

# Renaissance of Strong Metal–Support Interactions

Ming Xu,<sup>#</sup> Mi Peng,<sup>#</sup> Hailian Tang, Wu Zhou, Botao Qiao,<sup>\*</sup> and Ding Ma<sup>\*</sup>



Cite This: *J. Am. Chem. Soc.* 2024, 146, 2290–2307



Read Online

ACCESS |

Metrics & More

Article Recommendations

**ABSTRACT:** Strong metal–support interactions (SMSIs) have emerged as a significant and cutting-edge area of research in heterogeneous catalysis. They play crucial roles in modifying the chemisorption properties, interfacial structure, and electronic characteristics of supported metals, thereby exerting a profound influence on the catalytic properties. This Perspective aims to provide a comprehensive summary of the latest advancements and insights into SMSIs, with a focus on state-of-the-art *in situ/operando* characterization techniques. This overview also identifies innovative designs and applications of new types of SMSI systems in catalytic chemistry and highlights their pivotal role in enhancing catalytic performance, selectivity, and stability in specific cases. Particularly notable is the discovery of SMSI between active metals and metal carbides, which opens up a new era in the field of SMSI. Additionally, the strong interactions between atomically dispersed metals and supports are discussed, with an emphasis on the electronic effects of the support. The chemical nature of SMSI and its underlying catalytic mechanisms are also elaborated upon. It is evident that SMSI modification has become a powerful tool for enhancing catalytic performance in various catalytic applications.

## 1. INTRODUCTION

Heterogeneous catalysis plays a central role in the modern chemical industry, accounting for over 80% of catalytic transformation processes.<sup>1–3</sup> Among the various types of heterogeneous catalysts, supported metal catalysts consisting of highly dispersed metal species on high-surface-area materials such as oxides, carbons, ceramics, and zeolites have gained prominence.<sup>4–6</sup> Initially, these high-surface-area materials, known as supports or carriers, were used to provide a platform for the fine dispersion of metals, resulting in stable metal nanoparticles (NPs) with a larger ratio of exposed atoms. This allowed the formation of catalytically active sites that were resistant to sintering during use. However, subsequent investigations revealed the existence of metal–support interactions (MSIs), which have significant and distinct influences on the electronic and geometric structures of the supported metals, consequently affecting their catalytic performance.<sup>7,8</sup> Prof. Liu has comprehensively summarized<sup>9</sup> different kinds of MSIs, among which one notable type, strong metal–support interactions (SMSIs), gained particular attention in the field of heterogeneous catalysis from the late 1970s to the late 1990s. This term—SMSI—was first coined in 1978 by Tauster et al., who observed that the chemisorption of small molecules like H<sub>2</sub>, O<sub>2</sub>, and CO on TiO<sub>2</sub>-supported group VIII noble metals was significantly inhibited after reduction at high temperatures (500 °C) in a hydrogen atmosphere,<sup>10</sup> to describe this phenomenon which has been gradually developed into one of the most important concepts in the field of heterogeneous catalysis. This concept is denoted as “classic SMSI” (C-SMSI) hereinafter in this Perspective to distinguish it from the newly identified types of SMSIs.

Tauster’s discovery marked the beginning of research on this important topic in the field of heterogeneous catalysis. Following this discovery, extensive exploration of C-SMSI

ensued, expanding the range of catalyst systems capable of exhibiting C-SMSI to various reducible transition metal oxide-supported metal catalysts (e.g., V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, MnO, and Ta<sub>2</sub>O<sub>5</sub>).<sup>11</sup> Through extensive investigations, it has been revealed that electron transfer occurs from partially reduced oxide cations (e.g., Ti<sup>3+</sup> or Nb<sup>4+</sup>)<sup>12</sup> to adjacent metal atoms at the interface, resulting in negatively charged metal (M<sup>δ-</sup>) species.<sup>13–15</sup> Additionally, partially reduced oxide thin layers migrate onto the surface of metals, driven by SMSIs,<sup>16–19</sup> and form partial or complete encapsulation structures in most cases.<sup>20–25</sup> The surface disordered oxide clusters or particles that migrate on the top of metal endow its unique properties, which cannot be seen for the bulk oxides, leading to special chemical and catalytic properties. These phenomena can be attributed to the d-orbital interactions between the metal and oxide supports.<sup>26,27</sup> Importantly, this electron transfer and overlayer encapsulation<sup>28</sup> exhibit complete reversibility upon an inverse oxidation treatment at high temperatures,<sup>29</sup> accompanied by an inverse catalytic performance, further illustrating the dynamic nature of this phenomenon.<sup>30</sup> These typical characteristics serve as powerful criteria to identify the presence of C-SMSI, including (i) significant suppression of small-molecule adsorption (such as CO and H<sub>2</sub>), (ii) electron transfer from the support to the metal, resulting in negatively charged metal species, (iii) mass migration from the support to encapsulate metal NPs with a thin overlayer of support

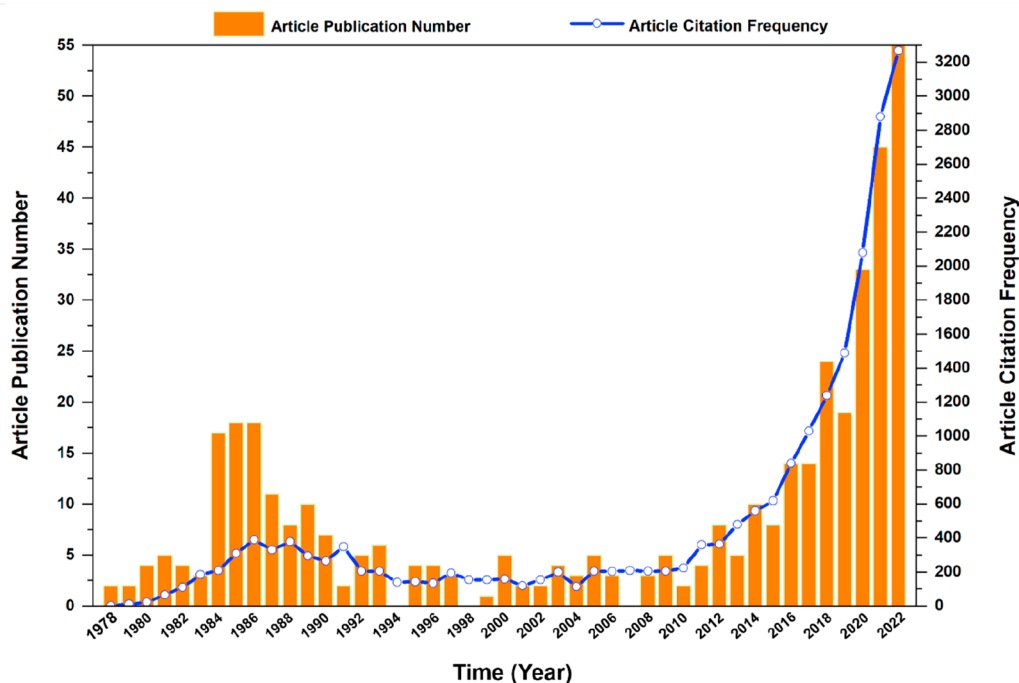
**Received:** August 21, 2023

**Revised:** December 19, 2023

**Accepted:** December 20, 2023

**Published:** January 18, 2024





**Figure 1.** Article publication number and citation frequency. The number of articles published and the corresponding article citation frequency are charted for the research on SMSIs from 1978 to 2022 (data comes from a literature search using “strong metal–support interactions” as the subject and title).

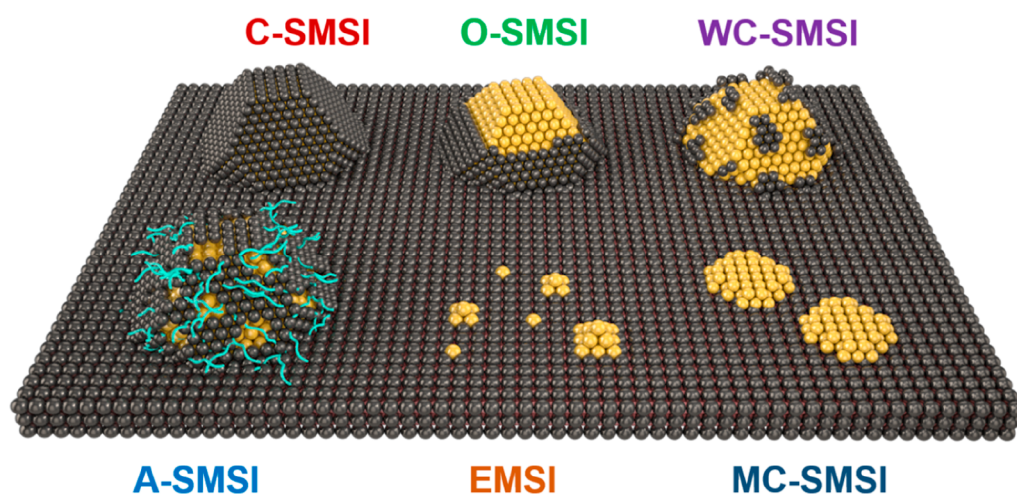
materials, and (iv) complete reversal of the preceding phenomena upon reoxidation.

Since the discovery of C-SMSI, it has gained considerable attention due to its remarkable influence on catalytic activity and selectivity, primarily attributed to the drastic changes in chemisorption behavior,<sup>31,32</sup> as well as its potential to improve catalyst stability through the encapsulation of metal NPs. In the early stages, C-SMSI was mainly regarded as a factor in catalyst passivation and deactivation, as metal active sites were encapsulated and the chemisorption of reactants was inhibited.<sup>33,34</sup> However, subsequent studies revealed that the formation of C-SMSI is beneficial for certain reactions, such as the selective hydrogenation of 3-nitrostyrene,<sup>35</sup> methane reforming with carbon dioxide,<sup>36</sup> and the water–gas shift (WGS) reaction.<sup>37</sup> Recent demonstrations have shown that various types of SMSIs can modify catalytic performance (including activity, selectivity, and stability) in certain reactions, including selective hydrogenation,<sup>38–47</sup> Fischer–Tropsch synthesis,<sup>48–52</sup> catalytic oxidation,<sup>53–55</sup> gas/liquid phase reforming,<sup>56–63</sup> and dehydrogenation of hydrocarbons,<sup>64–66</sup> among others. *In situ/operando* spectroscopy characterization has identified strong chemical bonding during the formation of the SMSI state,<sup>67–69</sup> leading to the rearrangement of the interfacial structure and redistribution of electrons at the interface. Additionally, strong electron perturbation<sup>70–73</sup> has been observed based on characterization and DFT calculation results, both of which contribute to its distinct catalytic properties. For instance, C-SMSI can enhance the adsorption and activation of reaction molecules, facilitate the stabilization of reactive intermediate states, and promote the activation and cleavage of specific chemical bonds (e.g., C–O, C–H, and O–H bonds).<sup>74,75</sup> Interfacial synergistic catalysis also plays a critical role in remarkably enhancing the catalytic performance. However, the understanding of the

underlying mechanisms through which SMSI influences catalytic activity and selectivity is still in its early stages.

Through continuous and in-depth exploration, the scope of catalyst systems exhibiting SMSI has expanded beyond transition metal oxides-supported group VIII metals to include group IB metals (e.g., Au/TiO<sub>2</sub> and Cu/ZnO).<sup>47,76,77</sup> For example, the C-SMSI phenomenon between Au NPs and TiO<sub>2</sub> support after high-temperature reduction was observed, filling a crucial gap in our understanding.<sup>76</sup> Moreover, novel types of SMSI catalyst systems have been discovered, exhibiting extraordinary catalytic properties, including metal/mixed oxides and metal/non-oxide supports (e.g., metal and carbide,<sup>61,74</sup> metal and nitride,<sup>78,79</sup> metal and nanocarbon,<sup>80,81</sup> metal and hydroxide<sup>82</sup>). Importantly, the SMSI between atomically dispersed Pt species/layer Au clusters and molybdenum carbide support ( $\alpha$ -MoC)<sup>59,74,83</sup> was identified, providing a new platform to explore SMSI phenomena. The regulation of catalyst pretreatment conditions is also an efficient approach to fabricate new types of SMSIs, such as oxidative strong metal–support interactions (O-SMSIs)<sup>84,85</sup> and adsorbate-mediated strong metal–support interactions (A-SMSIs).<sup>43</sup> More recently, researchers have reported the observation of SMSI phenomena under realistic reaction conditions, known as reactive metal–support interactions (RMSIs).<sup>86,87</sup> With the rapid development of single-atom catalysis, SMSIs between single atoms and supports have garnered increasing attention, facilitating the rational design of single-atom catalysts (SACs) with ultra-high stability and accelerating their industrialization. Therefore, the rational design and fabrication of diverse new types of SMSI catalysts are of vital importance in heterogeneous catalysis.

In recent years, several notable review papers have been published summarizing the advancements in this subfield of heterogeneous catalysis.<sup>5,6,88,89</sup> However, a relatively compre-



**Figure 2.** Schematic diagram of different types of catalysts with strong metal–support interactions (SMSIs). The classical strong metal–support interaction, the oxidative strong metal–support interaction, the wet-chemistry strong metal–support interaction, the adsorbate-mediated strong metal–support interaction, the electronic metal–support interaction, and the metal carbide-induced strong metal–support interaction are denoted as C-SMSI, O-SMSI, WC-SMSI, A-SMSI, EMSI, and MC-SMSI, respectively.

hensive summary of all new types of SMSIs, especially regarding their relationships and distinctions, has not been provided, requiring a deeper understanding of the nature of various SMSIs and the historical development of SMSIs. In this Perspective, we aim to present a relatively detailed account of the evolution of SMSIs by introducing and discussing various types of SMSIs. Finally, we provide a perspective on the further development of SMSIs.

## 2. NEWLY DISCOVERED SMSIS AND STATE-OF-THE-ART RESEARCH

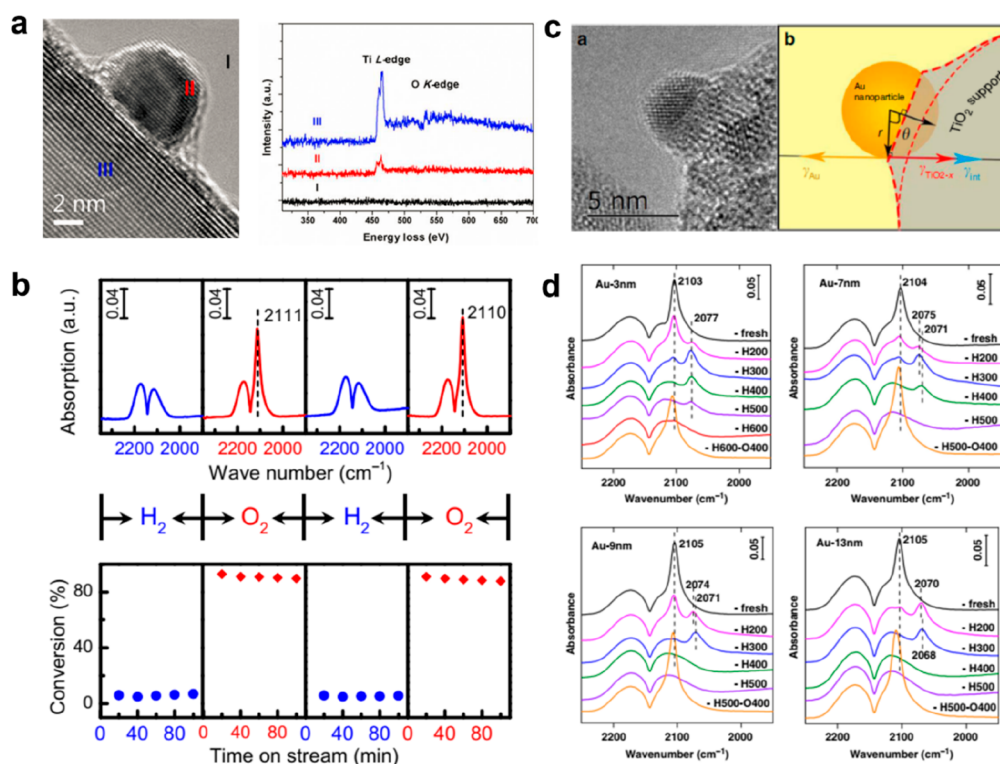
The interaction between the active metal and support in heterogeneous catalysis is strongly influenced by the pretreatment conditions of the catalysts, such as calcination temperature and atmosphere.<sup>43,53</sup> These conditions determine the magnitude and direction of electron transfer, as well as the encapsulation behavior of the supported metal.<sup>62</sup> As the field has rapidly progressed, different types of SMSIs have been continuously discovered and reported. In 2012, Rodriguez et al. found that electron perturbation could occur when small platinum clusters came into contact with ceria,<sup>56</sup> which was termed “strong electronic metal–support interaction” (EMSI) by Campbell.<sup>71</sup> EMSI differs significantly from C-SMSI because C-SMSI requires an additional reduction treatment to form, whereas EMSI occurs naturally upon contact between the metal and the support, without the need of any treatment. In the same year, Mou’s group reported an O<sub>2</sub>-treatment-induced SMSI between Au NPs and ZnO nanorods, which was the opposite condition required for C-SMSI and was termed “oxidative SMSI” (O-SMSI).<sup>53</sup> This discovery marked a milestone in the historical development of SMSIs because conventional wisdom held that supported Au catalysts could not exhibit SMSIs due to gold’s relatively low work function and surface energy compared to other noble metals.<sup>90</sup> Building on this work, Tang et al. reported a new discovery of O-SMSI between Au NPs and hydroxyapatite (HAP), a non-oxide material.<sup>82</sup> This finding is equally important, as it demonstrates for the first time that non-oxide supports can exhibit SMSI with metals and may inspire the exploration of new types of SMSIs between metals and non-oxides such as carbides and nitrides. Furthermore, this work further confirmed that Au can

exhibit SMSI with a support, leading to the subsequent discovery of C-SMSI between Au and TiO<sub>2</sub> by the same research group.<sup>76</sup> These studies have reignited enthusiasm for the topic of SMSIs, particularly in the field of heterogeneous catalysis. Figure 1 illustrates the accelerated progress in the study of SMSIs since 2012.

