

Effect of UiO-66 precursors with different Ce/Zr ratios on the performance of Pt-based catalysts in dry methane reforming reactions

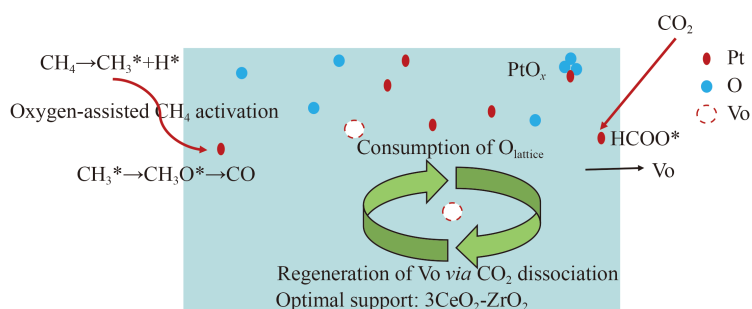
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Abstract: To address challenges of sintering and carbon deposition in the dry reforming of methane (DRM), this study employs UiO-66 as a precursor for modifying Pt-based catalysts. A series of Pt/CeO₂-ZrO₂ catalysts were synthesized *via* incipient wetness impregnation using supports with varying Ce/Zr ratios prepared through a hydrothermal method. Comprehensive characterization—

including CO₂-TPD, CH₄-TPD, XPS, XAFS, *in situ* DRIFTS, TG and Raman spectroscopy—revealed a volcano type correlation between DRM performance and the Ce/Zr ratio. Optimal catalytic activity and stability were achieved with the Pt/3CeO₂-ZrO₂ catalyst (Ce/Zr = 3:1). This catalyst features highly dispersed platinum, primarily existing as single atoms and thermally stable PtO_x clusters. Furthermore, it exhibits the highest concentration of Ce³⁺ and Zr³⁺ species, abundant oxygen vacancies (Vo), and a high defect density, all of which are indicative of a strong metal-support interaction. Mechanistically, the continuous and stable DRM reaction is facilitated by oxygen-assisted CH₄ dissociation and hydrogen-assisted CO₂ dissociation. At 800 °C, this catalyst exhibited outstanding performance, with CH₄ and CO₂ conversion rates reaching 86% and 93%, respectively. Notably, a 10 h stability test revealed no detectable carbon deposition. These results confirm that the catalyst significantly enhances reaction kinetics while demonstrating superior activity, stability, and resistance to both coking and sintering.

Key words: dry reforming of methane; platinum catalysts; UiO-66; CeO₂-ZrO₂



Global warming, driven by excessive greenhouse gas emissions, constitutes one of the most critical environmental challenges of our time. Carbon dioxide (CO₂) and methane (CH₄) serve as the primary contributors, accounting for approximately 71.6% and 21% of total emissions, respectively^[1–2]. As climate impacts intensify, there is an urgent imperative to shift toward need to transition towards sustainable energy frameworks by converting these greenhouse gases into high-value fuels and chemicals^[3–4]. Dry reforming of methane (DRM) represents a promising strategy for carbon recycling, as it simultaneously converts CH₄ and CO₂ into economically

valuable syngas with a unity H₂/CO ratio. Consequently, DRM has attracted considerable attention for its potential applications in sustainable energy and chemical synthesis^[5–7].

However, the highly endothermic nature of DRM requires elevated operating temperatures (typically exceeding 700 °C) to drive the reaction^[8–9]. Under these harsh conditions, catalysts are prone to rapid deactivation *via* carbon deposition (coking) and sintering, presenting a major bottleneck for industrial implementation^[10–11]. While non-noble metal catalysts, particularly nickel-based systems, exhibit reasonable considerable initial activity,

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they suffer from severe instability due to coking and sintering at high temperatures^[12–14]. In contrast, noble metals such as platinum (Pt) offer superior activity, stability and selectivity, attributed to their unique electronic structures and adsorption properties^[15–17]. Although the application of Pt is constrained by its high cost and limited abundance, cost-effective Pt-based catalysts can be engineered by maximizing atomic utilization, stabilizing active sites, enhancing metal-support interactions (MSI), and effectively suppressing carbon deposition. Notably, Jones et al.^[18] demonstrated that Pt atoms can be trapped by CeO₂, yielding a Pt/CeO₂ catalyst stable up to 800 °C during CO oxidation. This finding provides a critical foundation for designing Pt/CeO₂ catalysts capable of withstanding the rigorous thermal demands of DRM.

Metal-organic frameworks (MOFs), a class of emerging crystalline porous materials, have attracted widespread attention for DRM applications due to their abundant active sites, high specific surface areas, and tunable pore architectures^[19–21]. Among these, the UiO-66 series is particularly notable for its exceptional thermal and chemical stability, as well as its robust framework, which facilitates efficient gas adsorption and dissociation^[22–25]. For instance, Shao et al.^[26] utilized Zr-UiO-66 as a precursor to synthesize Ni@ZrO₂ catalysts *via* a controlled preparation strategy. Their Ni/ZrO₂-B variant exhibited superior DRM performance, which was attributed to the high dispersion of Ni species and strong metal-support interactions (SMSI). Concurrently, Ceria (CeO₂), an abundant and cost-effective rare-earth material with a cubic fluorite structure, is widely used in catalysis. Its rich surface oxygen vacancies play a critical role in promoting CO₂ activation^[27–29]. Leveraging MOF chemistry, Lammert et al.^[30] successfully synthesized Ce-based UiO-66 with an octahedral cage structure *via* a solvothermal method, achieving excellent thermal and chemical stability. However, pure CeO₂ is prone to sintering under high-temperature or reducing conditions, leading to surface area loss and catalytic deactivation^[31]. To address this, zirconium (Zr) doping has been proven effective due to the high compatibility between Ce and Zr^[32]. Zhou et al.^[33] demonstrated that substituting Ce⁴⁺ (0.092 nm) with the smaller Zr⁴⁺ ion (0.084 nm) creates a CeO₂-ZrO₂ solid solution, significantly enhancing thermal stability, redox properties, and oxygen storage capacity. Damyanova et al.^[34] further showed that pretreatment temperature and CeO₂ concentration significantly influence strongly affect Pt morphology. While their Pt/6CeO₂-ZrO₂ catalyst exhibited high Pt dispersion and favorable reducibility, it required a prolonged induction period to stabilize activity, indicating considerable potential for further performance optimization. Consequently, this study utilizes UiO-66 as a precursor to engineer Pt-based catalysts. A series of Pt/CeO₂-ZrO₂ catalysts were synthesized *via* impregnation, utilizing supports with varying Ce/Zr ratios prepared through a hydrothermal method. By systematically modulating the Ce/Zr ratio, this

work aims to enhance thermal stability, harness the redox properties of the support, and optimize defect concentrations. Ultimately, these findings provide valuable experimental insights for the rational design and optimization of Pt-based catalysts for DRM applications.

