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Methanol steam reforming performance and catalytic mechanism of bimetal-loaded cerium oxide-based thermal catalysts

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An activity evaluation was performed for the replacement of the noble metal Pt with non-precious metal active species while maintaining catalytic performance in methanol steam reforming. In this study, bimetallic cerium oxide-supported catalysts ($\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$) were prepared using Pt and non-precious metals. Among these catalysts, the Pt–Fe system exhibited the highest reforming performance. At 180 °C, the H_2 production rate reached 17.29 mmol $g_{\text{cat}}^{-1}\cdot\text{h}^{-1}$, with a CO selectivity of 15.58% and methanol conversion of 1.07%. Results indicated that the introduction of Fe effectively increased the specific surface area and the amount of lattice oxygen on the catalyst surface while promoting the formation of abundant oxygen vacancies. Under optimal reforming conditions, $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ showed the lowest energy consumption and the best reforming performance. Furthermore, based on the thermodynamic analysis of the methanol steam reforming reaction, the corresponding reaction pathways and catalytic mechanisms were proposed.

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1 Introduction

Transition metal oxides (TMOs) have been widely studied for their application as catalysts in low-temperature methanol steam reforming (LT-MSR) reaction due to their low cost and considerable catalytic activity.^{1–3} They have the advantages of variable valence states and tunable orbital occupancy in redox reactions, making them the most promising candidates to replace precious metals.^{4–6} The reported catalytic systems mainly include Ce-, Mo-, Cu- and Ti-based catalysts and multicomponent composite systems.^{7,8} Among these, the ceria-based catalysts exhibit a reversible $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox cycle, abundant oxygen vacancies within the structure, and strong metal–support interactions, which synergistically regulate the surface electronic structure. In addition, the exposure of different crystal facets further enhances surface reactivity. These combined effects enable ceria-based catalysts to display excellent redox properties and generate a large amount of highly active surface oxygen species.^{9–11} Thus, these catalysts show excellent redox activity, strong thermal stability, high surface reactive oxygen concentration and structural stability.^{12–14}

Studies show that transition metal oxide-loaded noble metal catalysts show great potential in methanol steam reforming (MSR) reactions, and their catalytic properties are sensitive to the structural features of the transition metal oxide interface, which are generally determined by the properties of the support and loaded metal.^{15–17} Compared with other metal (Au, Ag, Pd, Pt, Ru, Rh, and Ir)-loaded catalysts, cerium oxide-loaded Pt atomic catalysts exhibit significant advantages due to their high catalytic properties, abundance, and easy and affordable preparation process.^{18–20} Among transition metals, Fe, Ni, and Zn exhibit considerable catalytic activity and are much cheaper than Pt. Therefore, identifying alternative metals to replace noble metal loading without compromising catalytic performance is the focus of this study.

In this study, N-doped CeO_2 nanorods were prepared by thermal condensation. Under the condition that the Pt loading was set to 0.5 wt% and the Pt : M molar ratio was fixed at 1 : 1, a series of bimetallic Pt–M (M = Fe, Ni, Zn, Mg, Al, and Cu) catalysts supported on N- CeO_2 were prepared *via* an impregnation method, followed by drying and thermal treatment. Then, by adjusting the atomic ratio of Pt to non-precious metals (by adjusting the molar ratio), thermal catalysts with different atomic ratios ($\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$) were prepared by calcining the mixture at high temperatures. The crystal structure, microstructure, specific surface area, oxygen vacancy concentration, surface chemical composition, elemental state and chemical bond properties of the prepared thermal catalysts were investigated. In addition, their catalytic performance in methanol steam reforming was evaluated, and the possible reaction

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pathways and mechanisms of the $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$ catalysts were discussed.

2 Experiments

2.1 Materials

Cerium nitrate ($\text{Ce}(\text{NO}_3)_3$, AR) was purchased from Tianjin Damao Chemical Reagent Co., Ltd Sodium hydroxide (NaOH , AR) was obtained from Shanghai Macklin Biochemical Technology Co., Ltd Ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$, AR) was supplied by Xilong Scientific Co., Ltd Chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, AR) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd Copper sulfate (CuSO_4 , AR), aluminum nitrate ($\text{Al}(\text{NO}_3)_3$, AR), nickel nitrate ($\text{Ni}(\text{NO}_3)_2$, AR), iron nitrate ($\text{Fe}(\text{NO}_3)_3$, AR), zinc nitrate ($\text{Zn}(\text{NO}_3)_2$, AR), magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$, AR), anhydrous ethanol (AR), anhydrous methanol (AR), and sodium D-isoscorbate ($\text{C}_6\text{H}_7\text{NaO}_6$, AR) were all obtained from Aladdin Reagent Co., Ltd Deionized water was prepared in the laboratory.

2.2 Characterization

X-ray photoelectron spectroscopy (XPS, Kratos AXIS Nova) was employed to analyze the surface elemental composition and chemical states of the samples. The N_2 adsorption-desorption isotherms of the catalysts were measured using a surface area and pore structure analyzer (Beckman LS-230). The crystal structures of the samples were characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). Fourier transform infrared spectroscopy (FT-IR, VECTOR2, Bruker, Germany) was performed to identify the surface functional groups. The morphology and microstructure were examined using a field-emission scanning electron microscope (SEM, SU8100, Hitachi, Japan). Raman spectra were recorded on a Raman spectrometer (LabRAM Aramis, HORIBA, France). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Cyclic voltammetry (CV) curves were obtained using an electrochemical workstation (CHI660D, Chenhua Instruments, Shanghai, China).

2.3 Evaluation of catalytic performance

Catalytic performance in methanol steam reforming (MSR) for hydrogen production was evaluated in a fixed-bed quartz tubular reactor. A total of 200 mg of the catalyst (180–200 mesh) was loaded into the reactor. The catalyst was first reduced in a H_2/Ar mixed gas at a flow rate of 35 mL min^{-1} for 1 h under specified conditions. After reduction, the reactor was cooled to the desired reaction temperature under a 35 mL min^{-1} Ar atmosphere, and the fixed-bed reaction program was initiated. A $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ mixture with a molar ratio of 1 : 1.2 was fed into a vaporization chamber using a micro-pump at a flow rate of 0.1 mL min^{-1} . The vaporizer temperature was maintained at $200 \text{ }^\circ\text{C}$ to ensure complete evaporation of the liquid mixture into the gas phase. The corresponding weight hourly space velocity (WHSV) was 26 h^{-1} . The vapor was then carried into the reactor by Ar at a flow rate of 35 mL min^{-1} . The outlet gas mixture was first passed through a cold trap to condense the unreacted

components, and the remaining gas was subsequently analyzed online using a GC9790II gas chromatograph equipped with a chromatographic column (approximately $100 \text{ }^\circ\text{C}$) and a thermal conductivity detector (TCD, approximately $130 \text{ }^\circ\text{C}$), with 99.99% Ar as the carrier gas. The concentrations of H_2 , CO_2 , CH_4 and CO were monitored. Methanol conversion was calculated based on the carbon balance. For catalytic activity evaluation, measurements at each temperature were repeated three times, and the average values were reported.

$$X_{\text{MeOH}}(\%) = \frac{n_{\text{CO}} + n_{\text{CH}_4} + n_{\text{CO}_2}}{n_{\text{MeOH}}} \times 100\% \quad (1)$$

$$Y_{\text{H}_2} = \frac{n_{\text{H}_2}}{t \times m_{\text{cat}}} \quad (2)$$

$$S_{\text{CO}} = \frac{n_{\text{CO}}}{n_{\text{CO}_2} + n_{\text{CO}}} \times 100\% \quad (3)$$

$X(\text{MeOH})$: methanol conversion (%). $Y(\text{H}_2)$: hydrogen production rate ($\text{mmol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$); n : molar amount of gas (mmol); m_{cat} : mass of the catalyst (g); t : reaction duration (h); S : selectivity towards by-products CO (%).

2.4 Preparation of the N-CeO₂ and Pt_xM_{10-x}/N-CeO₂ catalysts

N-CeO₂ nanorods were prepared as follows: first, 2.605 g of cerium nitrate and 5 g of sodium hydroxide were dissolved in 80 mL of deionized water and stirred at $80 \text{ }^\circ\text{C}$ for 1 h. During the stirring process, 720 μL of ethylenediamine aqueous solution (75 vol%) was added dropwise. The resulting mixture was then transferred to a Teflon-lined autoclave and maintained at $120 \text{ }^\circ\text{C}$ for 24 h. After the reaction, the product was collected, ultrasonically washed, centrifuged, and freeze-dried. The obtained solid was then calcined in a muffle furnace at $450 \text{ }^\circ\text{C}$ for 5 h to yield yellow CeO₂ nanorods. Subsequently, 0.5 g of CeO₂ nanorods and 0.198 g of sodium D-isoscorbate were dispersed in 200 mL of deionized water and stirred at room temperature for 5 h. After ultrasonic washing, the N-doped CeO₂ nanorods were obtained.

$\text{Pt}_5\text{M}_5/\text{N-CeO}_2$ nanorods were prepared as follows: The $\text{Pt}_5\text{M}_5/\text{N-CeO}_2$ catalyst was prepared by the impregnation method. The specific procedure is as follows: firstly, 0.35 g of N-CeO₂ nanorods, 0.00226 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.00263 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.00269 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.00232 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.00339 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.00366 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and 938 μL of chloroplatinic acid solution (5 g L^{-1}) were dispersed in 60 mL of deionized water under continuous stirring. The mixture was stirred at room temperature for 5 h to ensure sufficient contact. Subsequently, the product was ultrasonically washed, centrifuged, and freeze-dried to obtain a gray flocculent solid. Finally, the obtained product was transferred to a crucible and calcined in a muffle furnace at $300 \text{ }^\circ\text{C}$ for 1 h. The resulting solid powders were denoted as $\text{Pt}_5\text{Cu}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Al}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Ni}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Zn}_5/\text{N-CeO}_2$, and $\text{Pt}_5\text{Mg}_5/\text{N-CeO}_2$ nanorods (Pt loading was 0.5 wt% and the molar ratio of Pt atoms to other metal atoms was 1 : 1).



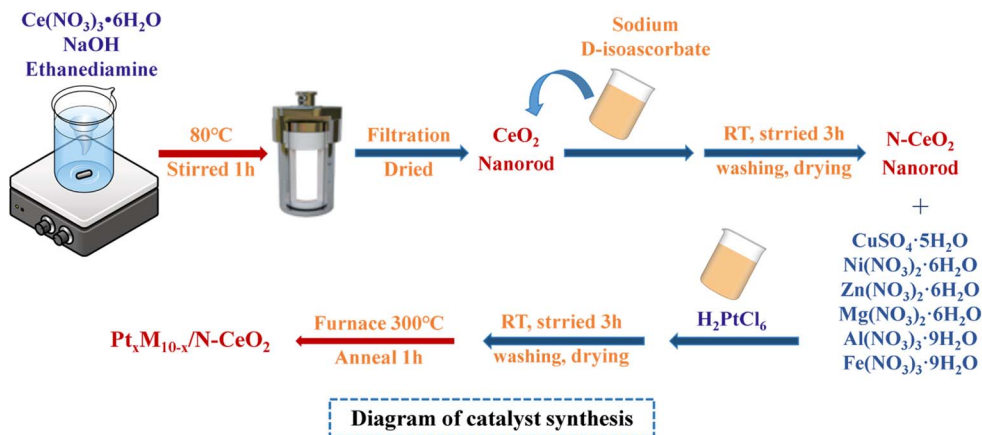


Fig. 1 Preparation process of $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$.