Subsequently, it was discovered that C-SMSI can also be extended to other group IB metals,<sup>91</sup> such as Cu and Ag. Furthermore, a series of new SMSI catalysts were constructed by modifying the pretreatment atmosphere, reducing agent, and synthesis methods, including WC-SMSI, A-SMSI, and EOMSI (each discussed below).<sup>92–94</sup> Generally, a reducing atmosphere promotes electron transfer from the oxide support to the interfacial atoms, while an oxidative atmosphere facilitates electron transfer from the supported metal to the oxide at the interface. In the field of SMSI research, the type of support also plays a central role in modulating MSIs, which in turn controls the metal morphology, particle size, and electronic structure of the supported metal. Particularly, with the emerging and rapid development of SACs, SMSIs between atomically dispersed metals and supports have garnered increasing interest and attention. In the following sections, we will briefly introduce these new types of SMSIs, as shown in Figure 2.

**2.1. New Findings in the Classical Strong Metal–Support Interaction (C-SMSI).** Supported Au catalysts have garnered significant attention in catalytic chemistry.<sup>95,96</sup> The particle size effect of Au strongly influences the catalytic properties for many important reactions.<sup>97</sup> However, due to the low Tammann temperature, Au NPs anchored on various supports tend to aggregate into larger particles, leading to a decrease in active interface area and interface reconstruction, which can result in passivation and deactivation. To overcome this challenge, an effective approach is to develop supported Au nanocatalysts with SMSIs.

Traditionally, it was believed that group IB metals could hardly form SMSIs with supports. However, Qiao et al. challenged this notion by demonstrating the occurrence of C-SMSI between Au and TiO<sub>2</sub> support.<sup>76</sup> Abundant TiO<sub>x</sub> overlayers migrated onto the surface of Au NPs to form stable encapsulation structures after high-temperature reduction, as



**Figure 3.** The classical strong metal–support interaction. (a) HRTEM image and EELS spectra of RR2Ti-H500 catalyst. (b) Reversibility of RR2Ti properties under redox treatment. From ref 76. Copyright The Authors, some rights reserved; exclusive licensee AAAS. Distributed under a CC BY-NC 4.0 license. (c) Thermodynamic equilibrium models. (d) *In situ* DRIFT spectra of CO adsorption over Au/TiO<sub>2</sub> with different particle sizes. Reprinted with permission under a Creative Commons Attribution 4.0 International license from ref 98. Copyright 2020 The Authors.

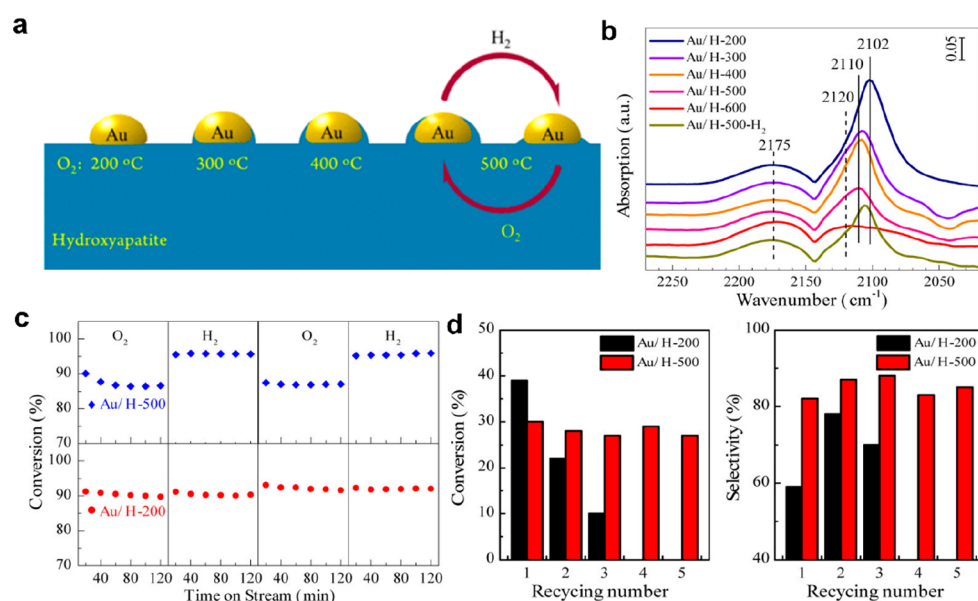
revealed by high-resolution transmission electron microscopy (HRTEM) and *in situ* electron energy loss spectroscopy (EELS) (Figure 3a). The reversible metal encapsulation by the TiO<sub>2</sub> support was also observed, consistent with TiO<sub>2</sub>-supported Pt group metals, resulting in a reversible catalytic performance (Figure 3b). Moreover, C-SMSI can be extended to other reducible oxide-supported Au catalyst systems, such as CeO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>. Further investigations indicated that other group IB metals supported on TiO<sub>2</sub> can also induce C-SMSI through high-temperature reduction. This discovery provides a new route to fabricate supported group IB metals with excellent stability while maintaining high catalytic activity.

More recently, Qiao et al. investigated the size effect on C-SMSI in Au/TiO<sub>2</sub> catalysts.<sup>98</sup> They confirmed that the size of the Au particles had a significant influence on the SMSI phenomenon at the metal–support interface. The study demonstrated that the enhancement of SMSIs occurred more prominently on larger Au particles (~9 and ~13 nm) compared to smaller ones (~3 and ~7 nm) in Au/TiO<sub>2</sub> catalysts (Figure 3d). It should be noted that at the same time Huang's group made a similar discovery of size-dependent SMSI on Pt/rutile (110) model catalyst,<sup>99</sup> further corroborating this finding. Furthermore, a thermodynamic equilibrium model was established to illustrate the size-dependent SMSI state (Figure 3c). This finding is of utmost importance, as it provides a novel approach to modulating catalytic hydrogenation selectivity by simply tuning the SMSI state, even in catalysts with uneven particle size distribution. Thus, controlling the particle size offers a promising avenue for optimizing the catalytic performance through SMSI engineering.

In addition to the size effect of Au NPs, the specific facets of the TiO<sub>2</sub> support also play a critical role in the state of Au–TiO<sub>2</sub> SMSIs. Huang et al. demonstrated that TiO<sub>2</sub>{100} facets supporting Au NPs undergo stronger Au–TiO<sub>2</sub> SMSIs compared to TiO<sub>2</sub>{101} facets.<sup>99</sup> The presence of TiO<sub>2-x</sub> overlayers on the surface of Au NPs generates abundant interfacial sites, which facilitate the activation of lattice oxygen, resulting in excellent performance in low-temperature CO oxidation. Furthermore, the 5 nm-Au/TiO<sub>2</sub>-H500 catalyst exhibited a lower performance than the 2 nm-Au/TiO<sub>2</sub>-H500 catalyst for CO oxidation (all TiO<sub>2</sub> NCs exhibit uniform morphologies and a pure anatase phase), attributed to the excessive encapsulation of Au NPs by TiO<sub>2-x</sub> overlayers. Therefore, manipulating the SMSI state through precise control of particle sizes and the exposure of specific oxide facets on supported metal catalysts represents an efficient strategy for tuning catalytic performance.

## 2.2. Electronic Metal–Support Interaction (EMSI).

Rodriguez et al. revealed significant electronic perturbations between small particles and ceria support via valence photoemission experiments combined with density functional theory (DFT) calculations.<sup>56</sup> These unique electronic properties between the active metal and the support strongly influence the adsorption strength of reactive molecules, resulting in exceptional catalytic properties. Particularly, the strong electronic perturbations significantly enhance the cleavage of the O–H bonds in water, facilitated by the intimate contact between small Pt clusters and the ceria support. Campbell confirmed the presence of strong electronic perturbations through DFT calculations and introduced the term “electronic metal–support interaction” (EMSI) to describe this special interaction.<sup>71</sup>



**Figure 4.** Fabrication of O-SMSI, spectral characterization, and its catalytic performance. (a) Schematic illustration of O-SMSI over Au-HAP catalysts. (b) *In situ* CO-DRIFTS over Au/H-X and Au/H500-H<sub>2</sub> catalysts. (c) CO conversions of Au/H-X at 100 °C via alternating treatment with a flow of O<sub>2</sub> and H<sub>2</sub> with the time stream on. (d) Conversion and selectivity of the Au/H-200 and Au/H-500 catalysts after five cycle experiments. Reprinted with permission from ref 82. Copyright 2016 American Chemical Society.

Libuda et al. further confirmed that the magnitude of charge transfer (CT) across the metal/support interface is size-dependent in the Pt/CeO<sub>2</sub> catalyst system, using synchrotron radiation photoelectron spectroscopy and scanning tunneling microscopy combined with DFT calculations.<sup>72</sup> The maximum CT occurs for Pt particles consisting of approximately 50 atoms, with a quantified transfer of 0.11 electron per Pt atom from the particle to the support. Importantly, CT strongly enhances the chemisorption of CO and H<sub>2</sub>O molecules by approximately 0.5 eV. Therefore, adjusting the particle size is an efficient approach to control the EMSI state in metal/oxide catalysts.

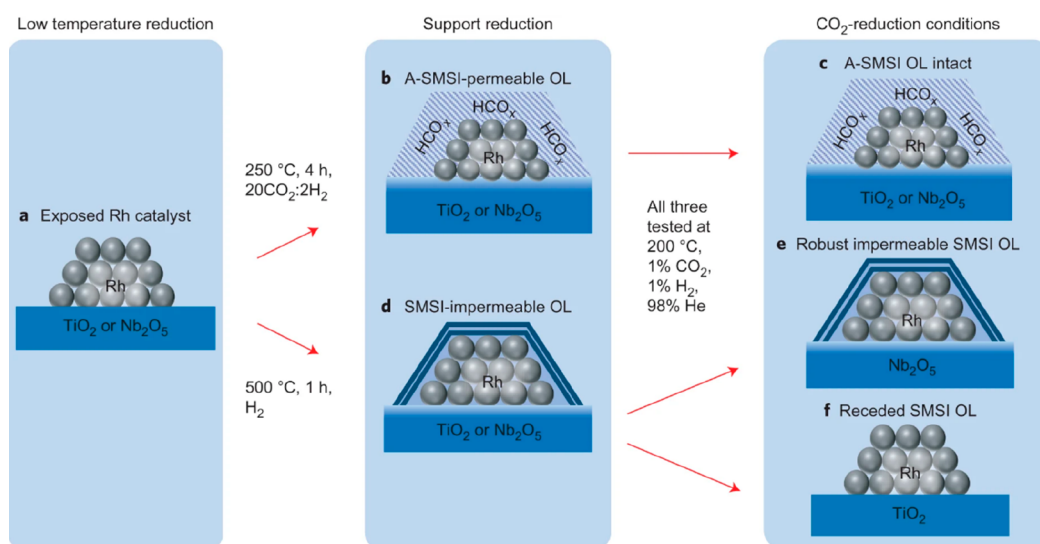
Tang et al. observed a strong EMSI between single-atom Ag and microporous hollandite manganese oxide (HMO) support, attributed to the higher depletion of 4d electronic states of Ag atoms driven by EMSI.<sup>70</sup> This stronger EMSI leads to a higher activation ability of the O<sub>2</sub> molecules in the Ag-HMO catalyst system, resulting in excellent performance in low-temperature formaldehyde oxidation. Additionally, the type of support also plays a critical role in enhancing catalytic activity and stability through strong EMSIs. Lu et al. demonstrated efficient tailoring of the 5d state of single-atom Pt by adjusting the support, including Co<sub>3</sub>O<sub>4</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, and graphene, due to strong EMSIs.<sup>73</sup> The optimum Pt<sub>1</sub>/Co<sub>3</sub>O<sub>4</sub> catalyst significantly improves the performance of the dehydrogenation of ammonia borane (AB). The presence of the EMSI state tailors the unoccupied 5d states to a moderate adsorption state for AB, facilitating H<sub>2</sub> desorption and contributing to its excellent performance.

**2.3. Oxidative Strong Metal–Support Interaction (O-SMSI).** Traditionally, SMSI formation requires a reducing atmosphere at high temperatures, while an oxidative atmosphere tends to disrupt the SMSI. However, an interesting phenomenon called “oxidative strong metal–support interaction” (O-SMSI) was reported between Au NPs and ZnO nanorod support after pretreatment under an oxidative atmosphere (O<sub>2</sub>).<sup>53</sup> Disordered ZnO overlayers migrated

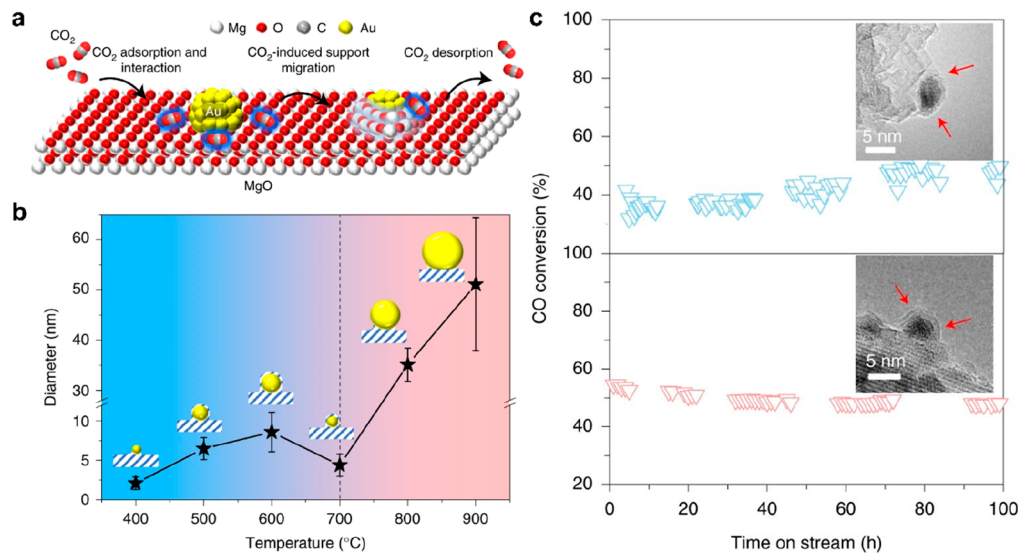
onto the surface of Au particles, forming a partially encapsulated structure, similar to C-SMSI. Surprisingly, this SMSI led to the formation of cationic gold (Au<sup>δ+</sup>) species at the interface, contrasting with the formation of negatively charged metal (M<sup>δ-</sup>) species in C-SMSI under reducing atmospheres. Furthermore, the de-encapsulation of Au/ZnO-nanorod catalysts could be observed after reduction in H<sub>2</sub> atmosphere at 300 °C, accompanied by the formation of Au<sup>δ-</sup> species due to the presence of AuZn alloy, as revealed by *in situ* extended X-ray absorption fine structure (EXAFS).

Another unconventional SMSI phenomenon between Au NPs and HAP was observed under oxidative treatment conditions, opposite to traditional reduction conditions in Figure 4a.<sup>82</sup> The presence of positively charged surface Au species was identified by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Figure 4b). A reversal in catalytic performance was also observed when the pretreatment was conducted in H<sub>2</sub> and O<sub>2</sub> flows (Figure 4c). This new type of SMSI between active metals and non-oxide support opens a path for the construction of phosphate-supported metal systems. Importantly, the Au/HAP SMSI catalyst system exhibited excellent cycling stability for the oxidation reaction of benzyl alcohol (Figure 4d,e), indicating that SMSI facilitates the resistance of supported metals against sintering through the encapsulation structure and special electron configuration.