1 Experimental

1.1 Materials

Ammonium cerium nitrate (Ce(NH₄)₂(NO₃)₆), zirconium chloride (ZrCl₄) and 2-aminoterephthalic acid were purchased from Aladdin. All reagents were of analytical grade. *N,N*-dimethylformamide (DMF, analytical grade) was obtained from Sinopharm Chemical Reagent Co., Ltd., while chloroplatinic acid solution (H₂PtCl₆, 8%) was procured from Alfa Aesar.

1.2 Catalyst preparation

1.2.1 Preparation of supports

CeO₂ and ZrO₂ supports were prepared *via* the thermal decomposition of hydrothermally synthesized Ce- and Zr-based UiO-66 precursors. Specifically, 2-aminoterephthalic acid (0.688 g) was dissolved in *N,N*-dimethylformamide (DMF, 180 mL) under magnetic stirring, followed by the addition of 60 mL of a 0.5 mol/L metal salt solution (either Ce(NH₄)₂(NO₃)₆ or ZrCl₄). The mixture was stirred at 500 r/min for 30 min at room temperature, transferred to a Teflon-lined autoclave, and heated at 180 °C for 6 h. The resulting precipitates were collected by vacuum filtration, washed and dried at 80 °C for 12 h. To obtain the final supports, the dried powders were calcined in air at 350 °C for 2 h (ramp heating rate: 2 °C/min). Mixed-oxide supports were prepared using the same procedure, substituting the single-metal solution with 60 mL of a mixed Ce(NH₄)₂(NO₃)₆ and ZrCl₄ solution (total concentration: 0.5 mol/L) with Ce/Zr ratios of 6:1, 3:1, 2:1, 1:1 and 0.5:1.

1.2.2 Preparation of catalyst

Catalysts with a nominal Pt loading of 0.8% were prepared *via* wet impregnation. Specifically, an aqueous H₂PtCl₆ solution (8%) was deposited onto the supports with varying Ce/Zr ratios using rotary evaporation. The resulting samples were dried at 80 °C for 12 h and subsequently calcined in a muffle furnace at 800 °C for 10 h (ramp rate: 2 °C/min). The final catalysts were designated as follows: Pt/6CeO₂-ZrO₂ (denoted as Pt/6Ce-Zr), Pt/3CeO₂-ZrO₂ (Pt/3Ce-Zr), Pt/2CeO₂-ZrO₂ (Pt/2Ce-Zr), Pt/CeO₂-ZrO₂ (Pt/Ce-Zr), Pt/CeO₂-0.5ZrO₂ (Pt/Ce-0.5Zr), Pt/CeO₂ and Pt/ZrO₂.

1.3 Catalytic performance evaluation

1.3.1 Catalytic activity tests

Catalytic activity tests were conducted in a stainless-steel fixed-bed reactor (12 mm inner diameter). The effluent gas composition was analyzed online using an Agilent 3000 Micro-GC. Reactions were performed at atmospheric pressure using 0.1 g of catalyst diluted with 1.0 g of inert SiC to mitigate thermal gradients. The feed gas consisted of a mixture of CH₄, CO₂ and N₂ (1:1:1 molar ratio) introduced at a gas hourly space velocity (GHSV) of 36 L/(g·h). Activity data were collected over a temperature range of 600–800 °C. The conversions of CH₄ and CO₂, as well as the H₂/CO ratio, were calculated according to the following equations^[35]:

$$x_{\text{CH}_4} = \frac{(F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}})}{F_{\text{CH}_4,\text{in}}} \times 100\% \quad (1)$$

$$x_{\text{CO}_2} = \frac{(F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}})}{F_{\text{CO}_2,\text{in}}} \times 100\% \quad (2)$$

$$\frac{\text{H}_2}{\text{CO}} = \frac{F_{\text{H}_2,\text{out}}}{F_{\text{CO},\text{out}}} \quad (3)$$

where x_{CH_4} and x_{CO_2} denote the conversions of CH₄ and CO₂, respectively, and F represents the reactant flow rate (L/h).

1.3.2 Catalyst stability tests

Stability tests were conducted using the same 12 mm (i.d.) stainless steel fixed-bed reactor described previously. The evaluation was performed at 800 °C for 10 h. Conditions remained identical to the activity tests, with the exception that the catalyst bed was undiluted (no SiC). Reactant conversions (CH₄, CO₂) and the H₂/CO ratio were calculated using the methods defined above.

1.4 Catalyst characterization

1.4.1 Temperature-programmed desorption (TPD)

The chemisorption behavior of CH₄ and CO₂ were investigated on an AMI-300 chemisorption analyzer (Zeton Altamira, USA). Prior to testing, 50.0 mg of the catalyst was loaded into a U-shaped quartz tube. The sample was pretreated in a helium flow (30 mL/min) at 150 °C for 1 h to remove impurities, then cooled to 50 °C in the same flow. The flow was then switched to the probe gas (CH₄ or CO₂, 30 mL/min) for a 1 h adsorption period. Subsequently, the system was purged with helium (30 mL/min) to remove physisorbed species until a stable baseline was obtained. Finally, desorption profiles were recorded by ramping the temperature to 750 °C at a rate of 10 °C/min.

1.4.2 X-ray absorption fine structure (XAFS)

The local coordination environment of Pt was investigated using X-ray absorption fine structure (XAFS) spectroscopy. Measurements were conducted at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), with the storage ring operating at an electron energy of 3.5 GeV. The incident beam was monochromatized using a Si(311) double-crystal monochromator. Data were collected using an argon-filled Lytle detector. The beam spot size was defined by horizontal and vertical slits to be approximately 1 mm×4 mm.

1.4.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Multilab 2000 spectrometer equipped with a monochromatic Al K α radiation ($h\nu=1486.6$ eV). Binding energies were calibrated using the adventitious C 1s peak at 284.8 eV to compensate for surface charging effects.

1.4.4 Raman spectroscopy

Raman spectroscopy was employed to characterize the carbon species on the spent catalysts using a Thermo Scientific DXR2 XI confocal Raman spectrometer. Spectra were collected at room temperature using a 532 nm Ar⁺ laser for excitation. Measurements were performed using a 50× objective lens with an exposure time of 30 s. The spectra were recorded over a range of 80–4000 cm^{−1} with a spectral resolution of 2 cm^{−1}.

