

Research progress on the role of oxygen vacancy in catalysts for dry reforming of methane

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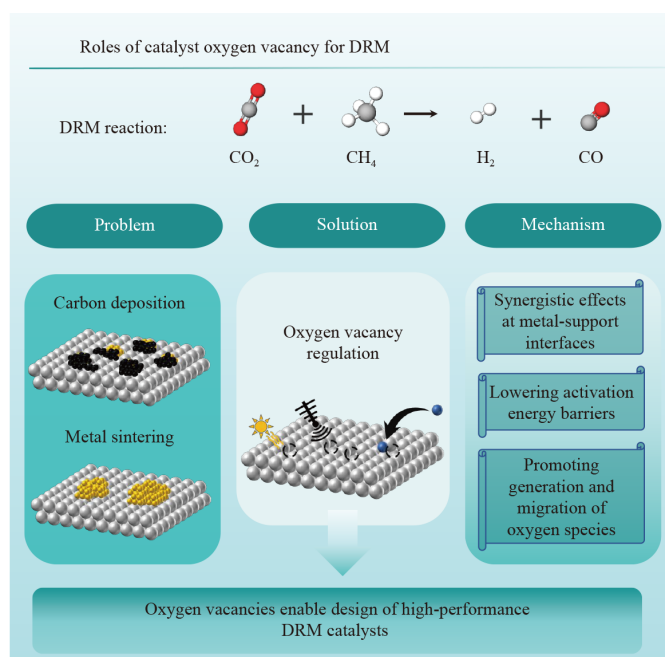
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Abstract: The extensive emission of greenhouse gases, primarily CO₂ and CH₄, has contributed to intensified global warming. Dry reforming of methane (DRM, CH₄ + CO₂ → 2CO + 2H₂) offers a pathway for the synergistic utilization of these two major greenhouse gases, presenting important implications for both environmental protection and energy sustainability. However, the catalysts still face the challenges such as carbon deposition and sintering of active metals, which adversely affect the catalytic performance and long-term stability. Oxygen vacancies, which are common lattice defects in metal oxides, have been demonstrated to improve the DRM performance by modulating the surface and interfacial properties of the catalysts. This review systematically summarizes research progresses in DRM over the past decade, outlines the major challenges and emphasizes the critical roles of oxygen vacancies in suppressing carbon deposition and inhibiting metal sintering.

Furthermore, the mechanisms through which oxygen vacancies influence DRM reactions are discussed, combined with their formation pathways and regulation strategies. These insights provide essential theoretical foundations for the design and synthesis of highly efficient and stable DRM catalysts.

Key words: dry reforming of methane; carbon deposition; oxygen vacancy; activation of methane; activation of carbon dioxide



Global warming triggered by greenhouse gases (primarily CO₂^[1] and CH₄^[2]) is a major issue of worldwide concern^[3]. The massive emissions and accumulation of greenhouse gases have already raised the global average temperature by 1.5 °C since the Industrial Revolution^[4]. According to the 2024 Global Carbon Budget released by the Intergovernmental Panel on Climate Change (IPCC)^[5], the global anthropogenic CO₂ emissions (the sources includes

fossil fuels, land use, land-use change and forestry) reached a record high of 41.6 billion tonnes of CO₂ in 2024. There is a 50% probability that the global average temperature will consistently exceed pre-industrial levels by more than 1.5 °C over the next 6 years and 1.7 and 2 °C within the next 14 and 27 years, respectively. To address the intensifying global greenhouse effect, carbon capture, utilization and storage (CCUS) technology has garnered

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widespread attention from both academia and industry^[6]. Amongst, dry reforming of methane (DRM) can convert both CH₄ and CO₂ into value-added syngas (CH₄ + CO₂ → 2CO + 2H₂)^[7], enabling the simultaneous reduction of the two major greenhouse gases. The produced syngas (CO and H₂) can be further converted into basic chemical feedstocks and high-value chemicals *via* routes like Fischer-Tropsch synthesis^[8]. However, the high reaction temperature (600–900 °C) often leads to the sintering of active metals, causing catalyst deactivation. Additionally, carbon deposition can also reduce the catalyst's durability and activity^[9–12]. To solve these problems, researchers have focused on modulating catalyst properties. Especially, oxygen vacancies, an important type of crystal defect, have demonstrated significant potential for optimization.

As a common defect in metal oxides, oxygen vacancies play crucial roles in heterogeneous catalysis^[13–14]. In DRM reactions, especially, oxygen vacancies can not only promote the activation of CH₄ and CO₂ and accelerate the elimination of carbon deposition, but also enhance the interaction between active metals and supports, preventing the sintering of active metals, thus stabilizing catalyst activity^[15–16]. Figure 1 shows the number of publications on DRM and the oxygen vacancies related to the reaction over the past decade. In the past five years, the concept of oxygen vacancies has appeared increasingly^[15,17–18]. Although some reviews have been published^[7,19–21], oxygen vacancies as a key influencing factor are less reviewed.

So, in this review, the key challenges are systematically reviewed based on the research progress over the past decade, among which carbon deposition and active metal sintering are the most critical issues. As oxygen vacancies play crucial roles in addressing these challenges, the formation mechanisms, regulation strategies and characterization methods of oxygen vacancies are further summarized to provide theoretical foundation for the rational design and precise construction of high-performance DRM catalysts.

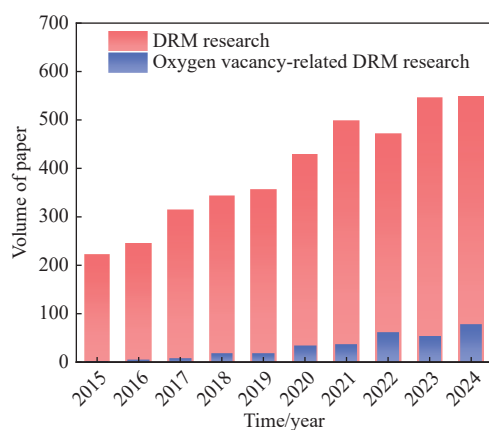


Fig. 1 Publication numbers of DRM research and oxygen vacancy-related DRM research over the past decade (Data source: Web of Science)

1 Summary of DRM reactions

1.1 DRM reactions and thermodynamic characteristics

The possible reactions are summarized in Table 1. For the main reaction (1), the H₂/CO ratio of the syngas produced by DRM is theoretically 1:1. However, the reverse water gas shift (RWGS) reaction (2) lowers the H₂/CO ratio to below 1. Other side reactions, such as CH₄ decomposition (8) and reverse Boudouard reaction (9), are the primary sources of carbon deposition. By controlling the reaction temperature for thermodynamically favorable reactions, the occurrence of side reactions can be suppressed. The thermodynamic calculations by Wang et al.^[22] shows that DRM occurs favorably at above 640 °C, while RWGS occurs only at below 820 °C. CH₄ decomposition and reverse Boudouard reaction occur at between 557 and 700 °C, respectively, favoring severe carbon deposition. Figure 2 illustrated the thermodynamic equilibrium diagram for DRM (CH₄/CO₂=1, 1 atm) as a function of temperature. Based on the thermodynamic characteristics of DRM, an appropriate reaction temperature can be optimized to achieve high conversion rates while simultaneously keeping high H₂/CO ratio and reducing carbon formation.