In the case of Au/TiO<sub>2</sub> catalysts, although they exhibit excellent catalytic performance in many important chemical reactions, they often suffer from poor on-stream stability during realistic reaction conditions, hindering their industrial applications. To address this issue, a melamine-mediated surface modification strategy was developed to construct sintering-resistant titania-supported Au catalysts with ultra-high stability and superior catalytic performance.<sup>100</sup> Instead of traditional high reduction conditions, the Au/TiO<sub>2</sub> catalyst was pretreated in N<sub>2</sub> gas (600 °C, 3 h), followed by calcination under an oxidative atmosphere (air condition) at 800 °C for 3



**Figure 5.** Schematic illustration of C-SMSI and A-SMSI. The overlayer structures of C-SMSI and A-SMSI for Rh/TiO<sub>2</sub> or Rh/Nb<sub>2</sub>O<sub>5</sub> catalysts are shown. Reprinted with permission from ref 43. Copyright 2016 Springer Nature Ltd.



**Figure 6.** (a) Schematic illustration of the CO<sub>2</sub>-induced A-SMSI on Au/MgO. (b) CO<sub>2</sub>-induced structure change of Au/MgO after pretreatment over various sizes of gold nanoparticles at different temperatures. (c) Durability of Au/MgO-C700 during CO oxidation at 300 °C. Reprinted with permission from ref 101. Copyright 2021 Springer Nature Ltd.

h. A permeable TiO<sub>x</sub> layer was observed to encapsulate the surface of Au NPs, facilitated by the presence of melamine under an oxidative atmosphere. Abundant Ti<sup>3+</sup> species in the TiO<sub>x</sub> cover layers were identified by EELS, and EXAFS fitting confirmed the formation of Au–Ti bonds in this encapsulated state. Importantly, this modified strategy can be extended to other commercially available supported Au catalysts, demonstrating its broad applicability and universality.

**2.4. Adsorbate-Mediated Strong Metal–Support Interaction (A-SMSI).** In the traditional view, the formation of SMSIs requires a high-temperature H<sub>2</sub> reduction. However, excessive encapsulation of the active metal by impenetrable oxide overlayers during reduction often leads to catalyst passivation and inactivation. The major challenge in this field for decades has been the significant reduction of active interfacial area. Therefore, it is crucial to construct new types

of SMSIs at milder conditions while maintaining a high exposure of interfacial sites.

Recently, an intriguing “adsorbate-induced SMSI” (A-SMSI) phenomenon was reported over Rh/TiO<sub>2</sub> and Rh/Nb<sub>2</sub>O<sub>5</sub> catalysts.<sup>43,46</sup> After pretreatment in a CO<sub>2</sub>–H<sub>2</sub> atmosphere at relatively low temperatures (150–300 °C), a thin HCO<sub>x</sub>-functionalized reducible oxide layer partially encapsulating the surface of the Rh NPs was observed (Figure 5). The surface-encapsulated layers exhibit a porous structure with abundant oxygen-vacancy (O<sub>v</sub>) defects, allowing reactive molecules to access the active sites on the Rh NPs. Surprisingly, the obtained A-SMSI Rh/TiO<sub>2</sub> and Rh/Nb<sub>2</sub>O<sub>5</sub> catalysts exhibit selective hydrogenation of CO<sub>2</sub> to CO, in contrast to traditional Rh SMSI catalysts that mainly produce CH<sub>4</sub>. *In situ* DRIFTS results show a ~50 cm<sup>-1</sup> redshift in the vibrational frequency of CO with decreased intensity of the IR band over the Rh/TiO<sub>2</sub> catalyst after treatment with

$2\text{CO}_2:2\text{H}_2$  compared to  $\text{H}_2$  treatment, indicating CT from the  $\text{TiO}_2$  support to Rh particles. However, it is intriguing that the negatively charged Rh species formed in this process do not promote excessive hydrogenation of  $\text{CO}_2$  to generate  $\text{CH}_4$ . Therefore, the chemical nature of A-SMSI and its catalytic mechanism have not been clearly elucidated for this new type of catalyst. Advanced *in situ* characterization techniques should be explored to gain a fundamental understanding of A-SMSI catalyst systems. The construction of A-SMSI catalysts opens up new possibilities for tuning the selectivity of hydrogenation reactions.

Bao et al. reported that permeable  $\text{BO}_x$  overlayers migrated onto the surface of Ni particles due to the formation of C-SMSI states adsorbate-induced by weak oxidizing gases (e.g.,  $\text{CO}_2$  or  $\text{H}_2\text{O}$ ).<sup>78</sup> EELS and *in situ* CO-DRIFTS experiments confirmed the formation of the  $\text{Ni}@\text{BO}_x$  encapsulation structure. Surface B–O and B–OH sites were observed in the  $\text{BO}_x$  encapsulation overlayers. Due to the presence of the SMSI state, metallic Ni remained the main component in the Ni/h-BN catalyst under  $\text{CO}_2$  or DMR atmospheres, protected by the  $\text{BO}_x$  overlayers, allowing for the formation of unique permeable overlayers. DFT calculations further indicated that the formation of  $\text{Ni}@\text{BO}_x$  nanostructures is thermodynamically favorable compared to that of the h-BN/Ni surface. Similar to C-SMSI catalysts, reversible structural transformations were also observed over metal/h-BN catalysts, with encapsulation occurring under oxidative treatment and de-encapsulation observed under reduction treatment. This modulation strategy can be extended to other metals, such as Fe, Co, Ru, and Pt, demonstrating its broad applicability. Furthermore, the presence of surface B–O and B–OH sites, in conjunction with adjacent active metal sites, synergistically promotes the catalytic reaction process, offering a new pathway for the design of high-performance catalysts.

Moreover, the A-SMSI phenomenon was also constructed between Au and MgO support by  $\text{CO}_2$  adsorbate-induced SMSIs ( $\text{MgO} + \text{CO}_2 \leftrightarrow \text{MgCO}_3$ ) following Le Chatelier's principle,<sup>101</sup> i.e., an irreducible thin MgO overlayers migrated on the surface of Au NPs to form an encapsulation structure in flowing  $\text{CO}_2$  (Figure 6). Notably, the MgO overlayer is permeable and even water-tolerant, which can enhance the stability of this type of Au-based catalyst with sinter resistance. The A-SMSI effect can be expanded to other Au/CaO or Au/HAP systems. This investigation provides us an avenue to rationally design the supported metal catalysts over irreducible oxides with an SMSI state. Apart from the  $\text{CO}_2$ -induced A-SMSI, alcohol adsorbate-induced SMSIs have gradually attracted attention. Polo-Garzon et al. found that 2-propanol can cause the carbon deposits and/or  $\text{TiO}_x$  overlayers to migrate on the surface of Au NPs and Pd NPs due to SMSIs at low temperature to form a partial or nearly complete encapsulation structure.<sup>93,102</sup> This gives us a method to construct A-SMSI catalysts under mild conditions.

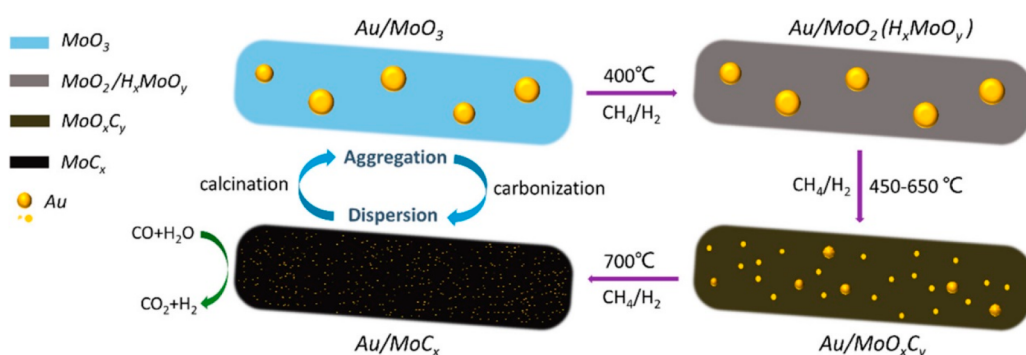
**2.5. Reactive Metal–Support Interaction (RMSI).** The concept of a “reactive metal–supported interaction” (RMSI) involves a chemical reaction between an admetal (active metal) and a support material, resulting in the formation of bimetallic alloys. Traditionally, RMSIs occur under reductive conditions using reductive oxides such as  $\text{TiO}_2$  and  $\text{CeO}_2$  as the supports. However, recent findings by Wu et al. have shown that RMSI can occur and form a Pt–Nb surface alloy between Pt and a two-dimensional (2D)  $\text{Nb}_2\text{CT}_x$  MXene at moderate reaction temperatures.<sup>86</sup> The formation of the bimetallic alloy structure

weakens the adsorption strength of the CO molecules compared to monometallic platinum. Simultaneously, the unique alloy–Mxene interface enhances the adsorption and activation of  $\text{H}_2\text{O}$  molecules. These combined effects contribute to the excellent catalytic performance of WGS reactions. This work provides a new strategy for fabricating bimetallic alloys through RMSI between an admetal and a non-oxide 2D metal carbide.

Recently, the C-SMSI state has been constructed over a Ru–Mo-oxide catalyst under  $\text{CO}_2$  hydrogenation conditions at 250 °C.<sup>92</sup> The defect  $\text{MoO}_{3-x}$  overlayers with abundant oxygen vacancies derived from the reduction of  $\text{MoO}_3$  support and subsequently migrated on the surface of Ru NPs to form a  $\text{Ru}@\text{MoO}_{3-x}$  encapsulation structure under the reaction conditions. Importantly, the CO selectivity is above 99% owing to the presence of the SMSI state, which is very different from the 100%  $\text{CH}_4$  selectivity on the surface of Ru NPs. The catalytic selectivity of the reverse water–gas shift (RWGS) reaction can switch back to 100%  $\text{CH}_4$  after  $\text{O}_2$  treatment. Thus, a reactive gas-induced encapsulation structure facilitates the modulation of catalytic properties in real reactions. Zhu et al. found that the  $\text{H}_2/\text{H}_2\text{O}/\text{CH}_3\text{OH}/\text{N}_2$  reactive gas mixture can accelerate the migration of  $\text{ZnO}_x$  species on the surface of Cu NPs over commercial  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst to form abundant Cu– $\text{ZnO}_x$  interfacial sites owing to the RMSI, which dramatically improves the catalytic activity and stability of the methanol steam reforming reaction. Further exploration of RMSIs with different metals and support materials holds exciting opportunities for tailoring catalytic properties and developing efficient catalysts for various chemical reactions.

**2.6. Wet-Chemistry Strong Metal–Support Interaction (WC-SMSI).** In a recent study by Xiao et al., a novel form of SMSIs called “wet-chemical SMSI” (WC-SMSI) was discovered.<sup>77</sup> In their study, C-SMSIs between Au NPs and a  $\text{TiO}_2$  support were found to form in a liquid environment via a wet-chemical method at room temperature, and thus it was defined as WC-SMSI. Disordered ultra-thin  $\text{TiO}_{2-x}$  overlayers were observed to encapsulate the surface of Au NPs, creating unique Au– $\text{TiO}_x$  interfacial sites. This led to the excellent stability and sinter resistance of the catalyst. The strong interactions between  $\text{Ti}^{3+}$  cations and Au NPs facilitated the formation of negatively charged Au species ( $\text{Au}^{\delta-}$ ), which promoted the activation of  $\text{O}_2$  molecules, resulting in the formation of  $\text{O}=\text{C}-\text{O}_2$  intermediates. Importantly, this preparation strategy was also applicable to other noble metals, such as Pt, Ru, Rh, and Pd, expanding the potential of WC-SMSIs in various catalytic systems. This discovery opens up new possibilities for the design and development of stable and efficient catalysts based on noble metals and oxide supports under mild reaction conditions.

**2.7. Electronic Oxide–Metal Strong Interaction (EOMSI).** In the field of catalysis, inverse-phase structural catalysts have garnered significant attention for their exceptional catalytic performance arising from their unique interfacial sites. Huang et al. have made significant contributions to this area by reporting on oxide–metal structural catalysts with strong electronic interactions and introducing the concept of “electronic oxide–metal strong interaction” (EOMSI).<sup>103</sup> In their study, they demonstrated that  $\text{CeO}_x$  oxide adlayers can stabilize on the surface of Ag nanocrystals with a low oxidation state. The presence of surface oxide adlayers imparts sinter resistance to oxidation, even at high temperatures in air. Furthermore, the thickness



**Figure 7.** New type of SMSI between metal and carbide. A schematic diagram of the formation of a SMSI between Au and the  $\alpha$ -MoC support is shown. Reprinted with permission from ref 61. Copyright 2018 American Chemical Society.

and size of the oxide adlayers were found to be closely related to the interfacial electronic properties. These findings provide new insights toward understanding strong interfacial interactions and offer a pathway to construct new types of structural catalysts.

**2.8. Metal Carbide-Induced Strong Metal–Support Interaction (MC-SMSI).** Metal carbide-supported metal catalysts have recently garnered significant attention due to the formation of SMSIs which can substantially enhance their catalytic performance.<sup>104</sup> One prominent example is molybdenum carbide, a transition metal carbide that incorporates carbon atoms into the lattices of molybdenum atoms, forming two distinct phases (i.e.,  $\alpha$ -MoC and  $\beta$ -Mo<sub>2</sub>C). Molybdenum carbide can serve as an efficient catalyst support, allowing for the modulation of the morphology, particle size, and electronic properties of the supported metals via SMSIs.

In the case of a Pt/Mo<sub>2</sub>C catalyst, strong interactions between Pt NPs and Mo<sub>2</sub>C support result in the formation of raft-like Pt NPs and the transfer of electrons from Pt NPs to the Mo<sub>2</sub>C support.<sup>105</sup> This leads to the formation of positively charged Pt species and enhances the catalytic activity. Similarly, with a Au/TiC(001) catalyst, strong electronic perturbations induced by SMSIs at the interface between Au and TiC dramatically enhance the catalytic properties of Au, particularly in the WGS reaction.<sup>106</sup> This electronic perturbation promotes the cleavage of O–H bonds in water.

Pure-phase  $\alpha$ -MoC with a face-centered cubic structure has also shown great potential as a catalyst support material.<sup>59,83</sup> Atomically dispersed Pt sites can be anchored on the surface of  $\alpha$ -MoC, accompanied by strong electron transfer from Pt<sub>1</sub> sites to the support, forming high-valence Pt species via SMSIs. This creates abundant active interfacial sites that substantially enhance catalytic performance, such as in the aqueous-phase reforming of the methanol reaction. The electron-deficient Pt<sub>1</sub> sites on  $\alpha$ -MoC promote the activation of C–H bonds while inhibiting the cleavage of C–O bonds. Additionally,  $\alpha$ -MoC exhibits high activity for the dissociation of H<sub>2</sub>O molecules at low temperatures. The synergy of both aspects contributes to the outstanding catalytic performance. Similarly,  $\alpha$ -MoC-supported single-atom Pt catalysts demonstrate highly CO-resistant catalytic properties in selective hydrogenation reactions, attributed to the presence of electron-deficient Pt species.<sup>107</sup> Through SMSIs between active metals and  $\alpha$ -MoC, layered Au clusters can be fabricated on the surface of  $\alpha$ -MoC. This unique interfacial structure confers exceptional performance to Au/ $\alpha$ -MoC catalysts in WGS reactions at ultra-low temperatures. The reversible dispersion/aggregation of Au

clusters can be observed through cycling carbonization and oxidation treatments (Figure 7), representing a new SMSI characteristic between metal and carbide support.<sup>61</sup>

In recent studies, atomically dispersed Co and Ni bimetallic catalysts were successfully fabricated over  $\alpha$ -MoC support, capitalizing on the SMSI effect.<sup>108</sup> The resulting CoNi/ $\alpha$ -MoC catalyst exhibited exceptional performance in the hydrolysis of AB, surpassing non-precious catalysts with a hydrogen generation rate of 321.1 mol H<sub>2</sub>·mol<sup>-1</sup> CoNi·min<sup>-1</sup> at 298 K. The spatial correlation between Co and Ni atoms was confirmed, and a strong synergistic interaction between the two metals was demonstrated, effectively activating the B–N bond in AB. Furthermore, the  $\alpha$ -MoC support demonstrated an excellent H<sub>2</sub>O dissociation ability, leading to the formation of abundant surface OH\* groups at low temperatures. The combination of the synergistic effects between Co and Ni atoms and the H<sub>2</sub>O dissociation ability of the  $\alpha$ -MoC support contributed to the outstanding catalytic performance in AB hydrolysis. This research represents a significant advancement in the design of atomically dispersed bimetallic catalysts with strong synergistic effects based on SMSIs, providing new opportunities for the development of efficient and cost-effective catalytic systems.

