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Identification of intrinsic active sites in ternary CuZnTi catalysts toward low-temperature water gas shift reaction

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ABSTRACT: In the heterogeneous field, modulation over strong metal-support interactions (SMSI) plays a crucial role in boosting catalytic performance toward interface-sensitive reactions (*e.g.*, water gas shift reaction, WGSR). Herein, a CuZnTi ternary catalyst was prepared *via in situ* structural topological transformation from CuZnTi-layered double hydroxides precursor (CuZnTi-LDHs). The resulting catalyst Cu/ZnTi-MMO(H350) exhibits an extraordinarily high catalytic activity toward low temperature-WGSR with a reaction rate of $19.7 \mu\text{mol}_{\text{CO}} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}$ at 250 °C, among the highest level in Cu-based catalysts. Advanced electron microscope and *in situ* spectroscopy characterizations verify that Cu nanoparticles (particle size: 7~10 nm) are modified by ZnTi-mixed metal oxides with abundant $\text{Cu}^{\delta+}-\text{O}_v-\text{Ti}^{3+}$ ($0 < \delta < 1$) interfacial sites. Incorporation of Ti element facilitates the reduction of ZnO to stabilize $\text{Cu}^{\delta+}$ species at the interface, which enhances the chemisorption of CO molecule. Simultaneously, neighboring $\text{O}_v-\text{Ti}^{3+}$ species significantly promotes the dissociation of H_2O molecule. The structure-activity correlation studies based on *quasi-in situ* XPS, *in situ* DRIFTS, *in situ* and *operando* EXAFS reveal that the interfacial sites ($\text{Cu}^{\delta+}-\text{O}_v-\text{Ti}^{3+}$) serve as the intrinsic active sites of WGS reaction. A combination of *in situ* characterization techniques and DFT calculations further substantiate that associative mechanism is the predominant reactive path below 200 °C whilst redox mechanism is overwhelming above 250 °C in the presence of Cu/ZnTi-MMO catalyst. This work demonstrates a facile modulation on metal-support interfacial structure *via* LDHs approach, which paves a way for rational design and preparation of heterogeneous catalysts.

Controlling the metal-support interactions is crucial to modulate the interfacial chemical properties of heterogeneous catalysts, which significantly affects the catalytic performance for a set of important interface-sensitive reactions, especially for water gas shift reaction (WGSR).^{1,2} The WGS reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$; $\Delta H^0 = -41.2 \text{ kJ mol}^{-1}$) plays an important role in industrial production of clean hydrogen as well as in eliminating residual CO in feed streams for fuel cells,³ which favors low reaction temperatures thermodynamically owing to its exothermic properties. Cu-based catalysts (*e.g.*, Cu-Zn-Al catalyst) have been employed industrially in low-temperature WGSR (LT-WGSR) for decades, but suffered from several difficulties in further promoting catalytic performance.⁴ Recently, oxide supported Cu based catalysts⁵⁻¹¹ (*e.g.*, Cu/CeO₂, Cu/SiO₂, Cu/ZnO, and Cu/TiO₂) exhibit tremendous potential for LT-WGSR, and great efforts have been devoted to demonstrating the key role of metal-support interfacial sites; however, a precise modulation over active site structure of Cu-based catalysts toward WGSR still remains a challenging goal.

Although great progress has been made in this area, the atomic structure and catalytic mechanism of intrinsic active sites toward WGSR have caused intensive debates. Moreover, the identification and characterization of intrinsic active sites at atomic/molecular level has long been a great challenge, especially under *in situ/operando* conditions. For instance, surface defect sites of small Cu particles, isolated Cu atoms or extended surfaces of Cu nanoparticles have been reported as active sites of WGSR.^{2,7,12-15} In addition, a great deal of studies^{2,16} verified that cationic Cu metal centers (*e.g.*, Cu ^{δ +} or Cu⁺) serve as the optimal active center for CO activation adsorption, but suffer from destruction under realistic reaction

conditions. Rodriguez *et al.* reported that oxygen vacancies located at the interface accelerate the water dissociation, followed by reaction between adsorbed CO and active OH species to produce CO₂ and H₂.¹⁷ Therefore, it is critical to modulate the interfacial structure of metal-support, so as to promote the catalytic performance of WGSR *via* tuning both CO adsorption and water dissociation. In this respect, modulation of strong metal-support interactions (SMSI) for heterogeneous metal catalysts is an effective route to control the interfacial geometric/electronic structure.^{1,18} Nevertheless, tuning SMSI by traditional methods usually requires harsh conditions (*e.g.*, high temperature), which results in excessive encapsulation and severe aggregation of active metal nanoparticles.¹⁹ This in turn deteriorates the catalytic behavior of interfacial active sites.