1.4.5 *In situ* diffuse reflectance fourier transform Infrared spectroscopy (*In situ* DRIFTS)

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted using a Thermo Scientific Nicolet iS50 spectrometer. All spectra were acquired by accumulating 64 scans at a resolution of 4 cm^{−1}.

For single-component adsorption experiments (CH₄ or CO₂), the sample was first pretreated at 250 °C for 1 h under an Ar flow (30 mL/min) with a heating rate of 5 °C/min to remove surface impurities. After cooling to room temperature (25 °C), a background spectrum was collected under the Ar atmosphere. The feed gas was then switched to a mixture of the adsorbate (CH₄ or CO₂) and Ar (5:30 mL/min), and the temperature was increased to the target reaction temperature of 350 °C at a rate of 2 °C/min for data acquisition.

To investigate surface species during the isothermal DRM reaction, *in situ* DRIFTS measurements were performed. Prior to the reaction, the catalyst was pretreated at 250 °C for 1 h under an Ar flow (30 mL/min) with a

heating rate of 5 °C/min. Subsequently, the temperature was increased to 350 °C at a rate of 5 °C/min under the same Ar flow, followed by a 30 min stabilization period to ensure thermal equilibrium. After collecting a background spectrum, the feed gas was switched to a reactant mixture of CH₄, CO₂ and Ar (5:5:30 mL/min) to initiate the DRM reaction, which was monitored for 1 h.

1.4.6 Thermogravimetric analysis (TGA)

The carbon content of the spent catalysts was determined using a simultaneous thermal analyzer (TA Instruments Q600 SDT), which records both mass loss (TG) and heat flow (DSC) signals. Analysis was conducted in an air atmosphere. The samples were heated from 50 to 800 °C at a rate of 10 °C/min.

2 Results and discussion

2.1 Catalytic performance evaluation

2.1.1 Catalytic activity tests

Catalytic performance was evaluated in a fixed-bed reactor, with the results presented in Figure 1. As expected for the highly endothermic DRM reaction, catalytic activity increased with rising temperature. The observed H₂/CO ratio of below 1 is attributed to the concurrent reverse water-gas shift (RWGS) side reaction. The Pt/ZrO₂ catalyst exhibited the lowest activity. However, incorporating Ce progressively enhanced performance; Figure 1(c) illustrates this trend, showing a positive correlation between CH₄ conversion and the Ce/Zr ratio. Optimal performance was achieved at a Ce/Zr ratio of 3, which yielded the highest

CH₄ and CO₂ conversions and H₂/CO ratio. Further increasing the ratio to 6 resulted in a decline in activity. Specifically, the Pt/3CeO₂-ZrO₂ catalyst achieved CH₄ and CO₂ conversions of 86% and 93%, respectively, at 800 °C, with an H₂/CO ratio close to unity.

2.1.2 Catalyst stability tests

Stability tests for the Pt/3CeO₂-ZrO₂, Pt/CeO₂ and Pt/ZrO₂ catalysts were conducted at 800 °C for 10 h (Figure 2). For all three catalysts, the H₂/CO ratio remained below unity due to the concurrent reverse water-gas shift (RWGS) side reaction. Notably, the Pt/3CeO₂-ZrO₂ catalyst exhibited superior catalytic performance and stability. Under these conditions, it achieved initial CH₄ and CO₂ conversions of 57% and 70%, respectively, along with the highest H₂/CO ratio among the tested samples. Its exceptional stability was evidenced by the absence of significant deactivation over the 10 h run. The robustness and high activity of Pt/3CeO₂-ZrO₂ at 800 °C can be attributed to several factors. First, the active Pt species are well-dispersed. Second, synchrotron radiation analysis reveals that, unlike the single-atom structure in Pt/CeO₂, Pt in Pt/3CeO₂-ZrO₂ catalyst exists primarily as thermally stable PtO_x nanoclusters. Third, XPS and CO-DRIFTS characterizations confirm that this catalyst possesses the highest concentration of surface defects, facilitating the reaction. These combined features underpin its superior stability and activity. In contrast, both Pt/CeO₂ and Pt/ZrO₂ catalysts suffered from varying degrees of deactivation. This is attributed to the thermal instability of Pt single atoms in Pt/CeO₂, and to severe carbon deposition on Pt/ZrO₂, caused by the lack of CH_xO* intermediate formation and a lower oxygen vacancy concentration.

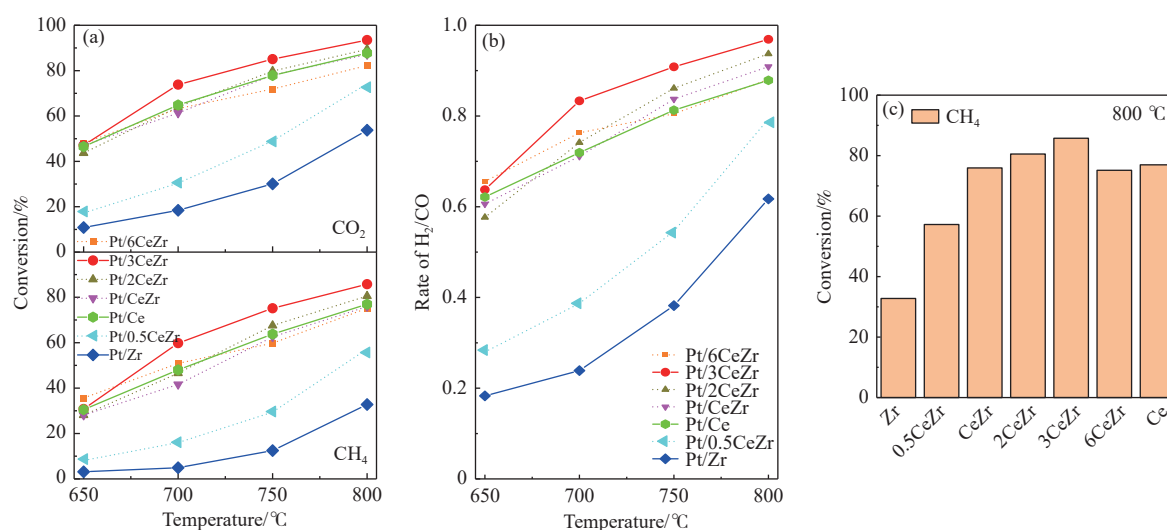


Fig. 1 Catalytic activity test: (a) conversion; (b) the rate of H₂/CO; (c) CH₄ conversion of catalyst at 800 °C
Reaction conditions: $t=650-800$ °C, $p=0.1$ MPa, CH₄:CO₂:N₂=1:1:1, GHSV=36 L/(g·h).