**2.9. SMSIs between Single Atoms and Supports.** In modern industrial catalysis, maximizing the utilization and catalytic efficiency of active metal centers is a key challenge. Single-atom catalysis has emerged as a promising approach due to its atomic economy<sup>109–111</sup> and the maximum utilization of interfacial active centers.<sup>1</sup> Interface engineering plays a crucial role in monitoring catalytic activity and selectivity, as interfacial sites often act as catalytically active centers. The fabrication and modulation of SMSIs between single atoms and supports have been recognized as an efficient approach to enhance the catalytic properties of SACs.<sup>112</sup> However, single atoms are prone to aggregation under realistic reaction conditions, making the regulation of interaction strength essential to fabricating sinter-resistant SACs and enhancing their stability.

The strength of interfacial binding between single atoms and the support can be predicted using theoretical calculations such as DFT. By calculation of the formation energy of oxides and oxygen vacancies, the oxophilicity and reducibility of the system can be assessed, providing insights into the strength of interfacial interactions. This theoretical approach aids in understanding and predicting the stability and catalytic performance of SACs.<sup>113</sup>

Recent studies have demonstrated SMSIs between single atoms, such as Pd and Cu, and nanodiamond–graphene



Table 1. Summary of Different Types of SMSIs

Entry	Type of SMSI	Description	Distinction	Example
1	Classic (C-SMSI)	Significant suppression of small-molecule adsorption; electron transfer from the support to the metal; mass migration from the support to encapsulate metal; complete reversal of the preceding phenomena upon reoxidation	Conventional SMSI	Transition metal oxides-supported group VIII metals and group IB metals
2	Electronic (EMSI)	Occurs naturally upon contact between the metal and the support, without the need of any treatment	Pretreatment condition	Pt/CeO <sub>2</sub> , Co <sub>3</sub> O <sub>4</sub> , ZrO <sub>2</sub> , graphene; Ag/HMO
3	Oxidative (O-SMSI)	O <sub>2</sub> -treatment-induced SMSI		Au-ZnO; Au-HAP; Au/TiO <sub>2</sub>
4	Adsorbate-mediated (A-SMSI)	Treatment under lower temperature in CO <sub>2</sub> /H <sub>2</sub> atmosphere		Rh/TiO <sub>2</sub> and Rh/Nb <sub>2</sub> O <sub>5</sub>
5	Wet-chemistry (WC-SMSI)	Interaction occurs at room temperature in a liquid environment		Au, Pt, Ru, Rh, and Pd with TiO <sub>2</sub>
6	Reactive (RMSI)	The metal reacts with the support to form an alloy phase	Mechanism	Pt/Nb <sub>2</sub> CT <sub>x</sub> MXene
7	Electronic oxide (EOMSI)	Strong metal interactions occur in inverse catalysts	Structure of metal/support	CeO <sub>x</sub> /Ag
8	Metal carbide-induced (MC-SMSI)	Highly dispersed metal species on carbides are significantly positively charged		Pt, Ni, Co, Pd with $\alpha$ -MoC
9	SMSI between single atoms and supports	Chemisorption of single atoms can also be prohibited due to the 18-electron rule instead of physical coverage		Pt/TiO <sub>2</sub> ; Pd, Cu with nanodiamond

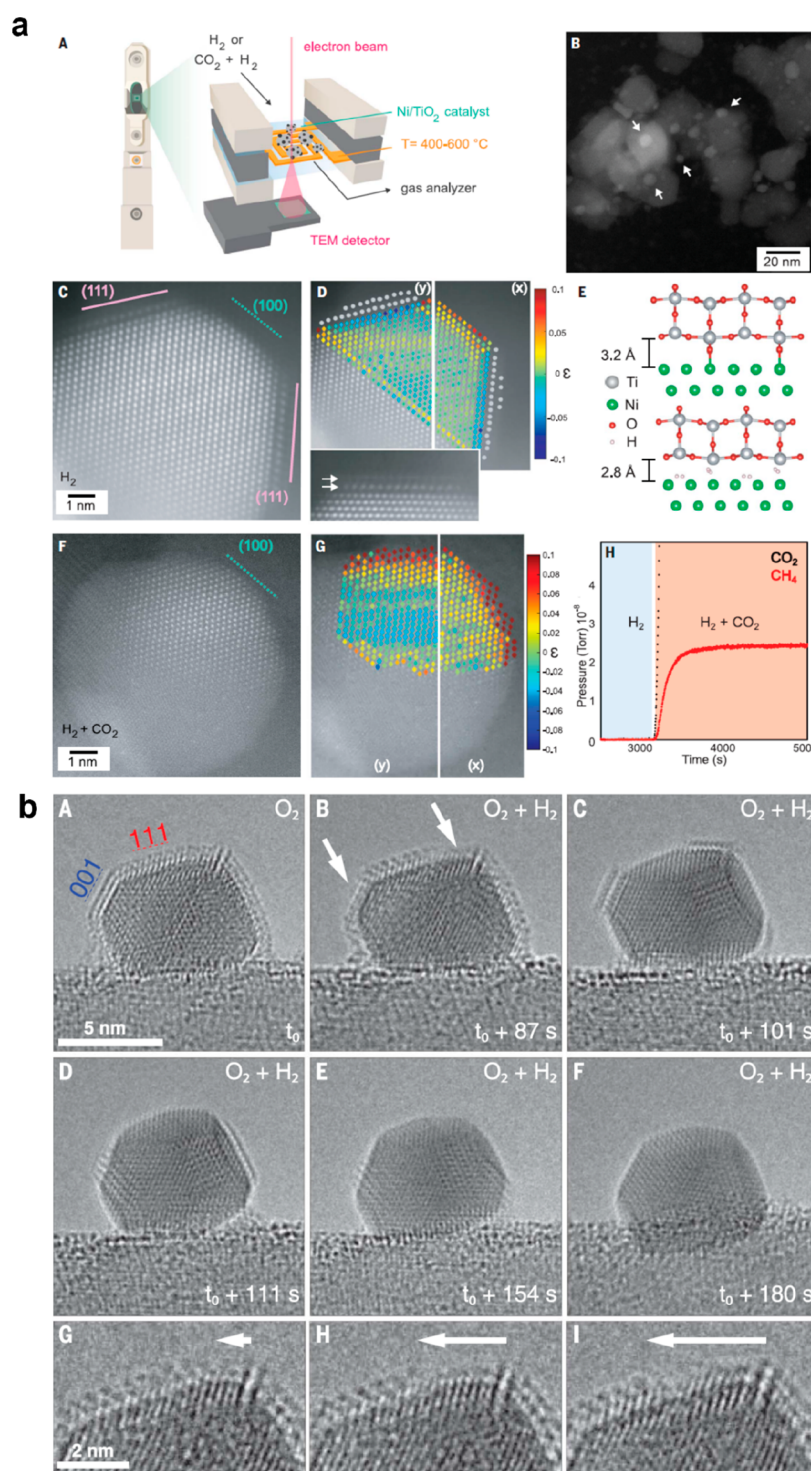
supports. This type of SMSI facilitates the full exposure of metal centers with well-defined electronic structures, leading to enhanced catalytic performance, such as high selectivity in the semi-hydrogenation of acetylene.<sup>114,115</sup> The formation of strong metal–carbon (M–C) bonds, such as Pd–C and Cu–C bonds, highlights the extraordinary interactions between metals and the nanodiamond–graphene support. These strong M–C bonds contribute to the stabilization of atomically dispersed metal species and the formation of well-defined electronic structures, resulting in significant influences on the catalytic properties of the supported metals.

Furthermore, recent findings by Qiao et al. revealed the occurrence of SMSIs between Pt single atoms and TiO<sub>2</sub> support at higher reduction temperatures compared to Pt NPs.<sup>112</sup> According to Born–Oppenheimer molecule dynamics simulations, charge distribution, and projected density of states analysis, the coordination saturation of Pt single atoms by two OH groups, two H atoms, and Ti<sup>3+</sup> species follows the 18-electron rule, and the optimized structure was denoted as (Pt(OH)<sub>2</sub>(H)<sub>2</sub>(Ti))–Ti<sub>23</sub>O<sub>47</sub>. The suppression of CO adsorption on Pt single atoms after high-temperature reduction stems from coordination saturation rather than physical coverage, which was confirmed by the low-energy ion scattering (LEIS) experiment and DFT calculations. In contrast, in Pt NP systems, the physical coverage of the support on Pt NPs is considered to be the primary factor for the suppressed adsorption of H<sub>2</sub> and CO. Furthermore, the exposure of Pt single-atom sites could be retained through the selective encapsulation of Pt NPs in the catalyst by TiO<sub>x</sub> overlayers. This discovery provides a new approach to identify the intrinsic catalytically active sites by precisely tuning the SMSI phenomenon. By investigating the interaction between single atoms and support materials, researchers can gain insights into the specific coordination environments and electronic structures that govern catalytic activity. The nine types of SMSIs are briefly summarized in Table 1.

### 3. UNVEILING THE CHEMICAL NATURE OF SMSIs VIA ADVANCED CHARACTERIZATION TECHNIQUES

Over the past several decades, extensive efforts have elucidated that SMSIs play a crucial role in significantly enhancing catalytic performance and selectivity in certain cases.<sup>116</sup> Gaining insight into the influence of SMSIs on catalytic properties is critical for the rational design and optimization of highly effective catalysts. The quest for a comprehensive understanding of SMSIs entails delving into their chemical nature and catalytic mechanisms, a long-standing challenge in the field. Cutting-edge *in situ/operando* characterization techniques, including electron microscopy (e.g., HRTEM, STEM, ETEM) and spectroscopy techniques (e.g., XPS, UPS, EXAFS, XRD, FT-IR, HS-LEIS, EPR, Raman) and temperature-programmed desorption and reduction experiments, combined with DFT calculations, have been utilized to decipher the chemical nature and the underlying catalytic mechanisms of SMSIs.<sup>29,51,117–120</sup> For example, the extent and direction of electron transfer can be identified via *in situ* X-ray photoelectron spectroscopy (XPS) and *in situ* X-ray absorption near-edge structure spectroscopy, coupled with *in situ* CO-DRIFTS.<sup>121,122</sup> The alteration of the metal d band center has been investigated using ultraviolet photoelectron spectroscopy (UPS) combined with DFT calculations, revealing substantial electronic perturbations at the interface.<sup>56,71</sup>

Electron microscopy techniques, including HRTEM and aberration-corrected scanning transmission electron microscopy (STEM), have been extensively applied to explore the geometric structure and composition of catalysts, including the morphology, size, defect structure, and encapsulation configuration of supported metals.<sup>123,124</sup> Cu/ZnO, a catalyst with important industrial applications, has been extensively applied in the low-temperature WGS reaction and the hydrogenation of CO/CO<sub>2</sub> to methanol, among others. The presence of SMSIs in this catalyst has been validated.<sup>47,125</sup> Aberration-corrected HRTEM and HAADF-STEM revealed abundant bulk/surface defects of Cu NPs, such as stacking faults, which led to the formation of twin boundary, kink, and step sites, confirming the strong interaction between Cu NPs and the



**Figure 8.** Restructuring and dynamical evolution of titanium oxide overlayers revealed by *operando* electron microscopy. (a)  $\text{TiO}_x$  overlayer formation and its restructuring of the Ni/ $\text{TiO}_2$  catalyst during  $\text{H}_2$  reduction and  $\text{CO}_2$  methanation, respectively. Reprinted with permission from ref 123. Copyright 2023 AAAS. (b) Morphological change of the particle surface upon transition into the redox-active regime on the Pt/ $\text{TiO}_2$  catalyst. Reprinted with permission from ref 29. Copyright 2022 AAAS.

$\text{ZnO}$  support. Furthermore, the migration of disordered  $\text{ZnO}_x$  overlayers onto the Cu NPs formed an encapsulation structure, as also confirmed by electron microscopy. Additionally, the presence of positively charged  $\text{Zn}^{\delta+}$  species at the interface, indicative of SMSI between Cu and  $\text{ZnO}$ , was revealed through the Zn- $\text{L}_{3}\text{M}_{45}\text{M}_{45}$  Auger spectra. Complementing these findings, DFT calculations established that the inclusion of Zn stabilizes active intermediates (e.g.,  $\text{HCO}$ ,  $\text{H}_2\text{CO}$ , and

$\text{H}_3\text{CO}$  species), a phenomenon facilitated by SMSIs that accounts for its exceptional catalytic performance.

High-sensitivity–low-energy ion scattering (HS-LEIS) is a unique technique to investigate the outermost atomic layer of supported catalysts, which can provide quantitative information on both the elemental composition and distribution. Zhang et al. confirmed that Pt NPs can be encapsulated by  $\text{TiO}_x$  layers after reduction at 250 °C via LEIS,<sup>112</sup> owing to the

significant decrement of Pt signal. Notably, there is no change anymore for the Pt single-atom signal after the high-temperature reduction at 600 °C, which directly demonstrates that the suppression of CO adsorption is not attributed to the physical coverage. HS-LEIS was also carried out to unveil the nature of surface overlayers over Fe<sub>2</sub>O<sub>3</sub>-CuO/SiO<sub>2</sub> catalyst with SMSIs.<sup>91</sup> The Cu HS-LEIS signal can be identified as continuously increasing up to a sputtered depth of 1.5 monolayer, indicating that a thin FeO<sub>x</sub> overlayer migrated on the surface of Cu NPs during the RWGS reaction.

In order to clearly decipher the chemical nature of SMSIs, electron paramagnetic resonance (EPR) spectroscopy, *in situ* Raman spectroscopy, and near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) are efficient techniques to reveal in-depth the surface and interfacial structures as well as the degree of encapsulation of supported metal catalysts with SMSIs. It is well known that surface defect structures can be formatted driven by the SMSIs, such as oxygen vacancy defects, Ti<sup>3+</sup>, Ce<sup>3+</sup>, and Mo<sup>δ+</sup> (5 < δ < 6) species. EPR measurements can confirm the partial reduction of TiO<sub>2</sub> species, especially sensitive to the Ti<sup>3+</sup> species and oxygen vacancy defects.<sup>126</sup> A strong signal at *g* = 1.934 can be assigned to the surface Ti<sup>3+</sup> species after reduction of Pt/TiO<sub>2</sub>-C at 250 °C. In addition, the signal at *g* = 2.002 is attributed to the oxygen vacancy.<sup>112</sup> Both of these can provide reliable information for the establishment of a theoretical calculation model. Bao et al. reported that the surface-defective MoO<sub>3-x</sub> species can be generated over Ru-Mo-O<sub>x</sub> catalyst under CO<sub>2</sub> hydrogenation conditions,<sup>92</sup> which is in sharp contrast to the pure MoO<sub>3</sub> sample. The MoO<sub>3-x</sub> surface phase can be revealed by *in situ* Raman spectroscopy, and the main signals are at 197, 221, 340, 485, 557, and 717 cm<sup>-1</sup>. *In situ* NAP-XPS confirmed the coexistence of Ru<sup>0</sup> species and unreduced Ru species as well as the formation of surface defective MoO<sub>3-x</sub> species. The peak at 230.5 eV is assigned to the Mo<sup>5+</sup>, while the peak at 231.4 eV is attributed to the Mo<sup>δ+</sup> (5 < δ < 6).

In a recent study, *operando* electron microscopy was employed to investigate the formation and dynamic reconstruction of thin TiO<sub>x</sub> overlayers on TiO<sub>2</sub>-based supported metal catalysts with SMSIs under various chemical environments.<sup>123</sup> The formation of thin TiO<sub>x</sub> overlayers was observed on Ni/TiO<sub>2</sub> catalysts after 400 °C reduction, resulting in a partially encapsulating bilayer structure (400-Ni/TiO<sub>2</sub>), as shown in Figure 8a. The selective coverage of Ni(111) facets by bilayers of TiO<sub>2</sub> rutile (110) was revealed by both electron microscopy observation and DFT calculations. The reconstructing behavior of Ni particles in the Ni/TiO<sub>2</sub> catalysts was investigated under the CO<sub>2</sub> hydrogenation working conditions. The proportion of Ni (111) facets decreased, while the Ni (100) facets remained due to the loss of the Ni-Ti interface, leading to the exposure of more active facets with lower atomic coordination. Consequently, the TiO<sub>x</sub> overlayers on 400-Ni/TiO<sub>2</sub> catalysts could be removed under CO<sub>2</sub> hydrogenation conditions, as also confirmed by NAP-XPS. Additionally, after 600 °C reduction, a more stable TiO<sub>x</sub> overlayer with complete encapsulation was formed on 600-Ni/TiO<sub>2</sub> catalysts. Interestingly, Ni re-exposure and the formation of Ni/TiO<sub>x</sub> interfacial sites were observed under CO<sub>2</sub> hydrogenation reaction conditions, resulting from the transformation of the completely encapsulating state to a partial coverage structure.

