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

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ABSTRACT

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



1 Introduction

Hydrogen (H₂) is widely recognized as a potential clean energy carrier, which could help reduce greenhouse gas emission. Number of hydrogen production process have been developed and studied by scientists, among which water-gas shift reaction (WGSR) is considered as a typically efficient way to produce and purify H₂¹ and it has been applied to many industrial processes, such as natural gas reforming, ammonia synthesize² and fuel cell application^{3, 4}.

The history of WGSR can be traced back to 1780s with their reaction depicted in the following equation: $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ ($\Delta H_r^\theta = -41.1 \text{ kJ}\cdot\text{mol}^{-1}$). As an exothermic reaction, it is thermodynamic suitable at low temperature with strict kinetic limit. Therefore, conventional WGSR system contained two adiabatic stages: high-temperature stage with Fe-Cr catalyst for high reaction rate and low-temperature stage with Cu-Zn-Al catalyst ($< 300^\circ\text{C}$) for forward conversion^{5, 6}. The reaction was not applied until 1888 that Mond utilized it for hydrogen production for fuel cell application. In 1914, Bosch and Wild had applied the reaction to industrial hydrogen production⁷. Because of the poisonousness of Cr and the high energy consumption, scientists struggled to optimize the performance of Fe-based catalysts by introducing different kinds of adjuvants until 1980s⁸. But the complexity and energy consumption of the system still encouraged scientists to develop new-style catalytic systems.



Encouraged by the proposal of associative mechanism and redox mechanism in 1920 and 1940¹, scientists realized that the reaction is mainly induced by the interfacial sites between loaded metals and the supports on the heterogeneous catalysts⁹. Increasing kinds of metal oxides are revealed by researchers with decent water dissociation performance and mild reaction condition, such as Al_2O_3 ^{10, 11}, CuFe_2O_4 ¹², ZrO_2 ¹³, CeZrO_4 ¹⁴. Also, the catalytic performance can be assisted by additives such as ZnO ¹⁵, Nb_2O_5 ¹⁶ which adjusting the physical and electronic structure of catalysts. Besides metal oxides, some advanced functional materials were noticed by researchers for their exclusive properties. For example, noble metal based catalysts putting α -MoC as a carrier was emphasized in the last few years for the excellent water dissociation activity¹⁷.

With the development of catalyst design strategies¹⁸, noble metal based catalysts aroused much attention in this field^{19, 20}. With moderate adsorption capacity for CO, metals like Au, Pt, Ru, Pd, 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 consists of single Pt atoms uniformly dispersed on a FeO_x support²³. With decent catalytic activity and new reaction mechanisms, SACs were further explored for better synthesis methods and catalytic properties and regarded as promising catalysts for WGS²⁴. However, in some occasions, nanoparticles show significant catalytic activity, whereas single atoms act as spectators²⁵. It is necessary to differentiate the function of nanoparticles and single atoms in different catalyst system for CO activation.





Table 1 Summary of the review perspective and proposed catalyst and active site design approach 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	1
The water gas shift reaction: Catalysts and reaction mechanism	2021	Catalyst component	Fe-based catalysts Cu-based catalysts Ni-based catalysts Co-Mo-based catalysts Noble-metal-based catalysts	8
Noble-metal based single-atom catalysts for the water-gas shift reaction	2021	Catalyst component and active species (noble-metal-based catalysts)	Single-atom catalysts with reducible oxide, irreducible oxide, carbides and nitrides supports Active metal species (positive state and metallic state)	21
Platinum based catalysts in the water gas shift reaction: Recent advances	2020	Catalyst component and mechanism study (platinum-based catalysts)	The influence of supports The influence of loading method and loading amount The influence of promoter addition Kinetic and mechanism study of Pt-based catalysts	22



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	7
Water gas shift catalysis	2009	Catalyst component	Iron oxide-Chromium oxide and Chromium free catalysts for 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	
The water-gas shift reaction	2006	Catalyst component and kinetic study	Iron-based shift catalysts Copper-based shift catalysts Cobalt molybdenum-based shift catalysts	6
Reasonable active site design for promoting water dissociation and carbon monoxide activation in low temperature water-gas shift reaction	/	Mechanism summary and active-site-design strategy for the two half-reactions of WGS	Mechanism study of WGS Active site design strategies for H ₂ O dissociation Active site design strategies for CO activation	This work

76 Up to now, most WGSR reviews mainly focus on the correlation between different
77 catalyst structure and performance, like noble metal catalysts, transitional metals-based
78 composite and so on. For example, Zhou et al. discussed different sorts of supported
79 metal nanoparticle catalysts for WGSR¹ and Chen et al. detailly summarized noble-
80 metal-based single-atom catalysts for WGSR²¹; Pal et al. provided a systematical review
81 for transitional-metal-based catalysts²⁶. Lee et al. focused on the impacts of reaction
82 conditions and catalysts on WGSR involving different feed gases²⁷. Some other reviews
83 with their review perspectives and proposed catalyst and active site design approaches
84 have been summarized in Table 1. These reviews demonstrated comprehensive
85 understanding of different catalytic systems and summarized the promising catalysts in
86 terms of material composition. However, to our best knowledge, few reviews conduct
87 their discussion based on the understanding of active site design, which triggered us to
88 summarize the first-class catalyst designs and attempt to find some possible correlation
89 between active site structure and promising catalytic performance. More importantly,
90 based on the proposal of surface catalytic theory²⁸ and the specificity of the WGSR, this
91 review considered it as the combination of two principal half-reactions: water
92 dissociation and CO activation, and emphasized that most excellent catalyst design
93 strategies focused on at least one of the half-reactions, whose significance was hardly
94 acknowledged by the previous reviews as shown in the last row of Table 1. Additionally,
95 on knowing that the deactivation of catalysts is still an inevitable phenomenon in actual