$\text{Pt}_x\text{Fe}_{10-x}/\text{N-CeO}_2$ nanorods were prepared as follows: The $\text{Pt}_x\text{Fe}_{10-x}/\text{N-CeO}_2$ catalyst was also prepared by the impregnation method. The specific procedure is as follows: firstly, 0.35 g of N-CeO₂ nanorods, 0.00658 g (0.00071 g, 0.00512 g, 0.00219 g, and 0.00366 g) of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 188 μL (1690 μL , 563 μL , 1314 μL , and 938 μL) of chloroplatinic acid solution (5 g L⁻¹) were dispersed in 60 mL of deionized water under continuous stirring. The mixture was stirred at room temperature for 5 h. After the reaction, the products were collected by filtration, washed with ethanol and deionized water, and then freeze-dried to obtain a gray flocculent solid. The dried samples were transferred to a crucible and calcined in a muffle furnace (heating rate of 5 °C min⁻¹) at 300 °C for 1 h. The resulting solid powders were denoted as $\text{Pt}_1\text{Fe}_9/\text{N-CeO}_2$, $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$, $\text{Pt}_9\text{Fe}_1/\text{N-CeO}_2$, $\text{Pt}_3\text{Fe}_7/\text{N-CeO}_2$, $\text{Pt}_7\text{Fe}_3/\text{N-CeO}_2$, and $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ nanorods (where $x:10 - x$ is the molar ratio of Pt to Fe). The preparation process is illustrated in Fig. 1.

3. Results and discussion

3.1 Morphology and structure analysis of the $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$ catalysts

Fig. 2a shows the XRD patterns of catalysts ($\text{Pt}_5\text{Cu}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Al}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Ni}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Zn}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$

and $\text{Pt}_5\text{Mg}_5/\text{N-CeO}_2$) prepared with 0.5 wt% Pt loading while keeping the molar ratio of Pt atoms to other metal atoms 1 : 1. Fig. 2a shows the XRD patterns of $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$ samples. All the samples exhibit diffraction peaks at $2\theta = 28.5^\circ$, 33.1° , 47.4° , 56.3° , 59.0° , 69.4° , 76.6° , and 79.1° ,^{21,22} which are attributed to the (111), (200), (220), (311), (222), (400), (331), and (420) crystal planes (PDF#34-0394), respectively. No characteristic peaks corresponding to the loaded metals were observed in the XRD patterns, which may be attributed to the low Pt loading (0.5 wt%) and the relatively low content of other metals, as well as their highly dispersed distribution within CeO₂. Notably, significant differences in the (111) diffraction peaks are observed among the samples, suggesting that metal loading affects the crystal structure of CeO₂ and may induce lattice distortion or crystallinity variations, resulting in different degrees of changes in the (111) plane.

The FTIR spectra of $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$ (M: Cu, Al, Ni, Zn, Fe, and Mg) samples are shown in Fig. 2b. The absorption peak at 3435 cm⁻¹ corresponds to the stretching vibration of adsorbed water molecules on the sample surface. The peak observed at 2350 cm⁻¹ can be attributed to the stretching vibration of C≡C-H or nitrile groups (C≡N). The absorption peak at 480 cm⁻¹ is assigned to the Ce-N stretching vibration, indicating that N atoms have been successfully introduced into the sample and that new

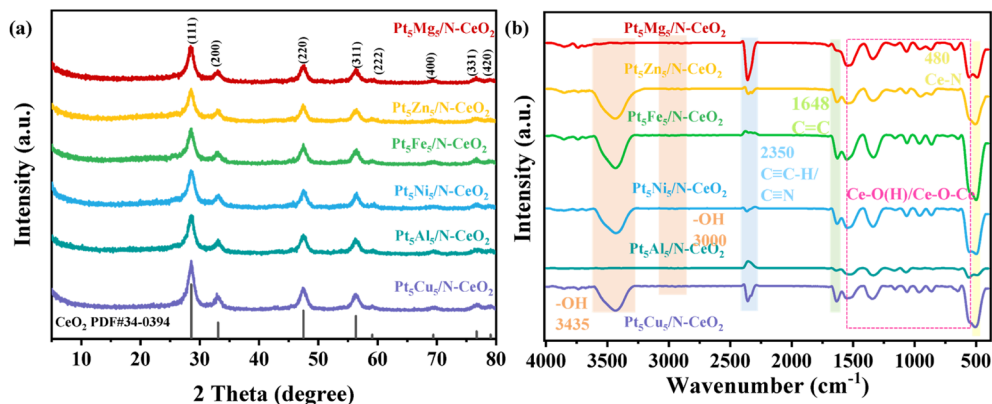


Fig. 2 (a) XRD patterns and (b) FT-IR spectra of the $\text{Pt}_5\text{M}_5/\text{N-CeO}_2$ catalysts.



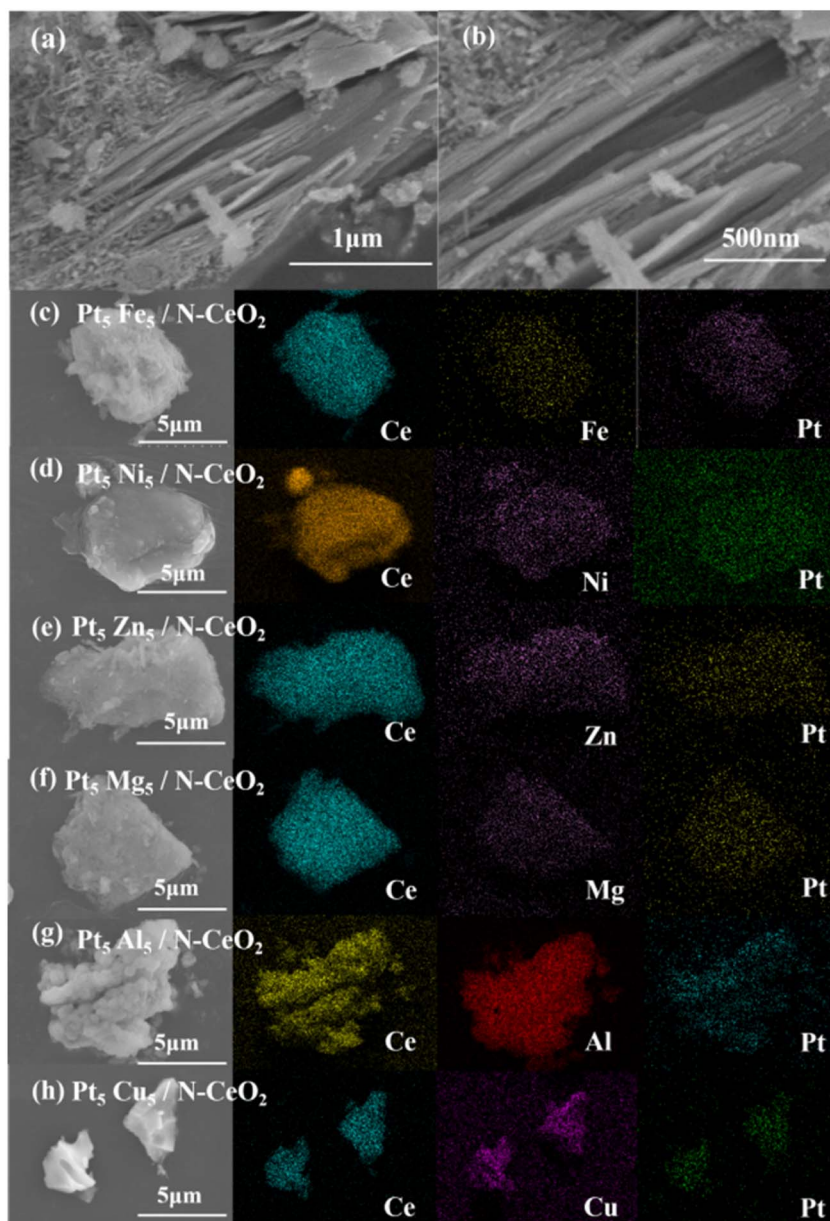


Fig. 3 (a and b) SEM image of $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$. (c–h) SEM-EDS elemental mapping of $\text{Pt}_5\text{M}_5/\text{N-CeO}_2$.

chemical bonds have been formed. The absorption peaks in the range of $510\text{--}1553\text{ cm}^{-1}$ correspond to the Ce–O stretching vibrations.^{21,23} It can be seen that the loaded metal elements have a negligible influence on the characteristic peaks of CeO_2 , and the product essentially maintains its original structure.

Fig. 3 shows the microscopic morphology and elemental distribution of the samples. Fig. 3a and b present the scanning electron microscopy (SEM) images of $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$. It can be observed that $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ exhibits a block-like structure assembled from nanorods, with an overall size of approximately $6\text{ }\mu\text{m}$, while the nanorods have an average diameter of about 10 nm . Some partially damaged regions can be observed on the surface of $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$, indicating a relatively rough surface. Such a rough surface is beneficial for increasing the specific

surface area of the catalyst and promoting the dispersion of active components. Fig. 3c–h show the SEM-EDS mapping images of $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Ni}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Zn}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Mg}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Al}_5/\text{N-CeO}_2$, and $\text{Pt}_5\text{Cu}_5/\text{N-CeO}_2$, respectively. It can be observed that Fe, Ni, Zn, Mg, Al, and Cu are uniformly distributed on the surface of CeO_2 .

Fig. 4 shows the N_2 adsorption–desorption equilibrium curves and pore size distribution curves of $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Ni}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Zn}_5/\text{N-CeO}_2$ and $\text{Pt}_5\text{Mg}_5/\text{N-CeO}_2$. As shown in Fig. 4a, all the samples exhibit a type IV isotherm with H_3 lag loop and rapid absorption under a low relative pressure. These results showed that the samples are characterized by the co-existence of mesopores and micropores. As shown in Table 1, the specific surface areas of each catalyst were calculated to be



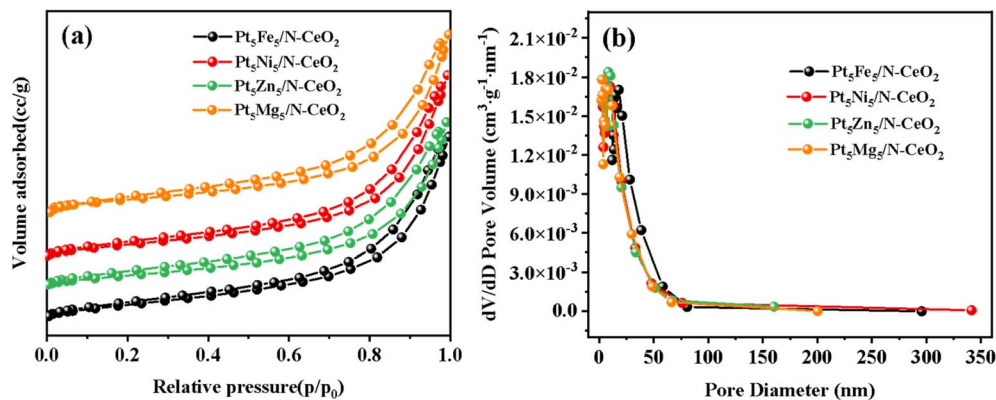


Fig. 4 (a) N_2 adsorption–desorption equilibrium curves of the $Pt_5M_5/N-CeO_2$ thermal catalysts and their (b) pore size distribution curves.

