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Reasonable active site design for promoting water dissociation and carbon monoxide activation in a low-temperature water-gas shift reaction

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To solve the energy crisis, the water–gas shift reaction (WGS) has been systematically studied for the effective production of pure hydrogen and removal of hazardous carbon monoxide. In typical industrial applications, the WGS commonly consists of two individual processes: a high-temperature shift reaction (320–450 °C) for a high reaction rate and a low-temperature shift reaction (150–300 °C) for high conversion due to their intrinsic thermodynamic and kinetic properties. Owing to the complexity of a traditional catalytic system, researchers have made great efforts to seek low-temperature (<300 °C) reaction catalysts with better performance and energy efficiency. Recent advancements have mainly focused on the correlation of the catalyst components and reactivities for low-temperature WGS. In contrast, this work considers different catalyst design ideas for enhancing the low-temperature WGS performance based on the combination of two half-reactions, namely, water dissociation and carbon monoxide activation, which occur on different active sites. Therefore, only an intentional design of the active sites for the two half-reactions can constitute an efficient catalyst. This review aims to summarize the advances made in the recent decade and provides some direction toward possible active site designs for future investigation.

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1 Introduction

Hydrogen (H₂) is widely recognized as a potential clean energy carrier that may help reduce greenhouse gas emissions. A number of hydrogen production processes have been developed and studied by scientists. Among them, the water–gas shift reaction (WGS) is considered an efficient way to produce and purify H₂.¹ It has been applied to many industrial processes, such as natural gas reforming, ammonia synthesis² and fuel cell applications.^{3,4}

The history of the WGS can be traced back to the 1780s, and its reaction is depicted in the following equation: CO + H₂O ↔ CO₂ + H₂ ($\Delta H_r^\theta = -41.1 \text{ kJ mol}^{-1}$). As an exothermic reaction, it is thermodynamically suitable at low temperatures with strict kinetic limits. Therefore, the conventional WGS system contains two adiabatic stages: a high-temperature stage with an Fe–Cr catalyst for a high reaction rate and a low-temperature stage with a Cu–Zn–Al catalyst (<300 °C) for the forward conversion.^{5,6} The reaction was not applied until 1888 when Mond utilized it for hydrogen production for fuel cell application. In 1914, Bosch and Wild applied the reaction in the

industrial production of hydrogen.⁷ Because of the toxicity of Cr and the high energy consumption, scientists struggled to optimize the performance of Fe-based catalysts by introducing different kinds of adjuvants until the 1980s.⁸ However, the complexity and energy consumption of the system still motivated scientists to develop new catalytic systems.

Encouraged by the proposal of an associative mechanism and redox mechanism in 1920 and 1940,¹ scientists realized that the reaction is mainly induced by the interfacial sites between loaded metals and the supports on heterogeneous catalysts.⁹ Increasing kinds of metal oxides have been revealed to have decent water dissociation performance and mild reaction conditions, such as Al₂O₃,^{10,11} CuFe₂O₄,¹² ZrO₂,¹³ and CeZrO₄.¹⁴ Also, the catalytic performance can be assisted by additives such as ZnO,¹⁵ Nb₂O₅,¹⁶ which adjust the physical properties and electronic structure of the catalysts. Besides metal oxides, some advanced functional materials were noted by researchers for their exclusive properties. For example, noble metal-based catalysts with α -MoC as a carrier were investigated in the last few years for their excellent water dissociation activity.¹⁷

With the development of catalyst design strategies,¹⁸ noble metal-based catalysts have attracted much attention in this field.^{19,20} With their moderate adsorption capacity for CO, metals like Au, Pt, Ru, Pd, and Ag are frequently selected as active components for WGS.^{21,22} Furthermore, in 2011, Zhang *et al.* firstly realized a single atom catalyst (SAC) that consisted

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of single Pt atoms uniformly dispersed on a FeO_x support.²³ With their decent catalytic activity and new reaction mechanisms, SACs were further explored for better synthesis methods and catalytic properties, and regarded as promising catalysts for WGS. ²⁴ However, in some occasions, the nanoparticles showed significant catalytic activity, whereas the single atoms acted as spectators.²⁵ Thus, it is necessary to differentiate the function of nanoparticles and single atoms in different catalyst systems for CO activation.

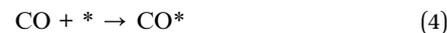
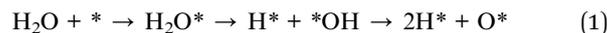
Up to now, most WGS reviews have mainly focused on the correlation between different catalyst structures and performances, like noble metal catalysts, transitional metal-based composites and others. For example, Zhou *et al.* discussed different sorts of supported metal nanoparticle catalysts for WGS,¹ and Chen *et al.* provided a detailed summary of noble metal-based single-atom catalysts for WGS.²¹ Pal *et al.* provided a systematic review for transitional metal-based catalysts,²⁶ and Lee *et al.* focused on the impacts of reaction conditions and catalysts on WGS involving different feed gases.²⁷ Some other reviews with their perspectives and proposed catalyst and active site design approaches have been summarized in Table 1. These reviews demonstrated the comprehensive understanding of different catalytic systems, and summarized the promising catalysts in terms of material composition. However, to our best knowledge, few reviews provided a discussion based on an understanding of designing the active site. This motivated us to summarize the first-class catalyst designs, and attempt to find some possible correlation between the active site structure and promising catalytic performance. More importantly, based on the proposal of surface catalytic theory²⁸ and the specificity of the WGS, this review considers it as a combination of two principal half-reactions: water dissociation and CO activation. This review also emphasizes that most of the excellent catalyst design strategies focus on at least one of the half-reactions, whose importance was hardly acknowledged in previous reviews, as shown in the last row of Table 1. Additionally, with the knowledge that the deactivation of catalysts is still an inevitable phenomenon under actual situations, some active site design strategies were directed toward inhibiting deactivation, which is worth discussing with their specific examples in this review.