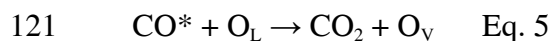
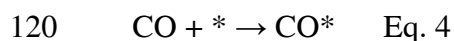
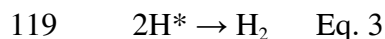
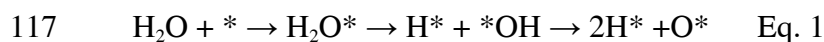
situation, some typical active site design strategies aimed at the inhibition of deactivation, which is worth discussing with their specific examples in this review.

2 Mechanisms

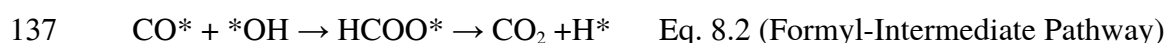
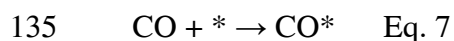
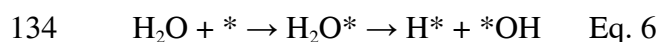
The studies on the mechanism of WGS have been conducted for a few decades because it is complex and still remain controversial. The most recognized mechanisms can be roughly divided into two categories, which mainly involves different routines of water dissociation and carbon monoxide activation: redox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

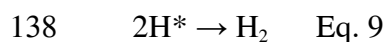
The redox mechanism was first proposed by Temkin in 1949²⁹. The shift reaction goes through a redox cycle as shown in the schematic in Figure 1 (a) and Eq. 1-5, where * represents the active site. To be specific, the H₂O will be directly adsorbed and activated on the active sites to be thoroughly dissociated 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, the 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 valance state noble metals; dark yellow balls: high valance state noble metals; yellow ellipse: noble metal sites). The reduction process is entirely independent from CO oxidation, and need enough activation energy to be thoroughly dissociated. Therefore, this mechanism is more favored by high-temperature shift reaction and active sites with better reduction capacity.





122 With the research trend for lower reaction temperature, the associative mechanism
 123 based on Langmuir-Hinshelwood model gradually came into scientists' eyesight. As
 124 shown in the schematic in figure 1 (b), different from the redox mechanism, the water
 125 dissociation will only be partially dissociated into H^* and $*\text{OH}$, and the $*\text{OH}$ will
 126 further react with CO^* to generate important free radical intermediates such as carboxyl
 127 ($*\text{COOH}$) and formyl (HCOO^*), thus the reduction and oxidation processes are not
 128 independent but associative. The intermediates will decompose into CO_2 and an extra
 129 H^* , which can combine with the former H^* to produce H_2 . This mechanism described
 130 by Eq. 6-9 revealed that the $*\text{OH}$ could directly react with activated CO and form
 131 important intermediates which could be further reform into CO_2 and H_2 , rather than
 132 indispensable exhaustive dissociation into O^* and H^* with higher activation energy,
 133 resulting in lower reaction temperature.





139 Both mechanisms above could be credible under different conditions with different
140 rate determining steps (RDS). For example, WGSR on classic high-temperature
141 catalysts like Fe_3O_4 composite tend to follow the redox mechanism. Huang et al.
142 conducted meticulous density functional theory calculation using Fe_3O_4 (111) surface
143 with the $\text{Fe}_{\text{oct}2\text{-tet}1}$ terminal and proved that redox mechanism was the primary reaction
144 routine with the RDS of CO_2 desorption because of the distinguishing water adsorption
145 ability of $\text{Fe}_{\text{oct}2}$ sites³⁰. Nevertheless, noble metal catalysts with abundant well-designed
146 interfacial active sites allowed easy combination of CO^* and $^*\text{OH}$, leading to the
147 associative mechanism. Vecchietti et al. studied Pt/CeO_2 catalyst and diffused
148 reflectance infrared Fourier transform spectroscopy (DRIFTS) results demonstrated the
149 existence of HCOO^* and COO^* species, which are typical intermediates of associative
150 mechanism. They also mentioned that on the contrast of the previous research, the
151 activation of water molecules in the WGSR mechanism is not the RDS in this system³¹.
152 These previous works emphasized the complexity of the reaction mechanisms with
153 various catalytic systems and reminded the future researchers that reasonable designing
154 of the interfacial site that initiated associative mechanism might be a common solution
155 for the first-class catalysts. Considering that the water dissociation and CO activation
156 are both inevitable for WGSR, these two vital processes could be thinking pivots for
157 the future active site design strategies, which would be further discussed in the
158 following section of the review.



159 3 Active sites design

160 3.1 Water Dissociation

161 Water dissociation is the key process of H_2 production and active intermediate
162 generation in WGS. Metal oxides have been widely studied in laboratory and
163 industrial process for water dissociation. As a kind of common defect site on the surface
164 of oxide catalysts, oxygen vacancies are regarded as the reaction sites and it has been
165 investigated for a long time because of its high activity and stability³². Mostly, the
166 activity of oxygen vacancies can be influenced by two factors: concentration and
167 species. Also, some metal sites can undertake the task of water dissociation by
168 purposive catalyst design. Therefore, it is worthwhile summarizing the ideas for active
169 sites design, which can be demonstrated in Figure 2.