142.827 $m^2 g^{-1}$, 133.858 $m^2 g^{-1}$, 129.307 $m^2 g^{-1}$ and 126.315 $m^2 g^{-1}$, respectively. The specific surface area of the samples varied from 126.315 to 142.8 $m^2 g^{-1}$, indicating that the type and shape of the loaded metal had an effect on surface area. Fig. 4b shows the pore size distribution curves of the samples, indicating that all the samples are mesoporous materials. The cumulative pore size distribution of the $Pt_5Fe_5/N-CeO_2$ catalyst was calculated by the BJH fitting method. The pore size of the $Pt_5Fe_5/N-CeO_2$ catalyst is approximately 8 nm, while the pore size of the other samples ranges from 6 to 8 nm. The experimental results demonstrate that large surface area and a high density of surface defects not only improve the dispersion of catalytically active species but also anchor Pt species, inhibiting their aggregation. In addition, the larger pore volume is conducive to facilitating the mass transfer of methanol and water molecules in the thermal catalytic reaction process to achieve better thermal catalytic activity.

Fig. 5a–f show the CV curves of $Pt_5Fe_5/N-CeO_2$, $Pt_5Ni_5/N-CeO_2$, $Pt_5Zn_5/N-CeO_2$, $Pt_5Mg_5/N-CeO_2$, $Pt_5Al_5/N-CeO_2$ and $Pt_5Cu_5/N-CeO_2$ at different scanning rates. Fig. 5g presents the relationship between the maximum current density of the sample and the scanning rate. It can be seen that the C_{dl} values of the sample are different under different bimetal loads. The C_{dl} value of $Pt_5Fe_5/N-CeO_2$ is 35.97 $\mu F cm^{-2}$. It is significantly higher than those for $Pt_5Ni_5/N-CeO_2$ (20.15 $\mu F cm^{-2}$), $Pt_5Zn_5/N-CeO_2$ (22.25 $\mu F cm^{-2}$), $Pt_5Mg_5/N-CeO_2$ (13.18 $\mu F cm^{-2}$), $Pt_5Al_5/N-CeO_2$ (13.58 $\mu F cm^{-2}$) and $Pt_5Cu_5/N-CeO_2$ (20.48 $\mu F cm^{-2}$), indicating that $Pt_5Fe_5/N-CeO_2$ exposes more active sites than the other samples. The introduction of Fe into the Pt-based catalyst significantly enhances the charge storage capacity compared with other non-precious metal promoters, thereby providing more catalytic sites and facilitating redox kinetics during the

catalytic reaction, suggesting that $Pt_5Fe_5/N-CeO_2$ is more effective in promoting the overall catalytic performance.

Defects and oxygen vacancies on the catalyst surface play a key role in the thermal catalytic water reforming of methanol. Raman spectroscopy can be used to characterize the structure of defects and oxygen vacancy concentration in catalysts. As shown in Fig. 6a, the Ce–O–Ce symmetric stretching vibration peak of the F_{2g} mode in the fluorite cubic cerium oxide structure is located at 462 cm^{-1} , and its position and shape can be adjusted by changing the microcrystal size. In contrast, the Raman peaks of the F_{2g} mode in the $Pt_5Fe_5/N-CeO_2$ sample are weaker than those of the other samples, which can be attributed to the sample having the smallest grain size. The weak peak observed at 257 cm^{-1} corresponds to the second-order transverse acoustic mode (2 TA), while another weak peak around 600 cm^{-1} is assigned to the defect induction band of the sample (the “D” band). The intensity can be used to measure the deformation of the anionic lattice, which is responsible for surface defects and oxygen vacancies in the sample.^{24,25} The relatively weak peak at 553.7 cm^{-1} was attributed to oxygen vacancies, and the relative intensity ratio of the D band to the F_{2g} mode (I_{600}/I_{462}) provides a quantitative measure of defect density and oxygen vacancy concentration. As shown in Fig. 6b, I_{600}/I_{462} of $Pt_5Fe_5/N-CeO_2$ is higher than those of $Pt_5Ni_5/N-CeO_2$ and $Pt_5Zn_5/N-CeO_2$. The results show that $Pt_5Fe_5/N-CeO_2$ has more structural defects and oxygen vacancy concentration than $Pt_5Ni_5/N-CeO_2$ and $Pt_5Zn_5/N-CeO_2$. The Fe–Pt–Ce interactions between the loaded metal and Ce promote the formation of defects and interfacial oxygen vacancies, which is consistent with XRD patterns and TEM results.

Electron paramagnetic resonance (EPR) is an important technique for directly detecting and studying crystal defects, and it provides further insights into the formation of oxygen vacancies in catalysts. As shown in Fig. 6c, $Pt_5Ni_5/N-CeO_2$, $Pt_5Zn_5/N-CeO_2$, and $Pt_5Fe_5/N-CeO_2$ exhibit defect signals at $g = 2.003$, indicating the presence of unpaired electrons associated with oxygen atoms. The intensity of these signals correlates with the concentration of oxygen vacancies.^{26,27} Among the samples, $Pt_5Fe_5/N-CeO_2$ shows the highest peak intensity, suggesting a higher concentration of oxygen vacancies, which is consistent with the Raman spectroscopy results. The increase in oxygen

Table 1 Specific surface area analysis of samples

Samples	S_{BET} ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Pore size (nm)
$Pt_5Fe_5/N-CeO_2$	142.827	0.446	9.135
$Pt_5Ni_5/N-CeO_2$	133.858	0.450	8.079
$Pt_5Zn_5/N-CeO_2$	129.307	0.408	7.501
$Pt_5Mg_5/N-CeO_2$	126.315	0.438	6.354



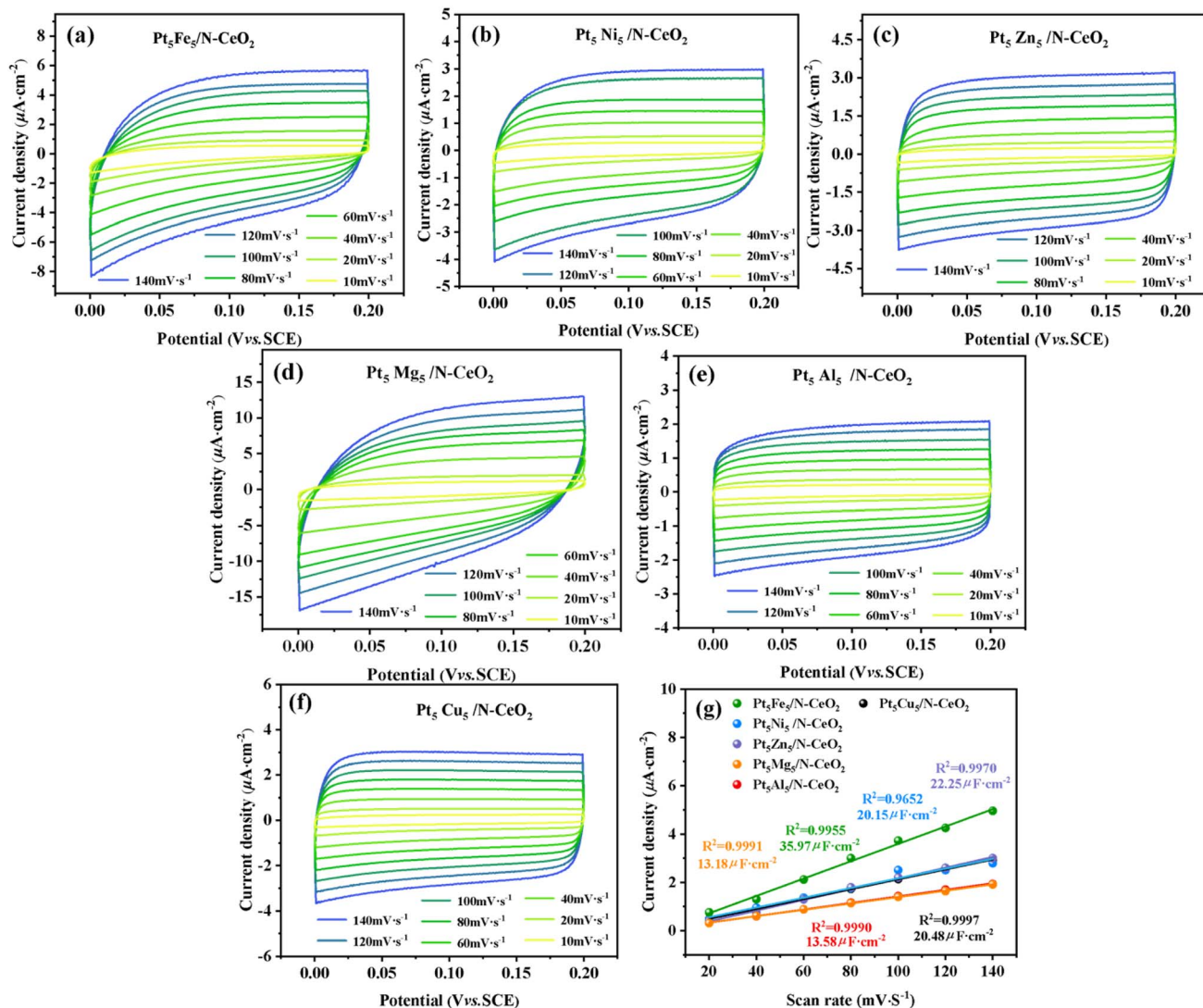


Fig. 5 (a–f) CV curves of Pt₅M₅/N-CeO₂ at different scan rates and (g) linear relation between the current density and scan rate of various metal-loaded catalysts.

vacancies leads to a greater number of active surface sites and facilitates their dynamic participation in the reaction cycle. These vacancies interact with adjacent metal species, synergistically enhancing the dehydrogenation reaction.