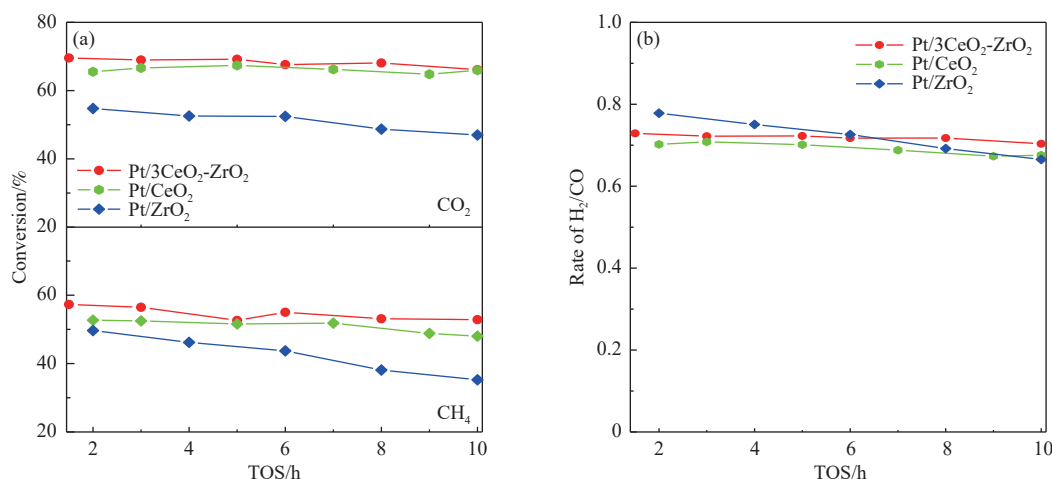


Fig. 2 Catalytic stability tests: (a) conversion; (b) the rate of H₂/CO
Reaction conditions: $t=800\text{ }^{\circ}\text{C}$, $p=0.1\text{ MPa}$, $\text{CH}_4:\text{CO}_2:\text{N}_2=1:1:1$, $\text{GHSV}=36\text{ L}/(\text{g}\cdot\text{h})$.

2.2 Catalyst characterization

2.2.1 Chemisorption analysis

The CO₂-TPD profiles are presented in Figure 3(a). Both Pt/3CeO₂-ZrO₂ and Pt/CeO₂ exhibited comparable desorption capacities, characterized primarily by weak adsorption peaks below 250 °C. The absence of significant medium-strength adsorption sites suggests these catalysts facilitate efficient CO₂ adsorption-desorption dynamics. In contrast, Pt/ZrO₂ displayed stronger CO₂ binding, with desorption peaks dominated by medium-strength sites above 250 °C. This indicates that the incorporation of CeO₂ effectively optimizes the CO₂ adsorption properties of the zirconia support. Figure 3(b) displays the CH₄-TPD profiles. The Pt/CeO₂ catalyst showed the highest CH₄ uptake, featuring weak adsorption sites (below 250 °C) and medium-strong adsorption sites (200–500 °C). Conversely, Pt/ZrO₂ exhibited the weakest CH₄ adsorption capacity, characterized by weak adsorption peak and a high-temperature desorption peak between 500 and 700 °C. The

Pt/3CeO₂-ZrO₂ catalyst demonstrated improved CH₄ adsorption capacity compared to Pt/ZrO₂, with a desorption profile similar to Pt/CeO₂ (weak adsorption below 250 °C and medium-strong adsorption at 200–500 °C). In summary, the TPD results confirm that Pt/3CeO₂-ZrO₂ and Pt/CeO₂ possess superior chemisorption properties for both reactants compared to Pt/ZrO₂, which is favorable for the DRM reaction.

2.2.2 Analysis of the coordination structure of active sites

Figure 4(a) displays the XANES spectra of the three catalysts alongside PtO₂ and Pt foil references. The near-edge absorption features of the catalysts closely resemble those of PtO₂, indicating that the Pt species exist primarily in an oxidized state. Figure 4(b) presents the Fourier-transformed EXAFS spectra. In the reference samples, the Pt–O coordination shell in PtO₂ appears at approximately 1.6 Å, while the metallic Pt–Pt bond in the Pt foil is centered between 2.5 and 2.7 Å.

