1, 2.5 and 5 g), while keeping the other preparation conditions unchanged.

1.4 Catalyst characterization

The crystal structure, textural properties, and surface chemical states of all synthesized catalysts were systematically characterized using various techniques. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 40 mA. The diffraction data were collected in the 2θ range of 10° – 90° at a scanning rate of $0.1^\circ/\text{s}$. The textural properties of the catalysts were analyzed by N_2 adsorption-desorption measurements using a Micromeritics ASAP 2020 automated physical adsorption analyzer. Prior to measurement, the samples were pretreated at 300°C under N_2 atmosphere for 6 h. The adsorption-desorption isotherms were obtained at -196°C under liquid nitrogen conditions. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, while the pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) model. The macroscopic morphology, surface structure, cross-sectional thickness of the monolithic *m*-NCM-*X* catalysts was characterized using a JSM-7001F field-emission scanning electron microscope (SEM) operated at 10 kV. H_2 temperature-programmed reduction (H_2 -TPR) measurements were carried out on a TP-5067 chemisorption analyzer. Typically, 0.05 g of catalyst (40–60 mesh) was heated from room temperature to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a 10% H_2/Ar flow (20 mL/min). The H_2 consumption was monitored using a thermal conductivity detector (TCD). X-ray photoelectron spectroscopy (XPS) analysis was performed on an AXIS SUPRA spectrometer equipped with a monochromatic Al $K\alpha$ X-ray source at a pass energy of 40 eV. All spectra were calibrated using the C 1s peak as the reference. Thermogravimetry-differential scanning calorimetry analysis (TG-DSC) was conducted on a NETZSCH STA-409 instrument. Approximately 30 mg of spent catalyst was heated from room temperature to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ under air atmosphere, and the corresponding weight loss was recorded. Raman spectra were collected on a Horiba Scientific LabRAM HR Raman spectrometer using a 532 nm laser source with a laser power of 0.1 mW. The coating adhesion strength was evaluated according to the coating weight loss ratio obtained from ultrasonic vibration tests. The calcined monolithic catalysts were immersed in deionized water and subjected to ultrasonic treatment for a total duration of 30 min. Samples were removed every 5 min, dried, and weighed. The coating weight loss ratio

was calculated based on the mass change before and after ultrasonic treatment, thereby evaluating the adhesion strength between the coating layer and the cordierite substrate. In addition, the mechanical properties of the monolithic catalysts were evaluated by compressive strength measurements. Both the coating adhesion strength and compressive strength tests were conducted in triplicate, and the average values obtained from parallel experiments were used as the final reported data to ensure good reliability and reproducibility.

1.5 Catalytic performance evaluation

The DRM reaction was carried out in a fixed-bed reactor under atmospheric pressure (Figure 1). The monolithic *m*-NCM-*X* catalyst was loaded into a quartz reaction tube with an inner diameter of 8 mm, and the remaining space was filled with quartz sand. Prior to the reaction, the catalyst was reduced at 750°C under an H_2/N_2 atmosphere (1:2). Subsequently, a reactant gas mixture with a CH_4/CO_2 ratio of 1:1 was introduced for catalytic performance evaluation at a gas hourly space velocity (GHSV) of $36000\text{ mL}/(\text{h}\cdot\text{g})$. The reaction products were analyzed online using a gas chromatograph.

The conversion (X) of the catalysts during catalytic performance evaluation was calculated as follows:

$$x_i = \frac{[F_i]_{\text{in}} - [F_i]_{\text{out}}}{[F_i]_{\text{in}}} \times 100\% \quad (1)$$

The H_2/CO ratio was calculated as follows:

$$\frac{\text{H}_2}{\text{CO}} = \frac{[F_{\text{H}_2}]_{\text{out}}}{[F_{\text{CO}}]_{\text{out}}} \times 100\% \quad (2)$$

where $[F_i]_{\text{in}}$ and $[F_i]_{\text{out}}$ represent the inlet and outlet gas flow rates (mL/min), respectively. The carbon balance during the reaction was maintained within $100\% \pm 5\%$.

2 Results and discussion

2.1 Cordierite pretreatment

In a typical dip-coating process, the amount of the pristine catalyst retained on the substrate is generally determined by the surface roughness of the cordierite substrate, the rheological properties of the slurry, and surface tension. In particular, surface grooves and pores on the cordierite substrate can provide anchoring sites for the coating slurry. Therefore, acid pretreatment of the pristine cordierite is employed to increase its surface roughness, which is beneficial for the sufficient penetration and adhesion of the slurry during the subsequent dip-coating process. As shown in Figure 2, the XRD patterns of the cordierite before and after acid pretreatment exhibit distinct diffraction peaks at $2\theta = 10.3^\circ, 21.6^\circ, 26.3^\circ, 28.1^\circ, 29.3^\circ, 53.3^\circ$ and 57.9° , which correspond to the cordierite phase $\text{Mg}_2\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ (JCPDS No. 09-0472).