Herein, CuZnTi-layered double hydroxides precursor (CuZnTi-LDHs) was synthesized by a facile co-precipitation method. By virtue of structural topological transformation of CuZnTi-LDH precursors in H₂/N₂ atmosphere, ZnTi-mixed metal oxides (ZnTi-MMO) decorated Cu nanoparticle catalysts (denoted as Cu/ZnTi-MMO) were obtained (Fig. 1A). A comprehensive study including X-ray diffraction (XRD), high resolution transmission electron microscope (HRTEM), *in situ* extended X-ray absorption fine structure spectroscopy (*in situ* EXAFS) and *quasi in situ* X-ray photoelectron spectroscopy (*quasi in situ* XPS) reveals the formation of Cu^{δ+}-O_v-Ti³⁺ interfacial site (0<δ<1; O_v: oxygen vacancy), attributed to the strong metal-support interactions (SMSI) between ZnTi-MMO and Cu nanoparticles. Moreover, the as-prepared Cu/ZnTi-MMO(H350) catalyst exhibits an extraordinary LT-WGSR catalytic performance with a reaction rate of 19.7 μmol_{CO} g_{cat}⁻¹s⁻¹ and turnover frequency value (TOF) of 5.7×10⁻² s⁻¹, which is among the highest level in

Cu-based catalysts. *In situ* DRIFTS measurements combined with *in situ/operando* EXAFS confirm that $\text{Cu}^{\delta+}$ species enhances CO chemisorption whilst $\text{O}_v\text{-Ti}^{3+}$ site accelerates water dissociation, accounting for the excellent catalytic performance of Cu/ZnTi-MMO catalyst. Furthermore, *in situ* time-resolved DRIFTS, TPSR measurements and DFT calculations demonstrate that the WGSR follows associative pathway below 200 °C whilst obeys redox pathway above 250 °C over Cu/ZnTi-MMO(H350) catalyst.

RESULTS AND DISCUSSION

Structural and morphological characterizations

The CuZnTi-LDHs precursor with $\text{Cu}^{2+}/\text{Zn}^{2+}/\text{Ti}^{4+}$ molar ratio of 1:2:1 was synthesized *via* a urea decomposition method. Its XRD pattern shows (003), (006), (110), and (113) plane for an LDHs phase at 2θ 12.9°, 23.8°, 57.2° and 59.7°, respectively (Fig. 1B a); and SEM images (Supplementary Fig. 1A) display a uniform nanosheet-like structure with a diameter of 8–10 nm. An *in situ* reduction treatment in H_2 atmosphere (at 300, 350, or 400 °C) results in structural transformation of CuZnTi-LDHs precursor to Cu nanoparticles supported on ZnTi-MMO (mixed metal oxides: ZnO and TiO_2), which are denoted as Cu/ZnTi-MMO(H300), Cu/ZnTi-MMO(H350) and Cu/ZnTi-MMO(H400). As shown in Fig. 1B b-d, XRD patterns of the three Cu-based samples show a series of reflections at 2θ 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, and 67.9° indexed to a ZnO phase (PDF#36-1451), and a weak peak at 25.3° attributed to an anatase TiO_2 phase (PDF#21-1272). In addition, with the increment of reduction temperature, the mean crystal size of Cu particles increases slightly from 9.4 to 10.1 nm calculated from Scherrer equation (Supplementary Table 1). The as-obtained three Cu/ZnTi-MMO samples inherit the original nanosheet-like morphology of

LDH precursor without obvious change (Supplementary Fig. 1B-D). For comparison, Cu/ZnO and Cu/TiO₂ were prepared by traditional precipitation-deposition method as reference samples, whose structure was identified as Cu+ZnO and Cu+TiO₂ phase (Fig. 1B e-f), with Cu crystal size of 15.6 nm and 23.2 nm (Supplementary Table 1), respectively.

Fig. 1 Synthesis and structure characterization of samples. XRD patterns of (a) CuZnTi-LDHs, (b) Cu/ZnTi-MMO(H300), (c) Cu/ZnTi-MMO(H350), (d) Cu/ZnTi-MMO(H400), (e) Cu/ZnO, and (f) Cu/TiO₂.