170 3.1.1 Oxygen Vacancy

171 3.1.1.1 Concentration of Oxygen Vacancy

172 For the reducible metal oxide supports, such as CuO ³³, Fe_2O_3 ³⁴, TiO_2 ³⁵, CeO_2 ³⁶ and so
173 on, the concentration of oxygen vacancy can be easily controlled by synthesizing and
174 pretreatment methods such as element doping. Jeong et al. prepared a series of Cu-
175 CeO_2 - ZrO_2 materials with different Ce/Zr ratio. They found that by the shrinkage of
176 lattice, Cu- $Ce_{0.8}Zr_{0.2}O_2$ contained a larger amount of oxygen vacancies and exhibited a
177 very stable WGS activity at about 300°C, which is correlated with the enhancement
178 of oxygen mobility. This work also mentioned that compared with tetragonal phase of
179 Cu- $Ce_{0.8}Zr_{0.2}O_2$, cubic phase shows higher WGS activity because it helps to achieve



higher concentration of oxygen vacancy¹⁴. Homogeneously, the design of La doped CeO₂^{37, 38} and Ga doped Pt/CeO₂³¹ achieved high concentration of oxygen vacancy and thereby promoted catalytic activity for WGSR. Therefore, element doping is regarded as a valid performance-promoting pathway³⁹. And similarly, the synthesis condition of catalysts can also change the O_v concentration, which needs to be further discussed.

In summary, there are direct evidences showing that materials with more oxygen vacancies tend to be more active in water dissociation process, because oxygen vacancies serve as the main active site of water dissociation and can stabilize the *OH, which enhance the WGSR activity.

3.1.1.2 Species of Oxygen Vacancy

Apart from gaining higher concentration of oxygen vacancy, recent advanced works mainly focus on the species of oxygen vacancy. Zhou* et al. successfully formed an asymmetric environment of oxygen vacancies also by element doping³². For example, the group doped Bi in CeO₂ and modified the surrounding of the oxygen vacancy by forming a distorted tetrahedral geometry of Bi-O_v-Ce₃. In comparison with traditional symmetric clusters like Ce₂-O_v-Ce₂, the asymmetric oxygen vacancy makes both the adsorption and desorption much easier (Figure 3 (a))⁴⁰. It is predictable that such asymmetric oxygen vacancy can be applied to some structure-sensitive reaction like the activation of H₂O in WGSR.

Researchers obtained a Zn-Ti mixed oxide support from a Zn-Ti layered double hydroxides 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 $\text{Au}^{\delta-}\text{-O}_v\text{-Ti}^{3+}$ shown in Figure 3 (b), and deep analysis of X-ray absorption near edge structure (XANES) results shown in Figure 3 (d) provided convincing evidence of the asymmetric oxygen vacancies. During the WGS, both $\text{Au}^{\delta-}$ and O_v species of the site directly participate in the H_2O dissociation process. Moreover, characterization results substantiated that the active oxygen vacancy also accelerated the CO chemisorption and H_2O dissociation⁴¹. The group also reported a TiO_{2-x} -modified Ni catalyst with tunable Ni- TiO_{2-x} interaction and the reaction process over $\text{Ni}^{\delta-}\text{-O}_v\text{-Ti}^{3+}$ site was discussed. By the in situ time-resolved DRIFTS results, a new redox mechanism was revealed and can be illustrated by two main steps: (1) the cleavage of O-H bond in H_2O molecule at the asymmetric oxygen vacancy site to generate H_2 and transform $\text{Ni}^{\delta-}\text{-O}_v\text{-Ti}^{3+}$ into $\text{Ni}^{\delta+}\text{-O-Ti}^{4+}$; (2) reaction between CO and $\text{Ni}^{\delta+}\text{-O-Ti}^{4+}$ to form CO_2 and $\text{Ni}^{\delta-}\text{-O}_v\text{-Ti}^{3+}$. These works focus on the establishment of asymmetric active oxygen vacancy and provide a new possible solution for construction of high-efficiency heterogeneous catalytic systems^{42, 43}. Many other works have successfully synthesized composites with asymmetric oxygen vacancies which also exhibited LT-WGS performance⁴⁴.

Additionally, based on the design of asymmetric oxygen vacancy, Chen et al. synthesized a bilayer Cu covered on CeO_2 (structure illustrated by Figure 3 (c)). The bottom layer of Cu can donate an electron to Ce^{4+} and coordinate with an O_v to form a $\text{Cu}^+\text{-O}_v\text{-Ce}^{3+}$ site, and the top layer of Cu can bond with the underlying Cu^+ to modify



the site to $\text{Cu}^0\text{-Cu}^+\text{-O}_v\text{-Ce}^{3+}$. Such interfacial active sites can optimize the plane-integrated bonding charge shown in Figure 3 (e) around Cu^+ and O_v sites, thereby enhance the CO adsorption and H_2O dissociation capacity⁴⁵.

Although the oxygen vacancy concentration is an important factor for the catalytic performance, the optimization of it is capped by the stability requirement of catalysts. Designing better oxygen vacancy species like the asymmetric oxygen vacancy is more crucial for more efficient catalytic system and can fundamentally reveal the H_2O dissociation mechanism.

3.1.2 Metal site

Except for oxygen vacancies, metal sites can also play 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 the interfaces between loaded metals and supports. Lucas et al. designed a $\text{Ni}/\text{Al}_2\text{O}_3$ composite and deeply tracked the oxygenate species (O^* and $^*\text{OH}$) from 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 reminded us that the combination of metal and support can be properly adjusted to obtain better water dissociation activity, and the WGS is a typical interface-sensitive reaction¹¹.