Table 1 Reaction networks in DRM^[23]

Reaction	$\Delta H_{298K}/(\text{kJ} \cdot \text{mol}^{-1})$	
CO ₂ +CH ₄ ↔ 2CO+2H ₂	247	(1)
CO ₂ +H ₂ ↔ CO + H ₂ O	41	(2)
2CH ₄ + CO ₂ ↔ C ₂ H ₆ + CO + H ₂ O	106	(3)
CH ₄ + 2CO ₂ ↔ C ₂ H ₄ + 2CO + 2H ₂ O	284	(4)
C ₂ H ₆ ↔ C ₂ H ₄ + H ₂	136	(5)
CO + 2H ₂ ↔ CH ₃ OH	-90.6	(6)
CO ₂ + 3H ₂ ↔ CH ₃ OH + H ₂ O	-49.1	(7)
CH ₄ ↔ C(s) + 2H ₂	74.9	(8)
2CO ↔ C(s) + CO ₂	-172.4	(9)
CO ₂ + 2H ₂ ↔ C + 2H ₂ O	-90	(10)
H ₂ + CO ↔ H ₂ O + C(s)	-131.3	(11)
CH ₃ OCH ₃ + CO ₂ ↔ 3CO + 3H ₂	258.4	(12)
3H ₂ O + CH ₃ OCH ₃ ↔ 2CO ₂ + 6H ₂	136	(13)
CH ₃ OCH ₃ + H ₂ O ↔ 2CO + 4H ₂	204.8	(14)
2CH ₃ OH ↔ CH ₃ OCH ₃ + H ₂ O	-37	(15)
CO ₂ + 4H ₂ ↔ CH ₄ + 2H ₂ O	-165	(16)
CO + 3H ₂ ↔ CH ₄ + H ₂ O	-206.2	(17)

1.2 DRM reaction mechanism

1.2.1 Mechanism summary

DRM is a multi-step process as shown Figure 3:

- (1) CH₄ adsorption and dissociative dehydrogenation on the active metal Ni to form CH_x* (x=1–3) and H*.
- (2) CO₂ adsorption and activation on basic sites or oxygen vacancies to form CO and active oxygen (O* or

OH*), either *via* direct dissociation ($\text{CO}_2 \rightarrow \text{CO} + \text{O}^*$) or hydrogen-assisted dissociation ($\text{CO}_2 + \text{H}^* \rightarrow \text{COOH}^* \rightarrow \text{CO} + \text{OH}^*$).

(3) CH_x^* reacts with active oxygen (O^* or OH^*) originated from CO_2 dissociation to form formate intermediates CH_xO^* , which is the key step for inhibiting carbon deposition.

(4) Decomposition of CH_xO^* into CO^* and H^* followed by H^* combination to yield H_2 .

Regarding to DRM kinetics, the rate-determining steps is still unclear. Zhang et al.^[24] deduced a Langmuir-Hinshelwood (LH) model over Ni/CaO- Al_2O_3 catalysts, identifying CH_4 dissociation as the rate-determining step. Olsbye et al.^[25] suggested both CH_4 dissociation and CO_2 activation are the rate-determining step: CH_4 dissociation forms carbon species, while CO_2 activation supplies active oxygen. Osaki et al.^[26] proposed that the reaction between CH_x^* and O^* is the rate-determining step. Some studies considered CH_xO^* decomposition as the rate-determining step^[27]. Anyway, CH_4 activation, CO_2 activation and reactions between intermediates all have significant influence on DRM reactions. Therefore, the mechanism is reviewed from the following three aspects: CH_4 activation, CO_2 activation and carbon deposition.

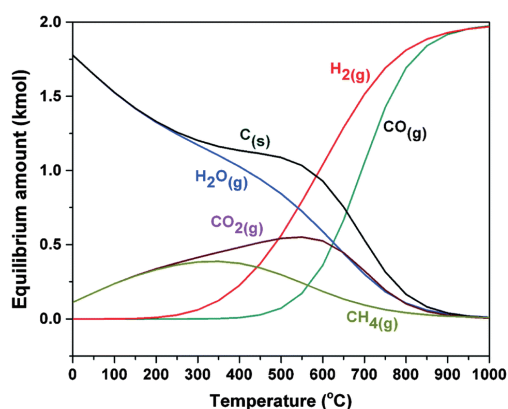


Fig. 2 Thermodynamic equilibrium plots for DRM^[7] (with permission from RSC Publications)

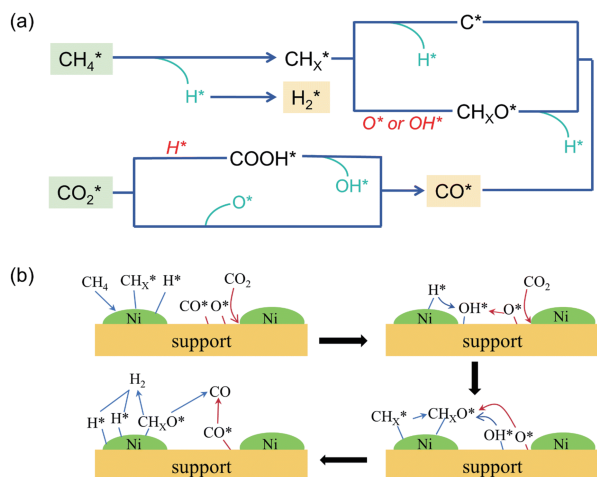


Fig. 3 Schematic of the DRM reaction steps (a) and molecular transformations on the catalyst surface (b)^[28] (with permission from RSC Publications)

1.2.2 CH_4 activation

CH_4 exhibits the highest C–H bond strength among all alkanes, with a first bond dissociation energy (BDE) of 439.3 kJ/mol (0 °C, 101.325 kPa)^[29] which generally requires substantial energy input. To mitigate the harsh conditions for CH_4 activation (high temperatures of above 1200 °C under non-catalytic conditions^[30]), electron exchange with metal active sites (e.g. Ni^[31], Co^[32]) or oxygen vacancies^[15] are utilized to promote C–H bond activation^[33], thereby lowering the reaction temperature. However, excessive dissociation of CH_4 can lead to carbon deposition and catalyst deactivation^[34]. Therefore, the catalyst's ability to promote CH_4 dissociation must be regulated.

1.2.3 CO_2 activation

CO_2 dissociates into CO and active oxygen on the catalyst surface which then oxidizes the carbon species generated from CH_4 dissociation, thereby reducing the carbon deposition^[35]. However, CO_2 is also chemically inert, with a high C=O bond energy of 806 kJ/mol. Therefore, the efficient CO_2 adsorption and dissociation are essential. Furthermore, the linear symmetric structure of CO_2 leads to a high adsorption energy barrier, particularly in the absence of suitable active sites^[36]. Thermodynamic analysis indicates that CO_2 dissociation requires high temperatures of above 700 °C^[37]. Beyond direct dissociation, other pathways exist for CO_2 activation. On basic supports, CO_2 is activated *via* carbonate intermediates^[38]. While on acidic supports, CO_2 activation is relatively weaker, which occurs primarily through reaction with surface hydroxyl groups forming formate intermediates. This process depends on the migration rate of hydroxyl groups on the supports or from metals to supports^[39].