Fig. 7 shows the XPS survey spectra of Pt₅Fe₅/N-CeO₂, Pt₅Ni₅/N-CeO₂ and Pt₅Zn₅/N-CeO₂. It can be observed that the peaks corresponding to N, Zn, and Pt are not clearly visible, which may be attributed to their low content and consequently weak signal

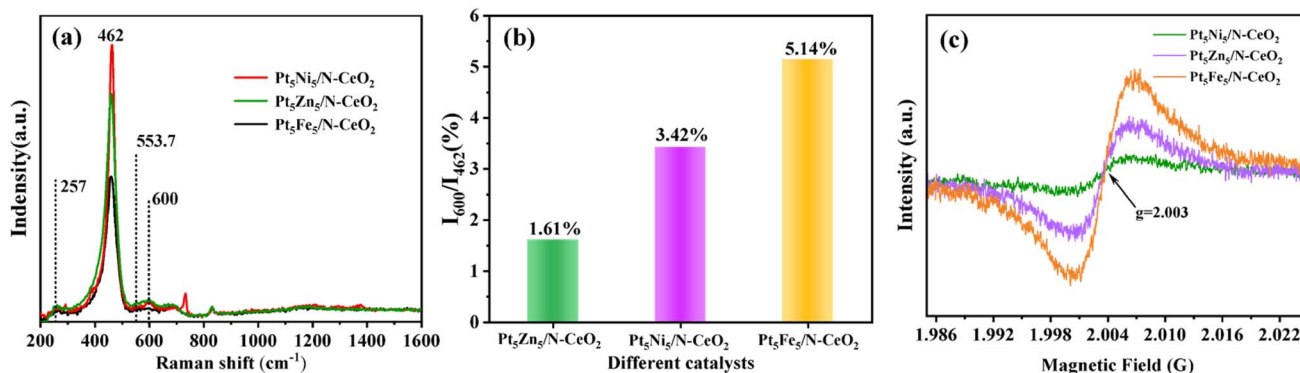


Fig. 6 (a) Raman spectra, (b) defect degree characterization, and (c) EPR spectra of Pt₅Ni₅/N-CeO₂, Pt₅Zn₅/N-CeO₂, and Pt₅Fe₅/N-CeO₂.



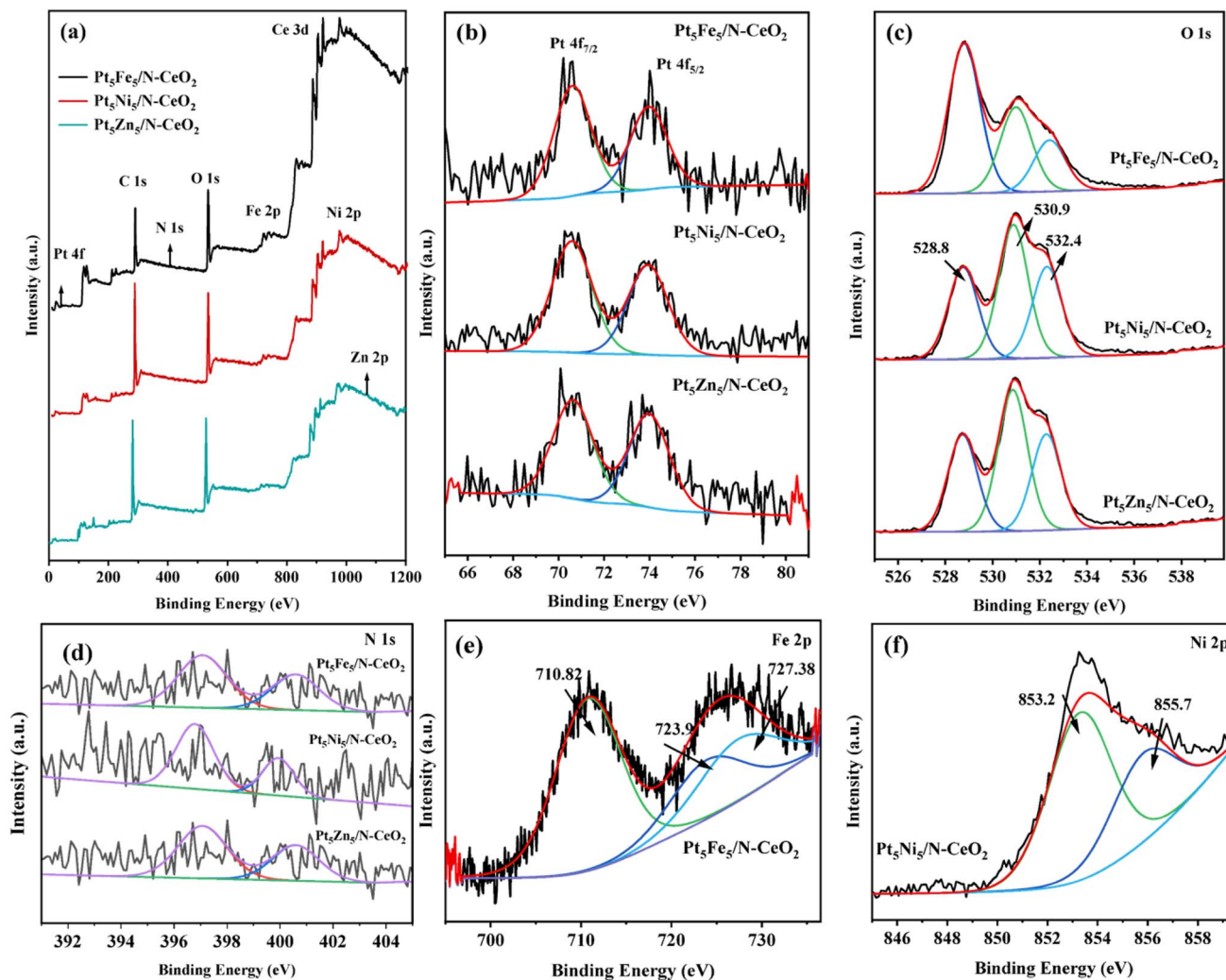


Fig. 7 XPS spectra of Pt₅Fe₅/N-CeO₂, Pt₅Ni₅/N-CeO₂ and Pt₅Zn₅/N-CeO₂: (a) survey spectrum and (b) Pt 4f, (c) O 1s, (d) N 1s, (e) Fe 2p, and (f) Ni 2p spectra.

intensity. Fig. 7b shows the Pt 4f spectra of the sample. The binding energies at 70.6 eV and 73.8 eV correspond to Pt²⁺ 4f_{7/2} and Pt⁰ 4f_{5/2}, respectively. The binding energy of the Pt⁰ 4f_{5/2} orbitals in Pt₅Fe₅/N-CeO₂ is higher than that of Pt₅Ni₅/N-CeO₂ and Pt₅Zn₅/N-CeO₂, indicating a stronger metal-support interaction and a higher proportion of metallic Pt species on the surface of the Pt₅Fe₅/N-CeO₂ catalyst, which is consistent with the results of Raman analysis. Fig. 7c shows the O 1s XPS spectra of the sample. The binding energy peaks at 528.8 eV, 530.9 eV and 532.4 eV are attributed to lattice oxygen, surface adsorbed oxygen and hydroxyl groups or adsorbed water, respectively. It is observed that the lattice oxygen peak of Pt₅Fe₅/N-CeO₂ shifts from 532.4 eV to 532.6 eV, suggesting that the introduction of Fe promotes the activation and migration of lattice oxygen compared with other samples. Fig. 7e shows the Fe 2p spectrum of Pt₅Fe₅/N-CeO₂. Three main peaks at 710.8 eV, 723.9 eV and 727.38 eV are observed, which are attributed to Fe³⁺ and Fe²⁺, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2} orbitals, respectively. This indicates the presence of Fe-Pt-Ce interfacial structures. In the Ni 2p spectrum (Fig. 7f), the peaks at

853.24 eV and 855.7 eV correspond to Ni⁰ and Ni²⁺, respectively.¹⁷ The N 1s XPS spectra (Fig. 7d) of Pt₅Fe₅/N-CeO₂, Pt₅Ni₅/N-CeO₂ and Pt₅Zn₅/N-CeO₂ show two peaks, corresponding to O-N and pyrrolic N, respectively.

3.2 Analysis of the methanol steam reforming reaction on the Pt_xM_{10-x}/N-CeO₂ catalysts

The methanol steam reforming performance of Pt₅M₅/N-CeO₂ was evaluated by measuring the H₂ production rate, CO selectivity, and methanol conversion. The reaction was carried out in a fixed-bed reactor using 0.2 g of 180–200 mesh catalyst particles mixed with 1 g of 120–180 mesh quartz sand. The temperature was increased to 180 °C at a heating rate of 5 °C min⁻¹ under an Ar flow of 35 mL min⁻¹. The molar ratio of methanol to water was 1 : 1.2, the space velocity was 30 mL h⁻¹ g⁻¹, and the feed rate of the methanol-water mixture was maintained at 0.1 mL min⁻¹. As shown in Fig. 8, the catalytic performances of all samples are summarized in terms of H₂ production rate, CO selectivity, and methanol conversion. Fig. 8a presents the H₂ production rate of the MSR reaction. Among all the bimetallic



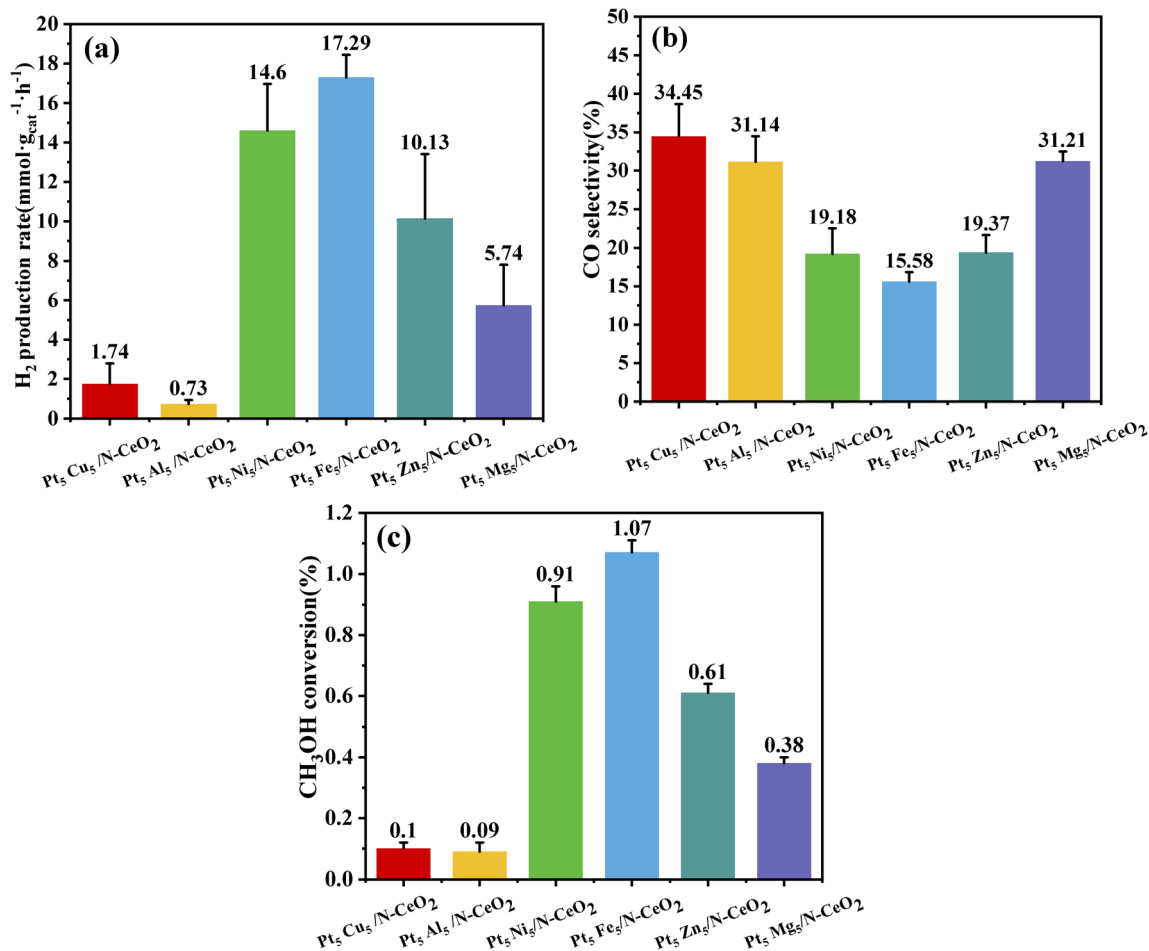


Fig. 8 (a) H₂ gas production rate, (b) CO selectivity, and (c) methanol conversion of various catalysts.