Plentiful studies center on MoC for production of high-purity H_2 was carried out and achieved intriguing advances^{46, 47}. Different from other oxides like SiO_2 or TiO_2 which cannot dissociate H_2O or can easily dissociate H_2O into H^+ and OH^- respectively, the



mass spectrum results have shown that after being adsorbed on α -MoC, the H_2O can be instantly dissociated into H^* and $*OH$ at almost room temperature, which are both important intermediates for WGS⁴⁸. Researchers composed a review to summarize the efforts they made on the development of M/MoC. The review mentioned that the wonderful 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 H_2O to a moderate level where the H_2O molecular can be solidly adsorbed on the surface and simultaneously dissociated by the energy released from adsorption⁴⁹. Furthermore, Zhang et al. designed Pt_1-Pt_n/α -MoC (morphology and structure shown in Figure 4 (a)) based on Pt_1/α -MoC with promising activity but disappointing stability and obtained better CO conversion than Cu-Zn-Al model catalyst and other MoC-based catalysts given in Figure 4 (b). The extra Pt clusters can change the interfacial structure by covering the redundant exposed surface of Pt_1/α -MoC, in order to preventing the oxidation of α -MoC by excess $*OH$, because the $*OH$ far from the interface of Pt and α -MoC cannot react with the activated CO. Also, the transient kinetic analysis (TKA) results of Pt_1-Pt_n/α -MoC revealed that except for H_2O dissociation, the CO can also be dissociated at low temperature to generate an extra carbon atom which can react with activated H_2O to produce additional 35% of H_2 in the total H_2 production. The reaction routines can be summarized by Figure 4 (c). By isotope labelling method, this work found some



different reaction routines based on the dissociation of CO, which means that the combination of 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 more active oxygen species supplement from CO dissociation⁵⁰. The fantastic performance of α -MoC based catalysts provided possibility for future research to investigate the electronic structure optimization of metal sites, in order to improve intrinsic H₂O dissociation ability, but there might be still many challenges to surpass the current performance of the α -MoC based catalysts.

MoC has been proved as an outstanding H₂O dissociation material, and other carbides like TiC^{51, 52} and Co₂C⁵³ are also under investigation. Additionally, metal-organic frameworks (MOFs) have been predicted as promising supports with controllable porous structure and changeable open metal sites (OMSs)⁵⁴. However, limited MOFs have been 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 of the oxygen atom in CO₂ are coming from H₂O. However, the synthesis of the MOF is complex and time-consuming, which needs further development⁵⁵.

The optimization of metal sites mainly focuses on adjusting the electronic structure by adjusting the surrounding environment. No matter loaded metal sites or support metal sites, it is vital to reveal the volcano-type relationship between metal sites and



surrounding atoms, which can really provide 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 oxygen vacancy can serve as CO adsorption site at the interfacial zone between loaded metal and supports, but in most LT-WGSR process, d-block elements, such as noble metals, can perform as the effective CO activation sites by cooperate 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 Figure 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 catalysts and substrates. For instance, metal loaded on supports can be controllably synthesized with varies of sizes, such as nanoparticles, clusters and single atoms⁵⁸. And based on the size effect, different sizes exhibited different catalytic performance and stability. Also, exposed facet of the catalysts is a key factor to the catalytic performance⁵⁹. It is essential to summarize the merits and drawbacks of different geometric structures, in order to provide clear strategies for reference.



305 Generally, it is well-known that as the maximization of interfacial site, single atom
306 catalysts should be divinely high-efficiency for WGS. However, works have been
307 delivered to identify the active sites of CO activation and prove that nanoparticles
308 performed better than single atom by time-dependent infrared spectrum. The result
309 proved that only CO adsorbed on Pt nanoparticles could be activated and participate in
310 the reaction (demonstrated in Figure 6 (a))²⁵. Therefore, with decent catalytic
311 performance and stability, they are widely investigated for LT-WGS since 1996^{19, 34}.
312 Andreas et al. designed TiO₂-supported Pt catalysts and used density functional theory
313 (DFT) calculations and microkinetic modeling to clarify the activity of the three-phase
314 boundary. Their results suggested the dominant catalytic process on Pt₈/TiO₂(110)
315 should be redox pathway and the better activity of three-phase boundary can be
316 correlated to reduced CO adsorption energy on Pt sites and increased number of oxygen
317 vacancies⁵⁹. Moreover, Zhao et al. synthesized a Pt-TiO₂ composite with ultra-small Pt
318 nanoparticles encapsulated in sub-50 nm hollow TiO₂ nanospheres. With the decrease
319 of Pt particle size, the catalyst shows a much higher turnover frequency (TOF) value,
320 which can be attributed to the size-dependent variation in the electronic structure of Pt
321 species and the sintering prevention effect from TiO₂ encapsulation. This work
322 provided a valid synthesis strategy for loading Pt on the internal surface of TiO₂
323 nanospheres and revealed a creative catalyst designing thought that the deactivation of
324 Pt could be avoided by controllable support encapsulation⁶⁰. CeO₂ is a typical reducible
325 support and is frequently selected as the support of noble metals such as Au⁶¹. Fu et al.



326 compared the activity of Au nanoparticles and clusters on CeO₂ and found that the
327 abundant interfacial sites between Au clusters and CeO₂ induced superior catalytic
328 performance than Au nanoparticles during WGS⁶². In short, the size of loaded metals
329 could directly determine the number of active sites.