1.2.4 Carbon deposition

Carbon deposition primarily originates from the deep dissociation of CH_4 ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) and the reverse Boudouard reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$). Deep dissociation of CH_4 is particularly significant on Ni-based catalyst^[40], whereas the reverse Boudouard reaction occurs more readily on weakly acidic supports (e.g. Al_2O_3)^[41]. The generated carbon species mainly include graphitic carbon, amorphous carbon and filamentous carbon^[42]. Graphitic carbon is the dense layers formed at high temperatures, leading to permanent deactivation by covering the active sites^[43]. Although amorphous carbon can be removed *via* oxidation, the high dispersion on catalyst surface or within catalyst micropores causes rapid deactivation^[44]. Filamentous carbon are generated in root-growth or tip-growth mechanism, which would encapsulate active components or be detached from supports, resulting in catalyst deactivation^[45]. By balancing the formation rates of carbon species and active oxygen on the catalysts, the carbon deposition can be avoided.

1.3 DRM catalysts system

1.3.1 Noble metal catalysts

Noble metal catalysts (e.g. Pt, Rh) exhibit excellent activity and stability for DRM. For instance, Rh/CeO₂ maintained over 95% CO₂ conversion after 100 h of reaction at 850 °C with negligible carbon deposition^[46]. However, the large-scale application of noble metal catalysts is constrained by the high cost (Rh price is around 1.25 million RMB/kg) and natural scarcity (crustal abundance $<1.0 \times 10^{-9}$)^[47]. Meanwhile, the noble metal catalysts suffer from the regeneration difficulty and high recovery costs. Although bimetallic designs can reduce noble metal loading, the issues such as active site competition^[48] and alloy structure instability need to be considered^[49]. Therefore, the industrial application of noble metal catalysts in DRM remains a distant prospect.

1.3.2 Ni-based catalysts

Ni-based catalysts have garnered significant attention due to their low cost and abundant active sites. However, they are prone to sintering at high temperatures (typically > 700 °C). The carbon species are more readily formed on the active centers of larger Ni particles, resulting in catalyst deactivation^[50]. Xu et al.^[51] found that the weak metal-support interaction in Ni/SiO₂ increased the Ni particle size during reactions, decreasing the CH₄ and CO₂ conversions from 78% and 85% to 51% and 65%, respectively, after reaction for 15 h. Akri et al.^[52] doped Ce into hydroxyapatite (HAP) support (Ni/HAP-Ce) to prevent carbon deposition and catalyst deactivation caused by Ni sintering. When Ce was incorporated into the HAP lattice, oxygen vacancies were generated in the vicinity for charge balance^[53], which served as ideal sites to trap and stabilize Ni atoms. Extended X-ray absorption fine structure (EXAFS) spectroscopy revealed the significant Ni-Ce scattering paths (~2.60) and an extremely low Ni-Ni coordination number (~0.7) in the Ni/HAP-Ce catalyst, indicating that oxygen vacancies prevented Ni agglomeration and enhanced the dispersion. Ullah et al.^[54] synthesized a Ni/CeO₂ (MD) catalyst with high oxygen vacancy concentration *via* microreactor. H₂ pulse chemisorption results showed that the Ni dispersion (9.65%) was significantly higher than that of a Ni/CeO₂ (SC) catalyst synthesized by simple co-precipitation with lower oxygen vacancy concentration (7.46%). This confirmed that oxygen vacancies could effectively improve the Ni dispersion. Furthermore, oxygen vacancies can promote the interaction between Ni atoms and supports, enabling partial electron transfer from Ni atoms to the electron-deficient supports. This granted Ni atoms anti-reduction ability, improving the anti-sintering capability of the Ni/HAP-Ce catalyst. Huang et al.^[55] prepared a catalyst in loosely packed platelet structure with high macroporosity by freeze-drying Ni-Mg-Al layered double hydroxide precursors, which improved the dispersion of active

component. The equilibrium CH₄ conversion of 95% was maintained over 100 h of continuous reaction. Although the methods mentioned above can greatly enhance the stability of Ni-based catalyst, the issue of Ni sintering deactivation remains challenging.

1.3.3 Co-based catalysts

Co metal behaves inferior DRM activity to other active metals but features with strong resistance to carbon deposition^[56]. Rosli et al.^[57] found that the excellent anti-coking capability of Co-based catalysts could be attributed to the strong oxophilicity, enabling immediate oxidation of carbon deposited on the catalyst surface. However, the high structural sensitivity of Co surfaces generally leads to catalyst deactivation. The deactivation of Co-based catalysts follows two pathways: oxidation and carbon deposition which are significantly affected by Co loading. High Co loading leads to deactivation *via* carbon deposition, while low Co loading results in oxidative deactivation^[58–59]. Joes-Alonso et al.^[60] observed that 1% of Co loading caused abrupt deactivation due to oxidation, whereas 9% of Co loading led to high carbon deposition rates due to larger Co particle sizes. Additionally, the exposed crystal facets also affect the Co deactivation mechanism. A density functional theory (DFT) computation combined with microkinetic modeling by Chen et al.^[61] demonstrated that the dominant reaction pathways on the Co(111) facet are C* + O* and CH* + O*. C* accumulation forming deposited carbon is prone to occur. On the Co(211) facet, the C* + O* pathway dominates, while high O* coverage leads to surface oxidation. The distribution of exposed Co facets is primarily influenced by Co nanoparticle size, resulting in the stability of Co-based catalysts highly dependent on the loading method and catalyst supports.

1.3.4 Catalyst support

Active metals are typically loaded on the support, which features with physicochemical properties such as high surface area, high dispersion of metal particles and supplies additional reaction sites^[62]. Support with large specific surface area, high porosity and high stability can maximize the dispersion of active metals. Materials such as Al₂O₃^[63–65] and SiO₂^[66–68] are commonly used^[69].

Typically, CO₂ activation occurs on the support, while CH₄ activation takes place on the active metals^[70]. This bifunctional mechanism makes the choice of catalyst supports critically important for both the activity and stability. During the catalyst preparation, when metal oxides are exposed to high temperature and reducing atmosphere, oxygen vacancies are generated, especially for reducible metal oxide supports such as TiO₂^[71–73] and CeO₂^[18,74–75]. When these metal oxides are used to combine with active metals, the mobility of the oxygen atoms is enhanced and the generation of oxygen vacancies is stimulated^[56]. The oxygen vacancies served as the sites for CO₂ activation and

C–H bond cleavage, thereby increasing the surface concentration of active oxygen and promoting the oxidative elimination of deposited carbon^[7]. Bahari et al.^[76] incorporated Y, La, Ce and Sm promoters into a Co/mesoporous alumina (MA) catalyst and found that the amount of carbon deposited followed the order of: Co/MA > Sm-Co/MA > La-Co/MA > Ce-Co/MA > Y-Co/MA, aligned with the oxygen vacancy concentration. Oxygen vacancies also play a positive role in CH₄ activation. Wang et al.^[77] performed *operando* studies and DFT calculations (Figure 4) on the Ir@CeO_{2-x} catalyst, and revealed that the interface sites were rich in oxygen vacancies (Ir^{δ+}-O_v-Ce³⁺), which acted as active centers for promoting CH₄ dissociation (the rate-determining step) and the oxidation of CH₂* to CH₂O*, effectively suppressing the carbon deposition.

2 Oxygen vacancy

2.1 Configuration of oxygen vacancy

Oxygen vacancy is a type of defect in metal oxides, which is formed when lattice oxygen escapes under specific external conditions (such as high temperature^[78] or reductive treatment^[79]). The concept of oxygen vacancy was firstly proposed by Tompkins et al.^[80] in 1960 s, when researchers discovered that metal oxides are not ideally perfect crystal structures as previously assumed but contain certain oxygen ion defect sites.