2 Mechanisms

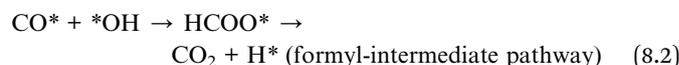
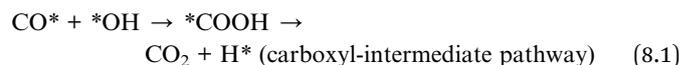
Studies on the mechanism of WGS have been conducted for a few decades because it is complex and still remains controversial. The most recognized mechanisms can be roughly divided into two categories, mainly involving different routes of water dissociation and carbon monoxide activation: redox mechanism and associative mechanism.

The redox mechanism was first proposed by Temkin in 1949.²⁹ The shift reaction goes through a redox cycle, as shown in the schematic in Fig. 1a and eqn (1)–(5), where * represents the active site. More specifically, H₂O will be directly adsorbed and activated on the active sites to be thoroughly dissociated into H₂ and O* (light blue balls: H atoms; dark blue balls: O atoms; dashed circle: oxygen vacancy; grey rectangle: support)

and consume much energy. Simultaneously, CO will be activated and react with the lattice oxygen to generate CO₂, leaving an oxygen vacancy which will be supplied by the O* from H₂O (black balls: C atoms; light yellow balls: low valence state noble metals; dark yellow balls: high valence state noble metals; yellow ellipse: noble metal sites). The reduction process is entirely independent from CO oxidation, and needs enough activation energy to be thoroughly dissociated. Therefore, this mechanism is more favored by the high-temperature shift reaction and active sites with better reduction capacity.



With the research trend for the lower reaction temperature, the associative mechanism based on the Langmuir–Hinshelwood model has gradually attracted much attention. As shown in the schematic in Fig. 1b, different from the redox mechanism, the water dissociation will only be partially dissociated into H* and *OH. The *OH will further react with CO* to generate important free radical intermediates, such as carboxyl (*COOH) and formyl (HCOO*). Thus, the reduction and oxidation processes are not independent, but associative. The intermediates will decompose into CO₂ and an extra H*, which can combine with the former H* to produce H₂. This mechanism described by eqn (6)–(9) revealed that the *OH could directly react with activated CO and form important intermediates, which could be further reformed into CO₂ and H₂, rather than undergo indispensable exhaustive dissociation into O* and H* with higher activation energy, resulting in a lower reaction temperature.



Both mechanisms above could be plausible under different conditions with different rate-determining steps (RDS). For example, WGS on classic high-temperature catalysts like the Fe₃O₄ composite tends to follow the redox mechanism. Huang *et al.* conducted a detailed density functional theory calculation using the Fe₃O₄ (111) surface with the Fe_{oct2-tet1} terminal, and proved that the redox mechanism was the primary reaction route with the RDS of CO₂ desorption because of the





Table 1 Summary of the review perspectives and proposed catalyst and active site design approaches of some published reviews and this work

Title	Published year	Review perspective	Proposed catalyst and active site design approach	Ref.
For more and purer hydrogen-the progress and challenges in water gas shift reaction	2023	Catalyst type and catalyst structure	Low and high temperature shift reaction catalysts Sulfur-tolerant and wide temperature shift reaction catalysts Nano catalysts and single-atom catalysts design Surface structure design Fe-based catalysts Cu-based catalysts Ni-based catalysts Co/Mo-based catalysts	1 8
The water gas shift reaction: catalysts and reaction mechanism	2021	Catalyst component	Noble metal-based catalysts Single-atom catalysts with reducible oxide, irreducible oxide, carbides and nitride supports	21
Noble metal-based single-atom catalysts for the water-gas shift reaction	2021	Catalyst component and active species (noble metal-based catalysts)	Active metal species (positive state and metallic state) The influence of supports The influence of the loading method and loading amount	22
Platinum-based catalysts in the water gas shift reaction: recent advances	2020	Catalyst component and mechanism study (platinum-based catalysts)	The influence of the promoter addition Kinetic and mechanism study of Pt-based catalysts	7
The review of Cr-free Fe-based catalysts for high-temperature water-gas shift reactions	2013	Catalyst component (Fe-Cr-based catalysts)	Iron oxide-chromium oxide catalysts Chromium-free catalysts	
Water gas shift catalysis	2009	Catalyst component	Iron oxide-chromium oxide and chromium free catalysts for the high-temperature shift reaction Cu-Zn-Al and promoted Cu catalysts for low-temperature shift reaction Sulfur-tolerant catalysts Noble-metal-based catalysts Monolith-coated catalysts for fuel cell	6
The water-gas shift reaction	2006	Catalyst component and kinetic study	Iron-based shift catalysts Copper-based shift catalysts Cobalt molybdenum-based shift catalysts	
Reasonable active site design for promoting water dissociation and carbon monoxide activation in a low temperature water-gas shift reaction	—	Mechanism summary and active-site-design strategy for the two half-reactions of WGSR	Mechanism study of WGSR Active site design strategies for H ₂ O dissociation Active site design strategies for CO activation	This work

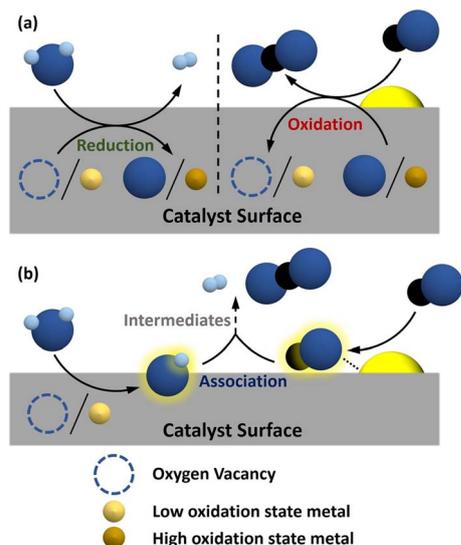


Fig. 1 (a) Process schematic of the redox mechanism. (b) Process schematic of the associative mechanism.

distinguishing water adsorption ability of the $\text{Fe}_{\text{Oct}2}$ sites.³⁰ Nevertheless, noble metal catalysts with abundant well-designed interfacial active sites allowed for the easy combination of CO^* and $^*\text{OH}$, leading to the associative mechanism. Vecchiotti *et al.* studied the Pt/ CeO_2 catalyst *via* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Their results demonstrated the existence of HCOO^* and COO^* species, which are typical intermediates of the associative mechanism. They also mentioned that in contrast to the previous research, the activation of water molecules in the WGS mechanism is not the RDS in this system.³¹ These previous works emphasized the complexity of the reaction mechanisms with various catalytic systems, suggesting that the reasonable design of the interfacial site that initiates the associative mechanism might be a common solution for the first-class catalysts. Considering that the water dissociation and CO activation are both inevitable for WGS, these two vital processes could be thinking pivots for future design strategies of the active site, which will be further discussed in the following section of the review.