*In situ* STEM and *in situ* TEM were employed to monitor the dynamic interactions between Pt metal particles and the

TiO<sub>2</sub> support with SMSIs. A non-classical O-SMSI state was observed on the Pt/TiO<sub>2</sub> catalyst upon exposure to an O<sub>2</sub> atmosphere.<sup>29</sup> The overlayers encapsulating the surface of Pt NPs could be completely removed after exposure to a mixture gas (60 mbar H<sub>2</sub> and 700 mbar O<sub>2</sub>) for 180 s, accompanied by shape change of the Pt NPs and a slight expansion of the Pt {100} facets, as shown in Figure 8b. The interfacial dynamics and redox-chemistry-driven directional migration of Pt NPs were also investigated by environmental TEM, revealing a strong dependence on NPs orientation. Upon exposure to a pure O<sub>2</sub> atmosphere, the SMSI state with an encapsulating structure for Pt/TiO<sub>2</sub> catalysts could be reestablished. These findings highlight the close relationship between the SMSI state and the chemical environment.

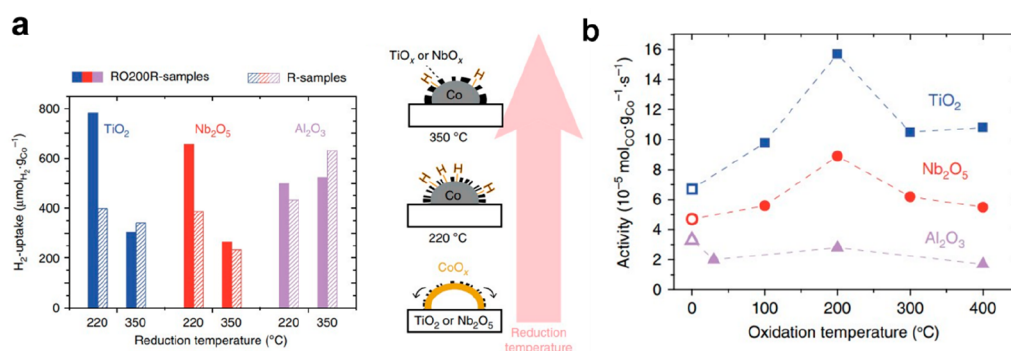
The use of *operando* electron microscopy techniques provides valuable insights into the formation, evolution, and transformation of SMSI structures in catalyst systems, shedding light on the interplay between metal NPs and support materials under different reaction conditions.

In the field of catalysis, the electronic state of the supported metal can significantly influence the catalytic activity. The formation of SMSIs can effectively modulate the d band center of the metal, thereby impacting its chemical properties. UPS has been an effective tool to probe the density of metal d states in SMSI systems, such as the Pt/CeO<sub>2</sub> catalyst.<sup>56</sup> The unique electronic properties of supported Pt were shown to enhance the activation and dissociation of H<sub>2</sub>O molecules. Most recently, the Ni@TiO<sub>2-x</sub> catalyst, featuring SMSIs, was synthesized based on the structural topotactic transformation from layered double hydroxides (LDHs).<sup>122</sup> The presence of strong electronic interactions between Ni and the TiO<sub>2</sub> support, leading to the formation of abundant Ni<sup>δ-</sup>-O<sub>v</sub>-Ti<sup>3+</sup> interfacial sites, was confirmed by a suite of *in situ* techniques: HRTEM, XPS, EXAFS, and DRIFTS. *In situ* EELS demonstrated that disordered TiO<sub>2-x</sub> overlayers partially coated Ni particles. *In situ* EXAFS and DFT calculations corroborated that H<sub>2</sub>O dissociation was significantly enhanced due to SMSIs, and interfacial Ni<sup>δ-</sup> species directly participated in the dissociation of H<sub>2</sub>O to generate Ni-O-Ti bonds, accounting for its extraordinarily high activity for the WGS reaction. *In situ* time-resolved DRIFTS was also carried out to monitor the whole catalytic process at the interface.

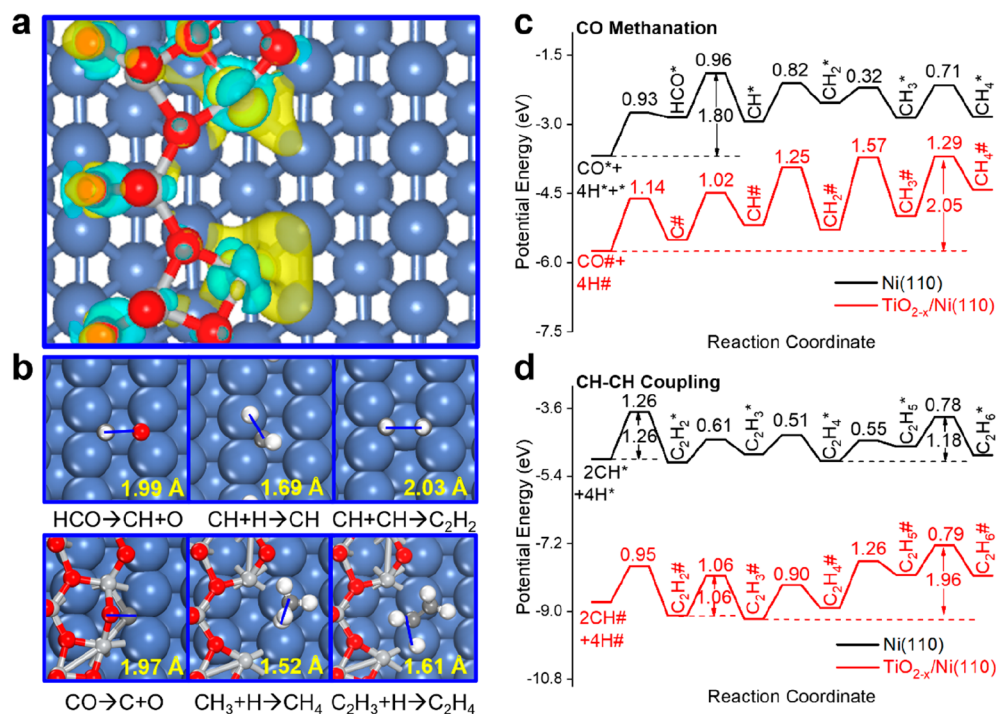
Leveraging a combination of these advanced *in situ* characterization techniques has provided researchers with profound insights into electronic interactions and catalytic mechanisms in SMSI systems. This knowledge is vital for the rational design and enhancement of catalysts that exhibit improved performance.

#### 4. IMPACT OF SMSIs ON CATALYTIC ACTIVITY, SELECTIVITY, AND STABILITY

The surface chemisorption properties of a catalyst have a significant bearing on its catalytic attributes. This is particularly pertinent in catalysts exhibiting SMSIs, where strong chemical bonds formed at the interface can dramatically alter the chemisorption behavior of the supported metal. As such, fine-tuning the strength of SMSIs is crucial to significantly augmenting the catalytic activity. Excessively strong interactions, however, can lead to catalyst passivation and deactivation, as uncovered in early research. A wealth of recent studies corroborate the assertion that SMSIs can dramatically enhance the catalytic activity, selectivity, and stability in select reactions.<sup>127-136</sup>



**Figure 9.** (a) Influence of the temperature of the second reduction on the exposed cobalt surface area and the schematic illustration. (b) Cobalt-weight-based catalytic activity in the Fischer–Tropsch synthesis after various reduction–oxidation–reduction (ROR) treatments. Reprinted with permission under a Creative Commons Attribution 4.0 International license from ref 49. Copyright 2018 The Authors.



**Figure 10.** DFT-optimized structures of  $\text{Ti}_6\text{O}_{11}/\text{Ni}(110)$  and the catalytic mechanism of the FTS reaction. Reprinted with permission under a Creative Commons Attribution 4.0 International license from ref 52. Copyright 2022 The Authors.

**4.1. Activity Enhancement.** In the field of heterogeneous catalysis, catalytic performance is dependent on the geometric and electronic structures of the active sites. SMSIs have the special advantage to modulate the CT between active metal and support, promote the formation of surface defect structures (e.g., oxygen vacancy defect), and improve the number of interface sites via regulating the suboxide overlayer on the surface of the active metal. Particularly, the magnitude and direction of electron transfer between metal and support can be tuned by precisely controlling the strength of SMSIs over different catalytic systems, resulting in the formation of SMSI-induced electron-rich or electron-deficient active sites, which dramatically enhance the catalytic performance.

de Jong et al. developed a reduction–oxidation–reduction (ROR) treatment method to tune the SMSI state of Co-based catalysts ( $\text{Co}/\text{TiO}_2$  and  $\text{Co}/\text{Nb}_2\text{O}_5$ ) and drastically improve the number of interfacial active sites (Figure 9).<sup>49</sup> After the second reduction, the cobalt surface area increases 2-fold,

accompanied by a proportional enhancement of the catalytic activity of Fischer–Tropsch synthesis (FTS). Zhang et al. regulated the  $\text{TiO}_x$  overlayer on the surface of Ru NPs to form the unique interface structure via SMSIs, which dramatically enhanced the cleavage of CO bonds during the FTS and boosted the catalytic activity of the  $\text{Ru}/\text{TiO}_2$  catalyst.<sup>51</sup> Wei et al. developed a LDH precursor to construct a  $\text{Au}@/\text{TiO}_{2-x}/\text{ZnO}$  catalyst with SMSIs at the lower temperature 300 °C under a  $\text{H}_2$  atmosphere. There is strong electron transfer from the ZnTi mixed metal oxide support to Au NPs, with the formation of abundant  $\text{Au}^{\delta-}-\text{O}_v-\text{Ti}^{3+}$  interfacial sites.<sup>62</sup> Study demonstrates that the electron-enriched  $\text{Au}^{\delta-}$  species facilitate the enhancement of CO chemisorption, while  $\text{O}_v-\text{Ti}^{3+}$  dramatically accelerates the dissociation of the  $\text{H}_2\text{O}$  molecule via interfacial synergy catalysis, accounting for the largely enhanced catalytic activity of the WGS reaction. Therefore, regulating SMSI states to increase the number and modify the active microzone structure of interfacial sites (e.g., electron

transfer and oxygen vacancy) are efficient strategies to enhance the catalytic activity in the heterogeneous catalysis.

It is well known that the activation, adsorption, and dissociation of H<sub>2</sub>O molecules play critical roles in various energy-related reforming reactions, including methanol/ethanol and water steam reforming reactions, the WGS reaction, etc.<sup>87,122</sup> Surface oxygen vacancies often serve as highly active sites for H<sub>2</sub>O dissociation. Reducible oxide-supported metal catalysts for SMSIs are gaining considerable attention due to the formation of abundant surface oxygen vacancy defects, which significantly facilitate the cleavage of the O–H bond in water. Ambient-pressure XPS on the Ni/CeO<sub>2</sub> system confirmed that H<sub>2</sub>O dissociation substantially increases due to the strong interactions between Ni and CeO<sub>2</sub> support.<sup>57</sup> Furthermore, DFT calculations substantiate that SMSI promotes water dissociation due to the strong electronic perturbation at the interface, accounting for the enhancement of catalytic activity of the WGS and ethanol steam reforming reactions.

**4.2. Selectivity Regulation.** Electron transfer is a typical characteristic of supported SMSI-type catalysts,<sup>52</sup> which is an efficient strategy to modulate the Fermi level of both the active metal and support, so as to construct abundant electron-rich or electron-deficient interfacial active sites. This can significantly alter the adsorption behavior of reactive molecules and active intermediate species and/or modify the catalytic reactive route to subsequently enhance the catalytic selectivity. Xu et al. reported a TiO<sub>2-x</sub>-modified Ni nanocatalyst with SMSIs based on the structural transformation of the NiTi-LDHs precursor.<sup>75</sup> The strong electron transfer between Ni NPs and TiO<sub>2-x</sub> support generated abundant Ni<sup>δ-</sup> species and Ni<sup>δ-</sup>–O<sub>v</sub>–Ti<sup>3+</sup> interfacial sites. The synergic catalysis between Ni<sup>δ-</sup> sites and oxygen vacancies promotes a large enhancement of the WGS reaction. More recently, Xu et al. further reported that the presence of Ni<sup>δ-</sup>/TiO<sub>2-x</sub> interfacial sites facilitates C–C chain propagation during the FTS reaction owing the stronger binding ability to carbon atoms based on the DFT calculations in Figure 10.<sup>52</sup> The selectivity of C<sub>2+</sub> paraffins was enhanced to ~64.6% over a Ni-based catalyst, efficiently inhibiting the formation of methane.

Furthermore, in CO<sub>2</sub> hydrogenation, isolated metal atoms facilitate the selective hydrogenation of CO<sub>2</sub> molecules to CO, whereas metal NPs promote the hydrogenation of CO<sub>2</sub> to CH<sub>4</sub>. Our recent findings,<sup>45</sup> however, reveal that the chemical state of the metal Ir species in the Ir/CeO<sub>2</sub> system significantly influences the selectivity of CO<sub>2</sub> hydrogenation owing to the strong electron transfer from Ir NPs to CeO<sub>2</sub> support via SMSIs, which can promote the formation of partially oxidized Ir species at the interface, yielding 100% selectivity for CO from CO<sub>2</sub> hydrogenation. This happens because CO molecules preferentially desorb from the surface of positively charged Ir species (electron-deficient Ir species) driven by SMSIs rather than undergoing further hydrogenation to CH<sub>4</sub>.

Controlling the encapsulation behavior of supported metals to achieve the selective exposure of active metal via the SMSI effect is another strategy to dramatically enhance the catalytic selectivity. Hutchings et al. developed a Sn-containing Pd-based catalyst on a TiO<sub>2</sub> support, in which the tin oxide overlayers encapsulate the small Pd-rich NPs and allow selective exposure of larger Pd-Sn alloy particles via the SMSI effect on the surface of the catalyst.<sup>137</sup> This unique Pd-based catalyst can promote the direct production of H<sub>2</sub>O<sub>2</sub> with a high selectivity. Zhang et al. reported that Pt NPs were

encapsulated by the TiO<sub>2</sub> support over the Pt/TiO<sub>2</sub> catalyst by coordination saturation via SMSIs, while Pt single atoms were selectively exposed, which substantially enhanced the catalytic selectivity of the semihydrogenation reactions.<sup>112</sup>

C-SMSI can considerably modify the surface coordination environment of supported metals by introducing an oxide overlayer onto the lower coordination metal sites (e.g., steps and corners). This alteration can significantly boost the catalytic selectivity. Hydrogenation reactions often demand simultaneous enhancement of both activity and selectivity. Metals such as Ni, Pt, and Ru, known for their potent hydrogenation activity, tend to over-hydrogenate, yielding undesirable products in certain reactions like the hydrogenation of substituted nitroaromatics. Interestingly, hydrogenation selectivity of TiO<sub>2</sub>-supported Ni, Pt, and Ru catalysts can achieve an exceptional enhancement in selectivity due to SMSIs. This allows for a dramatic increase in selectivity from merely 1% to above 95%, alongside an activity increment of nearly 2 orders of magnitude.<sup>35</sup>

This elevated selectivity stems from the alteration of the surface coordination environment instigated by the SMSI effect. The coverage of an oxide overlayer on the metal surface, fostered by SMSIs, modifies the adsorption and reaction pathways. This change favors the desired hydrogenation pathway while suppressing undesired side reactions. This precise adjustment of the surface coordination environment plays an instrumental role in achieving high selectivity in these catalyst systems.

**4.3. Stability Improvement.** Utilizing the SMSI effect to construct supported metal catalysts with excellent stability is an efficient strategy under harsh conditions in heterogeneous catalysis. The surface suboxide overlayers encapsulated on the surface of active metals can effectively inhibit the migration of metal NPs to enhance the sinter resistance of catalysts. However, the physical coverage usually blocks the surface metal sites; therefore, it is very important to precisely control the encapsulation degree and thickness as well as the permeability of suboxide overlayers migrated on the surface of metals.