Oxygen vacancy disrupts the perfect periodic arrangement of the crystal and alters the electronic structure around the vacancies^[81]. Consequently, the electron charge associated with the departed O atom (2e⁻) redistributes

within the surrounding lattice. As illustrated in Figure 5, due to the multiple oxidation states of metal oxides, the extra electrons tend to transfer to adjacent cations, reducing them into lower valence states^[82]. This endows some metal oxides crucial role in some catalytic reactions^[83]. Theoretical calculations indicate that oxygen vacancies create abundant localized electrons, which influence the physical and chemical properties of metal oxides (e.g. optical characteristics, electron transport, surface/interface structures etc.) and provide unique active sites for catalytic reactions^[83].

2.2 Regulation strategy of oxygen vacancy

2.2.1 Thermal or reductive treatment

Calcination at elevated temperatures in an oxygen-deficient atmosphere can induce lattice oxygen migration to form oxygen vacancies^[84]. Typical procedures involve high-temperature treatment under inert atmospheres (Ar^[78], N₂^[85]) or vacuum^[86], where the oxygen vacancy concentration depends on a temperature-time synergy^[87]. Hou et al.^[88] calcined nanotubular titanate (NTA) at varying temperatures in air or vacuum, producing TiO₂ with distinct types and concentrations of oxygen vacancies. The NTA calcined in air formed only bulk oxygen vacancies. Whereas those calcined in vacuum contains both bulk and surface oxygen vacancies as confirmed by Photoluminescence (PL) and Electron paramagnetic resonance (EPR) characterizations. However, the method requires careful balance between the thermodynamic stability of the materials and the formation of oxygen vacancy because that high temperatures may degrade the materials^[89].

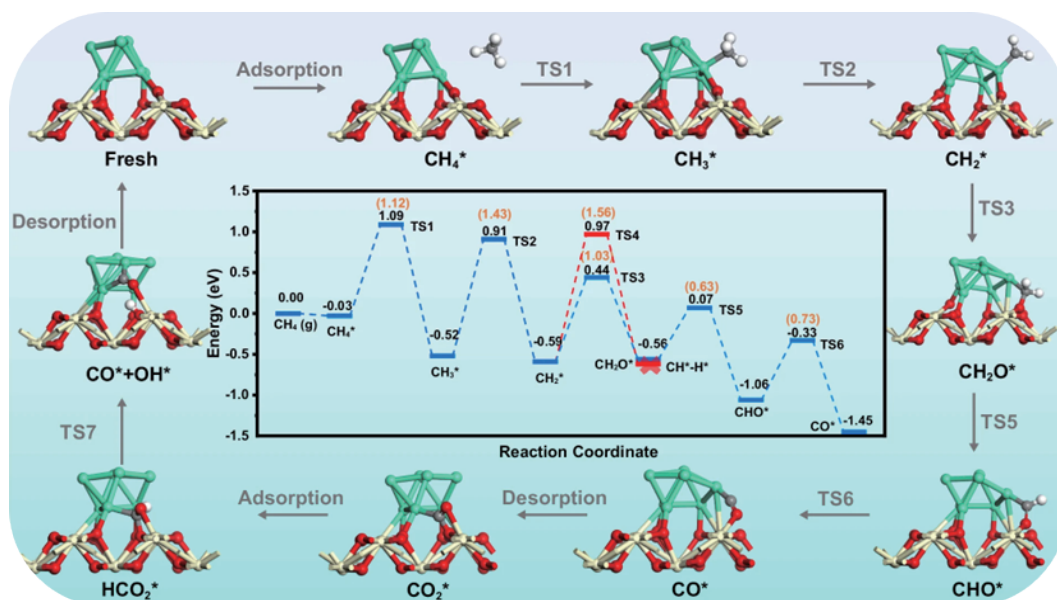


Fig. 4 Schematic illustration for DRM reaction at the interface of Ir/CeO_{2-x}^[77]

Ir: green; Ce: yellow; C: gray; O: crimson; H: white. The inset shows potential energy profile of CH₄ decomposition by Ir/CeO_{2-x}(110).

“TS” represents a transition state. The black and orange numbers represent the adsorption energies and energy barriers of the elementary steps, respectively.

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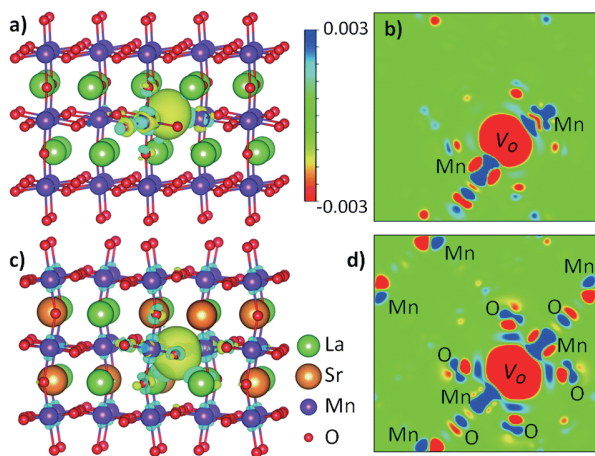


Fig. 5 Changes in electron density ($e \cdot \text{\AA}^{-3}$) upon oxygen vacancy formation in LaMnO_3 (a) and (b), and $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (c) and (d)^[82]

Yellow isosurfaces indicate lowered electron density; Cyan indicates increased electron density.
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Compared to thermal treatment, reductive treatment using gaseous or solid reducing agents (e.g. H_2 ^[90], NH_3 ^[91] and NaBH_4 ^[92]) can produce oxygen vacancies in metal oxides at relatively lower temperatures. The reducing molecules firstly adsorb onto the metal oxide surface to facilitate the transfer of lattice oxygen to the surface *via* electron transfer, thereby generating oxygen vacancies^[93]. Hou et al.^[94] employed NaBH_4 as reducing agent to prepare TiO_2 materials feathered with tunable ratio of bulk and surface oxygen vacancies concentrations by adjusting the amount of NaBH_4 and the treatment time.

2.2.2 Field control

The regulation of oxygen vacancies can be achieved by applying external fields, such as electric^[95], lighting^[74], microwave radiation^[96] and high-energy particle bombardment^[97]. Jiao et al.^[98] regulated oxygen vacancy concentration by applying electric field (particularly a negative field) to the catalyst.

The negative field accelerated oxygen vacancy formation by promoting hydrogen spillover to generate water. Li et al.^[99] prepared oxygen vacancy-rich $\text{Ru/TiO}_2\text{-CeO}_2$ catalyst *via* photothermal synergy, which utilizes light-induced intermetal charge transfer to accelerate the oxygen migration. EPR characterization results showed that the oxygen vacancy signal under light conditions was significantly stronger than that under dark conditions, indicating that light irradiation promoted the oxygen vacancy formation. Rapid microwave heating also facilitates oxygen vacancy generation. Wang et al.^[100] found that microwave heating resulted in an oxygen defect degree of 0.6 in $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}$ catalysts, compared to the value of 0.2 under conventional heating. High-energy particle bombardment utilizes high-energy electrons, protons or ion beams to irradiate the metal oxide surface, causing lattice

oxygen desorption *via* energy transfer to form oxygen vacancies^[101]. The oxygen vacancy concentration can be regulated by adjusting treatment time, irradiating particles and intrinsic structure of the metal oxide^[102]. Liu et al.^[103] used water plasma to etch a layered double hydroxide (LDH) structure and revealed the partial oxidation of Co^{2+} to Co^{3+} . The valence change accompanied by charge imbalance leads to oxygen atom loss that maintain the electrical neutrality, thereby forming oxygen vacancies.