3 Active site design

3.1 Water dissociation

Water dissociation is a key process of H_2 production and active intermediate generation in WGS. Metal oxides have been widely studied in laboratories and industrial processes for water dissociation. As a kind of common defect site on the surface of oxide catalysts, oxygen vacancies are regarded as the reaction sites, and it has been extensively investigated because of its high activity and stability.³² Mostly, the activity of oxygen vacancies can be influenced by two factors: concentration and species. Some metal sites can perform water dissociation by intentional catalyst design. Therefore, it is worthwhile to summarize the design ideas for active sites, which is shown in Fig. 2.

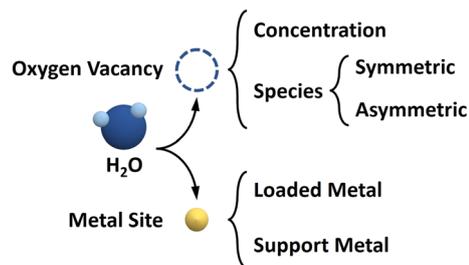


Fig. 2 Summary of the active site design for H_2O dissociation.

3.1.1 Oxygen vacancy

3.1.1.1 Concentration of the oxygen vacancy. For reducible metal oxide supports, such as CuO ,³³ Fe_2O_3 ,³⁴ TiO_2 ,³⁵ CeO_2 (ref. 36) and others, the concentration of the oxygen vacancy can be easily controlled by synthesis and pretreatment methods, such as element doping. Jeong *et al.* prepared a series of $\text{Cu-CeO}_2\text{-ZrO}_2$ materials with different Ce/Zr ratios. They found that by shrinking the lattice, $\text{Cu-Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ contained a larger amount of oxygen vacancies and exhibited very stable WGS activity at about 300 °C, which is correlated with the enhancement of the oxygen mobility. This work also mentioned that compared with the tetragonal phase of $\text{Cu-Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, the cubic phase shows higher WGS activity because it helps to achieve a higher concentration of oxygen vacancy.¹⁴ Homogeneously, the design of La-doped CeO_2 (ref. 37 and 38) and Ga-doped Pt/ CeO_2 (ref. 31) achieved a high concentration of oxygen vacancies, thereby promoting the catalytic activity for WGS. Therefore, element doping is regarded as a valid performance-promoting pathway.³⁹ Similarly, the synthesis condition of the catalysts can change the O_v concentration, which will be further discussed.

In summary, there are direct evidences showing that materials with more oxygen vacancies tend to be more active in the water dissociation process. This is because oxygen vacancies serve as the main active site of water dissociation and can stabilize the $^*\text{OH}$, which enhance the WGS activity.

3.1.1.2 Species of oxygen vacancy. Apart from gaining a higher concentration of oxygen vacancies, recent advanced works mainly focus on the species of oxygen vacancy. Zhou *et al.* successfully formed an asymmetric environment of oxygen vacancies by element doping.³² For example, the group doped Bi in CeO_2 and modified the surrounding of the oxygen vacancy by forming a distorted tetrahedral geometry of $\text{Bi-O}_v\text{-Ce}_3$. In comparison with traditional symmetric clusters like $\text{Ce}_2\text{-O}_v\text{-Ce}_2$, the asymmetric oxygen vacancy facilitates both the adsorption and desorption processes (Fig. 3a).⁴⁰ It is predictable that such asymmetric oxygen vacancy can be applied to some structure-sensitive reactions like the activation of H_2O in WGS.

Researchers obtained a Zn-Ti mixed oxide support from a Zn-Ti layered double hydroxide precursor. Because of the strong metal-support interaction, after loading Au nanoparticles, the electrons will transfer from the TiO_{2-x} overlayer to Au atoms to form the asymmetric oxygen vacancy site $\text{Au}^{\delta-}\text{-O}_v\text{-Ti}^{3+}$, as shown in Fig. 3b. An in-depth analysis of the X-ray