The supported Cu and Au catalysts have been used extensively in industrial catalysis, but Cu NPs and Au NPs tend to sinter during the catalytic reactions, owing to the low Tamman temperature. Taking advantage of the SMSI effect can construct Au and Cu nanocatalysts with excellent thermal stability under harsh reaction conditions. Zhang et al. developed a new route to prepare ultra-stable Au catalysts by loading Au NPs on the surface of mixed TiO<sub>2</sub> and HAP supports.<sup>84</sup> The incorporation of TiO<sub>2</sub> in HAP facilitates manipulation of the SMSI state between Au NPs and HAP, which can efficiently control the encapsulation degree of the Au NPs to expose the interfacial active sites. The optimal Au/TH-800 catalyst exhibits excellent durability for a variety of catalytic reactions at high temperature. Willinger et al. reported that the ZnO support migrated on the surface of Cu NPs to form stable encapsulation layers by SMSIs over the industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, which explain the ultra-high stability for methanol synthesis.<sup>23</sup>

## 5. CONCLUSIONS AND FUTURE PERSPECTIVES

Research on novel SMSIs in heterogeneous catalysis has emerged as a vibrant and forefront field. Modulating SMSIs offers a robust strategy to tailor the catalytic performance of supported metal catalysts. SMSI state formation induces

atomic rearrangements and charge redistribution, leading to the development of unique interfacial structures that dictate the chemical and catalytic behaviors. The exploration and advancement of new types of SMSI catalyst systems have spurred rapid progress in the field, providing an efficient pathway to design innovative catalyst systems. By leveraging SMSIs, we can fabricate electron-rich and electron-deficient metal species by controlling electron transfer at the interface. The unique interfacial structure confers extraordinary catalytic properties, including strong electron perturbations. Furthermore, the encapsulation structure formed around the supported metal provides efficient protection against coke deposition and metal loss, ensuring enhanced stability under realistic reaction conditions. As a result, catalyst systems incorporating various forms of SMSIs present exciting opportunities for fabricating high-performance catalysts with excellent stability, making them well-suited for practical applications.

The application of advanced electron microscopy and spectroscopy techniques has greatly enhanced our comprehension of the chemical intricacies of SMSIs at the atomic and molecular levels. Nevertheless, due to the inherent complexity of SMSIs and the limitations in current synthesis and characterization methodologies, research into the chemical nature and catalytic mechanisms of SMSIs is still in its nascent stages, sparking debates and controversies. The disclosure of the chemical nature and catalytic mechanisms under *in situ* or *operando* conditions is paramount, given that the intrinsic geometric and electronic structure of a catalyst undergoes transformation after air exposure. Moreover, in certain scenarios, the dynamic reconstruction of the catalyst's intrinsic active site occurs under realistic reaction conditions. The homogeneity of the catalyst's surface structure coupled with the complex chemical nature of SMSIs poses a formidable challenge in unambiguously elucidating the formation mechanism of SMSIs and attaining comprehensive insights. Consequently, the pursuit of a thorough understanding of SMSIs and their catalytic properties remains a complex and ongoing endeavor.

It is vitally important to develop new characterization techniques to further shed light on the SMSI mechanism. The rational design and construction of new types of SMSI catalyst systems could notably advance the field of heterogeneous catalysis. Additionally, the investigation into the formation of SMSIs between active metals and nanocarbon supports presents a promising avenue that could broaden the scope of this field. Given the rapid progress in single-atom catalysis and atomically dispersed catalysts (fully exposed catalysts), the study of SMSIs between atomically dispersed metal active centers and supports is becoming increasingly critical, as their catalytic performance often predominantly depends on the MSI, compared to traditional nanocatalysts.<sup>138,139</sup> This underscores the escalating importance of exploring and harnessing the SMSI phenomenon for the design of robust SAC systems, which could consequently accelerate their industrial applications.

The combination of advanced *in situ/operando* characterization techniques with DFT calculations is essential to provide a more profound fundamental understanding of SMSIs and their catalytic mechanisms. To gain fundamental insights into the chemical nature of SMSIs and the underlying catalytic mechanisms, the establishment of multiple *in situ/operando* characterization methodologies is requisite. These techniques

would reveal the inherent active center structure of the SMSI catalyst and the dynamic structural evolution of active sites at atomic/molecular levels. It is worth noting that our understanding of the chemical nature and formation mechanism of SMSI still lacks depth.

Nearly half a century has elapsed since the discovery of the first SMSI phenomenon. Extensive studies have been conducted to decipher the nature of SMSIs, and considerable progress has been made in understanding C-SMSI. However, as new variants of SMSIs emerge, particularly those that do not exhibit similar phenomena or meet the criteria of C-SMSI, there is a pressing need for new insights into these diverse SMSI phenomena. In many instances where the term "SMSI" is applied, the true nature of these phenomena and how to definitively classify them as SMSIs remain unresolved. Gaining consensus within the scientific community on the nature of different types of SMSIs, as well as their similarities and differences, necessitates open dialogue and extensive discourse in this specialized field.

## ■ AUTHOR INFORMATION

### Corresponding Authors

**Ding Ma** – Beijing National Laboratory for Molecular Sciences, New Cornerstone Science Laboratory, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China; [orcid.org/0000-0002-3341-2998](https://orcid.org/0000-0002-3341-2998); Email: [dma@pku.edu.cn](mailto:dma@pku.edu.cn)

**Botao Qiao** – CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China; [orcid.org/0000-0001-6351-455X](https://orcid.org/0000-0001-6351-455X); Email: [bqiao@dicp.ac.cn](mailto:bqiao@dicp.ac.cn)

### Authors

**Ming Xu** – Beijing National Laboratory for Molecular Sciences, New Cornerstone Science Laboratory, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China; State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

**Mi Peng** – Beijing National Laboratory for Molecular Sciences, New Cornerstone Science Laboratory, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China; [orcid.org/0000-0001-7713-4398](https://orcid.org/0000-0001-7713-4398)

**Hailian Tang** – School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, P. R. China

**Wu Zhou** – School of Physical Sciences, CAS Key Laboratory of Vacuum Physics, University of Chinese Academy of Sciences, Beijing 100049, P. R. China; [orcid.org/0000-0002-6803-1095](https://orcid.org/0000-0002-6803-1095)

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/jacs.3c09102>

### Author Contributions

#M.X. and M.P. contributed equally to this work.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (Grant Nos. 2021YFA1501102, 2021YFB3800300),

the National Natural Science Foundation of China (NSFC: 21725301, 21932002, 22232001, 22202004, 22102007), the Fundamental Research Funds for the Central Universities (buctrc202112), and the China Postdoctoral Science Foundation (Grants 2019M650306 and 2020T130010). This work has been supported by the New Cornerstone Science Foundation. D.M. acknowledges support from the Tencent Foundation through the XPLOER PRIZE.

## REFERENCES

- (1) Wang, A.; Li, J.; Zhang, T. Heterogeneous single-atom catalysis. *Nat. Rev. Chem.* **2018**, *2*, 65.
- (2) Li, S.; Wang, F.; Liu, Y.; Cao, Y. Highly Chemoselective Reduction of Nitroarenes Using a Titania-Supported Platinum-Nanoparticle Catalyst under a CO Atmosphere. *Chin. J. Chem.* **2017**, *35*, 591.
- (3) Zhang, J.; Zhu, D.; Yan, J.; Wang, C. A. Strong metal-support interactions induced by an ultrafast laser. *Nat. Commun.* **2021**, *12*, 6665.
- (4) van Deelen, T. W.; Hernández Mejía, C.; de Jong, K. P. Control of metal-support interactions in heterogeneous catalysts to enhance activity and selectivity. *Nat. Catal.* **2019**, *2*, 955.
- (5) Pu, T.; Zhang, W.; Zhu, M. Engineering Heterogeneous Catalysis with Strong Metal-Support Interactions: Characterization, Theory and Manipulation. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202212278.
- (6) Luo, Z.; Zhao, G.; Pan, H.; Sun, W. Strong Metal-Support Interaction in Heterogeneous Catalysts. *Adv. Energy Mater.* **2022**, *12*, 2201395.
- (7) Zhang, L.; Zhou, M.; Wang, A.; Zhang, T. Selective Hydrogenation over Supported Metal Catalysts: From Nanoparticles to Single Atoms. *Chem. Rev.* **2020**, *120*, 683.
- (8) Lang, R.; Du, X.; Huang, Y.; Jiang, X.; Zhang, Q.; Guo, Y.; Liu, K.; Qiao, B.; Wang, A.; Zhang, T. Single-Atom Catalysts Based on the Metal-Oxide Interaction. *Chem. Rev.* **2020**, *120*, 11986.
- (9) Liu, J. J. Advanced Electron Microscopy of Metal-Support Interactions in Supported Metal Catalysts. *ChemCatChem* **2011**, *3*, 934.
- (10) Tauster, S. J.; Fung, S. C.; Garten, R. L. Strong Metal-Support Interactions. Group 8 Noble Metals Supported on TiO<sub>2</sub>. *J. Am. Chem. Soc.* **1978**, *100*, 170.
- (11) Tauster, S. J.; Fung, S. C. Strong metal-support interactions: Occurrence among the binary oxides of groups IIA-VB. *J. Catal.* **1978**, *55*, 29.
- (12) Tauster, S. J.; Fung, S. C.; Baker, R. T. K.; Horsley, J. A. Strong Interactions in Supported-Metal Catalysts. *Science* **1981**, *211*, 1121.
- (13) Herrmann, J. M. Electronic Effects in Strong Metal-Support Interactions on Titania Deposited Metal Catalysts. *J. Catal.* **1984**, *89*, 404.
- (14) Lu, A.; Sun, H.; Zhang, N.; Che, L.; Shan, S.; Luo, J.; Zheng, J.; Yang, L.; Peng, D.-L.; Zhong, C.-J.; Chen, B. Surface Partial-Charge-Tuned Enhancement of Catalytic Activity of Platinum Nanocatalysts for Toluene Oxidation. *ACS Catal.* **2019**, *9*, 7431.
- (15) Hernández Mejía, C.; Vogt, C.; Weckhuysen, B. M.; de Jong, K. P. Stable niobia-supported nickel catalysts for the hydrogenation of carbon monoxide to hydrocarbons. *Catal. Today* **2020**, *343*, 56.
- (16) Sadeghi, H. R.; Henrich, V. E. SMSI in Rh/TiO<sub>2</sub> model catalysts: Evidence for oxide migration. *J. Catal.* **1984**, *87*, 279.
- (17) Logan, A. D.; Braunschweig, E. J.; Datye, A. K.; Smith, D. J. Direct Observation of the Surfaces of Small Metal Crystallites: Rhodium Supported on TiO<sub>2</sub>. *Langmuir* **1988**, *4*, 827.
- (18) Belzunegui, J. P.; Sanz, J.; Rojo, J. M. Contribution of physical blocking and electronic effect to establishment of strong metal-support interaction in rhodium/titanium dioxide catalysts. *J. Am. Chem. Soc.* **1992**, *114*, 6749.
- (19) Singh, A. K.; Pande, N. K.; Bell, A. T. Electron microscopy study of the interactions of rhodium with titania. *J. Catal.* **1985**, *94*, 422.
- (20) Bernal, S.; Calvino, J. J.; Cauqui, M. A.; Gatica, J. M.; López Cartes, C.; Pérez Omil, J. A.; Pintado, J. M. Some contributions of electron microscopy to the characterisation of the strong metal-support interaction effect. *Catal. Today* **2003**, *77*, 385.
- (21) Bowker, M.; Fourné, E. Direct interactions between metal nanoparticles and support: STM studies of Pd on TiO<sub>2</sub>(110). *Appl. Sur. Sci.* **2008**, *254*, 4225.
- (22) Willinger, M. G.; Zhang, W.; Bondarchuk, O.; Shaikhutdinov, S.; Freund, H. J.; Schlogl, R. A case of strong metal-support interactions: combining advanced microscopy and model systems to elucidate the atomic structure of interfaces. *Angew. Chem. Int. Ed.* **2014**, *53*, 5998.
- (23) Lunkenbein, T.; Schumann, J.; Behrens, M.; Schlogl, R.; Willinger, M. G. Formation of a ZnO overlayer in industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts induced by strong metal-support interactions. *Angew. Chem. Int. Ed.* **2015**, *54*, 4544.
- (24) Shi, X. Y.; Zhang, W.; Zhang, C.; Zheng, W. T.; Chen, H.; Qi, J. G. Real-space observation of strong metal-support interaction: state-of-the-art and what's the next. *J. Micr.* **2016**, *262*, 203.
- (25) Zhang, S.; Plessow, P. N.; Willis, J. J.; Dai, S.; Xu, M.; Graham, G. W.; Cargnello, M.; Abild-Pedersen, F.; Pan, X. Dynamical Observation and Detailed Description of Catalysts under Strong Metal-Support Interaction. *Nano Lett.* **2016**, *16*, 4528.
- (26) Horsley, J. A. A Molecular Orbital Study of Strong Metal-Support Interaction between Platinum and Titanium Dioxide. *J. Am. Chem. Soc.* **1979**, *101*, 2870.
- (27) Sakellson, S.; McMillan, M.; Haller, G. L. EXAFS Evidence for Direct Metal-Metal Bonding in Reduced Rh/TiO<sub>2</sub> Catalysts. *J. Phys. Chem.* **1986**, *90*, 1733.
- (28) Bernal, S.; Blanco, G.; Calvino, J. J.; López-Cartes, C.; Pérez-Omil, J. A.; Gatica, J. M.; Stephan, O.; Colliex, C. Electron Microscopy (HREM, EELS) Study of the Reoxidation Conditions for Recovery of NM/CeO<sub>2</sub> (NM: Rh, Pt) Catalysts from Decoration or Alloying Phenomena. *Catal. Lett.* **2001**, *76*, 131.
- (29) Frey, H.; Beck, A.; Huang, X.; van Bokhoven, J. A.; Willinger, M. G. Dynamic interplay between metal nanoparticles and oxide support under redox conditions. *Science* **2022**, *376*, 982.
- (30) Tauster, S. J. Strong Metal-Support Interactions. *Acc. Chem. Res.* **1987**, *20*, 389.
- (31) Baker, L. R.; Kennedy, G.; Van Spronsen, M.; Hervier, A.; Cai, X.; Chen, S.; Wang, L. W.; Somorjai, G. A. Furfuraldehyde hydrogenation on titanium oxide-supported platinum nanoparticles studied by sum frequency generation vibrational spectroscopy: acid-base catalysis explains the molecular origin of strong metal-support interactions. *J. Am. Chem. Soc.* **2012**, *134*, 14208.
- (32) Yoon, S.; Oh, K.; Liu, F.; Seo, J. H.; Somorjai, G. A.; Lee, J. H.; An, K. Specific Metal-Support Interactions between Nanoparticle Layers for Catalysts with Enhanced Methanol Oxidation Activity. *ACS Catal.* **2018**, *8*, 5391.
- (33) Bonanni, S.; Ait-Mansour, K.; Brune, H.; Harbich, W. Overcoming the Strong Metal-Support Interaction State: CO Oxidation on TiO<sub>2</sub>(110)-Supported Pt Nanoclusters. *ACS Catal.* **2011**, *1*, 385.
- (34) Xu, X.; Fu, Q.; Gan, L.; Zhu, J.; Bao, X. Interface-Confined FeO<sub>x</sub> Adlayers Induced by Metal Support Interaction in Pt/FeO<sub>x</sub> Catalysts. *J. Phys. Chem. B* **2018**, *122*, 984.
- (35) Corma, A.; Serna, P.; Concepción, P.; Calvino, J. J. Transforming Nonselective into Chemoselective Metal Catalysts for the Hydrogenation of Substituted Nitroaromatics. *J. Am. Chem. Soc.* **2008**, *130*, 8748.
- (36) Bradford, M. C. J.; Vannice, M. A. Catalytic reforming of methane with carbon dioxide over nickel catalysts I. Catalyst characterization and activity. *Appl. Catal. A: Gen.* **1996**, *142*, 73.
- (37) Yeung, C. M. Y.; Yu, K. M. K.; Fu, Q. J.; Thompsett, D.; Petch, M. I.; Tsang, S. C. Engineering Pt in Ceria for a Maximum Metal-Support Interaction in Catalysis. *J. Am. Chem. Soc.* **2005**, *127*, 18010.
- (38) Zhao, E. W.; Zheng, H.; Ludden, K.; Xin, Y.; Hagelin-Weaver, H. E.; Bowers, C. R. Strong Metal-Support Interactions Enhance the

Pairwise Selectivity of Parahydrogen Addition over Ir/TiO<sub>2</sub>. *ACS Catal.* **2016**, *6*, 974.

(39) Behrens, M.; Studt, F.; Kasatkin, I.; Kuhl, S.; Havecker, M.; Abild-Pedersen, F.; Zander, S.; Girgsdies, F.; Kurr, P.; Knief, B. L.; Tovar, M.; Fischer, R. W.; Norskov, J. K.; Schlogl, R. The active site of methanol synthesis over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> industrial catalysts. *Science* **2012**, *336*, 893.

(40) Yang, X.; Kattel, S.; Senanayake, S. D.; Boscoboinik, J. A.; Nie, X.; Graciani, J.; Rodriguez, J. A.; Liu, P.; Stacchiola, D. J.; Chen, J. G. Low Pressure CO<sub>2</sub> Hydrogenation to Methanol over Gold Nanoparticles Activated on a CeO<sub>x</sub>/TiO<sub>2</sub> Interface. *J. Am. Chem. Soc.* **2015**, *137*, 10104.