2.2.3 Ion doping

Doping enables the regulation of oxygen vacancies by incorporating ions with different valence states or radii into the host material. Electronic structure difference between the dopant ions and the host lattice induces charge imbalance. To maintain overall electrical neutrality in the system, oxygen vacancies are formed for charge compensation^[104]. For example, when Cu^{2+} dopes into CeO_2 (where Ce^{4+} is the primary lattice ion), the substitution of Ce^{4+} by Cu^{2+} creates a local charge deficiency, which is balanced by the formation of oxygen vacancies (one oxygen vacancy is created for every two Cu^{2+} substitutions for one Ce^{4+})^[105]. Wu et al.^[106] modulated the concentration of oxygen vacancies on the CeO_2 surface by substituting Ce^{4+} with smaller cations M ($M = \text{Mg}, \text{Co}, \text{Zn}$). Additionally, differences in ionic radii between the dopant and host ions cause lattice distortion, which lowers the oxygen vacancy formation energy^[107]. Xia et al.^[108] demonstrated that doping with redox inert cations with smaller radii ($\text{Sc}^{3+} > \text{Fe}^{3+} > \text{Ga}^{3+} > \text{Al}^{3+}$) reduced the tilting of FeO_6 octahedra, significantly decreasing the oxygen vacancy formation energy and accelerating the oxygen mobility. Furthermore, ion exchange provides a simple method for regulating oxygen vacancies. For instance, oxygen vacancy-rich NiO nanorods were produced *via* ion exchange between ZnO precursor and Ni^{2+} ^[109]. Similarly, oxygen vacancy-rich CoO was generated through ion exchange between ZnO and Co^{2+} ^[110].

2.2.4 Interfacial engineering

Metal-support interface engineering (e.g. Ni-ZrO_2 ^[111], Ni-CeO_2 ^[112]) induces oxygen vacancy formation *via* charge transfer between metals and the supports^[113]. Jin et al.^[114] deposited ZrO_2 onto $\text{Ni/Al}_2\text{O}_3$ catalyst using atomic layer deposition (ALD) and employed high-temperature H_2 reduction to transform the ZrO_2 film into tetragonal phase, cracking the film surrounding Ni sites and thereby forming a Ni-ZrO_x interface. Active H species generated from H_2 dissociation on the Ni surface promoted the desorption of surface oxygen from adjacent ZrO_2 *via* hydrogen spillover, inducing the formation of interfacial oxygen vacancies. During the DRM reaction, these interfacial oxygen vacancies dissociate CO_2 to release active oxygen, thereby limiting the carbon deposition. Li et al.^[115] introduced

ultrafine CeO₂ nano-islands (1–1.5 nm) onto SiO₂ support and found that charge transfer between Ni and CeO₂ induced oxygen vacancy formation. These interfacial oxygen vacancies modulated the CH₄ dissociation, significantly enhanced the CO₂ adsorption and activation, accelerated the surface carbon elimination reactions and effectively promoted the removal of carbon species from the catalyst surface, achieving high catalyst activity and stability.

Yang et al.^[116] summarized the formation methods for oxygen vacancy defects in different types of metal oxides (Figure 6), which require distinct regulation strategies in applicability, cost and operational complexity (Table 2). Through rational selection of regulation strategies, the electronic structure and surface properties of the metal oxides can be tailored, thereby providing highly efficient active sites for DRM reactions.

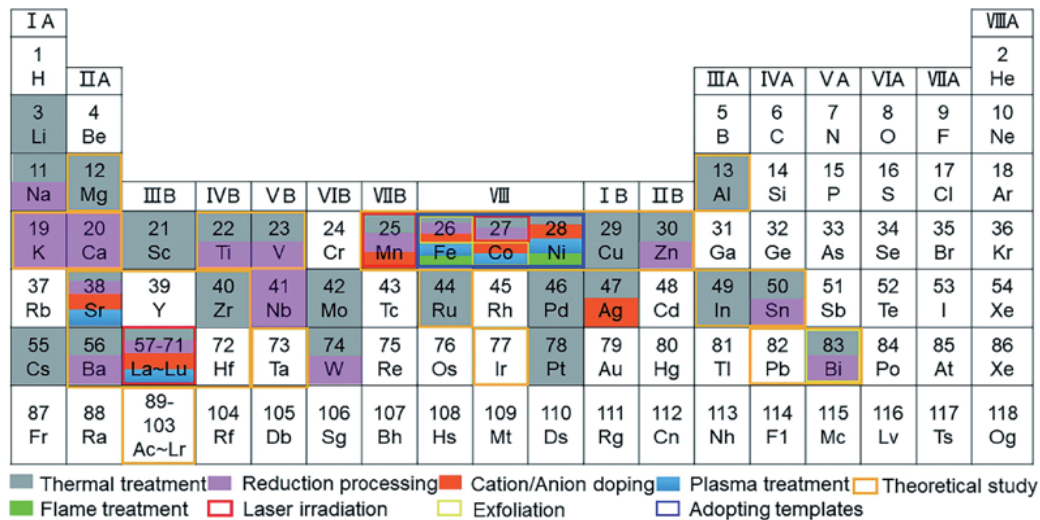


Fig. 6 Statistical diagram of oxygen vacancy formation methods in different types of metal oxides^[116]
(with permission from Progress in Chemistry)

Table 2 Comparison in regulation strategies of oxygen vacancy

Strategy	Applicability	Cost	Operational difficulty
Thermal treatment and reductive treatment	Suitable for most metal oxides ^[87,117]	Overall costs relatively low ^[92]	Relatively mature, and the parameters are easily controlled
Field control	Dynamic, reversible regulation through external field (electric field ^[95] , lighting ^[74] , etc.)	Despite the high costs for research and energy spent, the sustainable benefits are available ^[102]	The requirements for both equipment and technology are extremely high. Most works remain at the laboratory stage, with significant challenges for scaling up
Ion doping	Introducing heteroatoms to modify the local electronic structure of catalyst ^[105–106,118]	Costs for raw materials and doping process are the primary influencing factors	Precise controlling the dopant elements, concentration and uniformity is required. Once mature, the industrial production will become easy
Interfacial engineering	Suitable for complex materials to regulate the oxygen vacancies and ion/electron transport at the interface, by designing structures or compositions at heterogeneous interfaces ^[114–115]	Costs vary depending on the technology. For example, atomic layer deposition (ALD) requires substantial capital investment ^[119]	It is critically in precisely engineering interfaces, with control over their structure and chemistry making the process inherently complex

2.3 Research method for oxygen vacancy

2.3.1 Electron paramagnetic resonance (EPR)

EPR technique can directly prove the presence of oxygen vacancies by detecting the paramagnetic signals of unpaired

electrons in materials^[120]. Li et al.^[121] investigated the oxygen vacancies in BiOCl samples *via* EPR and observed a representative signal at $g=2.002$. The advantages lie in high sensitivity to unpaired electrons and providing direct evidence of defect types^[122], without any destruction of samples. However, the method is only effective to the paramagnetic oxygen vacancies instead of the vacancies

without unpaired electrons^[123].