H₂-TPR measurements (Supplementary Fig. 2) for CuZnTi-LDHs precursor give primary reduction peak shifting to higher temperature compared with the two reference samples (Cu/ZnO and Cu/TiO₂), indicating a strong interaction between Cu and ZnTi-MMO support.^{20,21} TEM images (Supplementary Fig. 3A₁-C₁) of Cu/ZnTi-MMO(H300), Cu/ZnTi-MMO(H350) and Cu/ZnTi-MMO(H400) display that Cu nanoparticles (Cu loading: ~15%; average size: ~8 nm) are anchored on the ZnTi-MMO matrix with a well-defined dispersion, in good agreement with the result of XRD patterns (Supplementary Table 1). HRTEM images (Supplementary Fig. 3A₂-C₂) illustrate the lattice fringe of 0.245 and 0.281

nm ascribed to the (101) and (002) planes of ZnO, 0.351 nm assigned to the (101) plane of TiO₂, and 0.208 nm indexed to the (111) plane of Cu phase. This indicates that the Cu nanoparticles are highly dispersed on ZnO and TiO₂ nanosheets with heterostructure interfaces. In marked contrast, the reference samples (Cu/ZnO and Cu/TiO₂) show much larger Cu nanoparticles (~15 nm and ~25 nm, Supplementary Fig. 3D_{1,2} and E_{1,2}).

As a typical sample, Cu/ZnTi-MMO(H350) was further studied by high-angle annular dark field scanning transmission electron microscopy (ac-HAADF-STEM) and electronic energy-loss spectroscopy (EELS). Element EDS mapping images (Fig. 2a₂-a₄) of Cu, Zn, and Ti illustrate that Cu nanoparticles are uniformly distributed on the ZnTi-MMO matrix; moreover, ZnO and TiO₂ overlayers partially cover the surface of Cu nanoparticles (Fig. 2a₅, a₆). To explore the interfacial electronic properties, EELS of Cu L_{2,3} edges (Fig. 2a₇) were collected at Spot I (support), Spot II (interface) and Spot III (Cu particle), respectively. The Cu L₃ edge of interface site (Spot II) displays an asymmetric peak at ~934.3 eV, with an obvious high energy shift (0.8 eV) relative to metal Cu (Spot III), indicating the formation of electron-deficient metallic Cu species (Cu^{δ+}) at the interface.²² The results above demonstrate that Cu nanoparticles are partially covered by ZnTi-MMO support with electron transfer at the interface, which is a typical characteristic of SMSI. For the control sample of Cu/ZnO, Cu nanoparticles are completely encapsulated by ZnO overlayer observed from element EDS mapping images of Cu, Zn, and O (Fig. 2b₂-b₆), but electron transfer is not apparent at the interface (Fig. 2b₇). In contrast, for the Cu/TiO₂ sample, no obvious coating layer is detected on the surface of Cu nanoparticles (Supplementary Fig. 4) due to a weak metal-support interaction, in consistent with the previous studies.²³

Fig. 2 Morphology characterizations and composition of samples. (a₁) Low magnification ac-HAADF-STEM image of the Cu/ZnTi-MMO(H350) sample. (a₂-a₆) Element EDS mapping images of Cu, Zn, Ti, Cu+Zn and Cu+Ti, respectively. (a₇) High resolution ac-HAADF-STEM image of the pink ellipse region in a₁; EELS collected at spots I, II, and III. (b₁) High resolution ac-HAADF-STEM image of the Cu/ZnO sample. (b₂-b₆) Element EDS mapping images of Cu, Zn, O, Cu+Zn and Cu+Zn+O of Cu/ZnO in b₁, respectively. (b₇) EELS collected at spots I, II, and III.

Identification of $\text{Cu}^{\delta+}\text{-O}_\text{v}\text{-Ti}^{3+}$ interface structure