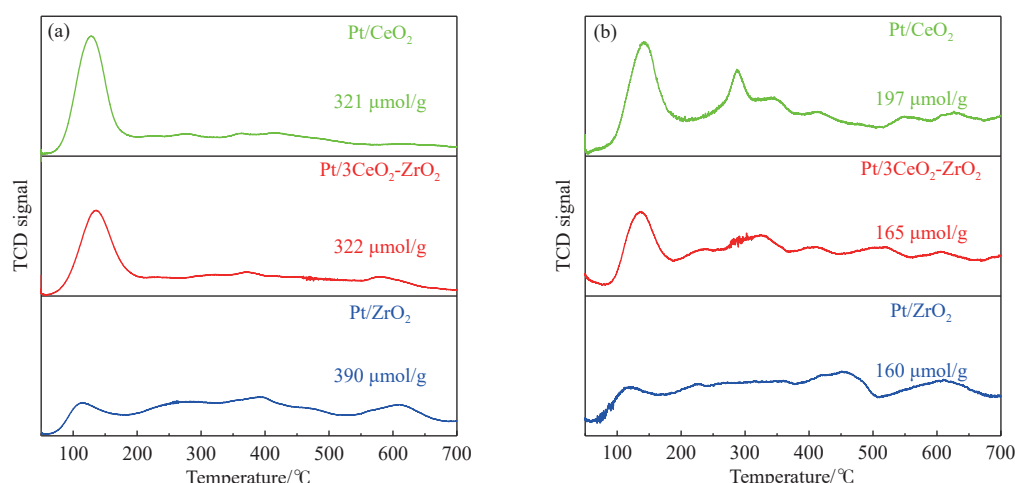


Fig. 3 (a) CO₂-TPD of catalysts; (b) CH₄-TPD of catalysts

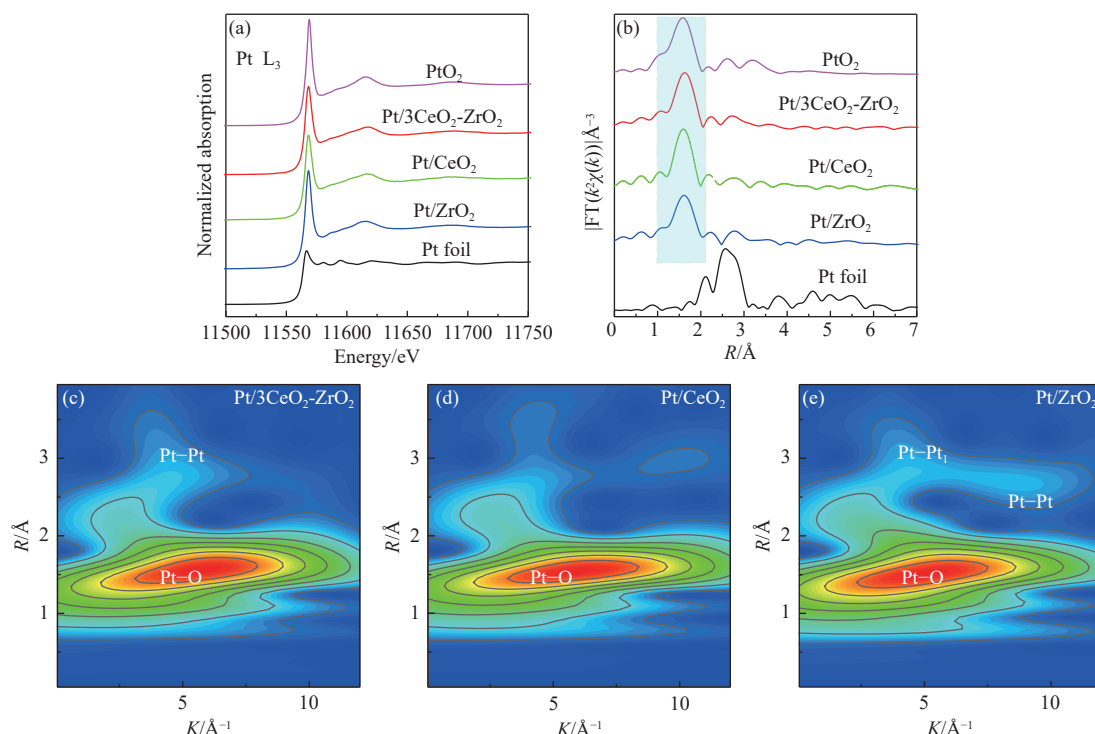


Fig. 4 XAFS spectra of catalysts: (a) XANES spectra; (b) EXAFS spectra; (c)–(e) Wavelet transforms spectra

All three catalysts exhibited a prominent signal at $\sim 1.6 \text{ \AA}$, corresponding to Pt–O coordination. Wavelet transform (WT) analysis was conducted to resolve both K-space and R-space information simultaneously (Figure 4(c), (d)). In these contour plots, red regions indicate high signal intensity. For the Pt/3CeO₂-ZrO₂ catalyst, Pt–Pt scattering was observed, attributed to the formation of PtO_x clusters. In contrast, the detection of metallic Pt–Pt bonding—consistent with Pt⁰ clusters—suggests that the Pt species in Pt/ZrO₂ exist as a mixed phase.

2.2.3 Analysis of the electronic structure of active sites

Figure 5 presents the XPS and CO-DRIFTS spectra of the catalysts. As illustrated in Figure 5(a), the Pt/3CeO₂-ZrO₂ and Pt/CeO₂ catalysts exhibit similar Pt 4f spectral profiles.

For Pt/3CeO₂-ZrO₂, the characteristic peaks at 72.84 eV (Pt 4f_{7/2}) and 76.16 eV (Pt 4f_{5/2}) are assigned to Pt²⁺, while the doublets at 71.35 and 74.67 eV correspond to Pt⁰. Similarly, Pt/CeO₂ displays Pt²⁺ features at 72.70 and 76.04 eV, with Pt⁰ signals appearing at 71.32 and 74.57 eV. These results indicate that the Pt species exist predominantly in the Pt²⁺ oxidation state, which is consistent with the XAFS characterization. Compared to Pt/CeO₂, the Pt²⁺ peaks in Pt/3CeO₂-ZrO₂ exhibit a small but distinct positive shift of $\sim 0.1 \text{ eV}$ toward higher binding energy. This shift suggests that Zr incorporation facilitates electron transfer, thereby stabilizing the Pt²⁺ species and enhancing the electronic metal-support interaction (EMSI). In CO chemisorption, the adsorption geometry depends on the nature of the active site: linear adsorption typically occurs on oxidized Pt, while both linear and bridging configurations are observed on Pt nanoclusters or nanoparticles^[36].

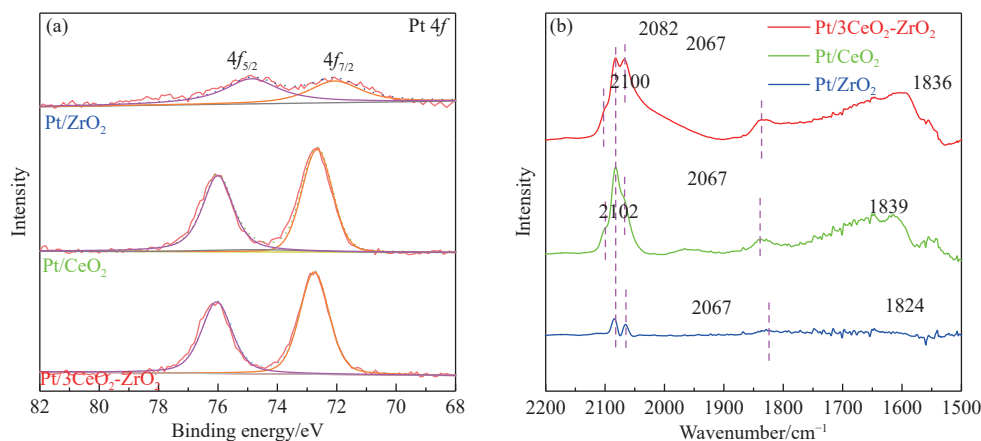


Fig. 5 (a) Pt 4f XPS spectra of catalysts; (b) *in situ* CO-DRIFT spectra of catalysts after CO desorption for 30 min

As shown in Figure 5(b), Pt/3CeO₂-ZrO₂ exhibits absorption bands at 2100, 2082 and 2067 cm⁻¹, which are assigned to linear CO adsorption on oxidized Pt and Pt nanoclusters. A characteristic band at 1836 cm⁻¹ is attributed to bridging CO adsorbed on Pt nanoclusters. Corroborated by the XAFS data, these results confirm that Pt/3CeO₂-ZrO₂ primarily consists of oxidized Pt alongside a fraction of PtO_x clusters, whereas Pt/CeO₂ is dominated by oxidized Pt species. In contrast, Pt/ZrO₂ displays a coexistence of oxidized Pt, Pt nanoclusters, and metallic Pt. Notably, Pt/ZrO₂ exhibited the lowest overall CO absorption intensity among the samples, aligning well with the XPS findings.