330 Zhang et al. synthesized Pt clusters and single atoms by changing the loaded facets
331 shown in Figure 6 (b). They deeply investigated the CO adsorption on Pt by IR spectrum
332 given in Figure 6 (c) and proved that the binding energy between CO and Pt
333 nanoparticles is weaker than CO and Pt single atoms by the blue shift of PtO₄²⁺ peak
334 compared with Pt^{δ+} and Pt⁰ peaks, which means that single atom catalysts (SACs) could
335 be well designed to show promising research value⁶³. Therefore, for WGS, single atom
336 sites with appropriate geometry design can still effectively activate CO for further
337 reaction with other intermediates such as *OH. Lin et al. synthesized Ir₁/FeO_x SAC for
338 WGS whose performance is one order of magnitude higher than its cluster and
339 nanoparticle counterparts⁶⁴. Furthermore, Liang et al. studied the redox mechanism of
340 Ir₁/FeO_x for WGS by detailed calculation and experiments and proved that the CO will
341 be adsorbed and activated on the Ir single atom with a dual active site of Fe³⁺-O...Ir²⁺-
342 O_v⁶⁵. And Guan et al. from the same group also fabricated Rh₁/TiO₂ SAC and obtained
343 an overall CO conversion of ~95%, which indicated that there are multiple choices of
344 noble metal for LT-WGS⁶⁶. Some kinds of SACs have also broken the traditional
345 cognition that noble metal sites are the actual CO activation sites. Sun et al. designed a
346 Ir₁/α-MoC catalyst for LT-WGS. 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 which 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 a obviously reduction of the activation energy (E_a)⁶⁷. These works provided abundant possibilities for the utilization of SACs in the future research with rational catalyst design to avert excessively adsorption.

As for the influence of exposed facets, Zhang et al. synthesized uniform cubic, dodecahedral and octahedral Cu nanocrystal by partial reduction of Cu₂O nanocrystal. They found that cubic Cu nanocrystal exposed (100) facets was more active than dodecahedral Cu nanocrystal exposed (110) facets for H₂O dissociation and CO activation, and octahedral Cu nanocrystal exposed (111) facets was inactive. By theoretical calculation results of surface structures and H₂O adsorption energy change, it is confirmed that the formate species adsorbed on Cu (111) need 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 will be self-poisoning during the reaction⁶⁸. On the basis, the research group deeply studied ZnO/Cu and revealed that the catalysts would undergo an in situ restructuring process during WGS to form the Cu-hydroxylated ZnO ensemble⁶⁹. These results suggested that controlling the exposed facet of crystalized catalysts like traditional Cu-based catalysts might also be a considerable strategy for performance optimization.

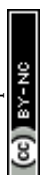


As is shown above, a reasonable geometric structure is important for better catalytic performance. The size and morphology effect need to be detailly investigated and discussed based on the experience and future works, aiming to summarize some universal catalyst design rules.

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 1978⁷⁰. 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 water dissociation section, SMSI can optimize the electron distribution of metal sites. Similarly, Abdel-Mageed et al. employed operando X-ray absorption spectrum (XAS) and FT-IR to identify the active Au species in highly active Au/CeO₂ catalyst. By synthesizing 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 catalytic performance test, they revealed a volcano-style pattern between the specific activity for LT-WGSR and the coordination number of Au-Au. These results offered a reference for the geometric and electronic structure design in the future⁷². The SMSI designed in these



works noticed us that for better CO activation performance, the interaction should be moderate. Excessively weak SMSI cannot form qualified active sites and the CO molecules are uneasy to react with oxygenate species if the SMSI is too strong.

In order to obtain an appropriate SMSI between loaded metals and supports, scientists offer varieties 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 CeO₂ lattice within 3-4 atomic layers. Such embedding structure optimizes the SMSI between Pt clusters and CeO₂ for more productive Pt sites⁷³. Similarly, the Pt/TiO₂ with overlayer structure can also optimize the SMSI⁷⁴. The results remind us that SMSI could be optimized by adjusting the geometric structure of materials.

Another important factor of SMSI is the component and concentration of active sites. Cu/Fe₃O₄ is a simple and non-toxic material. The formation of CuFe₂O₄ spinel structure can enhance the thermostability and change the electronic state of Cu and Fe by Jahn-Teller effect⁷⁵. Lin et al. prepared a Cu/Fe₃O₄ catalyst by co-precipitation method to gain larger amount of CuFe₂O₄, better which were responsible for CO activation³³. Han et al. further optimized the composition of Cu/Fe₃O₄ and found the Cu_{0.3}Fe_{0.7}O_x exhibited the highest CO conversion. The group reported that excessive loaded Cu will sinter and insufficient loaded Cu will suffer from lack of active sites and poisoning¹². For future investigation, it is necessary to figure out the most applicable component for a promising material.