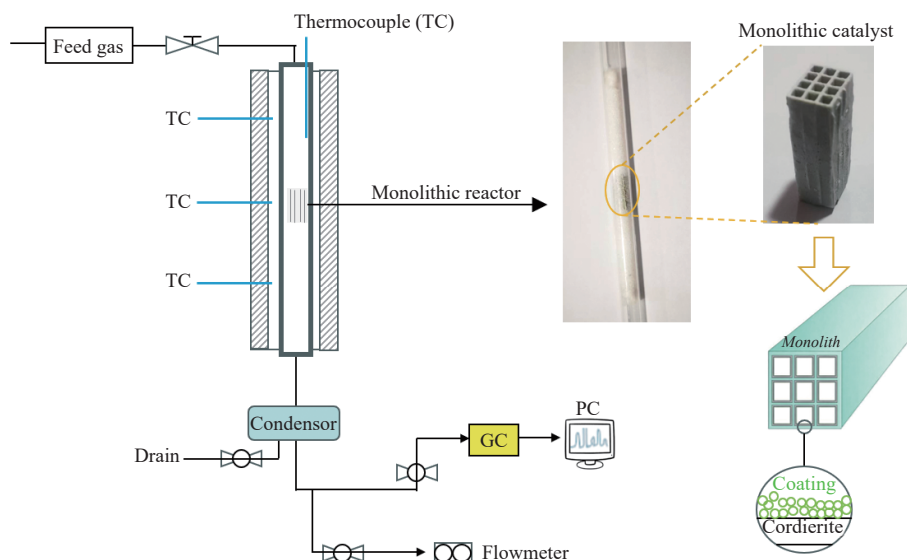


Fig. 1 Schematic diagram of the laboratory setup for DRM performance testing

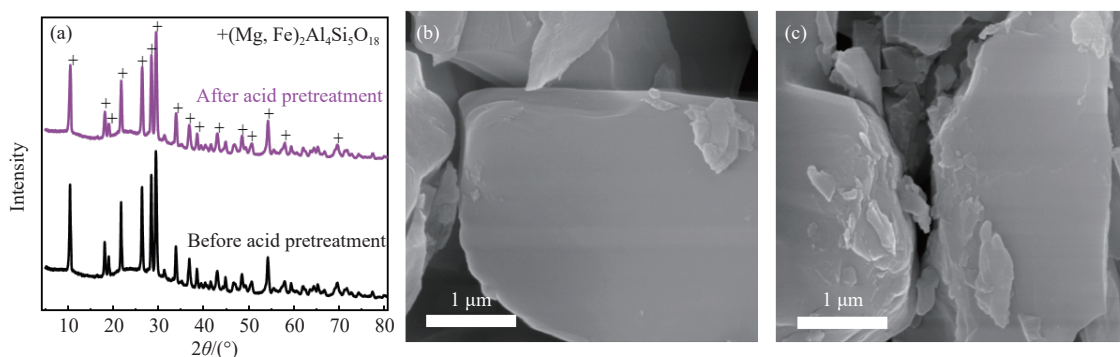


Fig. 2 (a) XRD and (b), (c) SEM patterns of cordierite before and after acid pretreatment

No obvious shift in diffraction peak positions or formation of new crystalline phases was detected after pretreatment, indicating that the acid etching process did not induce detectable phase transformation or structural degradation of the cordierite framework. However, a slight decrease in the relative intensity of several characteristic peaks was observed after acid treatment, which may be attributed to the etching effect of H^+ on the originally smooth cordierite surface, resulting in the formation of surface pits.

The evolution of the cordierite surface morphology, observed by SEM (Figure 2(b), (c)), further supports the above interpretation. The untreated pristine cordierite exhibited a relatively smooth, plate-like surface, whereas numerous etched grooves and pores appeared on the acid-treated cordierite surface. In addition, textural characterization revealed that the specific surface area of the acid-treated cordierite ($11.99 \text{ m}^2/\text{g}$) was approximately twice that of the pristine cordierite ($5.38 \text{ m}^2/\text{g}$), accompanied by increases in both pore volume and pore diameter (Table 1). These changes can be attributed to the acid leaching of Al^{3+} and Mg^{2+} species from the surface and interior of cordierite during the pretreatment process, which increased the surface roughness and enlarged the pore volume and pore size, thereby generating more surface

voids. Therefore, the acid pretreatment effectively constructed a rough surface/interface favorable for the adhesion and anchoring of active coatings without destroying the crystalline structure of the cordierite.

Table 1 Specific surface area pore volume and pore diameter of cordierite before and after acid pretreatment

Cordierite	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$v_p/(\text{cm}^3 \cdot \text{g}^{-1})$	d_p/nm
Untreated	5.38	0.0041	3.80
After acid treatment	11.99	0.0094	5.27

2.2 Interfacial regulation and anti-peeling effect analysis of *m*-NCM-*X* catalyst coatings

Figure 3(a) presents the XRD patterns of the calcined NCM-*X* samples prepared using different binders. All catalysts exhibited characteristic diffraction peaks at $2\theta = 37.2^\circ, 43.3^\circ, 62.8^\circ, 74.8^\circ$ and 78.8° , which can be assigned to the rock-salt-type (Mg, Ni, Co, Al)O solid solution phase. In addition, weak diffraction peaks observed at $2\theta = 31.3^\circ$ and 65.2° correspond to the (220) and (440) crystal planes of the MgAl_2O_4 spinel phase (JCPDS No. 21-1152), respectively. These results indicate that the introduction of

different binders has little influence on the primary crystalline phase structure of the catalysts. SEM was used to investigate the macroscopic morphology, surface structure, and cross-sectional thickness of the monolithic *m*-NCM-*X* catalysts, aiming to elucidate the influence of binder type on the surface uniformity and coating thickness of the active coating. Figure 3(b) shows the macroscopic morphology and surface distribution of the active coating prepared using the organic binder HEC. Compared with the bare cordierite substrate, the active coating particles aggregated into large clusters, resulting in uneven coverage of the cordierite wall surface and partial channel blockage. It should be noted that such non-uniform structures may lead to poor adhesion, wall cracking or structural defects, which can further induce coating spallation and active metal sintering under high-temperature reaction conditions due to thermally induced stress generated by uneven heat and mass transfer. These phenomena are often considered major causes of monolithic catalyst deactivation. When inorganic Si-sol was used as the binder, the surface structure showed some improvement, yet the overall distribution of the active coating remained unsatisfactory. In contrast, the inorganic Al-sol binder yield a well-distributed coating structure with integrity of the honeycomb channels. Further surface morphology (Figure 3(e)) and cross-sectional observations (Figure 3(f)) revealed that the active coating layer in *m*-NCM-Al-sol adhered tightly to the cordierite interface, exhibiting a continuous outer surface, a uniform thickness (~20.6 μm), and no observable cracks. It is worth noting that the acid-etched cordierite surface originally contained numerous grooves and depressions, whereas the nearly flat surface of *m*-NCM-Al-sol confirms that the alumina-sol-derived coating could

effectively wet and fill the surface defects of cordierite. This uniform coating structure is beneficial for efficient heat transfer and strong interfacial adhesion during the reaction process, while simultaneously avoiding channel blockage and maintaining a high dispersion of active sites. Consequently, a favorable balance between interfacial adhesion strength and mass transfer performance was achieved, which may contribute to enhanced reforming activity and catalytic stability.

To further elucidate the effect of different binders on the microscopic pore structure of the active coatings, the textural properties of NCM-*X* (*X* = HEC, Al-sol and Si-sol) coating catalysts were characterized by N_2 adsorption-desorption measurements. As shown in Figure 4(a), all catalysts exhibited typical type-IV adsorption isotherms of mesoporous materials. Notably, the pristine NCM catalyst displayed a distinct H3-type hysteresis loop, which can be attributed to slit-shaped pores formed by the stacking of plate-like particles. In contrast, the binder-modified NCM-*X* catalysts exhibited H2-type hysteresis loops, indicating the presence of typical “ink-bottle” pores or interconnected tubular pores with non-uniform pore-size distributions. In addition, the NCM-*X* coating catalysts reached adsorption saturation at relatively low relative pressures, suggesting the presence of smaller mesopores. The pore-size distribution shown in Figure 4(b) further confirms that the pore diameters of the active coatings were mainly concentrated in the range of 10–20 nm, which is significantly smaller than that of the pristine NCM catalyst. The specific regulatory effects of different binders on the textural parameters are summarized in Table 2.