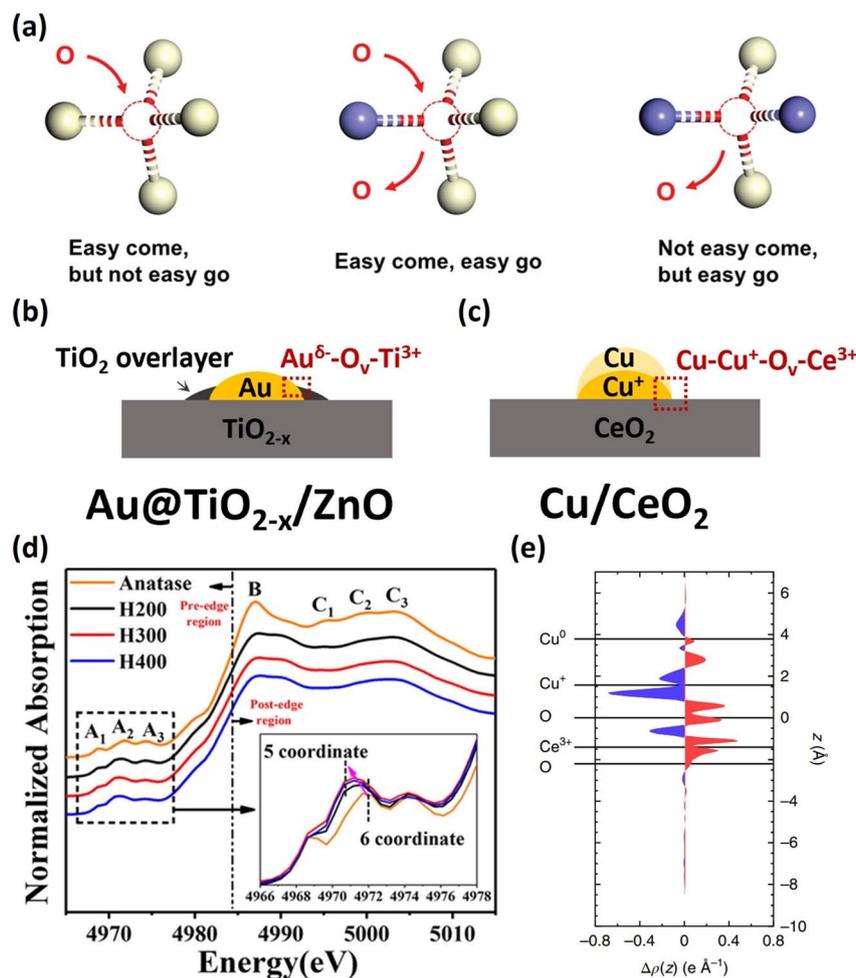


Fig. 3 (a) Schematic of the relationship between the microstructure of the oxygen vacancy and its redox property. (b) Diagram of the active site structure on Au@TiO_{2-x}/ZnO. (c) Diagram of the active site structure on Cu/CeO₂. (d) Normalized XANES spectra of Au@TiO_{2-x}/ZnO with different synthesizing conditions, providing direct evidence for the existence of an asymmetric oxygen vacancy site (Au^{δ-}-O_v-Ti³⁺). (e) Plane-integrated bonding charge $\Delta\rho(z)$ as a function of position across the Cu-Ce interface. Red and blue areas represent charge accumulation and depletion, respectively. (d) Copyright © 2019, American Chemical Society. (e) Copyright 2019, The Author(s), under exclusive license to Springer Nature Limited.

absorption near edge structure (XANES) results shown in Fig. 3d also provided convincing evidence of the asymmetric oxygen vacancies. During the WGS, both Au^{δ-} and O_v species of the site directly participate in the H₂O dissociation process. Moreover, characterization results showed that the active oxygen vacancy also accelerated the CO chemisorption and H₂O dissociation.⁴¹ The group also reported a TiO_{2-x}-modified Ni catalyst with tunable Ni-TiO_{2-x} interaction, and the reaction process over Ni^{δ-}-O_v-Ti³⁺ site was discussed. By the *in situ* time-resolved DRIFTS results, a new redox mechanism was revealed, which can be illustrated by two main steps: (1) the cleavage of the O-H bond in the H₂O molecule at the asymmetric oxygen vacancy site to generate H₂ and transform Ni^{δ-}-O_v-Ti³⁺ into Ni^{δ+}-O-Ti⁴⁺; (2) the reaction between CO and Ni^{δ+}-O-Ti⁴⁺ to form CO₂ and Ni^{δ-}-O_v-Ti³⁺. These works focus on the establishment of an asymmetric active oxygen vacancy, and provide a new possible solution for the construction of high-efficiency heterogeneous catalytic systems.^{42,43} Many other works have

successfully synthesized composites with asymmetric oxygen vacancies, which also exhibited LT-WGSR performance.⁴⁴

Additionally, based on the design of the asymmetric oxygen vacancy, Chen *et al.* synthesized a bilayer Cu covered on CeO₂ (structure illustrated in Fig. 3c). The bottom layer of Cu can donate an electron to Ce⁴⁺ and coordinate with an O_v to form a Cu⁺-O_v-Ce³⁺ site, and the top layer of Cu can bond with the underlying Cu⁺ to modify the site to Cu⁰-Cu⁺-O_v-Ce³⁺. Such interfacial active sites can optimize the plane-integrated bonding charge shown in Fig. 3e around the Cu⁺ and O_v sites, thereby enhancing the CO adsorption and H₂O dissociation capacity.⁴⁵

Although the oxygen vacancy concentration is an important factor for the catalytic performance, its optimization is capped by the stability requirement of catalysts. Designing better oxygen vacancy species like the asymmetric oxygen vacancy is more crucial for achieving a more efficient catalytic system, and can fundamentally reveal the H₂O dissociation mechanism.



3.1.2 Metal site. Except for oxygen vacancies, metal sites can also serve as the core sites for water dissociation. For traditional metal oxide catalysts, the loaded metal can be the water adsorption sites, and the dissociation capacity can be enhanced by the establishment of interfaces between loaded metals and supports. Lucas *et al.* designed a Ni/Al₂O₃ composite and closely tracked the oxygenate species (O* and *OH) from the water dissociation process at interface sites in contrast to the bare Ni surface. They found that the surface species are only available at the interfacial sites. The results demonstrated that the combination of a metal and support can be properly adjusted to obtain better water dissociation activity, and the WGSR is a typical interface-sensitive reaction.¹¹

Many studies center on MoC for the production of high-purity H₂ have been carried out and achieved intriguing advances.^{46,47} Other oxides, like SiO₂ or TiO₂, cannot dissociate H₂O or can easily dissociate H₂O into H⁺ and OH⁻, respectively. Mass spectral results have shown that after being adsorbed on α -MoC, H₂O can be instantly dissociated into H* and *OH at almost room temperature, which are both important intermediates for WGSR.⁴⁸ Researchers composed a review to summarize the efforts they made on the development of M/MoC. The review mentioned that the exceptional catalytic performance of

MoC originated from the incorporation of carbon atoms at the interstitial sites, which endows MoC with higher density of states near the Fermi level and proper electronic interaction between carbon atoms and metals. Such electronic interaction can optimize the adsorption energy of H₂O to a moderate level, where the H₂O molecule can be solidly adsorbed on the surface and simultaneously dissociated by the energy released from adsorption.⁴⁹ Furthermore, Zhang *et al.* designed Pt₁-Pt_n/ α -MoC (morphology and structure shown in Fig. 4a) based on Pt₁/ α -MoC with promising activity but disappointing stability, and obtained better CO conversion than the Cu-Zn-Al model catalyst and other MoC-based catalysts given in Fig. 4b. The extra Pt clusters can change the interfacial structure by covering the redundant exposed surfaces of Pt₁/ α -MoC to prevent the oxidation of α -MoC by the excess *OH, because the *OH is far from the interface of Pt and α -MoC cannot react with the activated CO. Furthermore, transient kinetic analysis (TKA) of Pt₁-Pt_n/ α -MoC revealed that except for H₂O dissociation, CO can also be dissociated at low temperature to generate an extra carbon atom, which can then react with activated H₂O to produce an additional 35% of H₂ in the total H₂ production yield. The reaction routes are summarized in Fig. 4c. Using the isotope labelling method, this work found some different