(41) Kondrat, S. A.; Smith, P. J.; Wells, P. P.; Chater, P. A.; Carter, J. H.; Morgan, D. J.; Fiordaliso, E. M.; Wagner, J. B.; Davies, T. E.; Lu, L.; Bartley, J. K.; Taylor, S. H.; Spencer, M. S.; Kiely, C. J.; Kelly, G. J.; Park, C. W.; Rosseinsky, M. J.; Hutchings, G. J. Stable amorphous georgeite as a precursor to a high-activity catalyst. *Nature* **2016**, *531*, 83.

(42) Xu, J.; Su, X.; Duan, H.; Hou, B.; Lin, Q.; Liu, X.; Pan, X.; Pei, G.; Geng, H.; Huang, Y.; Zhang, T. Influence of pretreatment temperature on catalytic performance of rutile TiO<sub>2</sub>-supported ruthenium catalyst in CO<sub>2</sub> methanation. *J. Catal.* **2016**, *333*, 227.

(43) Matsubu, J. C.; Zhang, S.; DeRita, L.; Marinkovic, N. S.; Chen, J. G.; Graham, G. W.; Pan, X.; Christopher, P. Adsorbate-mediated strong metal-support interactions in oxide-supported Rh catalysts. *Nat. Chem.* **2017**, *9*, 120.

(44) Kuld, S.; Thorhauge, M.; Falsig, H.; Elkjær, C. F.; Helveg, S.; Chorkendorff, I.; Sehested, J. Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis. *Science* **2016**, *352*, 969.

(45) Li, S.; Xu, Y.; Chen, Y.; Li, W.; Lin, L.; Li, M.; Deng, Y.; Wang, X.; Ge, B.; Yang, C.; Yao, S.; Xie, J.; Li, Y.; Liu, X.; Ma, D. Tuning the Selectivity of Catalytic Carbon Dioxide Hydrogenation over Iridium/Cerium Oxide Catalysts with a Strong Metal-Support Interaction. *Angew. Chem., Int. Ed.* **2017**, *56*, 10761.

(46) Chandler, B. D. An extra layer of complexity. *Nat. Chem.* **2017**, *9*, 108.

(47) Kattel, S.; Ramirez, P. J.; Chen, J. G.; Rodriguez, J. A.; Liu, P. Active sites for CO<sub>2</sub> hydrogenation to methanol on Cu/ZnO catalysts. *Science* **2017**, *355*, 1296.

(48) Happel, M.; Mysliveček, J.; Johánek, V.; Dvořák, F.; Stetsovykh, O.; Lykhach, Y.; Matolin, V.; Libuda, J. Adsorption sites, metal-support interactions, and oxygen spillover identified by vibrational spectroscopy of adsorbed CO: A model study on Pt/ceria catalysts. *J. Catal.* **2012**, *289*, 118.

(49) Hernández Mejía, C.; van Deelen, T. W.; de Jong, K. P. Activity enhancement of cobalt catalysts by tuning metal-support interactions. *Nat. Commun.* **2018**, *9*, 4459.

(50) Hernandez Mejia, C.; van der Hoeven, J. E. S.; de Jongh, P. E.; de Jong, K. P. Cobalt-Nickel Nanoparticles Supported on Reducible Oxides as Fischer–Tropsch Catalysts. *ACS Catal.* **2020**, *10*, 7343.

(51) Zhang, Y.; Yang, X.; Yang, X.; Duan, H.; Qi, H.; Su, Y.; Liang, B.; Tao, H.; Liu, B.; Chen, D.; Su, X.; Huang, Y.; Zhang, T. Tuning reactivity of Fischer–Tropsch synthesis by regulating TiO<sub>x</sub> overlayer over Ru/TiO<sub>2</sub> nanocatalysts. *Nat. Commun.* **2020**, *11*, 3185.

(52) Xu, M.; Qin, X.; Xu, Y.; Zhang, X.; Zheng, L.; Liu, J. X.; Wang, M.; Liu, X.; Ma, D. Boosting CO hydrogenation towards C<sub>2+</sub> hydrocarbons over interfacial TiO<sub>2-x</sub>/Ni catalysts. *Nat. Commun.* **2022**, *13*, 6720.

(53) Liu, X.; Liu, M. H.; Luo, Y. C.; Mou, C. Y.; Lin, S. D.; Cheng, H.; Chen, J. M.; Lee, J. F.; Lin, T. S. Strong metal-support interactions between gold nanoparticles and ZnO nanorods in CO oxidation. *J. Am. Chem. Soc.* **2012**, *134*, 10251.

(54) Naumann d'Alnoncourt, R.; Friedrich, M.; Kunkes, E.; Rosenthal, D.; Girgsdies, F.; Zhang, B.; Shao, L.; Schuster, M.; Behrens, M.; Schlögl, R. Strong metal-support interactions between palladium and iron oxide and their effect on CO oxidation. *J. Catal.* **2014**, *317*, 220.

(55) Wang, J.; Gu, X.; Pei, L.; Kong, P.; Zhang, J.; Wang, X.; Wang, R.; Waclawik, E. R.; Zheng, Z. Strong metal-support interaction

induced O<sub>2</sub> activation over Au/MNb<sub>2</sub>O<sub>6</sub> (M = Zn<sup>2+</sup>, Ni<sup>2+</sup> and Co<sup>2+</sup>) for efficient photocatalytic benzyl alcohol oxidative esterification. *Appl. Catal. B: Environ.* **2021**, *283*, 119618.

(56) Bruix, A.; Rodriguez, J. A.; Ramirez, P. J.; Senanayake, S. D.; Evans, J.; Park, J. B.; Stacchiola, D.; Liu, P.; Hrbek, J.; Illas, F. A new type of strong metal-support interaction and the production of H<sub>2</sub> through the transformation of water on Pt/CeO<sub>2</sub>(111) and Pt/CeO<sub>x</sub>/TiO<sub>2</sub>(110) catalysts. *J. Am. Chem. Soc.* **2012**, *134*, 8968.

(57) Carrasco, J.; Lopez-Duran, D.; Liu, Z.; Duchon, T.; Evans, J.; Senanayake, S. D.; Crumlin, E. J.; Matolin, V.; Rodriguez, J. A.; Ganduglia-Pirovano, M. V. In situ and theoretical studies for the dissociation of water on an active Ni/CeO<sub>2</sub> catalyst: importance of strong metal-support interactions for the cleavage of O-H bonds. *Angew. Chem., Int. Ed.* **2015**, *54*, 3917.

(58) Lee, J.; Burt, S. P.; Carrero, C. A.; Alba-Rubio, A. C.; Ro, I.; O'Neill, B. J.; Kim, H. J.; Jackson, D. H. K.; Kuech, T. F.; Hermans, I.; Dumesic, J. A.; Huber, G. W. Stabilizing cobalt catalysts for aqueous-phase reactions by strong metal-support interaction. *J. Catal.* **2015**, *330*, 19.

(59) Lin, L.; Zhou, W.; Gao, R.; Yao, S.; Zhang, X.; Xu, W.; Zheng, S.; Jiang, Z.; Yu, Q.; Li, Y. W.; Shi, C.; Wen, X. D.; Ma, D. Low-temperature hydrogen production from water and methanol using Pt/ $\alpha$ -MoC catalysts. *Nature* **2017**, *544*, 80.

(60) Li, M.; van Veen, A. C. Tuning the catalytic performance of Ni-catalysed dry reforming of methane and carbon deposition via Ni-CeO<sub>2</sub>-interaction. *Appl. Catal. B: Environ.* **2018**, *237*, 641.

(61) Dong, J.; Fu, Q.; Jiang, Z.; Mei, B.; Bao, X. Carbide-Supported Au Catalysts for Water-Gas Shift Reactions: A New Territory for the Strong Metal-Support Interaction Effect. *J. Am. Chem. Soc.* **2018**, *140*, 13808.

(62) Liu, N.; Xu, M.; Yang, Y.; Zhang, S.; Zhang, J.; Wang, W.; Zheng, L.; Hong, S.; Wei, M. Au<sup>δ-</sup>-O<sub>v</sub>-Ti<sup>3+</sup> Interfacial Site: Catalytic Active Center toward Low-Temperature Water Gas Shift Reaction. *ACS Catal.* **2019**, *9*, 2707.

(63) Nelson, N. C.; Szanyi, J. Heterolytic Hydrogen Activation: Understanding Support Effects in Water-Gas Shift, Hydrodeoxygenation, and CO Oxidation Catalysis. *ACS Catal.* **2020**, *10*, 5663.

(64) Jiang, F.; Zeng, L.; Li, S.; Liu, G.; Wang, S.; Gong, J. Propane Dehydrogenation over Pt/TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Catalysts. *ACS Catal.* **2015**, *5*, 438.

(65) Liu, G.; Zeng, L.; Zhao, Z.-J.; Tian, H.; Wu, T.; Gong, J. Platinum-Modified ZnO/Al<sub>2</sub>O<sub>3</sub> for Propane Dehydrogenation: Minimized Platinum Usage and Improved Catalytic Stability. *ACS Catal.* **2016**, *6*, 2158.

(66) Deng, L.; Miura, H.; Shishido, T.; Hosokawa, S.; Teramura, K.; Tanaka, T. Strong metal-support interaction between Pt and SiO<sub>2</sub> following high-temperature reduction: a catalytic interface for propane dehydrogenation. *Chem. Commun.* **2017**, *53*, 6937.

(67) Wang, L.; Wang, L.; Meng, X.; Xiao, F. S. New Strategies for the Preparation of Sinter-Resistant Metal-Nanoparticle-Based Catalysts. *Adv. Mater.* **2019**, *31*, No. e1901905.

(68) Ro, I.; Resasco, J.; Christopher, P. Approaches for Understanding and Controlling Interfacial Effects in Oxide-Supported Metal Catalysts. *ACS Catal.* **2018**, *8*, 7368.

(69) Farmer, J. A.; Campbell, C. T. Ceria maintains smaller metal catalyst particles by strong metal-support bonding. *Science* **2010**, *329*, 933.

(70) Hu, P.; Huang, Z.; Amghouz, Z.; Makkee, M.; Xu, F.; Kapteijn, F.; Dikhtiarenko, A.; Chen, Y.; Gu, X.; Tang, X. Electronic metal-support interactions in single-atom catalysts. *Angew. Chem., Int. Ed.* **2014**, *53*, 3418.

(71) Campbell, C. T. Catalyst-support interactions: Electronic perturbations. *Nat. Chem.* **2012**, *4*, S97.

(72) Lykhach, Y.; Kozlov, S. M.; Skala, T.; Tovt, A.; Stetsovykh, V.; Tsud, N.; Dvorak, F.; Johánek, V.; Neitzel, A.; Mysliveček, J.; Fabris, S.; Matolin, V.; Neyman, K. M.; Libuda, J. Counting electrons on supported nanoparticles. *Nat. Mater.* **2016**, *15*, 284.

(73) Li, J.; Guan, Q.; Wu, H.; Liu, W.; Lin, Y.; Sun, Z.; Ye, X.; Zheng, X.; Pan, H.; Zhu, J.; Chen, S.; Zhang, W.; Wei, S.; Lu, J.



Highly Active and Stable Metal Single-Atom Catalysts Achieved by Strong Electronic Metal-Support Interactions. *J. Am. Chem. Soc.* **2019**, *141*, 14515.

(74) Yao, S.; Zhang, X.; Zhou, W.; Gao, R.; Xu, W.; Ye, Y.; Lin, L.; Wen, X.; Liu, P.; Chen, B.; Crumlin, E.; Guo, J.; Zuo, Z.; Li, W.; Xie, J.; Lu, L.; Kiely, C. J.; Gu, L.; Shi, C.; Rodriguez, J. A.; Ma, D. Atomic-layered Au clusters on  $\alpha$ -MoC as catalysts for the low-temperature water-gas shift reaction. *Science* **2017**, *357*, 389.

(75) Xu, M.; He, S.; Chen, H.; Cui, G.; Zheng, L.; Wang, B.; Wei, M. TiO<sub>2-x</sub>-Modified Ni Nanocatalyst with Tunable Metal-Support Interaction for Water-Gas Shift Reaction. *ACS Catal.* **2017**, *7*, 7600.

(76) Tang, H.; Su, Y.; Zhang, B.; Lee, A. F.; Isaacs, M. A.; Wilson, K.; Li, L.; Ren, Y.; Huang, J.; Haruta, M.; Qiao, B.; Liu, X.; Jin, C.; Su, D.; Wang, J.; Zhang, T. Classical strong metal-support interactions between gold nanoparticles and titanium dioxide. *Sci. adv.* **2017**, *3*, No. e1700231.

(77) Zhang, J.; Wang, H.; Wang, L.; Ali, S.; Wang, C.; Wang, L.; Meng, X.; Li, B.; Su, D. S.; Xiao, F. S. Wet-Chemistry Strong Metal-Support Interactions in Titania-Supported Au Catalysts. *J. Am. Chem. Soc.* **2019**, *141*, 2975.

(78) Dong, J.; Fu, Q.; Li, H.; Xiao, J.; Yang, B.; Zhang, B.; Bai, Y.; Song, T.; Zhang, R.; Gao, L.; Cai, J.; Zhang, H.; Liu, Z.; Bao, X. Reaction-Induced Strong Metal-Support Interactions between Metals and Inert Boron Nitride Nanosheets. *J. Am. Chem. Soc.* **2020**, *142*, 17167.

(79) Lin, L.; Liu, J.; Liu, X.; Gao, Z.; Rui, N.; Yao, S.; Zhang, F.; Wang, M.; Liu, C.; Han, L.; Yang, F.; Zhang, S.; Wen, X. D.; Senanayake, S. D.; Wu, Y.; Li, X.; Rodriguez, J. A.; Ma, D. Reversing sintering effect of Ni particles on  $\gamma$ -Mo<sub>2</sub>N via strong metal-support interaction. *Nat. Commun.* **2021**, *12*, 6978.

(80) Lou, Y.; Wu, H.; Liu, J. Nanocarbon-Edge-Anchored High-Density Pt Atoms for 3-nitrostyrene Hydrogenation: Strong Metal-Carbon Interaction. *iScience* **2019**, *13*, 190.

(81) Ma, J.; Habrioux, A.; Morais, C.; Lewera, A.; Vogel, W.; Verde-Gómez, Y.; Ramos-Sanchez, G.; Balbuena, P. B.; Alonso-Vante, N. Spectroelectrochemical Probing of the Strong Interaction between Platinum Nanoparticles and Graphitic Domains of Carbon. *ACS Catal.* **2013**, *3*, 1940.

(82) Tang, H.; Wei, J.; Liu, F.; Qiao, B.; Pan, X.; Li, L.; Liu, J.; Wang, J.; Zhang, T. Strong Metal-Support Interactions between Gold Nanoparticles and Nonoxides. *J. Am. Chem. Soc.* **2016**, *138*, 56.

(83) Zhang, X.; Zhang, M.; Deng, Y.; Xu, M.; Artiglia, L.; Wen, W.; Gao, R.; Chen, B.; Yao, S.; Zhang, X.; Peng, M.; Yan, J.; Li, A.; Jiang, Z.; Gao, X.; Cao, S.; Yang, C.; Kropf, A. J.; Shi, J.; Xie, J.; Bi, M.; van Bokhoven, J. A.; Li, Y. W.; Wen, X.; Flytzani-Stephanopoulos, M.; Shi, C.; Zhou, W.; Ma, D. A stable low-temperature H<sub>2</sub>-production catalyst by crowding Pt on  $\alpha$ -MoC. *Nature* **2021**, *589*, 396.

(84) Tang, H.; Liu, F.; Wei, J.; Qiao, B.; Zhao, K.; Su, Y.; Jin, C.; Li, L.; Liu, J.; Wang, J.; Zhang, T. Ultrastable Hydroxyapatite/Titanium-Dioxide-Supported Gold Nanocatalyst with Strong Metal-Support Interaction for Carbon Monoxide Oxidation. *Angew. Chem., Int. Ed.* **2016**, *55*, 10606.

(85) Tang, H.; Su, Y.; Guo, Y.; Zhang, L.; Li, T.; Zang, K.; Liu, F.; Li, L.; Luo, J.; Qiao, B.; Wang, J. Oxidative strong metal-support interactions (OMSI) of supported platinum-group metal catalysts. *Chem. Sci.* **2018**, *9*, 6679.

(86) Li, Z.; Cui, Y.; Wu, Z.; Milligan, C.; Zhou, L.; Mitchell, G.; Xu, B.; Shi, E.; Miller, J. T.; Ribeiro, F. H.; Wu, Y. Reactive metal-support interactions at moderate temperature in two-dimensional niobium-carbide-supported platinum catalysts. *Nat. Catal.* **2018**, *1*, 349.