3.2.2.2 Synergistic effect

Besides normal nanoparticle-based materials, bimetallic sites and alloys arouses much more attention because the synergistic effect between two different metals is intriguing and contains profound scientific principles^{76, 77}. Recent research trend of bimetallic catalysts for WGS focus on the bimetal size adjustment and composition optimization to reduce the cost and enhance the performance⁷⁸⁻⁸⁰. As typical active components, Cu and Ni can be loaded on Fe_2O_3 simultaneously. The H_2 -TPR results indicated that the SMSI between the dopants (Cu or Ni) and Fe_2O_3 , which was beneficial to LT-WGS⁸¹. Zhang et al. anchored well-dispersed Pt single atoms on Co_3O_4 nanorods, forming a $\text{Pt}_1\text{Co}_n/\text{Co}_3\text{O}_4$ composite shown by structure schematic in Figure 7 (b), and found that the singly dispersed Pt_1Co_n nanoclusters were the active sites of WGS in the temperature range of 150-200°C. After increasing the temperature to about 300°C, the Co_3O_4 demonstrated by Figure 7 (a) will be reduced to CoO_{1-x} and Pt will sinter, resulting in the formation of $\text{Pt}_m\text{Co}_m/\text{CoO}_{1-x}$ demonstrated by Figure 7 (c) with more abundant surface oxygen vacancies. Both H_2O dissociation and CO activation process take advantage of the Pt_mCo_m active sites and achieve a lower activation energy, which suggested a effective method to tune the reactivity through reconstructing the oxide catalyst in the gas phase⁸². Xia et al. prepared Au and AuM (M=Ni, Cu, Pt) alloy nanoparticles supported on layered double hydroxides (LDHs) and found Au_2Cu_1 exhibited the highest TOF value with modulation to the redox process at the interface of AuM/LDHs interfaces⁸³. These works of bimetallic catalysts



construction with optimized structure show great potential for LT-WGSR, but the type and structure of metals need to be carefully designed for reacting 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 noticeable works have been reported and provided plentiful solutions. Au loaded on zeolites and mesoporous MCM-41 were found to be stabilized by the addition Na^+ and K^+ . The single site species of $\text{Au-O(OH)}_x\text{-(Na or K)}$ are active for the LT-WGSR below 200°C , and the $\text{AuO}_{6-7}(\text{OH})_2\text{Na}_9$ clusters exhibited the best catalytic performance and stabilization with the applicable CO adsorption energy because the addition of alkali ions performed as an electron acceptor and shared part of the electrons transferring to Au atoms to form a moderate Bader charge on Au⁸⁴. Coincidentally, Pt-Na/ SiO_2 has also been synthesized and showed better activity than Pt/ SiO_2 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/ Al_2O_3 . They assured that formates are the primary intermediate on uncoated Pt/ Al_2O_3 , while a film of hydroxides and carbonates is observed on the KOH-coated sample. It is interesting that the change of electronic structure by alkali species can affect the dominant routine of WGSR. Additionally, the strong red shift of CO adsorption peak in DRIFTS suggested that K-coadsorption can weaken the C-O bond and strengthen the Pt-C bond, leading to hinderance for CO desorption and facilitation for the reaction of CO with $^*\text{OH}$ ⁸⁵. Ang et al. suppressed the formation of methane by

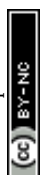


covering a layer of Na/NaO_x on Ni loaded CeO₂. The Na⁺ could replace the Ce⁴⁺ in the lattice and generate abundant lattice defects thus increasing the oxygen mobility, which will make the redundant CO adsorbed on Ni rapidly degraded and prevent the catalyst from being poisoning⁸⁶. These works revealed that the alkali metal doping can change the electron distribution of catalysts, in order to enhance the performance of active sites and change the reaction routine.

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

4 Summary and Prospect

Being regarded as a promising reaction fulfilling two expectations of converting CO and generating H₂ simultaneously, WGSR is a promising reaction but faces the problem that the temperature cannot overcome the thermodynamic and kinetic limits synchronously, thus bunches of 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 sites design. The combination of active site design for the two side reactions makes high-efficient WGSR for CO removal and H₂ production possible. In the past one-decade, numerous research has achieved important advances in the following prospects. For water dissociation, the concentration and structure of oxygen vacancies



473 can be designed for better catalytic performance and reasonable metal sites design can
474 help them efficiently participate in the process. For carbon monoxide activation
475 currently happening on d-block element sites, selectively synthesizing suitable size and
476 exploring providential electronic structure of the sites are both considered as valid ideas
477 for designing first-class catalysts. Some catalysts stood out with promising activity and
478 industrial application potential, such as noble metal loaded on CeO₂, α -MoC. But the
479 comparing with the relatively mature applied catalysts like Cu/Zn/Al system, the harsh
480 synthesis process and costly ingredients hindered their industrial application prospects
481 and research on the resistance of catalyst deterioration need to be further conduct in the
482 future. The future active site design strategies should take the industrial costs and
483 production scenarios into consideration and target at economical, stable and efficient
484 catalytic system.

485 Taken together, although WGSR has been investigated for a long period of time, there
486 is still room for improvement of the catalytic systems, which triggered extensive
487 interest from the scientific community. With the proposing of more novel theories and
488 the development of large language model, the catalysts for WGSR also need to stay up-
489 to-date and the designing methods could be assisted by AI prediction. We hope that the
490 development of active sites design for WGSR can make it a really efficient pathway for
491 H₂ generation and CO oxidation in the future.