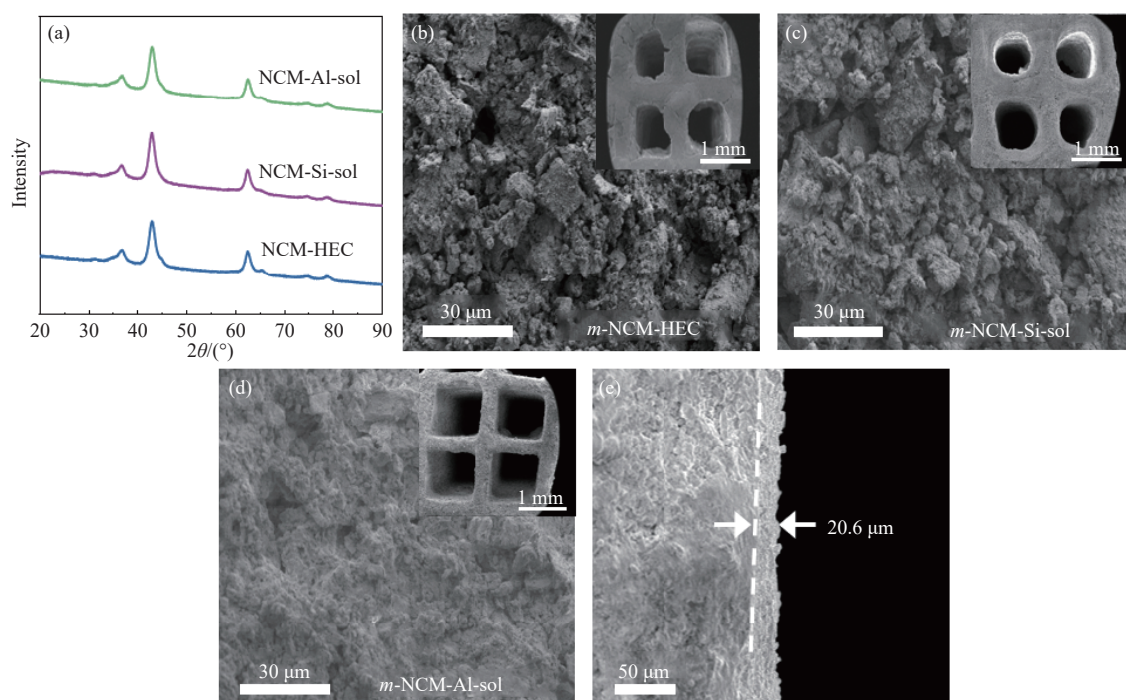


Fig. 3 (a) XRD patterns of NCM-*X* catalysts after calcination; SEM images showing the (b) macroscopic morphology, (c) surface structure and (d), (e) cross-sectional thickness of monolithic *m*-NCM-*X* catalysts

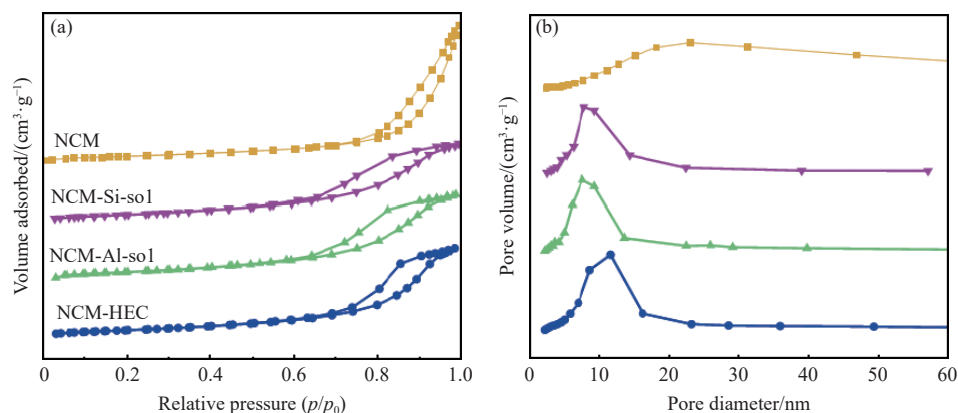


Fig. 4 (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of NCM-*X* (*X*=HEC, Al-sol, Si-sol) monolithic catalysts

Table 2 Physicochemical properties of the NCM-*X* catalysts

Catalyst	Specific surface area/(m ² ·g ⁻¹)	Average pore size/nm	Pore volume/(cm ³ ·g ⁻¹)
NCM-HEC	144.4	13.92	0.50
NCM-Al-sol	162.8	11.85	0.48
NCM-Si-sol	153.6	11.53	0.42

Among them, the catalysts prepared using inorganic binders (NCM-Al-sol and NCM-Si-sol), exhibited higher specific surface areas (162.8 and 153.6 m²/g, respectively) and smaller mesopore sizes (11.85 and 11.53 nm, respectively). In contrast, the catalyst prepared using the organic binder showed the largest average pore diameter and pore volume. It should be noted that although all NCM-*X* catalysts possessed mesoporous characteristics, the origin of their porosity differed. In NCM-Al-sol and NCM-Si-sol, the mesoporous structure mainly originated from the rigid framework formed by the high-temperature polycondensation of inorganic sols that interconnected the active particles. In contrast, the mesoporous structure of NCM-HEC was mainly derived from the voids generated after the removal of the organic binder during calcination, resulting in relatively broader mesopores and a weaker confinement effect. Similar phenomena were reported by Agueniou et al.^[20], who pointed out that, given the negligible intrinsic porosity of cordierite, alumina sol as a binder favored the formation of new pores smaller than 10 nm between catalyst particles. A high specific surface area is essential for the dispersion of active species and the exposure of abundant catalytic active sites, while small-sized mesopores can provide an effective confinement effect during DRM reactions. On the one hand, the confined pore space can suppress the continuous three-dimensional growth of carbon species, thereby facilitating coke gasification and removal. On the other hand, the interconnected mesoporous network can physically isolate active metal particles through pore-wall confinement, effectively inhibiting surface migration and sintering of metal nanoparticles under high-temperature reaction conditions. These results further demonstrate that the Al-sol-derived slurry can form a strongly adherent Al₂O₃ framework with an interconnected mesoporous confinement networks, uniform heat/mass transfer characteristics, and a

high specific surface area on the cordierite surface after the coating process.

Since organic binders are inevitably oxidized and removed during thermal treatment, they are unable to form a rigid framework layer or establish effective interactions with active particles. In contrast, inorganic binders undergo polycondensation and crystallization at high temperature, generating a mesoporous network framework layer that adhered to the cordierite interface and embedded dispersed active particles, thereby forming a support layer with distinct interactions toward the active species. Accordingly, XPS and H₂-TPR analyses were performed to investigate the surface chemical states and possible metal-support interactions of the reduced NCM-*X* catalysts (Figure 5). For the NCM-HEC catalyst prepared using the organic binder, the Ni 2p_{3/2} spectrum exhibited a Ni⁰ characteristic peak at 851.9 eV, which is close to the metallic Ni peak (~852.0 eV) previously reported for LDH-derived solid-solution catalysts^[21–23], indicating the formation of active metallic Ni species after reduction. In comparison, the Ni⁰ peaks of the catalysts prepared using inorganic binders shifted to lower binding energies (851.7 eV for NCM-Si-sol and 851.5 eV for NCM-Al-sol, respectively). In particular, the Ni⁰ peak of NCM-Al-sol was downshifted by approximately 0.4 relative to NCM-HEC and 0.2 eV relative to NCM-Si-sol, respectively, suggesting a significant increase in the electron density around Ni sites, which is generally associated with stronger metal-support interactions^[24]. Further semi-quantitative analysis of the Ni⁰/Ni²⁺ ratio (Table 3) revealed that NCM-Al-sol possessed the highest Ni⁰ proportion (63.5%), followed by NCM-Si-sol (60.5%) and NCM-HEC (58.7%). Meanwhile, Co⁰ characteristic peaks were observed at approximately 775.6–776.2 eV in the Co 2p_{3/2} spectra of all catalysts, confirming the formation of Ni-Co alloy phases^[25].