(87) Li, D.; Xu, F.; Tang, X.; Dai, S.; Pu, T.; Liu, X.; Tian, P.; Xuan, F.; Xu, Z.; Wachs, I. E.; Zhu, M. Induced activation of the commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst for the steam reforming of methanol. *Nat. Catal.* **2022**, *5*, 99.

(88) Wu, G.; Liu, Y.; Wang, J. Oxidative-Atmosphere-Induced Strong Metal-Support Interaction and Its Catalytic Application. *Acc. Chem. Res.* **2023**, *56*, 911.

(89) Wang, H.; Wang, L.; Xiao, F.-S. New routes for the construction of strong metal-support interactions. *Sci. Chi. Chem.* **2022**, *65*, 2051.

(90) Fu, Q.; Wagner, T.; Olliges, S.; Carstanjen, H. Metal-Oxide Interfacial Reactions: Encapsulation of Pd on TiO<sub>2</sub> (110). *J. Phys. Chem. B* **2005**, *109*, 944.

(91) Zhu, M.; Tian, P.; Kurtz, R.; Lunkenbein, T.; Xu, J.; Schlogl, R.; Wachs, I. E.; Han, Y. F. Strong Metal-Support Interactions between Copper and Iron Oxide during the High-Temperature Water-Gas Shift Reaction. *Angew. Chem., Int. Ed.* **2019**, *58*, 9083.

(92) Xin, H.; Lin, L.; Li, R.; Li, D.; Song, T.; Mu, R.; Fu, Q.; Bao, X. Overturning CO<sub>2</sub> Hydrogenation Selectivity with High Activity via Reaction-Induced Strong Metal-Support Interactions. *J. Am. Chem. Soc.* **2022**, *144*, 4874.

(93) Polo-Garzon, F.; Blum, T. F.; Fung, V.; Bao, Z.; Chen, H.; Huang, Z.; Mahurin, S. M.; Dai, S.; Chi, M.; Wu, Z. Alcohol-Induced Low-Temperature Blockage of Supported-Metal Catalysts for Enhanced Catalysis. *ACS Catal.* **2020**, *10*, 8515.

(94) Wu, P.; Tan, S.; Moon, J.; Yan, Z.; Fung, V.; Li, N.; Yang, S. Z.; Cheng, Y.; Abney, C. W.; Wu, Z.; Savara, A.; Momen, A. M.; Jiang, D. E.; Su, D.; Li, H.; Zhu, W.; Dai, S.; Zhu, H. Harnessing strong metal-support interactions via a reverse route. *Nat. Commun.* **2020**, *11*, 3042.

(95) Pan, M.; Brush, A. J.; Pozun, Z. D.; Ham, H. C.; Yu, W. Y.; Henkelman, G.; Hwang, G. S.; Mullins, C. B. Model studies of heterogeneous catalytic hydrogenation reactions with gold. *Chem. Soc. Rev.* **2013**, *42*, 5002.

(96) Yamazoe, S.; Koyasu, K.; Tsukuda, T. Nonscalable Oxidation Catalysis of Gold Clusters. *Acc. Chem. Res.* **2014**, *47*, 816.

(97) Haruta, M. Chance and necessity: my encounter with gold catalysts. *Angew. Chem., Int. Ed.* **2014**, *53*, 52.

(98) Du, X.; Huang, Y.; Pan, X.; Han, B.; Su, Y.; Jiang, Q.; Li, M.; Tang, H.; Li, G.; Qiao, B. Size-dependent strong metal-support interaction in TiO<sub>2</sub> supported Au nanocatalysts. *Nat. Commun.* **2020**, *11*, 5811.

(99) Zhang, Y.; Liu, J. X.; Qian, K.; Jia, A.; Li, D.; Shi, L.; Hu, J.; Zhu, J.; Huang, W. Structure Sensitivity of Au-TiO<sub>2</sub> Strong Metal-Support Interactions. *Angew. Chem., Int. Ed.* **2021**, *60*, 12074.

(100) Liu, S.; Xu, W.; Niu, Y.; Zhang, B.; Zheng, L.; Liu, W.; Li, L.; Wang, J. Ultrastable Au nanoparticles on titania through an encapsulation strategy under oxidative atmosphere. *Nat. Commun.* **2019**, *10*, 5790.

(101) Wang, H.; Wang, L.; Lin, D.; Feng, X.; Niu, Y.; Zhang, B.; Xiao, F.-S. Strong metal-support interactions on gold nanoparticle catalysts achieved through Le Chatelier's principle. *Nat. Catal.* **2021**, *4*, 418.

(102) Polo-Garzon, F.; Blum, T. F.; Bao, Z.; Wang, K.; Fung, V.; Huang, Z.; Bickel, E. E.; Jiang, D.-e.; Chi, M.; Wu, Z. In Situ Strong Metal-Support Interaction (SMSI) Affects Catalytic Alcohol Conversion. *ACS Catal.* **2021**, *11*, 1938.

(103) Qian, K.; Duan, H.; Li, Y.; Huang, W. Electronic Oxide-Metal Strong Interaction (EOMSI). *Chem. Eur. J.* **2020**, *26*, 13538.

(104) Deng, Y.; Ge, Y.; Xu, M.; Yu, Q.; Xiao, D.; Yao, S.; Ma, D. Molybdenum Carbide: Controlling the Geometric and Electronic Structure of Noble Metals for the Activation of O-H and C-H Bonds. *Acc. Chem. Res.* **2019**, *52*, 3372.

(105) Schweitzer, N. M.; Schaidle, J. A.; Ezekoye, O. K.; Pan, X.; Linic, S.; Thompson, L. T. High activity carbide supported catalysts for water gas shift. *J. Am. Chem. Soc.* **2011**, *133*, 2378.

(106) Rodriguez, J. A.; Ramirez, P. J.; Asara, G. G.; Vines, F.; Evans, J.; Liu, P.; Ricart, J. M.; Illas, F. Charge polarization at a Au-TiC interface and the generation of highly active and selective catalysts for the low-temperature water-gas shift reaction. *Angew. Chem., Int. Ed.* **2014**, *53*, 11270.

(107) Lin, L.; Yao, S.; Gao, R.; Liang, X.; Yu, Q.; Deng, Y.; Liu, J.; Peng, M.; Jiang, Z.; Li, S.; Li, Y. W.; Wen, X. D.; Zhou, W.; Ma, D. A highly CO-tolerant atomically dispersed Pt catalyst for chemoselective hydrogenation. *Nat. Nanotechnol.* **2019**, *14*, 354.

- (108) Ge, Y.; Qin, X.; Li, A.; Deng, Y.; Lin, L.; Zhang, M.; Yu, Q.; Li, S.; Peng, M.; Xu, Y.; Zhao, X.; Xu, M.; Zhou, W.; Yao, S.; Ma, D. Maximizing the Synergistic Effect of CoNi Catalyst on  $\alpha$ -MoC for Robust Hydrogen Production. *J. Am. Chem. Soc.* **2021**, *143*, 628.
- (109) Liu, L.; Corma, A. Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles. *Chem. Rev.* **2018**, *118*, 4981.
- (110) Wang, Y.; Mao, J.; Meng, X.; Yu, L.; Deng, D.; Bao, X. Catalysis with Two-Dimensional Materials Confining Single Atoms: Concept, Design, and Applications. *Chem. Rev.* **2019**, *119*, 1806.
- (111) Li, Z.; Ji, S.; Liu, Y.; Cao, X.; Tian, S.; Chen, Y.; Niu, Z.; Li, Y. Well-Defined Materials for Heterogeneous Catalysis: From Nanoparticles to Isolated Single-Atom Sites. *Chem. Rev.* **2020**, *120*, 623.
- (112) Han, B.; Guo, Y.; Huang, Y.; Xi, W.; Xu, J.; Luo, J.; Qi, H.; Ren, Y.; Liu, X.; Qiao, B.; Zhang, T. Strong Metal-Support Interactions between Pt Single Atoms and TiO<sub>2</sub>. *Angew. Chem., Int. Ed.* **2020**, *59*, 11824.
- (113) O'Connor, N. J.; Jonayat, A. S. M.; Janik, M. J.; Senftle, T. P. Interaction trends between single metal atoms and oxide supports identified with density functional theory and statistical learning. *Nat. Catal.* **2018**, *1*, 531.
- (114) Huang, F.; Deng, Y.; Chen, Y.; Cai, X.; Peng, M.; Jia, Z.; Ren, P.; Xiao, D.; Wen, X.; Wang, N.; Liu, H.; Ma, D. Atomically Dispersed Pd on Nanodiamond/Graphene Hybrid for Selective Hydrogenation of Acetylene. *J. Am. Chem. Soc.* **2018**, *140*, 13142.
- (115) Huang, F.; Deng, Y.; Chen, Y.; Cai, X.; Peng, M.; Jia, Z.; Xie, J.; Xiao, D.; Wen, X.; Wang, N.; Jiang, Z.; Liu, H.; Ma, D. Anchoring Cu<sub>1</sub> species over nanodiamond-graphene for semi-hydrogenation of acetylene. *Nat. Commun.* **2019**, *10*, 4431.
- (116) Sun, Y.; Yang, Z.; Dai, S. Nonclassical Strong Metal-Support Interactions for Enhanced Catalysis. *J. Phys. Chem. Lett.* **2023**, *14*, 2364.
- (117) Jin, S.; Zhang, Z.; Li, D.; Wang, Y.; Lian, C.; Zhu, M. Alcohol-Induced Strong Metal-Support Interactions in a Supported Copper/ZnO Catalyst. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202301563.
- (118) Zhang, J.; Ma, J.; Choksi, T. S.; Zhou, D.; Han, S.; Liao, Y. F.; Yang, H. B.; Liu, D.; Zeng, Z.; Liu, W.; Sun, X.; Zhang, T.; Liu, B. Strong Metal-Support Interaction Boosts Activity, Selectivity, and Stability in Electrosynthesis of H<sub>2</sub>O<sub>2</sub>. *J. Am. Chem. Soc.* **2022**, *144*, 2255.
- (119) Zhou, J.; Gao, Z.; Xiang, G.; Zhai, T.; Liu, Z.; Zhao, W.; Liang, X.; Wang, L. Interfacial compatibility critically controls Ru/TiO<sub>2</sub> metal-support interaction modes in CO<sub>2</sub> hydrogenation. *Nat. Commun.* **2022**, *13*, 327.
- (120) Tang, M.; Li, S.; Chen, S.; Ou, Y.; Hiroaki, M.; Yuan, W.; Zhu, B.; Yang, H.; Gao, Y.; Zhang, Z.; Wang, Y. Facet-Dependent Oxidative Strong Metal-Support Interactions of Palladium-TiO<sub>2</sub> Determined by In Situ Transmission Electron Microscopy. *Angew. Chem., Int. Ed.* **2021**, *60*, 22339.
- (121) James, T. E.; Campbell, C. T. Catalysis: Quantifying charge transfer. *Nat. Energy* **2016**, *1*, 1.
- (122) Xu, M.; Yao, S.; Rao, D.; Niu, Y.; Liu, N.; Peng, M.; Zhai, P.; Man, Y.; Zheng, L.; Wang, B.; Zhang, B.; Ma, D.; Wei, M. Insights into Interfacial Synergistic Catalysis over Ni@TiO<sub>2-x</sub> Catalyst toward Water-Gas Shift Reaction. *J. Am. Chem. Soc.* **2018**, *140*, 11241.
- (123) Monai, M.; Jenkinson, K.; Melcherts, A. E. M.; Louwen, J. N.; Irmak, E. A.; Van Aert, S.; Altantzis, T.; Vogt, C.; van der Stam, W.; Duchon, T.; Smid, B.; Groeneveld, E.; Berben, P.; Bals, S.; Weckhuysen, B. M. Restructuring of titanium oxide overlayers over nickel nanoparticles during catalysis. *Science* **2023**, *380*, 644.
- (124) Beck, A.; Frey, H.; Huang, X.; Clark, A. H.; Goodman, E. D.; Cargnello, M.; Willinger, M.; van Bokhoven, J. A. Controlling the Strong Metal-Support Interaction Overlayer Structure in Pt/TiO<sub>2</sub> Catalysts Prevents Particle Evaporation. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202301468.
- (125) Laudenschleger, D.; Ruland, H.; Muhler, M. Identifying the nature of the active sites in methanol synthesis over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts. *Nat. Commun.* **2020**, *11*, 3898.
- (126) Wei, S.; Ni, S.; Xu, X. A new approach to inducing Ti<sup>3+</sup> in anatase TiO<sub>2</sub> for efficient photocatalytic hydrogen production. *Chi. J. Catal.* **2018**, *39*, 510.
- (127) Yang, J.; Huang, Y.; Qi, H.; Zeng, C.; Jiang, Q.; Cui, Y.; Su, Y.; Du, X.; Pan, X.; Liu, X.; Li, W.; Qiao, B.; Wang, A.; Zhang, T. Modulating the strong metal-support interaction of single-atom catalysts via vicinal structure decoration. *Nat. Commun.* **2022**, *13*, 4244.
- (128) Wu, C.; Cheng, D.; Wang, M.; Ma, D. Understanding and Application of Strong Metal-Support Interactions in Conversion of CO<sub>2</sub> to Methanol: A Review. *Energy Fuels* **2021**, *35*, 19012.
- (129) Zabilskiy, M.; Sushkevich, V. L.; Palagin, D.; Newton, M. A.; Krumeich, F.; van Bokhoven, J. A. The unique interplay between copper and zinc during catalytic carbon dioxide hydrogenation to methanol. *Nat. Commun.* **2020**, *11*, 2409.
- (130) Zhang, B.; Sun, G.; Ding, S.; Asakura, H.; Zhang, J.; Sautet, P.; Yan, N. Atomically Dispersed Pt<sub>1</sub>-Polyoxometalate Catalysts: How Does Metal-Support Interaction Affect Stability and Hydrogenation Activity? *J. Am. Chem. Soc.* **2019**, *141*, 8185.
- (131) Li, J.; Lin, Y.; Pan, X.; Miao, D.; Ding, D.; Cui, Y.; Dong, J.; Bao, X. Enhanced CO<sub>2</sub> Methanation Activity of Ni/Anatase Catalyst by Tuning Strong Metal-Support Interactions. *ACS Catal.* **2019**, *9*, 6342.
- (132) Zhao, X.; Wu, X.; Wang, H.; Han, J.; Ge, Q.; Zhu, X. Effect of Strong Metal-Support Interaction of Pt/TiO<sub>2</sub> on Hydrodeoxygenation of *m*-Cresol. *ChemistrySelect* **2018**, *3*, 10364.
- (133) Zhang, S.; Xia, Z.; Ni, T.; Zhang, Z.; Ma, Y.; Qu, Y. Strong electronic metal-support interaction of Pt/CeO<sub>2</sub> enables efficient and selective hydrogenation of quinolines at room temperature. *J. Catal.* **2018**, *359*, 101.
- (134) Xu, S.; Li, H.; Du, J.; Tang, J.; Wang, L. Subnanometric Gold Clusters with Maximized Strong Metal-Support Interactions for Aerobic Oxidation of Carbon-Hydrogen Bonds. *ACS Sus. Chem. & Eng.* **2018**, *6*, 6418.
- (135) Guo, Y.; Mei, S.; Yuan, K.; Wang, D.-J.; Liu, H.-C.; Yan, C.-H.; Zhang, Y.-W. Low-Temperature CO<sub>2</sub> Methanation over CeO<sub>2</sub>-Supported Ru Single Atoms, Nanoclusters, and Nanoparticles Competitively Tuned by Strong Metal-Support Interactions and H-Spillover Effect. *ACS Catal.* **2018**, *8*, 6203.
- (136) Wang, L.; Zhang, J.; Zhu, Y.; Xu, S.; Wang, C.; Bian, C.; Meng, X.; Xiao, F.-S. Strong Metal-Support Interactions Achieved by Hydroxide-to-Oxide Support Transformation for Preparation of Sinter-Resistant Gold Nanoparticle Catalysts. *ACS Catal.* **2017**, *7*, 7461.
- (137) Freakley, S. J.; He, Q.; Harrhy, J. H.; Lu, L.; Crole, D. A.; Morgan, D. J.; Ntainjua, E. N.; Edwards, J. K.; Carley, A. F.; Borisevich, A. Y.; Kiely, C. J.; Hutchings, G. J. Palladium-tin catalysts for the direct synthesis of H<sub>2</sub>O<sub>2</sub> with high selectivity. *Science* **2016**, *351*, 965.
- (138) Zhang, T. Single-Atom Catalysis: Far beyond the Matter of Metal Dispersion. *Nano Lett.* **2021**, *21*, 9835.
- (139) Yang, H.; Wu, Y.; Zhuang, Z.; Li, Y.; Chen, C. Factors Affecting the Catalytic Performance of Nano-catalysts. *Chi. J. Chem.* **2022**, *40*, 515.