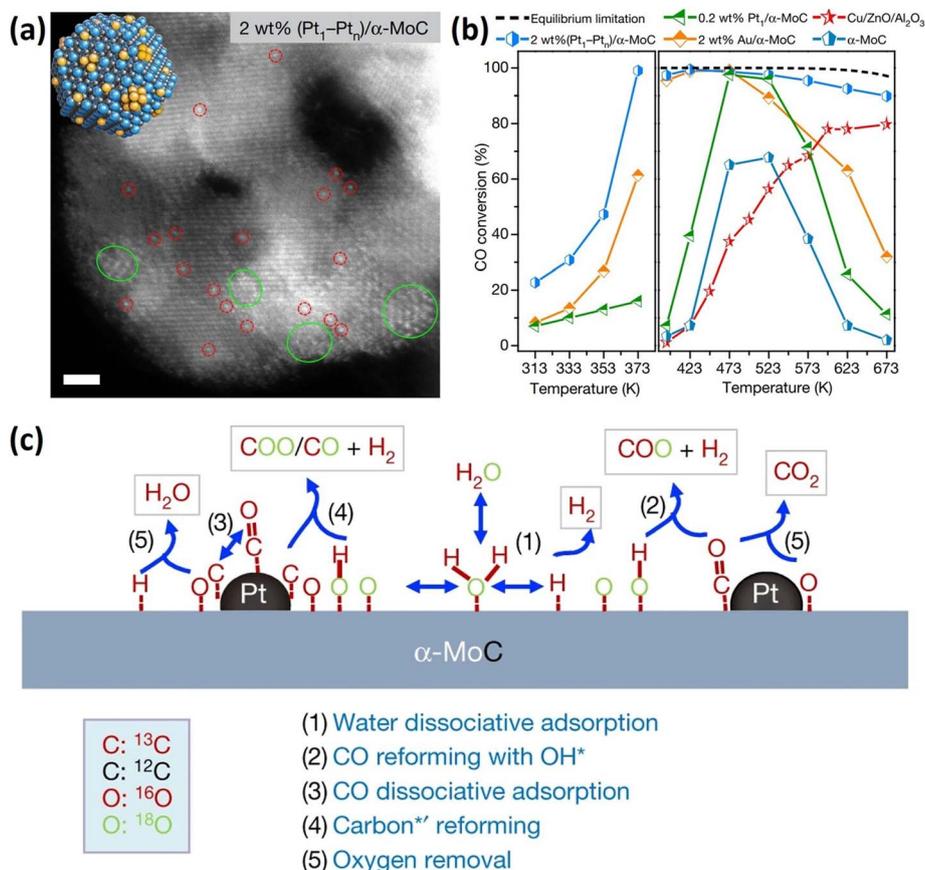


Fig. 4 (a) TEM image and a diagram of the distribution of Pt single atoms and clusters on Pt₁-Pt_n/ α -MoC. (b) CO conversion over different catalysts at various temperatures. (c) Schematic of the reaction routes for the WGS reaction over Pt/ α -MoC: (1) water dissociation; (2) the conventional WGS reaction routes (redox or associative intermediate mechanism); and (3)–(5) the unconventional WGS reaction routes. The asterisk represents the active site. Copyright 2021, The Author(s), under exclusive license to Springer Nature Limited.



reaction routes based on the dissociation of CO. This meant that the combination of a noble metal and α -MoC can not only make full use of the water dissociation capacity of MoC, but also enhance the CO activation process, resulting in a greater active oxygen species supplement from CO dissociation.⁵⁰ The exceptional performance of α -MoC-based catalysts provides a possibility for future research to investigate the electronic structure optimization of metal sites to improve their intrinsic H₂O dissociation ability, but there might be still many challenges to improving the current performance of the α -MoC-based catalysts.

MoC has been proved as an outstanding H₂O dissociation material. Other carbides like TiC^{51,52} and Co₂C⁵³ are also under investigation. Additionally, metal-organic frameworks (MOFs) have been predicted as promising supports with a controllable porous structure and changeable open metal sites (OMSs).⁵⁴ However, there have been limited MOFs applied in LT-WGSR because of their instability in vapor atmosphere. Recently, Rivero-Crespo *et al.* synthesized a robust and highly crystalline MOF, which can stabilize Pt⁺ single atom sites by a water cluster. The work reported a double water attack mechanism for the MOF to give CO₂, in which both oxygen atoms in CO₂ come from H₂O. However, the synthesis of the MOF is complex and time-consuming, requiring further development.⁵⁵

The optimization of metal sites mainly focuses on adjusting the electronic structure by adjusting the surrounding environment. Regardless of the loaded metal sites or support metal sites, it is vital to reveal the volcano-type relationship between metal sites and surrounding atoms, which can provide a valid active site design reference for future research.

3.2 Carbon monoxide activation

Meanwhile, carbon monoxide activation is essential for CO elimination in WGSR. Sometimes, an oxygen vacancy can serve as a CO adsorption site at the interfacial zone between the loaded metal and supports. However, in most LT-WGSR processes, d-block elements such as noble metals can serve as effective CO activation sites by cooperating with the supports.^{56,57} Opinions on how to optimize the activation sites for better performance remains unclear and contradictory. In this section, optimizing the geometric structure and electronic structure are considered as two feasible choices for the enhancement of d-block element performance (shown in Fig. 5), which will be discussed below.

3.2.1 Geometric structure. The geometric structure can directly affect the catalytic performance by changing the interaction between the catalysts and substrates. For instance, metal loaded on supports can be controllably synthesized with various

sizes, such as nanoparticles, clusters and single atoms.⁵⁸ Based on the size effect, different sizes exhibited different catalytic performances and stabilities. In addition, the exposed facet of the catalysts is a key factor of the catalytic performance.⁵⁹ Thus, it is essential to summarize the merits and drawbacks of different geometric structures to provide clear strategies for reference.