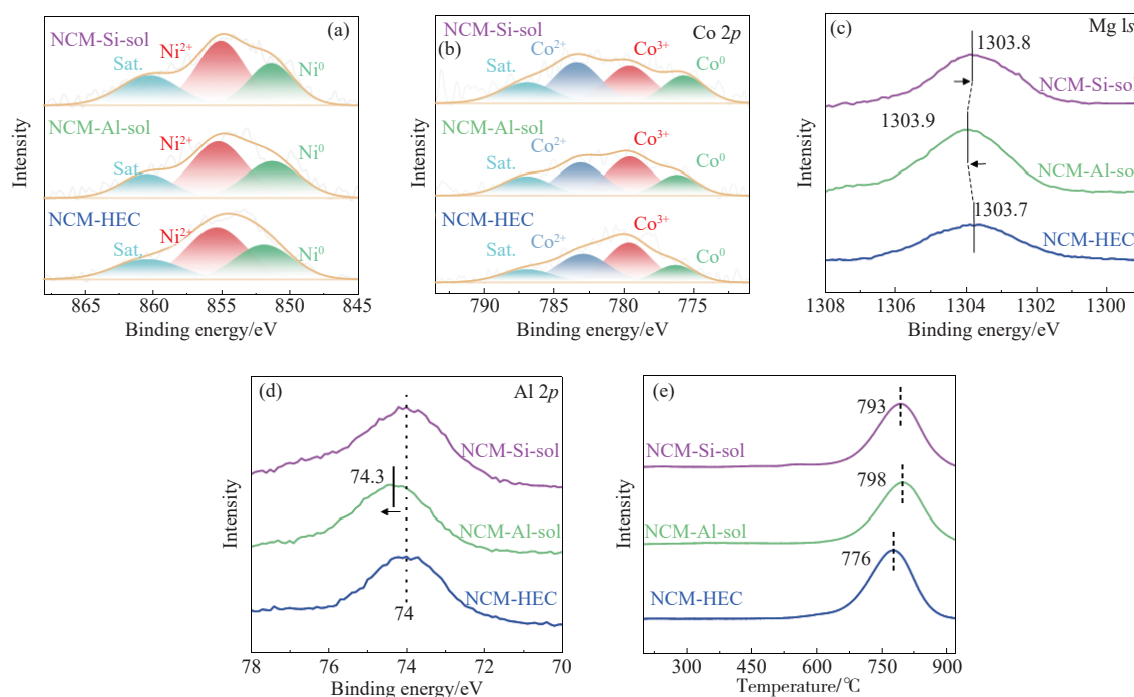


Fig. 5 XPS spectra of reduced NCM- X (X =PVA, HEC, Al-sol, Si-sol) catalysts: (a) Ni 2 p , (b) Co 2 p , (c) Mg 1 s and (d) Al 2 p ; (e) H₂-TPR profiles of NCM- X catalysts

Table 3 The binding energy values of the support sample and the synthetic catalyst

Catalyst	Elements binding energy/eV					(Ni ⁰ /Ni ²⁺)/%
	Ni ⁰	Ni ²⁺	Co ⁰	Co ²⁺	Co ³⁺	
NCM-HEC	851.9	855.6	776.1	783.1	779.6	58.7
NCM-Al-sol	851.5	855.4	776.2	783.2	779.7	63.5
NCM-Si-sol	851.7	855.4	775.6	783.3	779.5	60.5

In addition, the Mg 1 s spectra showed that the Mg²⁺ binding energies of catalysts prepared using inorganic binders were higher than that of NCM-HEC prepared using the organic binder, with NCM-Al-sol exhibiting the highest Mg 1 s binding energy (1303.9 eV). This result indicates stronger interactions between Mg and Ni in the inorganic-binder-modified catalysts, especially in NCM-Al-sol, where obvious charge redistribution toward neighboring Ni species may occur. Interestingly, the Al 2 p spectra exhibited a distinct trend: only the NCM-Al-sol catalyst showed a significant increase in Al 2 p binding energy (74.3 eV), whereas the other two catalysts exhibited nearly identical values (~74 eV). This trend aligns well with the negative shift of the Ni peak, implying that part of the electron density from the framework Al species was transferred to Ni, thereby increasing the electron density around Ni sites^[26]. These results suggest that strong interactions were established between the active particles and the Al₂O₃ mesoporous support framework derived from Al-sol after calcination and reduction, leading to the formation of a (Ni-Mg)Al_xO₄ composite structure^[27]. Evidently, catalysts prepared using inorganic binders, particularly Al-sol, can effectively regulate the local electronic environment of the alloy phase through enhanced metal-support interactions, which is beneficial for CH₄ activation during the DRM

reaction^[28].

Further evidence was provided by the H₂-TPR results (Figure 5(e)). The main reduction peaks in the range of 750–850 °C are generally attributed to the reduction of Ni species strongly interacting with the support^[29]. Marked differences in the reduction profiles were observed among catalysts prepared using different binders. NCM-HEC exhibited the lowest main reduction peak temperature (776 °C), whereas the reduction peaks of NCM-Al-sol and NCM-Si-sol shifted toward higher temperatures overall. In particular, the reduction peak of NCM-Al-sol located near 800 °C can be assigned to NiAl₂O₄ crystalline phases or Ni species embedded within the Al₂O₃ support framework through strong metal-support interaction (SMSI). Chava et al.^[30] reported a coating reconstruction phenomenon during a study on the effect of calcination time on Ni/ γ -Al₂O₃-coated monolithic catalysts, in which a bidirectional diffusion mechanism occurred during high-temperature calcination: surface Ni species diffused inward into the coating, while Mg/Si species from the cordierite substrate simultaneously diffused outward into the coating layer, ultimately forming a MgAl₂O₄/NiAl₂O₄ mixed phase within the coating. Combined with the physicochemical characterization results of the NCM- X catalysts, a similar process is proposed for NCM-Al-sol during high-