catalysts, Pt₅Fe₅/N-CeO₂ exhibits the highest H₂ production rate (17.29 mmol g_{cat}⁻¹ h⁻¹), which is 1.18, 1.71, 3.01, 9.94, and 23.68 times higher than those of Pt₅Ni₅/N-CeO₂ (14.6 mmol g_{cat}⁻¹ h⁻¹), Pt₅Zn₅/N-CeO₂ (10.13 mmol g_{cat}⁻¹ h⁻¹), Pt₅Mg₅/N-CeO₂ (5.74 mmol g_{cat}⁻¹ h⁻¹), Pt₅Al₅/N-CeO₂ (1.74 mmol g_{cat}⁻¹ h⁻¹), and Pt₅Cu₅/N-CeO₂ (0.73 mmol g_{cat}⁻¹ h⁻¹), respectively. The enhanced activity can be attributed to the role of Fe as an additional active

site, which synergistically interacts with Pt and strengthens the metal-support interaction.

Fig. 8b shows the CO selectivity of catalysts during the MSR reaction. The CO selectivity values of Pt₅Fe₅/N-CeO₂, Pt₅Ni₅/N-CeO₂, Pt₅Zn₅/N-CeO₂, Pt₅Mg₅/N-CeO₂, Pt₅Al₅/N-CeO₂, and Pt₅Cu₅/N-CeO₂ are 34.45%, 31.14%, 19.18%, 15.58%, 19.37%, and 31.21%, respectively. Among these, the Fe-containing catalyst exhibits a relatively lower CO selectivity, indicating

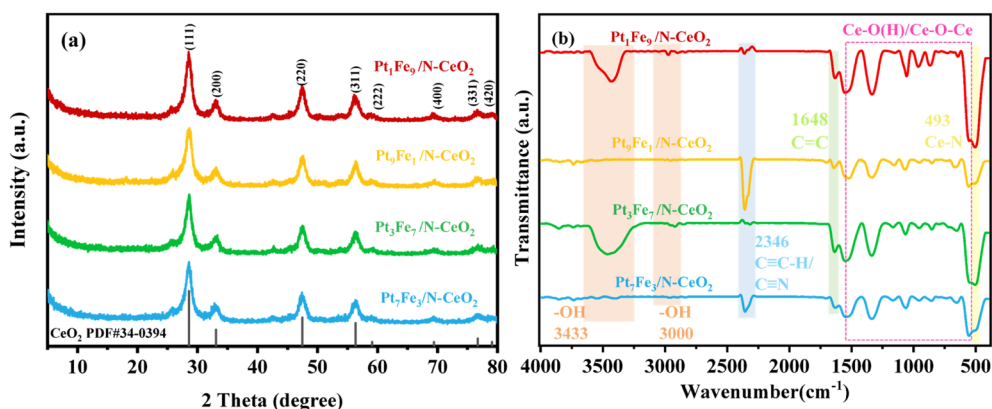


Fig. 9 XRD patterns (a) and FT-IR spectra (b) of the Pt_xFe_{10-x}/N-CeO₂ samples with bimetallic molar ratios of Pt and Fe at 7 : 3, 3 : 7, 9 : 1 and 1 : 9.



that Fe plays a positive role in suppressing by-product formation and improving the catalytic performance in the bimetallic system. Fig. 8c illustrates the methanol conversion of each catalyst. Pt₅Fe₅/N-CeO₂ exhibits the highest methanol conversion (1.07%), which is consistent with its superior H₂ production performance. These results demonstrate that the Pt-Fe bimetallic system exhibits the most favorable interaction with the CeO₂ support. Notably, this synergy enables a reduced usage of the noble metal Pt while maintaining high catalytic activity, thereby lowering the overall catalytic cost.

3.3 Morphology and structure analysis of the Pt_xFe_{10-x}/N-CeO₂ catalysts

Fig. 9a presents the XRD patterns of Pt_xFe_{10-x}/N-CeO₂ catalysts (where *x* denotes the molar ratio of Pt to Fe). All the samples display characteristic diffraction peaks at $2\theta = 28.5^\circ, 33.1^\circ, 47.4^\circ, 56.3^\circ, 59.0^\circ, 69.4^\circ, 76.6^\circ$ and 79.1° , which can be indexed to the (111), (200), (220), (311), (222), (400), (331), and (420) planes of fluorite-structured CeO₂ (PDF#34-0394). However, no discernible diffraction peaks associated with Pt or Fe species are detected, which can be reasonably ascribed to their ultralow loading, rendering them below the detection limit of XRD. In addition, it can be observed that the diffraction peak intensities of (111), (200), (220), and (311) planes of the Pt₁Fe₉/N-CeO₂ sample are significantly higher than those of the other samples. This may be attributed to the increased Fe content, which could alter the crystallinity of the catalyst or promote the growth of CeO₂, thereby enhancing the diffraction intensities of (111), (200), (220) and (311) planes.

Fig. 9b shows the FT-IR spectra of the catalysts. It can be observed that the characteristic peak positions of the four samples are similar. The peak near 3433 cm^{-1} corresponds to the O-H stretching vibration of adsorbed water. However, no corresponding peak is observed for Pt₉Fe₁/N-CeO₂ and Pt₇Fe₃/N-CeO₂ in this region, which may be related to the humidity of the ambient air during sample preparation and measurement. The

peak at 2346 cm^{-1} is associated with the stretching vibration of triple bonds (C≡C-H) or nitrile groups (C≡N), indicating that the N species are incorporated into the samples and form chemical bonds. The band at 493 cm^{-1} can be attributed to Ce-N vibrations. Meanwhile, the peaks below 1660 cm^{-1} (in the range of $493\text{--}1552\text{ cm}^{-1}$) are assigned to Ce-O(H) stretching modes, confirming the presence of the CeO₂ phase in all the samples. It is notable that the intensity of the peak at 493 cm^{-1} gradually increases with increasing Fe loading, suggesting that the Pt-to-Fe atomic ratio influences the crystal structure and growth behavior of the catalyst.

The morphology and microstructure of the Pt₅Fe₅/N-CeO₂ sample were examined by transmission electron microscopy (TEM). As shown in Fig. 10a, the sample exhibits a nanorod structure with a length of approximately 20 nm and an average diameter of about 6 nm. As shown in Fig. 10b, clear lattice fringes can be observed on the CeO₂ nanorods, with interplanar spacings of 0.310 nm and 0.280 nm, corresponding to the (111) and (200) planes of CeO₂, respectively. In addition, Pt nanoparticles in close contact with CeO₂ were observed, with a particle size of about 5 nm. These nanoparticles display distinct lattice fringes with a spacing of 0.198 nm, which can be assigned to the (200) plane of Pt. Furthermore, lattice fringes attributable to Fe₂O₃ were also observed, with an interplanar spacing of 0.264 nm, corresponding to the (104) crystal plane.

Fig. 11a-d present the CV curves of Pt₉Fe₁/N-CeO₂, Pt₃Fe₇/N-CeO₂, Pt₇Fe₃/N-CeO₂, and Pt₁Fe₉/N-CeO₂ at different scan rates. The bimetallic catalysts exhibit distinct current responses, indicating differences in their electrochemical properties. As shown in Fig. 11e, the Pt/Fe molar ratio significantly influences the *C*_{dil} of the samples. The variation can be attributed to changes in particle size and oxygen vacancy concentration, which affect the number of accessible active sites. In addition, the variation in Pt and Fe contents may alter the lattice structure, including porosity and thickness. Among all samples, Pt₉Fe₁/N-CeO₂ exhibits the highest *C*_{dil} value ($34.46\text{ }\mu\text{F cm}^{-2}$), which is approximately 1.7 times higher than that of Pt₁Fe₉/N-

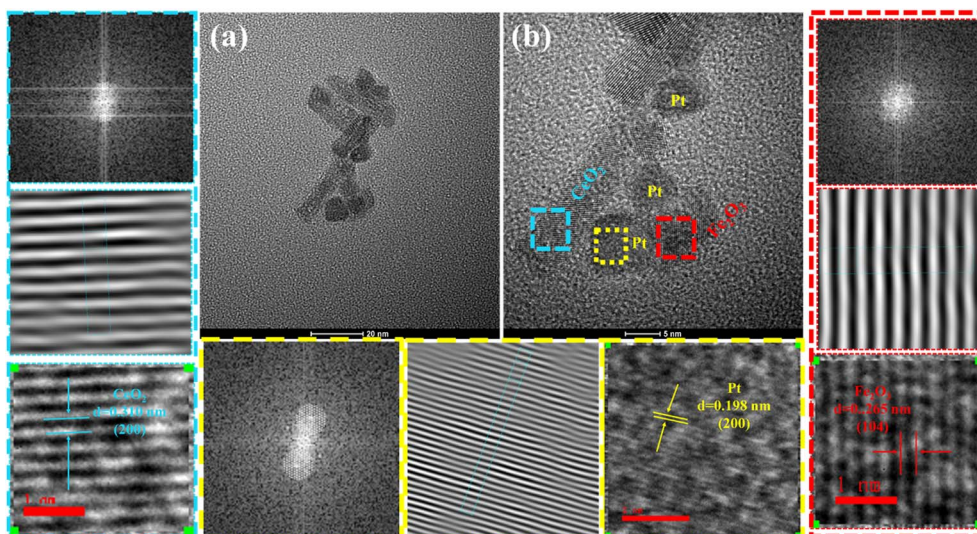


Fig. 10 (a and b) TEM images of Pt₅Fe₅/N-CeO₂.