FIGURES

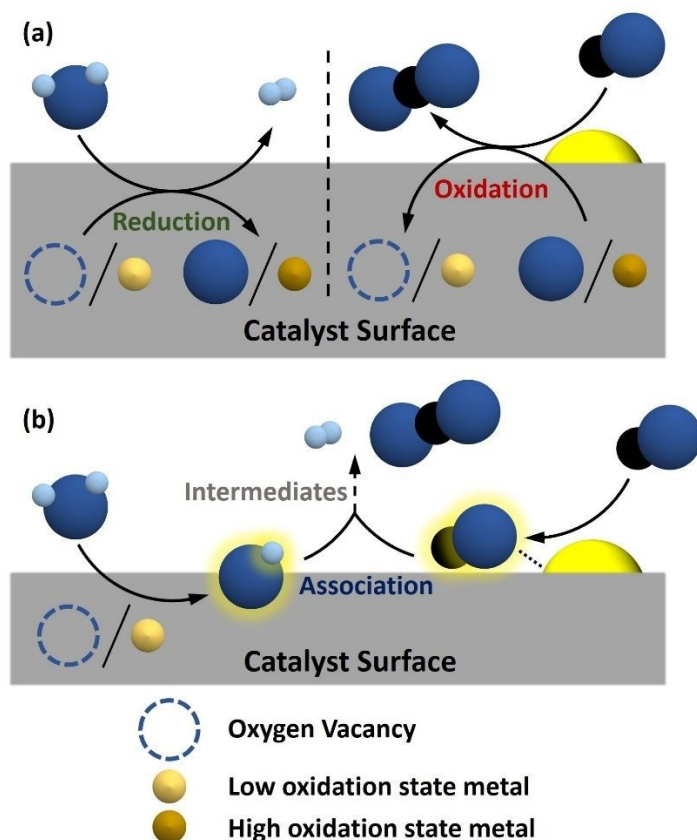


Figure 1 (a) Process schematic of redox mechanism. (b) Process schematic of associative mechanism.

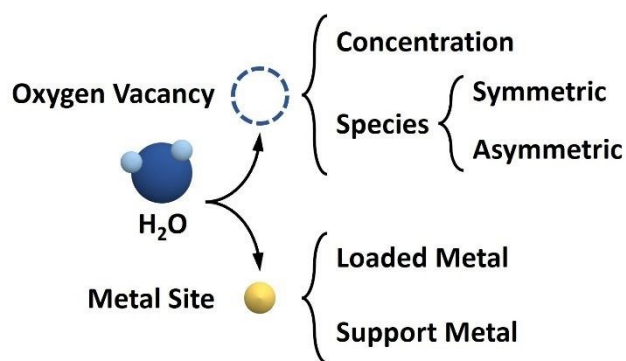


Figure 2 Summarization of active site design for H₂O dissociation.

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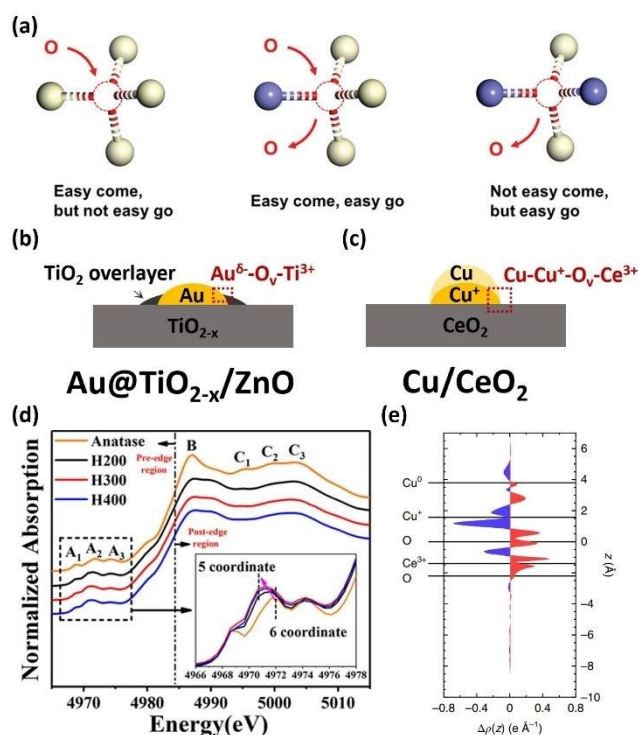
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Figure 3 (a) Schematic diagram of relationship between the microstructure of oxygen vacancy and its redox property. (b) A diagram of the active site structure on Au@TiO_{2-x}/ZnO. (c) A diagram of the active site structure on Cu/CeO₂. (d) Normalized XANES spectra of Au@TiO_{2-x}/ZnO with different synthesizing condition, which provided a direct evidence for the existence of asymmetric oxygen vacancy site (Au^{δ-}-O_v-Ti³⁺). (e) Plane-integrated bonding charge Δρ(z) as a function of position across the Cu-Ce interface. The red and blue areas represent charge accumulation and depletion, respectively.

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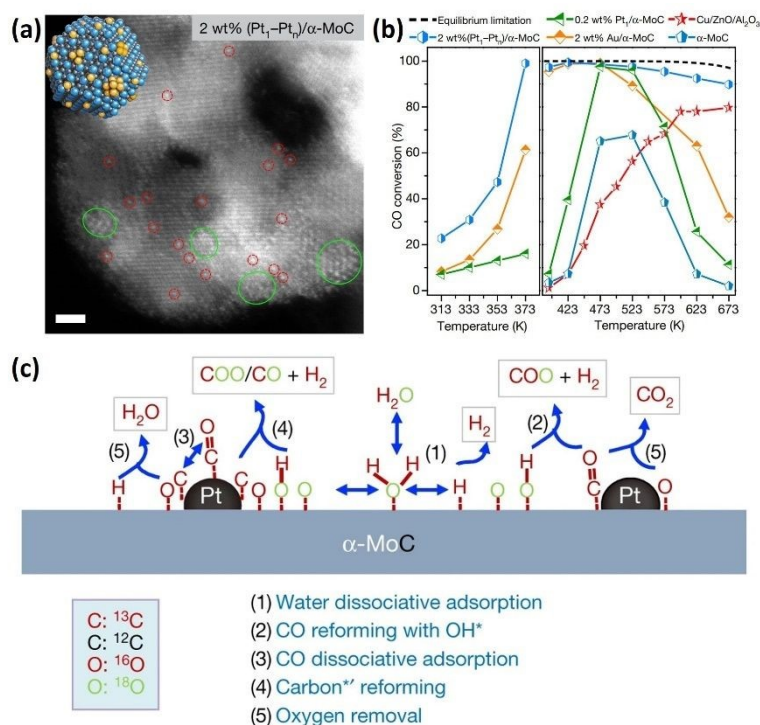