temperature calcination. Specifically, elevated temperatures promoted the diffusion of active particles into the Al_2O_3 mesoporous framework derived from Al-sol, resulting in the formation of a $(\text{Ni-Mg})\text{Al}_x\text{O}_4$ composite structure with strong SMSI characteristics. Such a composite structure can be reduced at high temperature to generate highly stable and active Ni-Co alloy phases with small particle sizes. Meanwhile, the intrinsic $\text{Al}(\text{Mg})\text{O}_x$ species from the cordierite substrate may gradually diffuse into the coating layer during prolonged high-temperature calcination and form bridging interactions with the Al-sol-derived Al_2O_3 mesoporous framework. This process improved thereby the coating distribution, adhesion strength, and the local electronic environment of the active metals. In contrast, although Si-sol formed an interconnected mesoporous SiO_2 network during calcination, the lack of sufficient Al species hindered the formation of additional $(\text{Ni-Mg})\text{Al}_x\text{O}_4$ composite structures. Consequently, the coating reconstruction process driven by the bidirectional diffusion mechanism was less effective, resulting in weaker interactions with both the cordierite interface and active particles, as well as inferior coating distribution. For the organic binder, the polymer chains gradually decomposed, oxidized, and burned off during high-temperature calcination, ultimately leaving the active particles in a loosely aggregated state after binder removal. Consequently, this led to the weakest interaction strength and poorest coating distribution. The FE-SEM results (Figure 3(e), (f)) further support the above interpretation, indicating that the calcined mesoporous Al_2O_3 network played a critical bridging role between the cordierite interface and the NCM active particles, which also implies the superior anti-peeling capability of the NCM-Al-sol coating.

The adhesion performance tests (Figure 6 and Table 4) further demonstrate the critical bridging role of the Al_2O_3 mesoporous framework and the anti-peeling property of the active coating in the monolithic $m\text{-NCM-Al-sol}$ catalyst. As the ultrasonic treatment time increased from 5 to 30 min, the weight loss ratios of all catalysts gradually increased, indicating that ultrasonic vibration weakened the interfacial stability between the coating layer and the support. Among them, the $m\text{-NCM-HEC}$ catalyst prepared using the organic binder exhibited a relatively high weight loss, reaching approximately $3.6\% \pm 0.06\%$ after 30 min, followed by $m\text{-NCM-Si-sol}$ catalyst ($3.94\% \pm 0.12\%$). In contrast, the $m\text{-NCM-Al-sol}$ catalyst exhibited the best coating adhesion performance, with a weight loss of only $1.82\% \pm 0.08\%$ after 30 min. This superior adhesion behavior can be attributed to the interfacial structural reconstruction between the Mg/Al species originating from the cordierite substrate and the Al-sol-derived Al_2O_3 support layer during high-temperature calcination. Table 4 further summarizes the compressive strengths of the monolithic $m\text{-NCM-X}$ catalysts. The results indicate that the $m\text{-NCM-Al-sol}$ catalyst exhibited the highest compressive strength (17.83 ± 0.25 MPa), followed by $m\text{-NCM-Si-sol}$ (16.03 ± 0.35 MPa),

while the organic-binder-modified $m\text{-NCM-HEC}$ catalyst showed significantly lower compressive strength (12.86 ± 0.40 MPa). These results suggest that inorganic binders, particularly alumina sol, can preserve the intrinsic mechanical strength of the cordierite substrate to the greatest extent. Evidently, the lowest weight loss ratio and highest compressive strength of $m\text{-NCM-Al-sol}$ indicate the formation of stronger interfacial chemical bonding between the active coating and the cordierite wall surface. Overall, compared with the organic binder and Si-sol, the use of Al-sol can bridge the cordierite substrate and active particles during the phase transformation process induced by high-temperature calcination. Ultimately, this formed an interconnected pore-confinement network, yielding a continuous crack-free coating with excellent anti-peeling properties. Simultaneously, it promoted charge redistribution through strong metal-support interactions and created mesoporous framework confinement at the microscopic level.

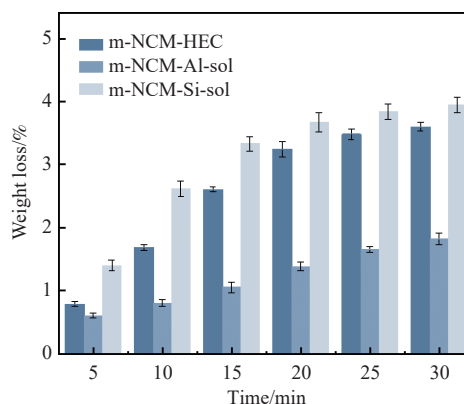


Fig. 6 Adherence stability of $m\text{-NCM-X}$ ($X = \text{HEC}, \text{Al-sol}, \text{Si-sol}$) catalyst

Table 4 Compressive strength of monolithic $m\text{-NCM-X}$ catalysts

Sample	Compressive strength/MPa
$m\text{-NCM-HEC}$	12.86 ± 0.40
$m\text{-NCM-Al-sol}$	17.83 ± 0.25
$m\text{-NCM-Si-sol}$	16.03 ± 0.35

2.3 Catalytic performance evaluation of monolithic $m\text{-NCM-X}$ catalysts

To investigate the effect of different binders on the DRM performance of $m\text{-NCM-X}$ catalysts, catalytic activity tests were conducted at 1 atm, 700 °C, a gas hourly space velocity (GHSV) of 36 L/(g·h), and a CH_4/CO_2 ratio of 1:1. As shown in Figure 7(a), the initial CH_4 conversion followed the order of $m\text{-NCM-Al-sol}$ (73%) > $m\text{-NCM-HEC}$ (71.6%) > $m\text{-NCM-Si-sol}$ (70.7%). In line with the XPS-derived differences in strong metal-support interaction (SMSI), the enhanced activity of the inorganic-binder catalysts can be attributed to enhanced electronic transfer,

which strengthened the activation of C–H bonds in adsorbed CH_4 species on Ni sites. In particular, the AlO_x species provided by Al-sol induced the strongest SMSI and charge redistribution with the metal sites, thereby leading to the highest catalytic activity. During prolonged reaction time, marked differences in catalyst stability were observed among the $m\text{-NCM-}X$ catalysts. The catalysts prepared using inorganic binders exhibited clearly superior stability compared to those prepared using the organic binder. Among them, $m\text{-NCM-Al-sol}$ showed the best stability, with the CH_4 conversion decreasing by only approximately 2.6% after 30 h of reaction. In comparison, $m\text{-NCM-Si-sol}$ exhibited moderate stability, with a CH_4 conversion decrease of approximately 7.9%, whereas, the $m\text{-NCM-HEC}$ catalyst prepared using the organic binder deactivated most rapidly, with the CH_4 conversion sharply dropping to 53% after 30 h (a loss of 18.6%). As shown in Figure 7(b), the variation trend of CO_2 conversion closely mirrored that of CH_4 conversion, further confirming the crucial role of binder type in regulating the performance of monolithic catalysts. As illustrated in Figure 7(c), the H_2/CO ratio of all catalysts remained around 0.83, which can be attributed to the reverse water-gas shift (RWGS) side reaction that consumes H_2 and produces additional CO ^[31].