2.2.4 Analysis of surface defect structures

The surface defect structures of the catalysts were characterized using XPS. Figures 6(a) and 6(b) display the Ce 3d and Zr 3d spectra, respectively. It is well established that the concentrations of Ce³⁺ and Zr³⁺ are linearly correlated with the abundance of oxygen vacancies^[37]. Notably, the relative proportions of Ce³⁺ and Zr³⁺ are significantly higher in Pt/3CeO₂-ZrO₂ than in Pt/CeO₂, confirming a higher density of oxygen vacancies in the ternary catalyst. The Ce peaks in Pt/3CeO₂-ZrO₂ exhibit a negative shift toward lower binding energy relative to Pt/CeO₂. This suggests that Zr incorporation enhances the electronic metal-support interaction (EMSI). Similarly, the Zr peaks in Pt/3CeO₂-ZrO₂ shift toward lower binding energy compared to Pt/ZrO₂, further supporting the presence of strong electronic interactions facilitated by Ce doping. Figure 6(c) presents the O 1s spectra. The peak at 529.4 eV (O_I) is attributed to lattice oxygen (O_{lattice}) in ZrO₂ and CeO₂, while the component at 531.4 eV (O_{II}) is ascribed to surface oxygen species associated with defect sites. Deconvolution analysis reveals that the Pt/3CeO₂-ZrO₂ catalyst possesses the highest relative ratio of O_{II} species. In summary, the elevated Ce³⁺ and Zr³⁺

concentrations, combined with the abundance of surface oxygen vacancies (Vo), demonstrate that Pt/3CeO₂-ZrO₂ possesses the highest defect density. This defect-rich structure is closely associated with the strong metal-support interactions within the catalyst.

2.2.5 In situ infrared spectroscopic investigation

To investigate the individual activation, adsorption, and dissociation behaviors of reactants, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed using CH₄ and CO₂ as probe molecules. Figure 7(a) illustrates the adsorption and dissociation of CO₂ at 350 °C. The bands located between 2260 and 2390 cm⁻¹ are attributed to gas-phase CO₂. Upon exposure to the catalysts, CO₂ undergoes dissociative adsorption to form linearly adsorbed CO on Pt sites, characterized by a peak at approximately 2060 cm⁻¹. The Pt/3CeO₂-ZrO₂ catalyst exhibits intermediate CO peak intensity. Notably, no linear or bridging CO bands were observed on the bare supports. This indicates that the interaction between Pt and the support is essential for facilitating CO₂ activation and subsequent dissociation. Figure 7(b) displays the spectra for CH₄ adsorption and dissociation. The peak at 3015 cm⁻¹ corresponds to gas-phase CH₄. Chemisorption and dissociation of CH₄ occur on all three catalyst surfaces, yielding linearly adsorbed CO on Pt sites (observed at 2040–1950 cm⁻¹). These results suggest the reaction pathway CH₄ + O* → CO + 4H*, where O* originates from lattice oxygen or surface oxygen species associated with defects. Consequently, this oxidation process generates oxygen vacancies (Vo). The absence of adsorbed CO on the bare supports indicates that the support oxygen alone is inactive for CH₄ activation. In contrast, the introduction of Pt induces a restructuring of surface defects, thereby activating a portion of the surface oxygen. These results confirm a synergistic effect between the Pt species and the CeO₂-ZrO₂, CeO₂ and ZrO₂ supports.

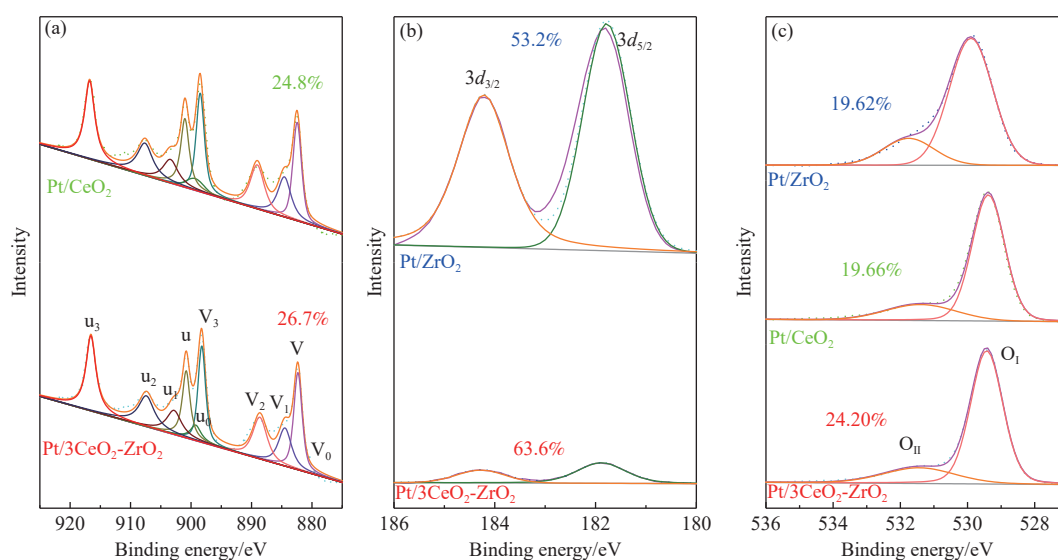


Fig. 6 (a) Ce 3d spectra of XPS; (b) Zr 3d spectra of XPS; (c) O 1s spectra of XPS

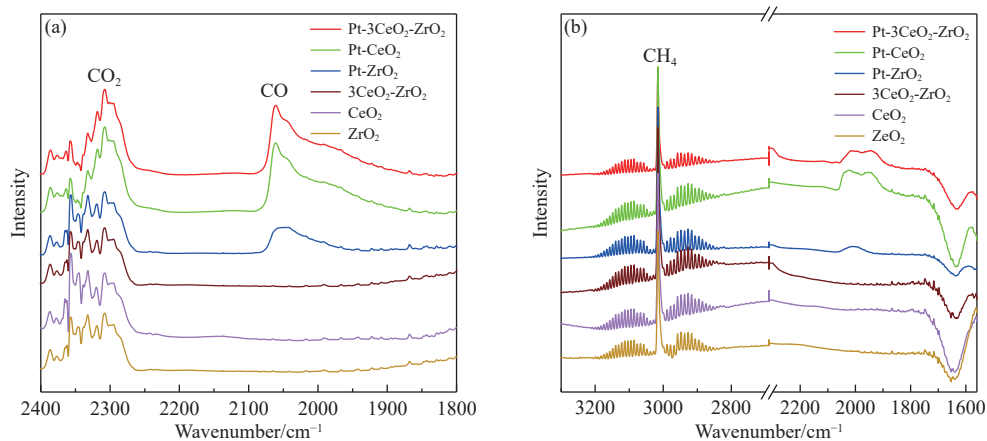


Fig. 7 CO₂ and CH₄ adsorption spectra of catalysts and supports *in situ* DRIFT at 350 °C: (a) CO₂; (b) CH₄