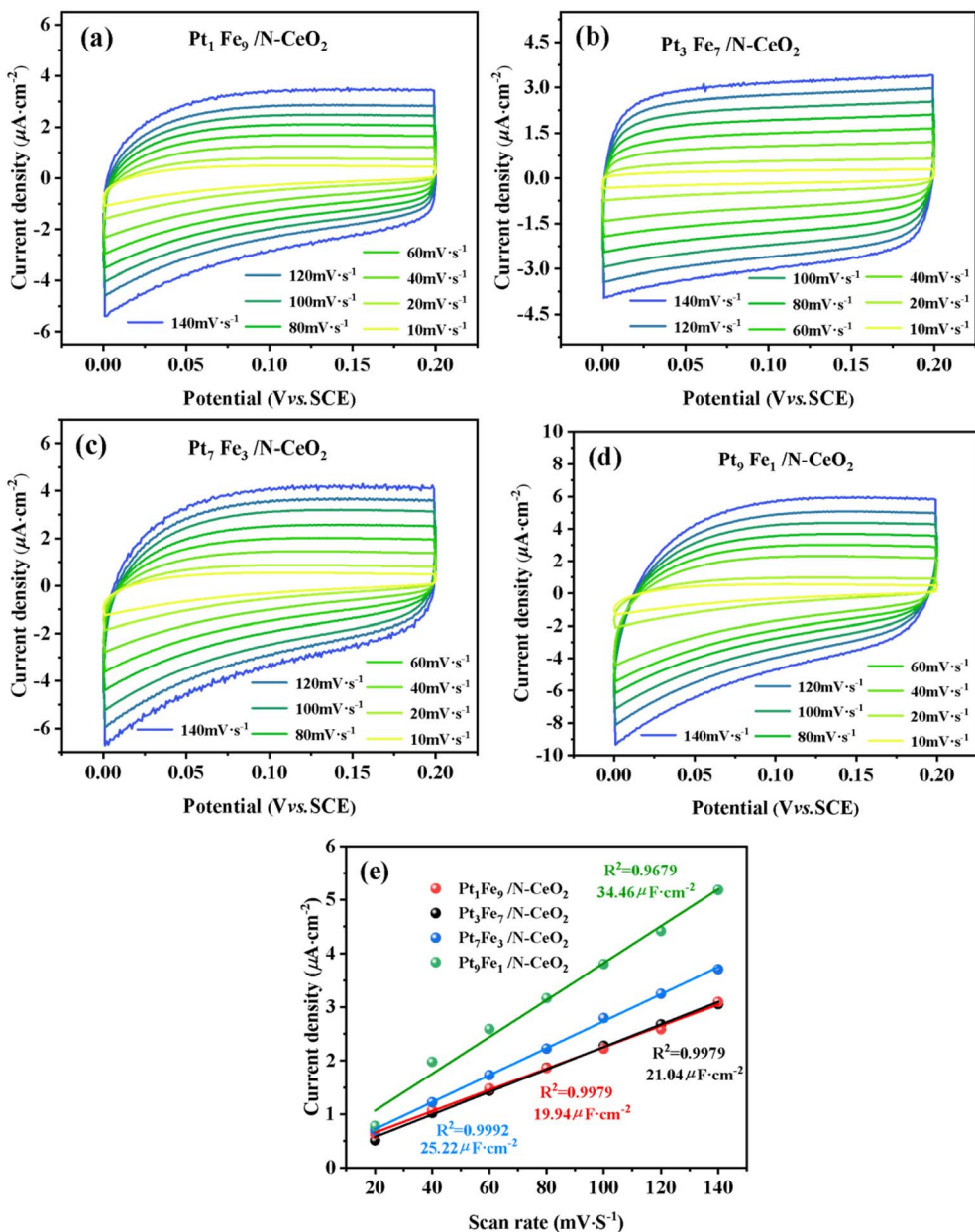


Fig. 11 (a–d) CV curves at different scan rates of Pt_xFe_{10-x}/N-CeO₂ and (e) linear relation between their current density and scan rate.

CeO₂ (19.94 μF cm⁻²), indicating a larger electrochemically active surface area and more exposed active sites. The C_{dl} values of Pt₇Fe₃/N-CeO₂ and Pt₃Fe₇/N-CeO₂ are 25.22 and 21.04 μF cm⁻², respectively. As Pt loading decreases, the C_{dl} value gradually declines, which can be attributed to the reduced number of highly active Pt sites.

To characterize the chemical states of the elements in the samples, X-ray photoelectron spectroscopy (XPS) was performed on Pt₃Fe₇/N-CeO₂, Pt₉Fe₁/N-CeO₂, Pt₇Fe₃/N-CeO₂, and Pt₃Fe₇/N-CeO₂. Fig. 12a presents the full survey spectra of four samples, showing the characteristic peaks for Ce 3d, Fe 2p, O 1s, N 1s, and C 1s at their corresponding binding energies. Peaks corresponding to Pt and Fe were not clearly observed in the survey spectra, which can be attributed to the low loading levels of

these metals. Fig. 12b presents the Pt 4f spectra of Pt₅Fe₅/N-CeO₂, Pt₉Fe₁/N-CeO₂, Pt₇Fe₃/N-CeO₂, and Pt₃Fe₇/N-CeO₂. Metallic Pt serves as the active site for methanol steam reforming, with characteristic binding energies located at approximately 70.6 eV (Pt 4f_{7/2}) and 73.8 eV (Pt 4f_{5/2}). As Pt is progressively substituted by Fe, the binding energy of Pt shifts to lower values, indicating a modification of its electronic environment due to metal–metal interactions. Fig. 12c shows the O 1s spectra of the samples. The peaks located at 528.8 eV, 530.9 eV, and 532.4 eV are assigned to lattice oxygen, surface-adsorbed oxygen, and hydroxyl groups or adsorbed water species, respectively.²⁸ With increasing Fe loading, the O 1s peaks shift toward higher binding energies, with the most pronounced shift observed for Pt₅Fe₅/N-CeO₂. The shift plays



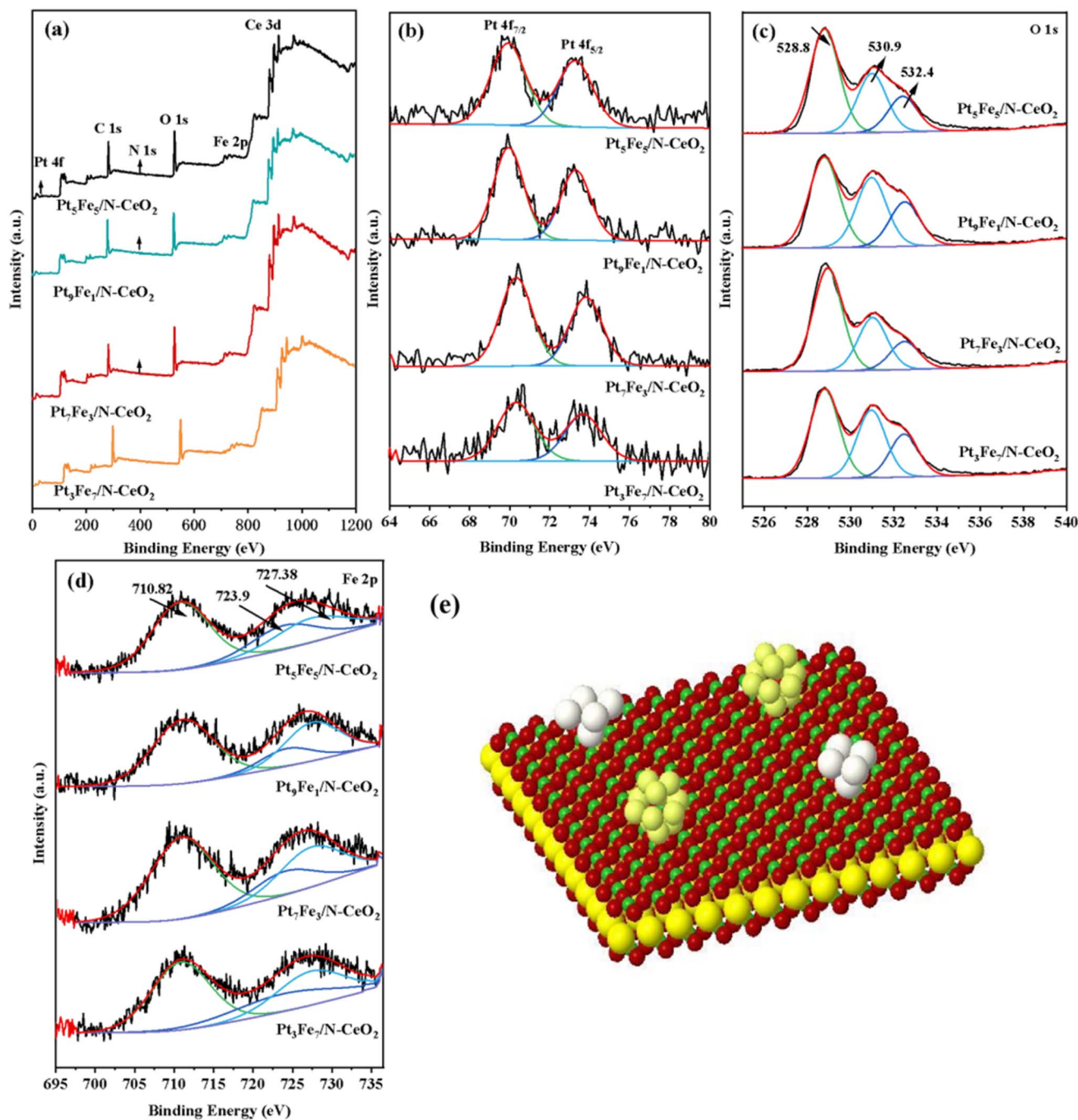


Fig. 12 XPS spectra of $\text{Pt}_x\text{Fe}_{10-x}/\text{N-CeO}_2$: (a) survey spectrum and (b) Pt 4f, (c) O 1s, and (d) Fe 2p spectra. (e) Metal atom-loaded doping structure.

a crucial role in facilitating the migration and activation of lattice oxygen species.²⁹ Meanwhile, the activation and mobility of lattice oxygen are closely associated with oxygen vacancies on the catalyst surface.^{30,31} The enhanced intensity of the lattice oxygen peak suggests a decrease in electron cloud density, indicating stronger metal-support interactions. Fig. 12d displays the Fe 2p spectra of the samples. Three main peaks at 710.8 eV, 723.9 eV, and 727.38 eV are observed in the Fe 2p spectra, corresponding to Fe^{3+} and Fe^{2+} species in the Fe

$2p_{3/2}$ and $\text{Fe} 2p_{1/2}$ orbitals.³² Slight shifts in the peaks at 710.8 eV and 723.9 eV for $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ indicate that the Pt/Fe molar ratio influences the strength of the chemical bonding and electronic interaction between the metal species. Fig. 12e illustrates the three-dimensional crystal structure of $\text{Pt}_x\text{Fe}_{10-x}/\text{N-CeO}_2$. In the model, green represents N dopants on the CeO_2 support, dark yellow corresponds to Ce atoms, red denotes O atoms, while the metallic sites are shown in silver-white for Fe and pale yellow for Pt.