TG-DSC and Raman analyses were performed on the spent $m\text{-NCM-}X$ catalysts to probe the catalyst deactivation mechanism with a focus on carbon deposition. As shown in the TG-DSC curves (Figure 7(d)), all catalysts underwent a slight weight loss within the range of 50–200 °C, accompanied by weak DSC signals, which was generally attributed to the removal of adsorbed water. In the temperature range of 200–300 °C, the slight weight increase was usually associated with the oxidation of metal species.

Notably, prominent weight loss occurred for all catalysts within 300–750 °C, corresponding mainly to the combustion of deposited carbon species. Among the catalysts, the catalyst prepared using the organic binder HEC exhibited the highest weight loss (24.2%), indicating severe carbon deposition. In contrast, catalysts prepared using inorganic binders showed lower weight losses. The values for $m\text{-NCM-Si-sol}$ and $m\text{-NCM-Al-sol}$ were recorded at 16.8% and 13.2%, respectively. The DSC profile of $m\text{-NCM-HEC}$ displayed the highest peak temperature (645 °C), consistent with the combustion of highly graphitized carbon. The DSC signal of $m\text{-NCM-Si-sol}$ became broader and shifted toward lower temperatures, indicating a decrease in both the amount and crystallinity of the deposited carbon. In comparison, $m\text{-NCM-Al-sol}$ exhibited the weakest thermal combustion signal and the lowest peak temperature (503 °C), confirming its superior ability to suppress the formation of inert carbon species during the DRM reaction. The Raman spectra further verified the above results. The D band ($\sim 1340\text{ cm}^{-1}$) and G band ($\sim 1580\text{ cm}^{-1}$) correspond to amorphous and graphitic carbon, respectively. Comparison of the I_D/I_G ratios further revealed distinct carbon structures, which increased in the order of $m\text{-NCM-HEC}$ (1.08) < $m\text{-NCM-Si-sol}$ (1.12) < $m\text{-NCM-Al-sol}$ (1.26). Among them, $m\text{-NCM-Al-sol}$ exhibited the highest I_D/I_G ratio, indicating that the deposited carbon was mainly amorphous carbon, which is more readily oxidized and removed. In addition, adhesion stability tests were performed on the spent $m\text{-NCM-}X$ catalysts after the high-temperature DRM reaction (Figure 7(f)). The results further corroborate the conclusion that monolithic $m\text{-NCM-Al-sol}$ exhibited superior resistance to coating spallation at high temperatures.

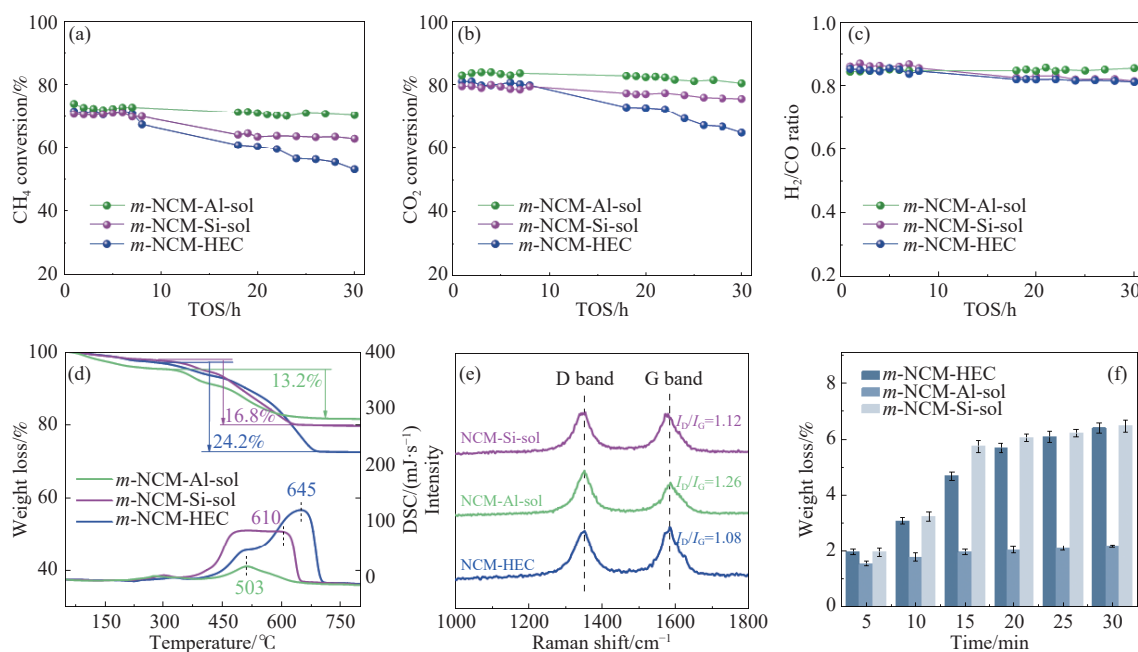


Fig. 7 (a)–(c) Effect of different binders on the performance of $m\text{-NCM-}X$ ($X = \text{HEC, Al-sol, Si-sol}$) catalysts in methane dry reforming, (d) TG-DSC, (e) Raman spectra and (f) adherence stability of $m\text{-NCM-}X$ catalyst after reaction

Even after 30 h of DRM reaction, excellent adhesion was maintained, with the coating showing minimal loss ($2.18\% \pm 0.05\%$). In contrast, the spent *m*-NCM-HEC and *m*-NCM-Si-sol catalysts exhibited substantially higher ultrasonic-induced mass losses of about $6.40\% \pm 0.17\%$ and $6.46\% \pm 0.21\%$ respectively after 30 min. Notably, these values were significantly larger than those of the freshly calcined samples, indicating progressive deterioration of their coating adhesion strengths under high-temperature and high-space-velocity reaction conditions. During the DRM reaction, insufficient bonding between the active coating and the cordierite substrate, along with structural defects such as cracks or poor mechanical strength, can induce local thermal stress at high temperatures, thereby leading to coating spallation, active phase migration, particle aggregation, and ultimately leading to catalyst deactivation^[32–33]. Moreover, carbon deposition on metal surfaces under high-temperature conditions represents another major deactivation pathway. Based on the comprehensive physicochemical characterization and adhesion stability tests before and after reaction, the coating derived from the organic binder HEC possessed a loose structure, unstable interfacial bonding, weak interfacial electronic interaction and limited pore-confinement effect, thereby resulting in the poorest catalytic performance. Although the inorganic binder Si-sol generated a mesoporous structure similar to that of Al-sol, its discontinuous coating distribution and relatively weak adhesion led to inadequate resistance to spallation at high temperatures. In contrast, the strongly bonded mesoporous network framework formed from Al-sol after calcination provided a more uniform and stable architecture, which facilitated efficient heat and mass transfer. Meanwhile, the interconnected mesoporous framework also promoted coke gasification through spatial confinement effects, thereby effectively mitigating the risks of deactivation by carbon deposition and coating failure.