2.3.2 X-ray photoelectron spectroscopy (XPS)

XPS can identify oxygen vacancies by analyzing the binding energy of the O 1s orbital on the material surface. It is generally accepted that oxygen vacancies produce a characteristic peak at around 531.4–531.5 eV, attributed to chemisorbed oxygen, which is distinct from lattice oxygen (approximately 529.5 eV)^[124], though this assignment remains debated^[125]. The method provides information of surface chemical states and semi-quantitative data, with a sampling depth of about 10 nm, which is one of the most widely used surface analysis techniques^[126]. As a surface-sensitive technique, nevertheless, XPS is insensitive to the defects within the material bulk. The high-energy X-ray beam may potentially cause sample damage.

2.3.3 Raman spectroscopy

Raman spectroscopy can indirectly detect oxygen vacancies by monitoring the changes in lattice vibration modes of the materials. The presence of oxygen vacancies may cause the shifts in Raman peaks or the appearance of new peaks^[127]. The Raman characterization Eu-doped CeO₂ by Huang et al.^[128] showed the appearance of a new peak at 600 cm⁻¹, confirming the formation of oxygen vacancies. Raman characterization is rapid, non-destructiveness and sensitivity to lattice distortions. However, the evidence of oxygen vacancies is indirect and is susceptible to interference from other factors (e.g. stress, doping), necessitating validation with complementary techniques.

2.3.4 X-ray absorption fine structure (XAFS)

XAFS provides an effective method for determining electronic structure and the presence of oxygen vacancies^[129]. It can provide structural information such as oxidation state, bond length, bond type and coordination number^[130]. Qualitative defect levels can be inferred by observing the shift in distance and peak intensity of neighboring coordinating atoms. Zhang et al.^[131] conducted XAFS characterization on defect-rich R-WO₃, less-defective D-WO₃ and commercial C-WO₃ samples. Fourier transform of the raw data into real-space atomic distance information revealed that the EXAFS peak intensity of R-WO₃ was significantly lower than that of C-WO₃ and D-WO₃, accompanied by a peak shift, indicating differences in local atomic arrangement and the presence of oxygen vacancies. The advantages of XAFS include element specificity, high sensitivity to local structure and applicability to both crystalline and amorphous materials due to the independence on long-range order. However, the

analysis on XAFS results requires complex data fitting and modeling. The technology relies on large-scale facilities (synchrotron radiation) as the light source.

2.3.5 Scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS)

STEM enables direct imaging of atomic structures, while EELS detects the distribution of oxygen vacancies from surface to bulk by analyzing the energy loss spectra^[132]. The technique accomplishes spatial resolution and chemical composition analysis in atomic-scale, with electronic structure information provided by EELS. However, the high equipment costs, complex sample preparation and limited view field making it difficult to represent the overall scenario. It is applicable for direct observation of oxygen vacancies at the nanoscale or even atomic level and investigation of local electronic structures of oxygen vacancies.

2.3.6 Density functional theory (DFT)

DFT calculation, based on quantum mechanical principles, can simulate the electronic structure of materials and oxygen vacancy^[133]. Zhao et al.^[134] employed DFT calculations to reveal the structural model of V_O-MnO₂ containing oxygen vacancies. Compared to non-defective MnO₂, the total and partial density of states of V_O-MnO₂ shifted closer to the Fermi level, in consistent with experimental results, demonstrating the assistant role of DFT in identifying the oxygen vacancies. The method can theoretically predict the formation energy, stability and electronic structure influences of oxygen vacancies, and thus assist the interpretation of experimental results. As a theoretical simulation rather than a direct experimental measurement, DFT still faces challenges in describing certain complex systems. It can serve as a complementary tool to integrate with experimental results, deepening the understanding of the formation mechanisms and electronic effects of oxygen vacancies.

3 Effects of oxygen vacancy in DRM

Oxygen vacancies have been widely recognized as key active sites for DRM catalysis: on one hand, they serve as preferred sites for CH₄ activation and dissociation of, promoting the cleavage of C–H bonds while suppressing excessive CH₄ dissociation; on the other hand, they act as centers for CO₂ adsorption and activation, facilitating CO₂ conversion to generate more active oxygen species, thereby inhibiting carbon deposition. Rational regulation of oxygen vacancies enables highly efficient and stable operation of DRM reactions (Table 3).

Table 3 Effects of oxygen vacancy in DRM

Catalyst	DRM condition	Catalytic performance				Effect of oxygen vacancy	Ref.
		$x_{\text{CH}_4}/\%$ ^a	$x_{\text{CO}_2}/\%$ ^b	H_2/CO ^c	Carbon deposits		
Ni/MgO-Ce/SBA-15	900 °C, $\text{CH}_4:\text{CO}_2 = 1:3$, $\text{GHSV}^{\text{d}} = 85000$	93	57	<1	Negligible (12 h)	Enhancing CO_2 activation, eliminating surface carbon species and improving catalyst activity	[135]
Ni-NiO-Sr ₂ Nb ₂ O ₇	500 °C, $\text{CH}_4:\text{CO}_2 = 1:1$, $\text{GHSV}^{\text{d}} = 240000$	50	58	0.85	Negligible (30 h)	Serving as sites for CO_2 adsorption and activation, and utilizing photoelectrons to reduce CO_2 to CO with the replenishment of lattice oxygen, and thereby inhabiting coke formation	[136]
Ni/Ce _{0.9} Eu _{0.1} O ₈	600 °C, $\text{CO}_2:\text{CH}_4:\text{N}_2 = 1:1:2$, $\text{GHSV}^{\text{d}} = 120000$	25	33	Not mentioned	Not mentioned	Serving as sites for promoting CO_2 dissociation and providing lattice oxygen to oxidize deposited carbon	[18]
Ni ₁ /HAP-Ce	750 °C, $\text{CO}_2:\text{CH}_4:\text{He} = 2:2:6$, $\text{GHSV}^{\text{d}} = 60000$	90	95	~1	Negligible (100 h)	Strengthening metal-support interactions to stabilize the single Ni atoms, and thereby reducing coking and sustaining catalyst stability	[52]
Co-Y ₂ O ₃ /MA	750 °C, $\text{CO}_2:\text{CH}_4:\text{N}_2 = 1:1:3.1$, $\text{GHSV}^{\text{d}} = 36000$	85.8	92.2	<1	7.02% (8 h)	Activating CO_2 and promoting carbon gasification, thereby reducing carbon deposition	[76]
Ir@CeO _{2-x}	700 °C, $\text{CH}_4:\text{CO}_2:\text{N}_2 = 4:4:1$, $\text{GHSV}^{\text{d}} = 240000$	72	82	Not mentioned	Negligible (100 h)	Forming interfacial sites ($\text{Ir}^{\delta+}\text{-O}_v\text{-Ce}^{3+}$) to promote CH_4 dissociation and conversion of intermediates, thereby reducing carbon deposition	[77]
Ni/Ce-SiO ₂	800 °C, $\text{CH}_4:\text{CO}_2:\text{N}_2 = 9:9:2$, $\text{GHSV}^{\text{d}} = 9000$	92	96	0.96	10.7% (2000 h)	Enhancing CO_2 adsorption and activation, thereby promoting the gasification of deposited carbon	[115]
1.5CeO _{2-x} -NSNT	750 °C, $\text{CH}_4:\text{CO}_2:\text{N}_2 = 1:1:2$, $\text{GHSV}^{\text{d}} = 96000$	85	88	<1	6% (100 h)	Promoting CO_2 adsorption and activation with formation of reactive oxygen species, and enhancing the gasification of deposited carbon	[137]
Ni-ZrO ₂ /DMS	800 °C, $\text{CH}_4:\text{CO}_2 = 1:1$, $\text{GHSV}^{\text{d}} = 18000$	92	96	~1	Negligible (100 h)	Reducing the activation energy for CH_4 dissociation, thereby promoting CH_4 activation and dissociation	[138]
Ni-Ce _{0.25} Zr _{0.75} O ₂ /ZSM-5	750 °C, $\text{CH}_4:\text{CO}_2:\text{Ar} = 1:1:8$, $\text{GHSV}^{\text{d}} = 45000$	91.9	93.8	0.98	0.61 mg/(g·h)	Enhancing the interaction between Ni and the support, and modulating the electronic structure of Ni, thereby promoting the CH_4 adsorption and activation	[139]
LaNi _{0.6} Mn _{0.4} O ₃	750 °C, $\text{CH}_4:\text{CO}_2:\text{N}_2 = 1:1:2$, $\text{GHSV}^{\text{d}} = 15000$	92	84	>1	Negligible (10 h)	Improving oxygen mobility <i>via</i> reversible conversion of $\text{Mn}^{4+}/\text{Mn}^{3+}$, thereby reducing coke formation	[140]