To further elucidate the reaction mechanism, *in situ* DRIFTS measurements were conducted under reaction conditions at 350 °C. The resulting spectra are presented in Figure 8, divided into four spectral regions corresponding to: hydroxyl groups (–OH, panel a), carbonyl species (CO, panel b), carbonate/carboxylate species (OCOO–C–O, panel c), and oxygenated hydrocarbon intermediates (CH_xO, panel d). An analysis of the –OH, CO and OCO bands reveals that the Pt/CeO₂ catalyst exhibits the highest abundance of hydroxyl species (particularly Type III–OH), the largest amount of desorbable linear CO, and the strongest signal intensities for carbonate and bicarbonate

intermediates. The Pt/3CeO₂–ZrO₂ catalyst shows intermediate intensities for these species, whereas Pt/ZrO₂ exhibits the weakest signals. Moreover, as observed in Figure 8(d), no CH_xO* intermediates were detected on the Pt/ZrO₂ catalyst at 350 °C.

Based on the *in situ* DRIFTS results, the reaction mechanisms for the Pt/3CeO₂–ZrO₂ and Pt/CeO₂ catalysts are illustrated in Figure 9. Methane activation occurs at the Pt–O_{lattice} interface *via* an oxygen-assisted dissociation pathway, proceeding through CH_xO* intermediates to form CO.

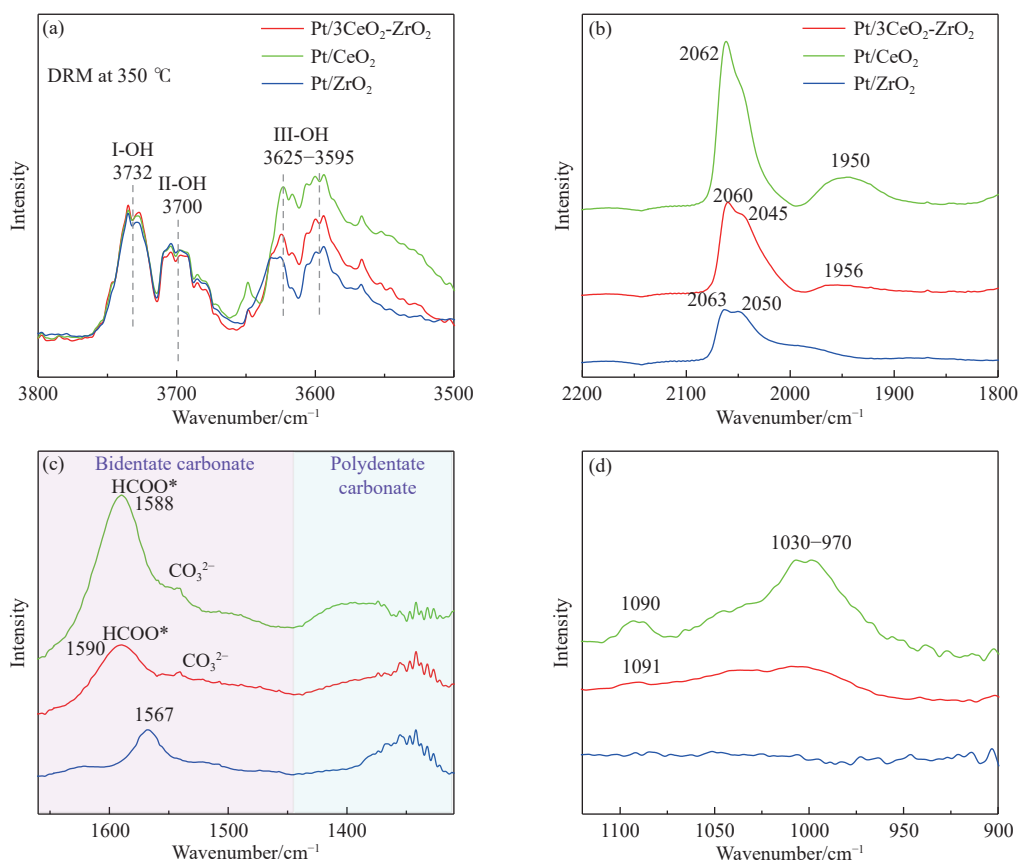


Fig. 8 The spectra of catalysts *in situ* DRIFT during DRM reaction at 350 °C for 1 h: (a) –OH band; (b) CO band; (c) OCO band; (d) CH_xO band

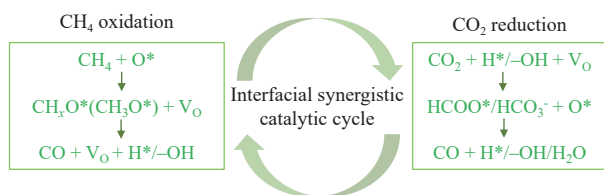


Fig. 9 Reaction mechanism diagrams of Pt/3CeO₂-ZrO₂ and Pt/CeO₂

The dissociated hydrogen species (H*) primarily recombine to generate H₂, while a portion migrates to adjacent oxygen atoms to form hydroxyl groups (–OH), which subsequently participate in the activation of CO₂. Thus, CO₂ is reduced by the H* species or –OH groups derived from methane. This process involves dissociation through formate (HCOO*), bicarbonate (HCO₃[–]) and carbonate (CO₃^{2–}) intermediates, ultimately yielding CO and a small amount of H₂O. Furthermore, the oxidation of CH₄ consumes lattice oxygen (O_{lattice}), resulting in the generation of oxygen vacancies (V_O). Concurrently, the dissociative reduction of CO₂ produces surface oxygen species (O*) that refill these vacancies, thereby establishing a self-sustained catalytic cycle between the oxidation and reduction steps^[38].