2.4 Adhesion mechanism of the anti-peeling coating in *m*-NCM-Al-sol, mesoporous confinement and local electronic effects

Based on the above results, a possible mechanism is proposed to elucidate the influence of different binders on the coating structure and catalytic performance of monolithic catalysts. In the system employing the organic binder, the continuous organic adhesive layer formed by HEC, which encapsulates the active particles initially, undergoes decomposition of its long-chain carbon structures during high-temperature calcination. Subsequently, oxidation and removal of the organic components induce significant coating shrinkage and stress concentration, causing the active particles to aggregate and form loosely packed mesoporous structures^[34]. Under continuous thermal stress, cracks gradually initiate and propagate within the coating, evolving into cohesive or interfacial failure,

ultimately leading to coating agglomeration, non-uniform distribution, and severe cracking. As a result, under conditions of accumulated thermal stress, the coating becomes prone to spallation, metal sintering, and deactivation *via* coking during high-temperature reactions^[35]. These results indicate that organic binders mainly provide temporary physical adhesion and are incapable of forming a rigid mesoporous support framework. This inherent limitation makes it challenging to maintain stable structural support and confinement effects under high-temperature conditions. When inorganic Si-sol was employed as the coating binder, the layer of SiO₂ colloidal particles layer encapsulating the active particles underwent dehydration and condensation during calcination and interconnected, forming a continuous mesoporous inorganic network framework. As the temperature increased, the coating gradually solidified developing a mesoporous framework that provided a degree of spatial confinement. However, due to the absence of external Al species required for reconstructing the (Ni-Mg)Al_xO₄ coating structure *via* the bidirectional diffusion mechanism, the interactions between the solidified SiO₂ network, the cordierite interface and the active particles remained relatively weak. Consequently, the coating was prone to cracking due to accumulated thermal stress during high-temperature calcination, leading to a significant degradation in its adhesive properties. Therefore, although *m*-NCM-Si-sol exhibited improved coking resistance owing to its mesoporous confinement effect, its overall structural stability was limited being compromised by its relatively poor adhesion and resistance to spallation. In contrast, the inorganic Al-sol binder transformed into a continuous and compact mesoporous network structure upon calcination and established stable interfacial connections between the active particles and the cordierite substrate (Figure 8). On the one hand, the Al-sol-derived coating infiltrated and filled the surface defects of cordierite and subsequently formed a “bridging-anchor” structure between the cordierite interface and active particles during the high-temperature-induced phase transformation^[36–37]. This significantly enhanced the coating adhesion strength and surface uniformity, thereby improving the coating’s resistance to spallation under prolonged high-temperature reaction conditions. On the other hand, the embedding of active particles into the Al₂O₃ mesoporous framework formed a (Ni-Mg)Al_xO₄ composite structure, creating strong metal-support interactions. This structure ensured high dispersion of active particles within the coating and promoted electron transfer from framework Al species to Ni after reduction, thereby enhancing catalytic activity. Meanwhile, the inherent confinement effect of the interconnected Al₂O₃ mesoporous channels effectively restricted the uncontrolled growth of carbon species and facilitated coke gasification. As a result, the monolithic *m*-NCM-Al-sol catalyst exhibited excellent coating structural integrity and superior stability in catalytic performance.

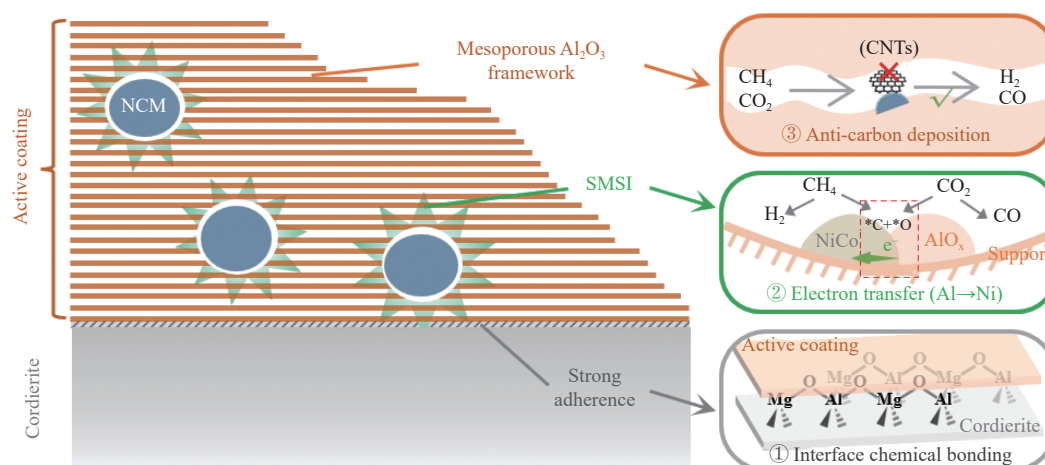


Fig. 8 Schematic diagram of the binder-controlled mechanism of anti-detachment coating and the confinement effect of the mesoporous network skeleton and electronic effect in the *m*-NCM-Al-sol catalyst

2.5 Optimization of coating process parameters for monolithic catalysts

After identifying alumina sol as the optimal binder, the effects of key coating process parameters, including Al-sol content, pristine catalyst loading amount, and coating cycles, on the performance of the *m*-NCM-Al-sol catalyst were systematically investigated to gain deeper insight into the relationship between coating structure and catalytic behavior. As shown in Figure 9, the Al-sol content significantly influenced catalytic performance. Among the samples, *m*-NCM-3%-Al-sol exhibited the highest and most stable CH₄ and CO₂ conversions, whereas lower (1%) or higher (5%–7%) Al-sol contents led to performance

degradation. At low binder content, the coating layer was relatively thin and incomplete, resulting in weak interfacial adhesion and non-uniform dispersion of active species. Conversely, excessive Al-sol content produced a thicker and denser coating that partially blocked the channels, thereby increasing diffusion resistance. Catalytic performance exhibited a volcano-shaped dependence on the amount of pristine catalyst loaded, with the 2.5 g formulation demonstrating the optimal activity and stability. Insufficient loading provided an inadequate number of active sites, while excessive loading tended to induce overly thick coatings and particle agglomeration. Furthermore, the number of coating cycles markedly affected catalyst performance.