^a: Conversion of CH_4 ; ^b: Conversion of CO_2 ; ^c: Ratio of H_2 to CO produced from the reaction; ^d: Gas hourly space velocity is in mL/(g·h).

3.1 CH₄ activation

Most studies^[98,137,141–142] suggested that oxygen vacancies play an indirect role in CH_4 activation by promoting CO_2 activation to supply active oxygen and then oxidatively remove the deposited carbon from CH_4 activation. Furthermore, oxygen vacancies modulated the electronic structure of the catalyst surface/interface, thereby optimizing the adsorption strength of intermediates derived

from CH_4 decomposition and thus preventing its excessive dissociation into carbon deposits^[143]. Meng et al.^[144] found that the oxygen vacancy-rich Ni/La₂O₃ exhibited better durability compared to the oxygen vacancy-deficient Ni/La₂Zr₂O₇, during which the enhanced CO_2 activation could generate more active oxygen for the oxidation of deposited carbon, preventing the loss of CH_4 activation capability of Ni from coking. Consequently, Ni/La₂O₃ showed only 10.8% decrease in H_2 yield during 50 h of photothermal catalytic reaction, verifying the indirect role

of oxygen vacancies to promote CH₄ activation. In contrast, significant filamentous carbon formed on Ni/La₂Zr₂O₇, encapsulating Ni particles and then degrading the ability of catalyst for CH₄ dissociation. Additionally, oxygen vacancies as defect sites provided anchoring points that strengthened metal-support interactions, maintaining the high dispersion of active sites and suppressing sintering^[74]. Niu et al.^[145] observed that Ni²⁺ species interacted with oxygen vacancies on the CeO₂ support, forming Ni⁺-CeO₂ structures, which effectively immobilized the metal species and thus prevented them from migration and agglomeration. This effect was particularly pronounced in the Pt_{0.2}/Ni_{0.6}@CeO₂ catalyst prepared with dispersants (polyethylene glycol and ethylene glycol), which possessed more oxygen vacancies. The Ni 2p_{3/2} XPS spectra indicated a shift in the binding energy of Ni²⁺ species towards higher values in the catalyst containing dispersants, demonstrating the enhanced interaction between Ni²⁺ and the CeO₂ support. This confirmed that oxygen vacancies could stabilize the Ni species by facilitating the formation of Ni⁺-CeO₂ structures, thereby maintaining active site dispersion and inhibiting sintering.

In addition to the indirect action on CH₄ activation, oxygen vacancies could synergize with active components to directly promote CH₄ activation^[18,138,146]. Yang et al.^[139] increased the concentration of oxygen vacancies by adjusting the Ce/Zr ratio, which strengthened the interaction between Ni and the Ce_xZr_{1-x}O₂ support, thereby promoting the formation of Ni-O-M (M = Ce/Zr) species. These Ni-O-M species shifted the catalyst's *d*-band center closer to the Fermi level, resulting in higher surface electron/charge density on the active components. This strengthened the orbital interaction with CH₄, facilitating its adsorption and activation, consequently promoting the reaction^[147–148]. Both experimental and theoretical results indicated that C–H bond activation was more sensitive to coordinatively unsaturated metal sites^[149]. For instance, Lustemberg et al.^[150], based on experimental and DFT calculation results, demonstrated that Ni²⁺ species facilitated C–H bond dissociation at lower temperatures compared to metallic Ni. Therefore, oxygen vacancies could enhance the ability of active components for CH₄ adsorption and C–H bond cleavage. Furthermore, the transition between two oxidation states of reducible supports (e.g., Ce⁴⁺ and Ce³⁺) generated oxygen vacancies, which could accommodate electrons transferred from the active metal to the support, creating coordinatively unsaturated metal sites^[151]. These coordinatively unsaturated metal sites formed at interface sites acted as electron acceptors for CH₄ dissociation, lowering the T_d symmetry of CH₄ molecule and promoting its activation and dehydrogenation to CH_x*^[152]. DFT calculation by Cheng et al.^[153] showed that oxygen vacancies reduced the dissociation barriers of the radicals such as CH₃*, CH₂* and CH*, significantly promoting the CH₄ activation. In summary, the promoting roles of oxygen vacancies in CH₄ activation is multifaceted: when the interaction between the active component and the support is

weak, oxygen vacancies primarily promote CH₄ activation indirectly by activating CO₂ to supply active oxygen for carbon removal, thus indirectly facilitating CH₄ dissociation; when a strong interaction forms between the active component and the support, the resulting interfacial oxygen vacancies can lower the activation energy barrier for CH₄, directly promoting its dissociation^[77].

3.2 CO₂ activation

In DRM reactions, oxygen vacancies serve as key sites for CO₂ adsorption and activation i.e. CO₂ molecules adsorb onto oxygen vacancies and dissociate into active oxygen species (O*) and CO: CO₂ → CO + O*, where highly reactive O* participates in subsequent reactions (e.g. oxidizing the species derived from CH₄ dissociation)^[154]. Guo et al.^[137] reported a CeO_{2-x} interface-confined and nickel silicate nanotubes (NSNT)-derived Ni catalyst (CeO_{2-x}-NSNT) for DRM. The reduced CeO_{2-x}-NSNT catalyst possessed abundant extrinsic defects originated from the interfacial reaction between CeO₂ nanoparticles and NSNT supports, accompanied by interface reconstruction, forming oxygen vacancies, lattice distortion and electronic structure modifications, playing a significant role in DRM reactions. The Ni-CeSiO_{2-x} interface promoted the CO₂ adsorption and activation, enabling its rapid dissociation into CO and O*. The oxygen vacancies in CeO_{2-x}, associated with the generation of Ce³⁺ species, render CeO_{2-x} an electron donor, enhancing the reducibility of the support. These electrons transfer to the lowest unoccupied molecular orbital (LUMO) of CO₂ molecule, weakening the C=O bond. Furthermore, electron transfer induces a bent configuration of the adsorbed CO₂, significantly elongating the C=O bond and thereby reducing the dissociation energy barrier. DFT calculation by Qu et al.^[155] indicated that the Gibbs free energy barrier for direct dissociation of CO₂ on Ru cluster sites was relatively high (2.46 eV), while with oxygen vacancy assistance, the barrier was significantly reduced to 1.81 eV. Based on the CO₂ temperature-programmed desorption (CO₂-TPD) results, Dostagir et al.^[156] observed that, in the Co-doped ZrO₂ catalysts (CoZrO_x) where Co doping increased the oxygen vacancies, the intensity of the desorption peak corresponding to chemisorbed CO₂ (320 °C) enhanced with increasing cobalt loading, demonstrating that oxygen vacancies were crucial for CO₂ chemisorption. The dissociation of CO₂ on oxygen vacancies into CO and O* avoided hydrogen-assisted activation that produced COOH* intermediates, the formation of which was a primary factor driving the RWGS reaction^[157]. Therefore, the activation of CO₂ via oxygen vacancies can also suppress the occurrence of RWGS reaction.