2.3 Analysis of carbon deposition on spent catalysts

Figure 10(a) presents the thermogravimetric (TG) profiles of the spent catalysts. No significant carbon deposition was observed on the Pt/3CeO₂-ZrO₂ and Pt/CeO₂ catalysts, whereas the Pt/ZrO₂ sample exhibited minor carbon accumulation. The Raman spectra shown in Figure 10 (b) corroborate these findings. The absence of characteristic carbon bands for Pt/3CeO₂-ZrO₂ and Pt/CeO₂ confirms their superior resistance to coking, consistent with the TG results. In contrast, the Pt/ZrO₂ catalyst displayed distinct D and G bands with an intensity ratio (I_G/I_D) of 1.16, indicating a moderate degree of graphitization and confirming the formation of carbonaceous deposits during the reaction. The enhanced coking resistance of Pt/3CeO₂-ZrO₂ and Pt/CeO₂ is attributed to their specific reaction pathways. During the dissociative adsorption of CH₄ on Pt sites to form CH₃* and H*, the CH₃* species avoids the conventional dehydrogenation route; instead, it transforms into CH_xO* intermediates, effectively inhibiting complete cracking into elemental carbon (C*). Conversely, the absence of CH_xO* intermediates on Pt/ZrO₂ facilitates carbon accumulation, rendering it significantly more susceptible to coking compared to the Ce-containing catalysts.

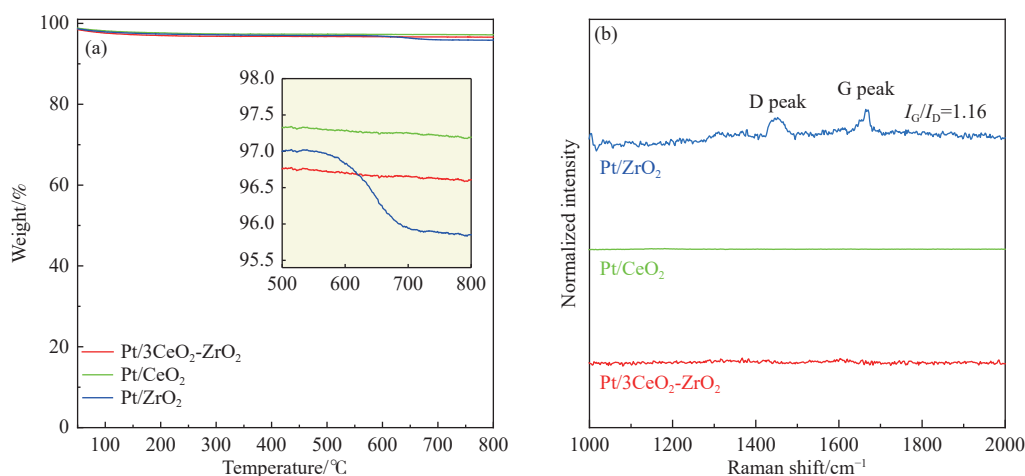


Fig. 10 Carbon analysis of used catalysts: (a) TG profiles; (b) Raman spectra

3 Conclusion

In this study, the defect concentration of Pt/CeO₂-ZrO₂ catalysts was modulated by adjusting the Ce/Zr ratio within UiO-66 precursors. Based on comprehensive characterization (CO₂/CH₄-TPD, XPS, XAFS, *in situ* DRIFTS, TG and Raman), the following conclusions were drawn: (1) Utilizing CeO₂-ZrO₂ supports derived from UiO-66 facilitates the high dispersion and stability of loaded platinum. Specifically, the Pt/3CeO₂-ZrO₂ catalyst exhibited the highest defect concentration and the strongest metal-support interaction. (2) Platinum exists predominantly in an oxidized state across all catalysts, though the specific speciation varies. Pt/3CeO₂-ZrO₂ consists mainly of PtO_x clusters and single atoms. In contrast, Pt exists exclusively

as single atoms on Pt/CeO₂, whereas the Pt/ZrO₂ catalyst contains a mixture of single atoms, PtO_x clusters, and metallic Pt_x clusters. (3) The catalytic cycles on Pt/3CeO₂-ZrO₂ and Pt/CeO₂ are driven by a synergistic combination of oxygen-assisted CH₄ dissociation and hydrogen-assisted CO₂ dissociation. Notably, the Pt/3CeO₂-ZrO₂ catalyst (Ce/Zr = 3:1) demonstrated superior catalytic activity, thermal stability against sintering, and resistance to coking at 800 °C. Specifically, it achieved CH₄ and CO₂ conversions of 86% and 93%, respectively, with a H₂/CO ratio near unity. Both TG and Raman analyses confirmed the absence of significant carbon deposition. Collectively, these findings provide valuable experimental insights for the design and optimization of Pt-based catalysts for the dry reforming of methane.

Declaration of Competing Interest

The authors declare no conflict of interest.

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不同 Ce/Zr 比的 UiO-66 前驱体对 Pt 基催化剂甲烷干重整反应性能的影响

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摘要: 本研究针对甲烷二氧化碳重整反应催化剂的烧结和积炭问题, 选取 UiO-66 作为前驱体对 Pt 基催化剂进行改性。利用水热法制备 Ce/Zr 比例不同的 CeO₂-ZrO₂ 载体, 采用浸渍法合成 Pt/CeO₂-ZrO₂ 系列催化剂。利用 CO₂-TPD、CH₄-TPD、XPS、XAFS、*in situ* DRIFT、TG、Raman 光谱等进行表征, 结果表明, 催化剂的 DRM 反应性能随着 Ce/Zr 利用比值的增加而增加, 呈现火山型趋势, 当 Ce/Zr=3:1 时, Pt/3CeO₂-ZrO₂ 表现出优异的 DRM 活性和稳定性。Pt/3CeO₂-ZrO₂ 催化剂中 Pt 高度分散, 其主要是以单原子 Pt 和在高温下更加稳定的 PtO_x 原子簇形式存在, 催化剂具有最高的 Ce³⁺、Zr³⁺ 的含量、丰富的 Vo、最高的氧空位含量, 存在强金属载体相互作用, 表现出最高的缺陷浓度。同时 Pt/3CeO₂-ZrO₂ 中 CH₄ 的氧助解离和 CO₂ 的氢助解离促进 DRM 反应连续稳定进行, 其 800 °C 时 CH₄ 转化率达到 86%, CO₂ 转化率达到 93%。催化剂稳定性测试 10 h 内没有积炭, 结果表明 Pt/3CeO₂-ZrO₂ 更有利于 CH₄ 和 CO₂ 的反应, 表现出更高的催化活性和稳定性以及抗积炭和抗烧结性能。

关键词: 甲烷干重整; 铂催化剂; UiO-66; CeO₂-ZrO

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