Figure 4 (a) TEM image and a diagram of the distribution of Pt single atoms and clusters on $(Pt_1-Pt_n)\alpha$ -MoC. (b) CO conversion over different catalysts at various temperatures. (c) Schematic of the reaction routes for the WGS reaction over Pt/ α -MoC: (1) water dissociation; (2) the conventional WGS reaction routes (redox or associative intermediate mechanism); and (3)–(5) the unconventional WGS reaction routes. The asterisk represents the active site.

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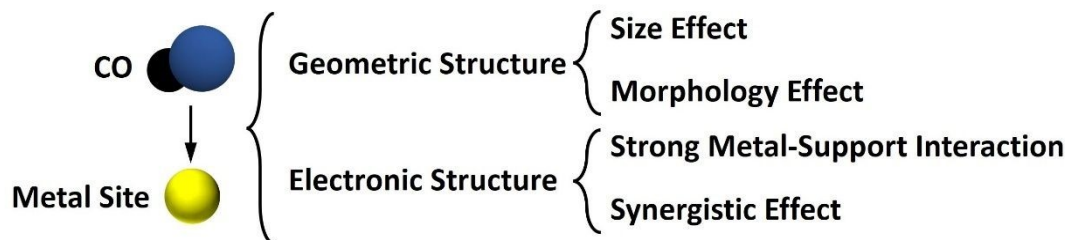
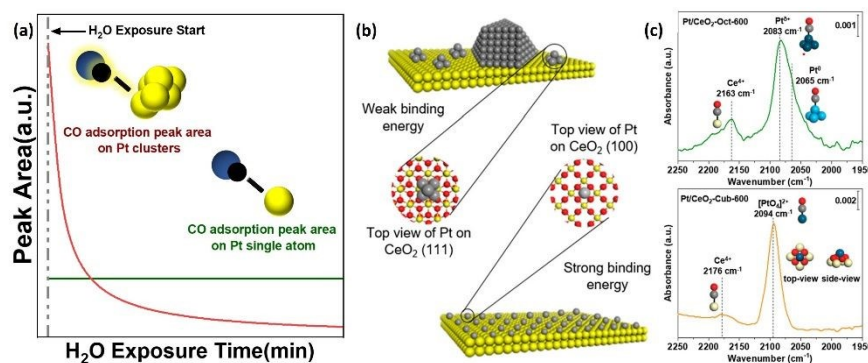


Figure 5 Summarization of active site design for CO activation.

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523 **Figure 6** (a) Time-dependent IR spectra of CO adsorbed on 1 wt.% Pt/SiO₂ upon H₂O
 524 exposure. The peaks in green zone corresponds to CO adsorbed on Pt single atoms and
 525 the peaks in blue zone corresponds to CO adsorbed on Pt nanoparticles. The diagrams
 526 on the right side shows the CO activation status on different sites. (b) A diagram of Pt
 527 cluster and single atom on different CeO₂ facets. (c) In situ CO-DRIFTS of Pt/CeO₂
 528 samples, showing the bonding energy differences between CO and Pt with different
 529 sizes.

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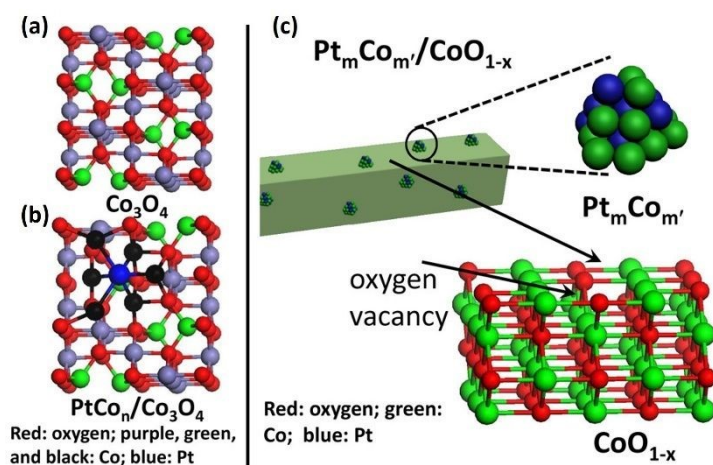
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540 **Figure 7** Structural models of surfaces of pure Co_3O_4 and active catalysts, (a) Top view
 541 of pure Co_3O_4 . (b) Top view of $\text{Pt}_m\text{Co}_{m'}/\text{Co}_3\text{O}_4$. (c) Diagrams of synergistic active sites
 542 in $\text{Pt}_m\text{Co}_{m'}/\text{CoO}_{1-x}$.

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565 Notes

566 The authors declare no competing financial interest.

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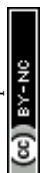
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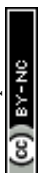


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Dear Editor:

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

Sincerely,

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