3.3 Carbon deposition suppression

The carbon deposition rate is a key index to evaluated the

DRM performance, which determine the operational lifespan of the catalysts^[42]. Regulating oxygen vacancies can effectively suppress the carbon deposition, which involves promoting the generation of active oxygen species and enhancing lattice oxygen mobility, thereby accelerating the elimination of deposited carbon.

During the DRM process, oxygen vacancies serve as active sites in lowering the dissociation barrier of the C=O bond, promoting CO₂ adsorption and activation into CO and O*. The generated O* immediately oxidized the deposited carbon, thereby accelerating the Boudouard reaction ($C + CO_2 \rightarrow 2CO$)^[115]. Singha et al.^[158] increased the Ce³⁺ concentration (32.8%) in CeO₂ via Pd doping, generating a high density of oxygen vacancies, where CO₂ dissociation occurred and the active oxygen was dynamically replenished. Simultaneously, the oxygen vacancies act as storage sites for active oxygen on the CeO₂ support surface. When CH₄ dissociation on Pd nanoparticle surfaces occurred to generate carbon deposit precursors, the active oxygen supplied from the adjacent oxygen vacancies could directly oxidize the carbon species. No graphitic carbon species were detected in the spent catalyst. The TGA/DTG analysis showed a very low carbon deposition (<1%), confirming the effective suppression of carbon deposition by oxygen vacancies.

Furthermore, oxygen vacancy enhances the mobility of lattice oxygen by weakening the metal-oxygen bond strength, thereby accelerating the oxidation of carbon deposited on the catalyst surface. In metal oxides, doping with metal cations altered the crystal structure and creates lattice defects which increased the oxygen desorption capacity and oxygen vacancy concentration, consequently promoting the oxygen migration within the crystal structure^[159]. During the reaction, the formation and filling of oxygen vacancies constituted the core mechanism driving lattice oxygen migration. Once oxygen vacancies were formed, lattice oxygen and metal cations rapidly migrated to establish a new equilibrium (until the concentration gradient dissipates)^[160]. Ren et al.^[161] observed a significant increase in oxygen vacancy concentration after doping La into CoMn₂O₄. The desorption temperature of surface lattice oxygen markedly decreased in the doped catalyst (with enhanced peaks at 300–500 °C in He-TPD), while the bulk lattice oxygen desorption peak shifted to lower temperatures (with increasing peak intensity at >500 °C and lowering peak temperature). H₂-TPR results showed a significant increase in the intensity of the low-temperature reduction peak (200 °C), indicating enhanced extraction of surface lattice oxygen. DFT calculations confirmed that the oxygen vacancy formation energy (E_{OV}) decreased from 1.68 eV in CoMn₂O₄ to 1.47 eV in CoMn_{1.9}La_{0.1}O₄, facilitating lattice oxygen migration. Shahnazi et al.^[140] developed a porous LaNi_{0.6}Mn_{0.4}O₃ perovskite catalyst for DRM, in which Mn substitution induced oxygen vacancy formation by creating Mn³⁺/Mn⁴⁺ mixed valence states, promoting the lattice oxygen mobility. The sufficient active oxygen transported from the lattice oxidized the carbon accumulated on the

catalyst surface, effectively suppressing the carbon deposition.

4 Conclusion and outlook

The DRM faces critical challenges of carbon deposition and active metals sintering. The introduction of oxygen vacancies is essential to address these challenges. This review focuses on the regulation strategy of oxygen vacancy and the roles of oxygen vacancy in DRM reactions. Currently, four primary regulation strategies are proposed: thermal treatment or reductive treatment, field control, ion doping and interface engineering. By rationally selecting the strategies and aligning with key DRM reaction steps and molecular transformation processes on catalyst surfaces, oxygen vacancy can be precisely introduced to provide highly active sites for DRM reactions. Mechanistic analysis reveals that oxygen vacancies promote the reactions via three main ways: (1) synergistically enhancing CH₄ activation at metal-support interfaces; (2) serving as active sites to directly adsorb and activate CO₂, thereby lowering the activation energy barrier; (3) facilitating the generation and migration of active oxygen species to accelerate the oxidative elimination of carbon deposits.

Precise regulation of oxygen vacancy represents an effective strategy for developing high-activity and high-stability DRM catalysts. Nevertheless, current research still faces challenges as: (1) The mechanistic understanding of oxygen vacancies in DRM requires combined experimental and theoretical approaches to elucidate their roles at atomic and electronic levels; (2) Oxygen vacancies are prone to annihilation during reactions. Achieving the spontaneous regeneration with external fields to enable cyclic participation represents a promising research direction; (3) The rational design of oxygen vacancies is still inadequate, necessitating targeted control of the distribution to fully exploit the functions in the reaction; (4) The synergistic effects between oxygen vacancies and other factors, such as active components, support properties (e.g. acidity, basicity) and promoters, need further in-depth exploration. With the multi-dimensional and cross-scale precise regulation, the design of ideal DRM catalysts with high activity, stability will be realized ultimately.

Declaration of Competing Interest

The authors declare no conflict of interest.

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甲烷干重整反应中催化剂氧空位作用的研究进展

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摘 要: 温室气体(主要是 CO₂ 和 CH₄)的大量排放加剧全球气候变暖。甲烷干重整反应(DRM, CH₄ + CO₂ → 2CO + 2H₂)可实现这两大温室气体的协同转化与资源化利用, 具有重要的环境与能源意义。然而, DRM 过程面临催化剂积炭和活性金属烧结的挑战, 严重制约了其反应性能与长期稳定性。氧空位作为金属氧化物中常见的晶格缺陷, 可通过调控催化剂表界面性质以促进 DRM 性能。本工作综述了近十年的 DRM 研究进展, 总结了其面临的主要问题, 指出催化剂氧空位在抑制积炭、防止烧结等方面的重要作用, 并结合其形成机制与调控策略归纳了氧空位在 DRM 反应中的作用机理。以上认识有助于为设计和合成高性能的 DRM 催化剂提供重要理论依据。

关键词: 甲烷干重整反应; 积炭; 氧空位; 甲烷活化; 二氧化碳活化

中图分类号: O643.36; TQ032.4

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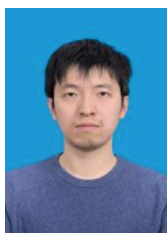
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