In situ EXAFS spectroscopy at Cu *K*-edge was carried out to explore the geometric structure, electronic state and coordination environment of Cu species. As shown in Fig. 3A, the normalized XANES spectra of Cu/ZnO, Cu/TiO₂ and Cu/ZnTi-MMO(H350) samples show a slightly stronger white line relative to the Cu foil, indicating a predominant metallic Cu with a bit of Cu oxidation state.^{24,25} The photon energy of adsorption edge is obviously lower than that of the Cu₂O reference for the three samples (Fig. 3A, inset). This indicates the formation of Cu species with partial positive valence (denoted as $\text{Cu}^{\delta+}$, $0 < \delta < 1$) for Cu/ZnTi-MMO(H350) sample, in accordance with the results of EELS. Moreover, Fig. 3B shows the fourier transform EXAFS spectra at Cu *K*-edge (R-space). The metallic Cu–Cu distance for Cu/ZnTi-MMO(H350) sample displays a slight decrease (0.03 Å) compared with Cu foil (~2.54 Å), indicating a strong bonding interaction between metal Cu and ZnTi-MMO support. Furthermore, the Fourier transform of k^3 -weighted EXAFS spectra of these samples at Cu *K*-edge (R-space plot) and corresponding curve fitting are obtained (Supplementary Fig. 5), and the fitting results are listed in Supplementary Table 2. Notably, the first Cu–O shell of Cu/ZnTi-MMO(H350) is observed at the atomic distance of ~1.9 Å, demonstrating the presence of $\text{Cu}^{\delta+}\text{-O}$ species,²⁴ but this is not detected for the samples of Cu/ZnO and Cu/TiO₂. Moreover, the Cu/ZnTi-MMO(H350) sample possesses the lowest Cu–Cu coordination number (6.2), which accords with the smallest particle size confirmed by XRD and HRTEM.

Fig. 3 *In situ* XAS measurements of samples. (A) XANES spectra and (B) Fourier-transform EXAFS spectra at the Cu *K*-edge (R-space) for Cu/ZnTi-MMO(H350), Cu/ZnO, Cu/TiO₂, CuO, Cu₂O and Cu foil. The inset in A shows the enlarged image of the absorption edge. (C) XANES spectra at the Ti *K*-edge for the three Cu/ZnTi-MMO samples, Cu/TiO₂ and reference anatase. (D) Enlarged view for the pre-edge region of (C). (E) Zn *K*-edge XANES and (F) EXAFS spectra for Cu/ZnTi-MMO(H350), Cu/ZnO, ZnO and Zn foil.

In situ XANES at Ti *K*-edge and Zn *K*-edge were carried out as shown in Fig. 3C and 3E. In post-edge region, the white line peak (at ~4987 eV, labeled as B) and three additional peaks (within 4990–5010 eV, labeled as C₁, C₂, and C₃) of Cu/ZnTi-MMO(H300), Cu/ZnTi-MMO(H350) and Cu/ZnTi-MMO(H400) samples are lower than that of anatase reference (Fig. 3C), indicating a decreased Ti–O coordination number.^{26,27} In addition, the pre-edge region gives rise to three pre-peaks denoted A₁, A₂, and A₃, attributed to transitions of the core electron to Ti 3*d*4*p*4*s* hybridized states.^{26,27} For the three Cu/ZnTi-MMO samples, the A₂ feature shows a stronger intensity with a shift to lower energy (Fig. 3D), indicating a

lower coordination numbers (5 coordination) and distorted Ti–O environment,²⁶⁻²⁸ which is associated with the presence of oxygen vacancies (*i.e.*, O_v–Ti³⁺ site). As shown in the Zn *K*-edge XANES spectra (Fig. 3E), the Cu/ZnTi-MMO(H350) sample shows the lowest intensity of white line relative to Cu/ZnO and ZnO samples, suggesting a significant reduction of ZnO. In terms of the R-space plot, no obvious change is observed in the first Zn–O shell and the second Zn–Zn shell for ZnO, Cu/ZnO and Cu/ZnTi-MMO(H350) (Fig. 3F).

In order to investigate surface chemical state of various samples, *quasi in situ* XPS was performed over Cu/ZnTi-MMO, Cu/ZnO and Cu/TiO₂, respectively. The three Cu/ZnTi-MMO samples show a ~0.6 eV shift toward higher binding energy of Cu 2_p_{3/2} and Cu 2_p_{1/2} peaks (Supplementary Fig. 6A), in comparison with Cu/ZnO and Cu/TiO₂, indicating a strong electronic interaction between Cu species and ZnTi-MMO supports. X-ray excited Auger electron spectra (XAES) measurements were executed to further distinguish Cu⁰ and Cu^{δ+} species. As shown in Fig. 4A, the peak centered at ~919.1 eV (kinetic energy values) belongs to Cu⁰ species. Notably, the three Cu/ZnTi-MMO samples display rather close characteristic peak centered at ~917.2 eV, which is ascribed to Cu^{δ+} species.^{28,29} The corresponding Auger parameter and relative proportion of Cu species for five samples are listed in Supplementary Table 3. In addition, the derivative spectra of Cu *K*-edge XANES spectra also confirm the change of valence state (Fig. 4B).^{30,31} As the reduction temperature increases from 300 to 400 °C, the ratio of Cu^{δ+} enhances first and then declines, and the maximum (50.0%) is present at 350 °C. In contrast, the reference samples (Cu/ZnO and Cu/TiO₂) have a low ratio of Cu^{δ+} (19.6% and 16.7%, respectively). *In situ* DRIFTS