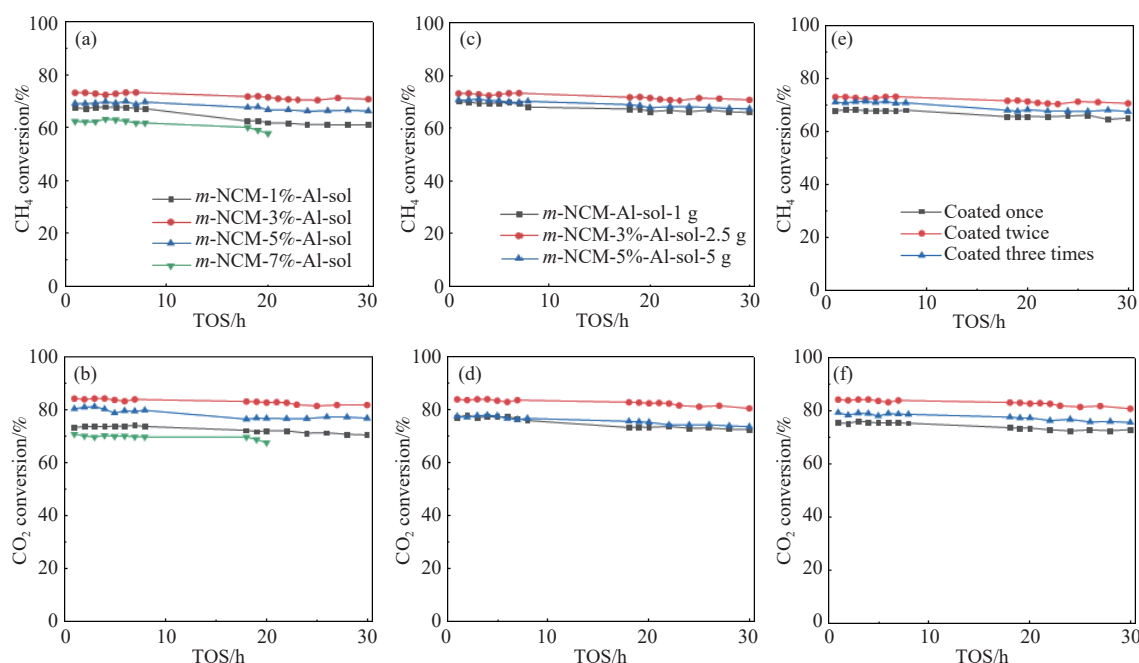


Fig. 9 Effect of coating parameters on the catalytic performance of *m*-NCM-Al-sol catalysts in DRM: (a), (b) CH₄ conversion and CO₂ conversion as a function of time on stream with different Al-sol contents; (c), (d) with different active component loadings; (e), (f) with different coating cycles

Compared with one or three coating cycles, two coating cycles produced a more uniform and continuous coating structure, thereby significantly enhancing both catalytic activity and stability. Notably, the H_2/CO ratio remained nearly constant within the range of 0.80–0.85 across all preparation conditions (not shown), indicating that the coating parameters mainly influenced catalytic performance through regulating structural characteristics and mass-transfer behavior, with minimal impact on the reaction pathway.

3 Conclusion

In summary, monolithic *m*-NCM-*X* catalysts for DRM reactions were successfully prepared *via* a dip-coating process, and the effects of inorganic and organic binders on the coating structure and catalytic performance of the monolithic catalysts were systematically investigated, together with the corresponding mechanism analysis. The results demonstrate that the alumina-sol-modified *m*-NCM-Al-sol catalyst formed a reconstructed coating with a (Ni-Mg) Al_xO_4 composite structure through the elemental diffusion mechanism between the cordierite substrate and active particles during the high-temperature phase transformation process. This coating exhibited a uniform and robust interfacial structure, featuring an interconnected mesoporous Al_2O_3 network and strong metal-support (Al-sol-derived framework) interfacial interactions that effectively regulated charge transfer around the metal sites. In contrast, when Si-sol was employed as the binder, although a rigid mesoporous network framework was formed, the lack of strong interactions between the coating layer, the cordierite surface and the NCM active particles resulted in the formation of numerous coating cracks after calcination, which was unfavorable for heat transfer and adhesion stability. Compared with inorganic binders, the organic binder was gradually oxidized and removed during high-temperature calcination, unable to form a permanent supporting framework. Consequently, the temporary coating connection failed to withstand accumulated thermal stress, eventually evolving into a poorly adhered structure with severe particle agglomeration, abundant cracks, and inadequate anti-peeling resistance. By correlating the coating characteristics of the monolithic catalysts with their catalytic performance, it was revealed that coating adhesion strength, mesoporous confinement effects and strong SMSI-induced regulation of the local electronic environment of metal sites are the key factors determining DRM performance. Among the catalysts, the strongly adhered coating of *m*-NCM-Al-sol effectively prevented the active component loss owing to its excellent high-temperature anti-peeling capability, while its mesoporous confinement structure suppressed coke deposition. Meanwhile, the interfacial charge transfer between the metal species and the support framework promoted C–H bond activation on Ni sites, thereby resulting in the best catalytic activity and

stability. In contrast, the catalyst modified using the organic binder HEC exhibited the poorest coating uniformity, adhesion strength, and coking confinement properties, leading to significantly inferior catalytic performance compared with catalysts prepared using inorganic binders. After further optimization of the coating process parameters, the monolithic *m*-NCM-Al-sol catalyst exhibited excellent and stable DRM performance, achieving CH_4 and CO_2 conversions of 73% and 83.6%, respectively, during continuous operation for 30 h.

Declaration of Competing Interest

The authors declare no conflict of interest.

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黏结剂对整体式催化剂涂层结构调控及 CH₄-CO₂ 重整性能研究

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摘 要: 甲烷 CO₂ 干重整反应 (DRM) 因降碳减排、增值转化等优势被视为“双碳”背景下的关键 CO₂ 利用技术, 但目前适用于工业化 DRM 过程的成型催化剂研究报道仍然较少。基于此, 本工作以蜂窝状堇青石为基体构建了整体式催化剂, 并重点考察了有机和无机黏结剂对涂层结构的不同作用形式及催化性能的调控机制。对比发现, 无机铝溶胶构建的活性涂层连续均匀且不易脱落; 同时, 外来 Al₂O₃ 网络经高温煅烧结构演变中的元素扩散机制桥联堇青石表界面和催化剂活性颗粒实现了涂层重构, 形成具有强金属担体相互作用的 (Ni-Mg)Al₂O₄ 复合结构, 且连通式介孔骨架展现出优良的孔道限域特性, 最终实现了整体式 *m*-NCM-Al-sol 催化剂的强涂层黏结性、活性提升及抗碳稳定运行。相比之下, 无机 SiO₂ 引导形成的介孔网络涂层因表界面结构不均和缺乏黏结性易导致活性涂层脱落及催化活性损失。当使用有机黏结剂时, 无论宏观涂层形貌和黏附性能, 还是微观介孔限域及局域电子效应, 均不如无机黏结剂调控有效, 因此, 其改性的样品展现出最差催化性能。此外, 通过优化铝溶胶涂覆工艺参数如黏结剂含量、活性组分用量及涂覆次数, 实现了涂层厚度与传质性能的协同平衡, 优化后的整体式催化剂在 DRM 反应中表现出优良性能。该工作可为高效整体式催化剂涂层的成型与调控提供有价值的参考。

关键词: 甲烷干重整; 整体式催化剂; 铝溶胶; 介孔骨架涂层; 双重扩散机制

中图分类号: O643.36

文献标识码: A

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