Generally, it is well-known that with the single atom catalysts providing the largest quantity of interfacial sites, it should exhibit an increase in efficiency for WGSR. However, various studies have aimed to identify the active sites of CO activation and prove that nanoparticles performed better than single atoms by time-dependent infrared spectroscopy. The result proved that only CO adsorbed on Pt nanoparticles could be activated and participate in the reaction (demonstrated in Fig. 6a).²⁵ Therefore, with decent catalytic performance and stability, they have been widely investigated for LT-WGSR since 1996.^{19,34} Andreas *et al.* designed TiO₂-supported Pt catalysts, and used density functional theory (DFT) calculations and microkinetic modeling to clarify the activity of the three-phase boundary. Their results suggested that the dominant catalytic process on Pt₈/TiO₂(110) should be the redox pathway, and the better activity of the three-phase boundary can be correlated with the reduced CO adsorption energy on Pt sites and increased number of oxygen vacancies.⁵⁹ Moreover, Zhao *et al.* synthesized a Pt-TiO₂ composite with ultra-small Pt nanoparticles encapsulated in sub-50 nm hollow TiO₂ nanospheres. With the decrease of the Pt particle size, the catalyst shows a much higher turnover frequency (TOF) value, which can be attributed to the size-dependent variation in the electronic structure of the Pt species and the sintering prevention effect from TiO₂ encapsulation. This work provided a valid synthesis strategy for loading Pt on the internal surface of TiO₂ nanospheres, and revealed a creative catalyst design in which the deactivation of Pt could be avoided by controllable support encapsulation.⁶⁰ CeO₂ is a typical reducible support, and is frequently selected as the support of noble metals such as Au.⁶¹ Fu *et al.* compared the activity of Au nanoparticles and clusters on CeO₂, and found that the abundant interfacial sites between Au clusters and CeO₂ induced superior catalytic performance when compared to Au nanoparticles during WGSR.⁶² In short, the size of the loaded metals directly determines the number of active sites.

Zhang *et al.* synthesized Pt clusters and single atoms by changing the loaded facets shown in Fig. 6b. They closely investigated the CO adsorption on Pt by IR spectroscopy, as given in Fig. 6c. Zhang *et al.* proved that the binding energy between CO and Pt nanoparticles is weaker than that between CO and Pt single atoms by the blue shift of the PtO₄²⁺ peak compared with the Pt^{δ+} and Pt⁰ peaks. This means that single atom catalysts (SACs) may show promising research value.⁶³ Therefore, for WGSR, single atom sites with appropriate geometry design can still effectively activate CO for further reaction with other intermediates, such as *OH. Lin *et al.* synthesized Ir₁/FeO_x SAC for WSGR, whose performance is one order of magnitude higher than its cluster and nanoparticle counterparts.⁶⁴ Furthermore, Liang *et al.* studied the redox

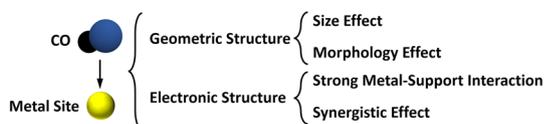


Fig. 5 Summary of the active site design for CO activation.



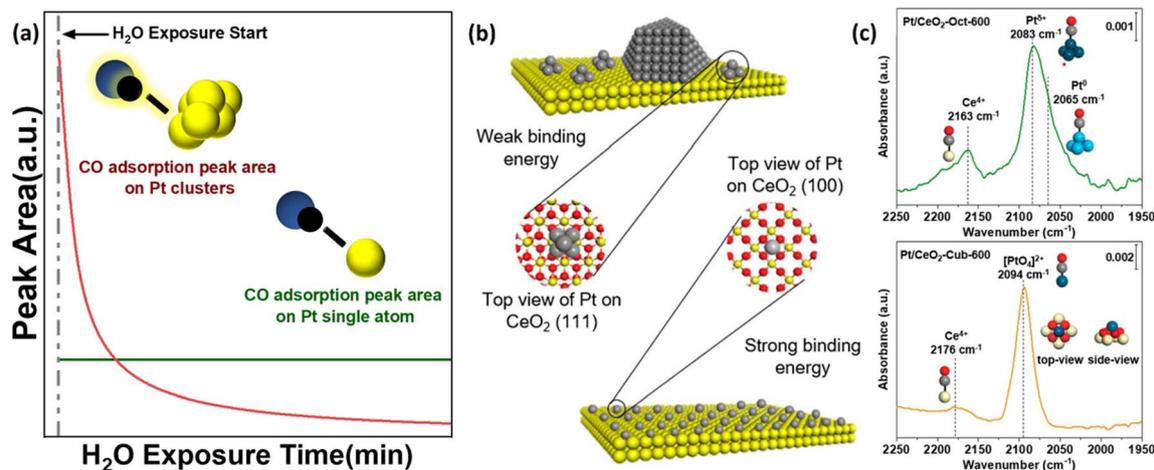


Fig. 6 (a) Time-dependent IR spectra of CO adsorbed on 1 wt% Pt/SiO₂ upon H₂O exposure. Peaks in the green zone correspond to CO adsorbed on Pt single atoms, and the peaks in blue zone correspond to CO adsorbed on Pt nanoparticles. Diagrams on the right side show the CO activation status on different sites. (b) Diagram of the Pt cluster and single atom on different CeO₂ facets. (c) *In situ* CO-DRIFTS of the Pt/CeO₂ samples, showing the bonding energy differences between CO and Pt with different sizes. Copyright © 2023, American Chemical Society.

mechanism of Ir₁/FeO_x for WGSR by detailed calculation and experiments, and proved that CO will be adsorbed and activated on the Ir single atom with a dual active site of Fe³⁺-O²⁻-Ir²⁺-O_v.⁶⁵ Guan *et al.* (from the same group) also fabricated Rh₁/TiO₂ SAC, and obtained an overall CO conversion of ~95%. This showed that there are multiple choices of noble metal for LT-WGSR.⁶⁶ Some kinds of SACs have also broken the traditional model that noble metal sites are the actual CO activation sites. Sun *et al.* designed an Ir₁/α-MoC catalyst for LT-WGSR. Different from other works, they revealed that the great performance does not originate from the direct participation of Ir single atoms in the CO activation. The Ir single atoms served as a promoter that assisted Mo sites to activate CO. With kinetic measurements and theoretical calculation, they proved that the addition of Ir single atoms effectively changed the electronic property of Mo sites, resulting in an obvious reduction of the activation energy (*E_a*).⁶⁷ These works provide abundant possibilities for the utilization of SACs in future research studies with rational catalyst design to avert excessive adsorption.