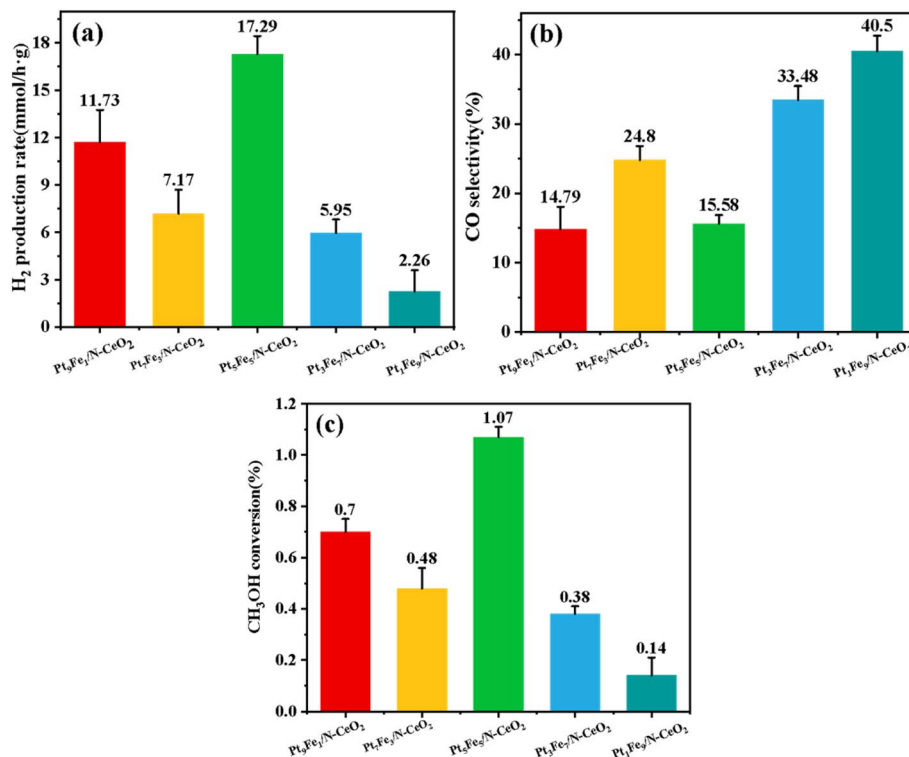


Fig. 13 (a) H_2 production rate, (b) CO selectivity, and (c) methanol conversion rate of various catalysts.

3.4 Analysis of the methanol steam reforming reaction on $\text{Pt}_x\text{Fe}_{10-x}/\text{N-CeO}_2$

The catalytic performance of $\text{Pt}_x\text{Fe}_{10-x}/\text{N-CeO}_2$ samples with varying Pt-to-Fe molar ratios ($\text{Pt}_1\text{Fe}_9/\text{N-CeO}_2$, $\text{Pt}_3\text{Fe}_7/\text{N-CeO}_2$, $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$, $\text{Pt}_7\text{Fe}_3/\text{N-CeO}_2$, and $\text{Pt}_9\text{Fe}_1/\text{N-CeO}_2$) in the MSR reaction was systematically investigated. As shown in Fig. 13a–c, the H_2 production rate, CO selectivity, and methanol conversion were evaluated. Fig. 13a indicates that the $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ sample exhibited the highest H_2 production rate among the catalysts. The optimal performance is attributed to the balanced ratio of Fe-Pt-Ce structures, which synergistically enhanced catalytic activity. The H_2 production rate of $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ is 1.47, 2.41, 3.01 and 7.65 times higher than that of $\text{Pt}_9\text{Fe}_1/\text{N-CeO}_2$ ($11.73 \text{ mmol } g_{\text{cat}}^{-1} \cdot \text{h}^{-1}$), $\text{Pt}_7\text{Fe}_3/\text{N-CeO}_2$ ($7.17 \text{ mmol } g_{\text{cat}}^{-1} \cdot \text{h}^{-1}$), $\text{Pt}_3\text{Fe}_7/\text{N-CeO}_2$ ($5.95 \text{ mmol } g_{\text{cat}}^{-1} \cdot \text{h}^{-1}$), and $\text{Pt}_1\text{Fe}_9/\text{N-CeO}_2$ ($2.26 \text{ mmol } g_{\text{cat}}^{-1} \cdot \text{h}^{-1}$), respectively. These results highlight the critical role of tuning the Pt–Fe molar

ratio in improving MSR performance, aligning with recent advancements in the design of bifunctional catalysts for selective hydrogen production. Fig. 13b presents the CO selectivity of catalysts in methanol steam reforming reactions. The CO selectivity of $\text{Pt}_9\text{Fe}_1/\text{N-CeO}_2$, $\text{Pt}_7\text{Fe}_3/\text{N-CeO}_2$, $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ and $\text{Pt}_1\text{Fe}_9/\text{N-CeO}_2$ is 14.79%, 24.8%, 33.48%, and 40.5%, respectively. Notably, the Pt:Fe molar ratio of 5:5 demonstrated the lowest CO selectivity in MSR, indicating that Fe optimally suppresses byproduct formation through bimetallic synergistic regulation. Fig. 13c displays methanol conversion of the samples, where a molar ratio of 5:5 exhibited the highest conversion efficiency, consistent with the H_2 production rate trends. Experimental results suggest that the Pt–Fe (5:5) bimetallic system achieves optimal metal–support interactions, facilitating accelerated C–H bond cleavage in methanol and water molecules with the lowest energy barrier (minimum energy level required for activation). The configuration exhibits the highest methanol reforming

Table 2 Comparison of the reaction conditions and catalytic performance of different catalysts for methanol steam reforming

Catalyst	Temperature ($^{\circ}\text{C}$)	WHSV (h^{-1})	S/C	X (CH_3OH) (%)	Y(H_2) $\text{mmol} \cdot \text{h}^{-1} \cdot g_{\text{cat}}^{-1}$	Ref.
Cu/CeO_2	250	—	1	66.3	490	33
$\text{PdCu}/\text{CeO}_2\text{-Al}_2\text{O}_3$	250	4	1.5	50	—	34
$\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$	200	6	1.3	—	95.5	35
CuO/ZnO	300	30	1.3	98.3	—	36
CuCo_2O_4	320	4.32	1.2	100	0.24	37
$\text{CuO-ZnO-Al}_2\text{O}_3/\text{CeO}_2$	280	6.05	1.2	100	0.672	38
$\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$	180	24	1.2	1.08	18.8	This work



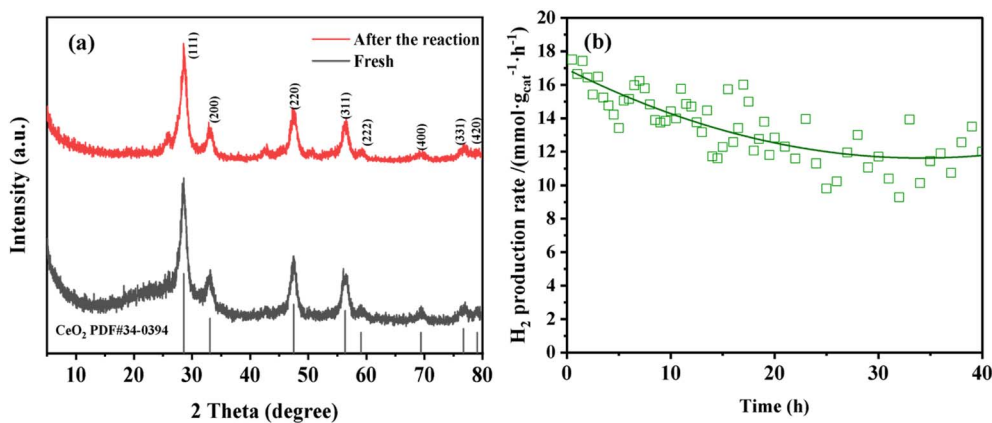


Fig. 14 (a) XRD patterns of the $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ sample after 40 h of methanol steam reforming reaction. (b) Stability evaluation of the $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ sample in the MSR reaction.

Table 3 Hydrogen production rates of $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$ ($M = \text{Fe, Ni, Zn, Mg, Al, and Cu}$) at different temperatures

T ($^{\circ}\text{C}$)	$\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$	$\text{Pt}_5\text{Ni}_5/\text{N-CeO}_2$	$\text{Pt}_5\text{Zn}_5/\text{N-CeO}_2$	$\text{Pt}_5\text{Mg}_5/\text{N-CeO}_2$	$\text{Pt}_5\text{Al}_5/\text{N-CeO}_2$	$\text{Pt}_5\text{Cu}_5/\text{N-CeO}_2$
170	16.5	10.87	5.22	3.56	0.01	1.03
180	17.29	14.60	10.13	5.74	0.73	1.74
190	25.88	18.74	11.64	10.34	7.88	6.44
200	37.58	35.86	20.89	13.45	10.76	11.67
210	56.42	48.59	35.92	17.94	15.45	14.84

performance due to favorable interfacial electronic effects and reduced energy barriers. Furthermore, a comparison of catalysts reported for hydrogen production *via* methanol steam reforming is presented in Table 2.

Fig. 14a and b present the stability evaluation results of the $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ catalyst after 40 h of operation in the methanol steam reforming reaction. The results indicate that the $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ catalyst maintains good stability after 40 h of continuous reaction. The H_2 production rate decreases from an initial value of approximately $17 \text{ mmol g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ to about $12 \text{ mmol g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, suggesting that the catalyst exhibits favorable structural integrity and catalytic stability during the long-term operation.

3.5 Analysis of the methanol steam reforming (MSR) reaction kinetics over $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$ -based catalysts

Based on the hydrogen production rates of $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$ at different temperatures Tables 3 and 4, the reaction energy barriers of bimetallic Pt-M ($M = \text{Fe, Ni, Zn, Mg, Al, Cu}$) sites in methanol steam reforming (MSR) were systematically investigated. Fig. 15a displays the Arrhenius plots for $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Ni}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Zn}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Mg}_5/\text{N-CeO}_2$, $\text{Pt}_5\text{Al}_5/\text{N-CeO}_2$, and $\text{Pt}_5\text{Cu}_5/\text{N-CeO}_2$. The calculated activation energies reveal that $\text{Pt}_5\text{Al}_5/\text{N-CeO}_2$ exhibits the highest activation energy ($312.82 \text{ kJ mol}^{-1}$), which is 5.5 times higher than that of $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ ($57.19 \text{ kJ mol}^{-1}$) and significantly exceeds those of $\text{Pt}_5\text{Ni}_5/\text{N-CeO}_2$ ($69.05 \text{ kJ mol}^{-1}$), $\text{Pt}_5\text{Zn}_5/\text{N-CeO}_2$

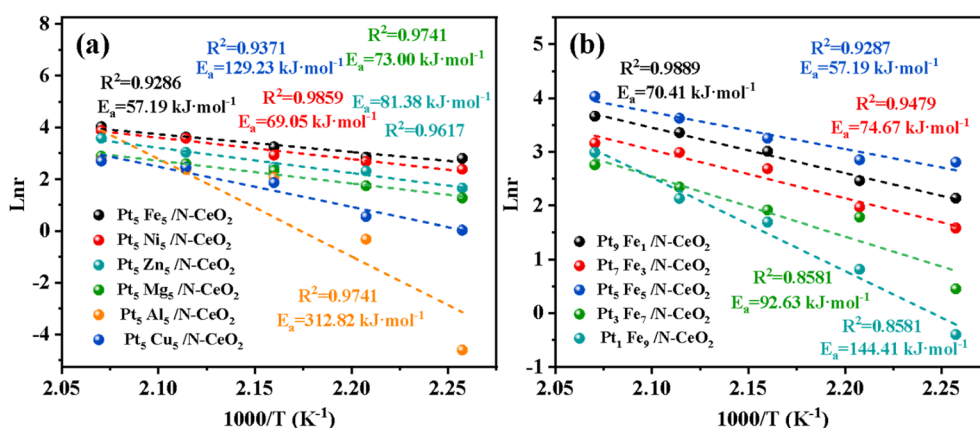


Fig. 15 (a and b) Reaction rate and temperature curves of $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$.