As for the influence of exposed facets, Zhang *et al.* synthesized uniform cubic, dodecahedral and octahedral Cu nanocrystals by partial reduction of the Cu₂O nanocrystal. They found that the cubic Cu nanocrystal exposed (100) facets were more active than the dodecahedral Cu nanocrystal exposed (110) facets for H₂O dissociation and CO activation, and the octahedral Cu nanocrystal exposed (111) facets were inactive. By theoretical calculation results of the surface structures and H₂O adsorption energy change, it was confirmed that the formate species adsorbed on Cu (111) needed to overcome a large barrier to decompose, leading to the accumulation of formate and finally covering the active sites. Therefore, the Cu (111) facets are initially active, but is self-poisoned during the reaction.⁶⁸ On this basis, the research group studied ZnO/Cu in detail, and revealed that the catalysts would undergo an *in situ* restructuring process during WGSR to form the Cu-hydroxylated ZnO ensemble.⁶⁹ These results suggested that controlling the

exposed facet of crystalized catalysts like traditional Cu-based catalysts might also be a potential strategy for performance optimization.

As shown above, a reasonable geometric structure is important to achieve better catalytic performance. The size and morphology effect should be investigated in detail and discussed based on prior experience and future works, with the goal of attaining some universal catalyst design rules.

3.2.2 Electronic structure

3.2.2.1 Strong metal-support interaction (SMSI). The strong metal-support interaction (SMSI) was first found by S. J. Tauster and S. C. Fung in 1978.⁷⁰ The interaction broadly exists in numerous kinds of supported catalysts and markedly adjusts their electronic structure, such as the electron states of loaded metals. For example, as we mentioned in the water dissociation section, SMSI can optimize the electron distribution of metal sites. Similarly, Abdel-Mageed *et al.* employed *operando* X-ray absorption spectroscopy (XAS) and FT-IR to identify the active Au species in the highly active Au/CeO₂ catalyst. By synthesizing the Au species with different electronic states (Au^{δ-}, Au⁰, Au^{δ+}) on purpose, they presented an idea that the nanometer-sized Au⁰ particles are the dominant active species rather than the cationic Au species (Au³⁺).⁷¹ Apart from that, the coordination number of active sites is related to the strength of SMSI. Jin *et al.* loaded Au atomic layers and isolated atoms on MoC to synthesize different Au/MoC catalysts. With XAS analysis and the catalytic performance test, they revealed a volcano-style pattern between the specific activity for LT-WGSR and the Au-Au coordination number. These results offered a reference for designing the geometric and electronic structure in the future.⁷² The SMSI designed in these works showed that for better CO activation performance, there should be moderate interactions. Excessively weak SMSI cannot form satisfactory active sites, and the CO molecules cannot easily react with the oxygenate species if the SMSI is too strong.



To obtain an appropriate SMSI between loaded metals and supports, scientists offer a variety of methods. For example, Yang *et al.* demonstrated the origin of SMSI by using Pt/CeO₂ as a model catalyst and WGS as a model reaction. On CeO₂(110), Pt clusters embed into the CeO₂ lattice within 3–4 atomic layers. Such embedding structure optimizes the SMSI between the Pt clusters and CeO₂ to achieve more productive Pt sites.⁷³ Similarly, Pt/TiO₂ with an overlayer structure can also optimize the SMSI.⁷⁴ The results demonstrate that SMSI may be optimized by adjusting the geometric structure of the materials.

Another important factor of SMSI is the component and concentration of the active sites. Cu/Fe₃O₄ is a simple and non-toxic material. The formation of the CuFe₂O₄ spinel structure can enhance the thermostability, and change the electronic state of Cu and Fe by Jahn-Teller effect.⁷⁵ Lin *et al.* prepared a Cu/Fe₃O₄ catalyst by co-precipitation method to gain a larger amount of CuFe₂O₄, which was responsible for CO activation.³³ Han *et al.* further optimized the composition of Cu/Fe₃O₄ and found that Cu_{0.3}Fe_{0.7}O_x exhibited the highest CO conversion. The group reported that an excessively loaded Cu will sinter and an insufficiently loaded Cu will suffer from a lack of active sites and poisoning.¹² Thus, future studies should determine the most applicable component for a promising material.

3.2.2.2 Synergistic effect. Besides normal nanoparticle-based materials, bimetallic sites and alloys have attracted much more attention. This is because the synergistic effect between two different metals is intriguing and contains profound scientific principles.^{76,77} The recent research trend of bimetallic catalysts for WGS focuses on adjustment of the bimetal size and optimization of the composition to reduce the cost and enhance the performance.^{78–80} As typical active components, Cu and Ni can be simultaneously loaded on Fe₂O₃. The H₂-TPR results indicated that the SMSI occurs between the dopants (Cu or Ni) and Fe₂O₃, which is beneficial to LT-WGS.⁸¹ Zhang *et al.* anchored well-dispersed Pt single atoms on Co₃O₄ nanorods, forming a Pt₁Co_n/Co₃O₄ composite (structure schematic shown in Fig. 7b). They found that the singly dispersed Pt₁Co_n nanoclusters were the active sites of WGS in the temperature range

of 150–200 °C. After increasing the temperature to about 300 °C, Co₃O₄ (as demonstrated in Fig. 7a) will be reduced to CoO_{1-x} and Pt will sinter. This results in the formation of Pt_mCo_m/CoO_{1-x}, as shown in Fig. 7c, with more abundant surface oxygen vacancies. Both H₂O dissociation and CO activation processes take advantage of the Pt_mCo_m active sites and achieve a lower activation energy, which suggested an effective method to tune the reactivity through reconstructing the oxide catalyst in the gas phase.⁸² Xia *et al.* prepared Au and AuM (M = Ni, Cu, Pt) alloy nanoparticles supported on layered double hydroxides (LDHs). They found that Au₂Cu₁ exhibited the highest TOF value with modulation to the redox process at the interface of the AuM/LDHs interfaces.⁸³ These works on constructing bimetallic catalysts with optimized structure show great potential for LT-WGS. However, the type and structure of the metals should be carefully designed to react in concert.

As a kind of electronic adjuvants, alkali elements are often doped in some supported catalysts to optimize the electronic structures of metal sites. Therefore, many notable works have been reported and provide a plethora of solutions. Au loaded on zeolites and mesoporous MCM-41 were found to be stabilized by the addition of Na⁺ and K⁺. The single site species of Au-O(OH)_x-(Na or K) are active for LT-WGS below 200 °C. Furthermore, AuO₆₋₇(OH)₂Na₉ clusters exhibited the best catalytic performance and stabilization as shown by the applicable CO adsorption energy. This is because the addition of alkali ions served as an electron acceptor and shared part of the electrons being transferred to Au atoms to form a moderate Bader charge on Au.⁸⁴ Coincidentally, Pt-Na/SiO₂ was also synthesized and showed better activity than Pt/SiO₂ at temperatures below 300 °C.²⁵ Kaftan *et al.* applied DRIFTS coupled with online quadrupole mass spectrometry (QMS) to observe the formation of surface species and demonstrate the enhancement of KOH-coated Pt/Al₂O₃. They assured that formates are the primary intermediate on uncoated Pt/Al₂O₃, while a film of hydroxides and carbonates is observed on the KOH-coated sample. It is interesting that changing the electronic structure by alkali species can affect the dominant reaction route of WGS. Additionally, the strong red shift of the CO adsorption peak in DRIFTS suggested that K-coadsorption can weaken the C–O bond and strengthen the Pt–C bond, leading to the hindrance of CO desorption and facilitating the reaction of CO with *OH.⁸⁵ Ang *et al.* suppressed the formation of methane by covering a layer of Na/NaO_x on Ni-loaded CeO₂. The Na⁺ replaces the Ce⁴⁺ in the lattice and generates abundant lattice defects, thus increasing the oxygen mobility, which will rapidly degrade the redundant CO adsorbed on Ni and prevent the self-poisoning of the catalyst.⁸⁶ These works revealed that alkali metal doping can change the electron distribution of catalysts, enhancing the performance of the active sites and changing the reaction route.

Generally, the electronic structure of active sites can be adjusted *via* the design of the bimetallic site and alkali doping based on the synergistic effect between the metals. For different sites with different performances, concrete analyses of their specific situations are necessary to ensure which elements can achieve the best optimization results.

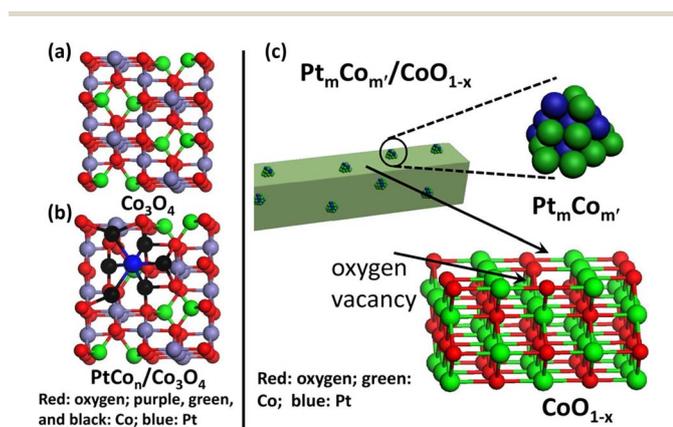


Fig. 7 Structural models of the surfaces of pure Co₃O₄ and active catalysts. (a) Top view of pure Co₃O₄. (b) Top view of Pt₁Co_n/Co₃O₄. (c) Diagrams of the synergistic active sites in Pt_mCo_m/CoO_{1-x}. Copyright © 2013, American Chemical Society.



4 Summary and prospect

WGSR is regarded as a promising reaction that can simultaneously fulfill the two expectations of converting CO and generating H₂. However, it is hindered by the fact that the temperature cannot synchronously overcome the thermodynamic and kinetic limits. Thus, many catalytic systems have been developed for high-efficiency WGSR. In this review, we considered WGSR as a combination of two half-reactions: H₂O dissociation and CO oxidation, which are the optimization targets of active site design. The combination of active site designs for the two side reactions makes it possible to achieve highly efficient WGSR for CO removal and H₂ production. In the past decade, numerous research studies have achieved important advances in the following prospects. For water dissociation, the concentration and structure of oxygen vacancies can be designed for better catalytic performance. Furthermore, the reasonable design of metal sites can help them efficiently participate in the process. For carbon monoxide activation that currently proceeds on d-block element sites, there are two valid options for designing first-class catalysts. This includes selectively synthesizing sites of suitable sizes and optimizing the electronic structure of the sites. Some catalysts have stood out with promising activity and industrial application potential, such as the loading of a noble metal on CeO₂, α -MoC. However, compared with relatively mature applied catalysts like the Cu/Zn/Al system, the harsh synthesis process and costly ingredients hindered their industrial application prospects. Further research studies should also examine how to reduce and minimize catalyst deterioration. Future design strategies for the active site should also take into consideration the industrial costs and production scenarios and specifically target economical, stable and efficient catalytic systems.

Taken together, although WGSR has been extensively investigated, there is still room for improvement of the catalytic systems. Thus, there is still much interest from the scientific community. With the proposal of more novel theories and the development of a large language model, the catalysts for WGSR must also stay up-to-date, and the designing methods can be assisted by AI prediction. We hope that the development of active site design for WGSR can help optimize H₂ generation and CO oxidation in the future.

Conflicts of interest

The authors declare no competing financial interests.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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