Table 4 Hydrogen production rates of $\text{Pt}_x\text{Fe}_{10-x}/\text{N-CeO}_2$ at different temperatures

T (°C)	$\text{Pt}_9\text{Fe}_1/\text{N-CeO}_2$	$\text{Pt}_7\text{Fe}_3/\text{N-CeO}_2$	$\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$	$\text{Pt}_3\text{Fe}_7/\text{N-CeO}_2$	$\text{Pt}_1\text{Fe}_9/\text{N-CeO}_2$
170	8.45	4.87	16.5	1.57	0.67
180	11.73	7.17	17.29	5.95	2.26
190	20.32	14.65	25.88	6.79	5.43
200	28.76	19.87	37.58	10.42	8.42
210	38.99	23.67	56.42	15.78	15.45

Table 5 Comparison of the kinetic data of samples

Samples	E_a (kJ mol ⁻¹)	A
$\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$	57.19	18.183
$\text{Pt}_5\text{Ni}_5/\text{N-CeO}_2$	69.05	21.078
$\text{Pt}_5\text{Zn}_5/\text{N-CeO}_2$	66.26	23.771
$\text{Pt}_5\text{Mg}_5/\text{N-CeO}_2$	74.74	21.152
$\text{Pt}_5\text{Al}_5/\text{N-CeO}_2$	312.82	81.795
$\text{Pt}_5\text{Cu}_5/\text{N-CeO}_2$	129.23	35.123
$\text{Pt}_9\text{Fe}_1/\text{N-CeO}_2$	70.41	21.236
$\text{Pt}_7\text{Fe}_3/\text{N-CeO}_2$	74.67	21.895
$\text{Pt}_3\text{Fe}_7/\text{N-CeO}_2$	92.63	25.939
$\text{Pt}_1\text{Fe}_9/\text{N-CeO}_2$	144.41	39.000

(129.23 kJ mol⁻¹), $\text{Pt}_5\text{Mg}_5/\text{N-CeO}_2$ (73.00 kJ mol⁻¹), and $\text{Pt}_5\text{Cu}_5/\text{N-CeO}_2$ (129.23 kJ mol⁻¹), indicating that Fe substitution for Pt provides the lowest energy barrier for MSR and minimizes energy consumption.

As shown in Table 5, $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ also exhibits the lowest pre-exponential factor, suggesting that under these conditions, the sample achieves the optimal collision frequency during the reaction. Consistent with Raman and BET analyses, the observed differences in the apparent activation energy are related to the concentration of surface oxygen species. The presence of oxygen vacancies creates unsaturated active sites, which serve as catalytic centers controlling the reaction rate and reducing the energy barrier. Moreover, C–H bond cleavage is a key rate-determining step in MSR. Experimental results show that, compared with other non-precious metals, Fe loading promotes C–H bond cleavage, which accounts for the superior catalytic activity of the sample.

Based on hydrogen evolution experiments at different temperatures, the reaction energy barriers of Pt–Fe bimetallic catalysts with varying molar ratios in methanol steam reforming (MSR) were systematically investigated. Fig. 15b shows the Arrhenius plots for $\text{Pt}_1\text{Fe}_9/\text{N-CeO}_2$, $\text{Pt}_9\text{Fe}_1/\text{N-CeO}_2$, $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$, $\text{Pt}_7\text{Fe}_3/\text{N-CeO}_2$, and $\text{Pt}_3\text{Fe}_7/\text{N-CeO}_2$. Calculations revealed that $\text{Pt}_5\text{Fe}_5/\text{N-CeO}_2$ exhibits the lowest activation energy (57.19 kJ mol⁻¹), significantly lower than $\text{Pt}_9\text{Fe}_1/\text{N-CeO}_2$ (70.41 kJ mol⁻¹), $\text{Pt}_1\text{Fe}_9/\text{N-CeO}_2$ (144.41 kJ mol⁻¹), $\text{Pt}_7\text{Fe}_3/\text{N-CeO}_2$ (74.67 kJ mol⁻¹), and $\text{Pt}_3\text{Fe}_7/\text{N-CeO}_2$ (92.63 kJ mol⁻¹). Table 5 demonstrates that increasing the Fe loading enhances the pre-exponential factor, indicating that Fe promotes the reactant-catalyst collision frequency and more Fe sites enhance the collision frequency between the catalyst and reactant molecules. Furthermore, the Pt-to-Fe molar ratio affects the number of active catalytic sites on the surface. When the Pt/Fe molar ratio is 5 : 5, the sample exhibits the lowest energy level

for electron transfer and the minimum energy barrier, achieving the most efficient catalytic performance.

3.6 Mechanism study of the methanol steam reforming reaction on $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$ -based catalysts

Based on the above experimental results, the possible reaction pathways for methanol–water reforming on $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$ are proposed: (i) CH_3OH spontaneously decomposes into CO and H_2 .

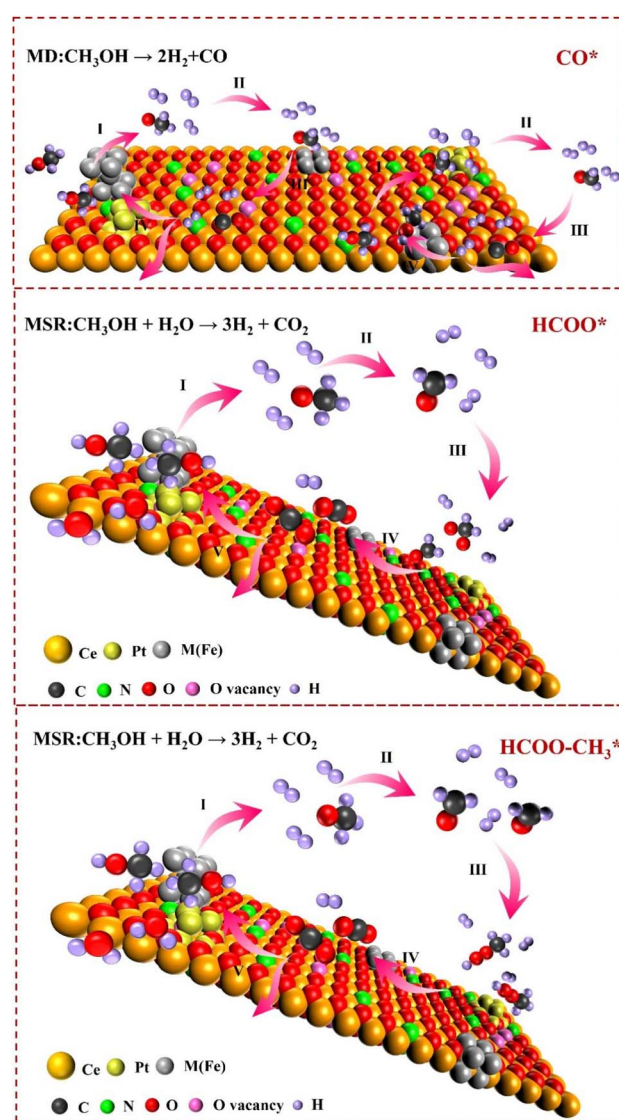


Fig. 16 Mechanism of the methanol steam reforming reaction over $\text{Pt}_x\text{M}_{10-x}/\text{N-CeO}_2$.



Part of the produced CO reacts with water vapor to form CO₂ and H₂, while the remaining CO remains in the reaction vessel and waits to react with the remaining water vapor or is discharged from the vessel (denoted as the CO* pathway); (ii) CH₃OH is further oxidized by the active oxygen generated by hydroxyl groups or H₂O to form HCOO*, and the intermediate product HCOO* decomposes to produce CO₂ and H₂ (denoted as the HCOO* pathway);³⁹ and (iii) CH₃OH undergoes dehydrogenation to form HCOO-CH₃, which then hydrolyzes to form HCOO*, and subsequently decomposes to produce CO₂ and H₂ (denoted as the HCOO-CH₃* pathway).^{40,41} Due to the low surface density of Pt and M atoms, gaseous methanol molecules first react with lattice oxygen or surface hydroxyl groups of the N-CeO₂ support to form top and bridging methoxy species. The N-CeO₂ support itself exhibits negligible methanol decomposition activity, and the methoxy species must diffuse to the Pt and M sites for further reaction. Among these, the top methoxy species is more reactive than the bridging methoxy species. Considering that these pathways occur almost simultaneously, a sequential MSR reaction mechanism over Pt_xM_{10-x}/N-CeO₂ is proposed (Fig. 16). Methanol dehydrogenation occurs at the Pt metal sites, releasing hydrogen and generating CO intermediates. The adjacent oxygen vacancies facilitate the dissociation and adsorption of gaseous methanol. The introduction of M atoms provides additional metal active sites and promotes the formation of oxygen vacancies near the cations, enhancing the reaction of hydroxyl species adsorbed on these vacancies with nearby methanol molecules, thereby minimizing the diffusion limitation of intermediates. Among the possible methanol-water reforming pathways, the CO* pathway is a key factor contributing to catalyst deactivation. Based on the evaluation of catalytic activity with varying bimetallic loadings and atomic ratios, partially substituting Pt sites with Fe appears beneficial for suppressing CO formation. This strategy increases the number of exposed active sites and enhances the overall catalytic activity in methanol steam reforming.

4 Conclusion

In this study, a bimetallic cerium-based catalyst (Pt_xM_{10-x}/N-CeO₂) was prepared using the high-temperature calcination method. Based on the performance evaluation of MSR, the optimal bimetallic catalyst was found to be Pt₅Fe₅/N-CeO₂. Subsequently, the influence of the Pt-to-Fe atomic ratio on MSR performance was investigated. The results indicate that loading different bimetallics can increase the specific surface area, surface defects, and reactive active sites of CeO₂. XPS testing revealed that the loading of Pt and Fe on the N-CeO₂ support promotes the migration of lattice oxygen species. The results of the methanol steam reforming experiments show that Pt₅Fe₅/N-CeO₂ exhibits the highest H₂ production rate and the lowest CO selectivity, with a H₂ production rate of 17.29 mmol g_{cat}⁻¹·h⁻¹, CO selectivity of 15.58%, and methanol conversion rate of 1.07%, demonstrating the best catalytic performance. Compared with Pt_xFe_{10-x}/N-CeO₂, the H₂ production rate of Pt₅Fe₅/N-CeO₂ increases, indicating that the difference in activity evaluation is not significant and the cost is reduced while maintaining the catalytic performance. According to the Arrhenius equation, Pt₅Fe₅/N-CeO₂ has the

lowest apparent activation energy, suggesting that the sample requires the lowest energy to overcome in the MSR reaction and the reaction occurs to the greatest extent.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

All data included in this study are available upon request to the corresponding author.

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