measurements (Fig. 4C) were performed to further study the electronic structure of Cu species for the five Cu-based samples. Generally, the $\text{Cu}^{\delta+}$ species strengthens the back-donation of Cu d electrons into the CO $2\pi^*$ anti-bonding orbitals, giving rise to enhanced CO chemisorption.³² As shown in Fig. 4C, the three Cu/ZnTi-MMO samples exhibit a stronger CO adsorption (IR band at 2103 cm^{-1}) than that of Cu/ZnO and Cu/TiO₂ (2107 cm^{-1}). The results above demonstrate that a strong metal-support interaction in Cu/ZnTi-MMO results in the formation of $\text{Cu}^{\delta+}$ species at the interface, which therefore enhances CO chemisorption.

Fig. 4 Chemical composition and state of samples. *Quasi in situ* XAES spectra of (A) Cu LMM, (D) Zn LMM, (E) Ti 2p and (F) O 1s for various samples: (a) Cu/ZnO, (b) Cu/TiO₂,

(c) Cu/ZnTi-MMO(H300), (d) Cu/ZnTi-MMO(H350), (e) Cu/ZnTi-MMO(H400). (B) The first derivative from *in situ* Cu *K*-edge XANES spectra. (C) *In situ* DRIFTS spectra for the five Cu-based samples recorded within 2200–2000 cm⁻¹ after CO chemisorption at 25 °C and subsequently flushing with He for 30 min. *Quasi in situ* XAES spectra of Cu LMM spectra for Cu/TiO₂ are shown in Supplementary Fig. 6B.

Zn LMM Auger peak was also conducted and deconvoluted into a main peak (Zn²⁺, ~988.2 eV) and a shoulder peak (Zn⁰, ~991.5 eV) *via* a Gaussian peak fitting approach. As shown in Fig. 4D, in comparison with the Cu/ZnO sample, the Zn LMM Auger peak of Cu/ZnTi-MMO(H350) shifts to higher energy with apparently enhanced shoulder peak (~991.5 eV), which can be ascribed to the presence of metallic Zn.³³ The SMSI between the Cu species and ZnTi-MMO support promotes the reduction of ZnO species, in accordance with the result of EXAFS. Fig. 4E shows a broad Ti 2*p* spectrum deconvoluted to two peaks at 459.1 eV and 458.5 eV, corresponding to Ti⁴⁺ and Ti³⁺ species, respectively.^{34,35} The ratio of the Ti³⁺ enhances first and then declines, and the maximum is obtained for Cu/ZnTi-MMO(H350) sample (Supplementary Table 4). In the case of O 1*s* region (Fig. 4F), the peak at 530.1 eV for Cu/ZnTi-MMO samples is ascribed to surface adsorbed oxygen species at oxygen vacancy,³⁵ whose intensity shows a similar trend as Ti³⁺ in these samples (*i.e.*, O_v-Ti³⁺ sites). A comprehensive study of *in situ* EXAFS, *quasi in situ* XPS and *in situ* DRIFTS substantiates the formation of Cu^{δ+}-O_v-Ti³⁺ interface structure, and the Cu/ZnTi-MMO(H350) sample possesses the most abundant interface sites.

Studies on the catalytic performance and structure-performance correlation

The catalytic performance of various samples toward LT-WGSR was evaluated within the reaction temperature from 120 to 350 °C. As shown in Fig. 5A, the catalytic performance

of Cu/ZnTi-MMO catalysts display the following sequence: Cu/ZnTi-MMO(H350) > Cu/ZnTi-MMO(H300) > Cu/ZnTi-MMO(H400). The Cu/ZnTi-MMO(H350) catalyst exhibits the optimal catalytic activity, with a CO conversion of 96.5% at 250 °C, which is superior to the commercial Cu/ZnO/Al₂O₃ catalyst under the same WGS condition (Supplementary Fig. 7). A long-term running test shows a satisfactory catalytic stability with CO conversion loss of ~15% within 60 h at 250 °C (Supplementary Fig. 8). HRTEM image of the used catalysts displays a slight growth or agglomeration of Cu nanoparticles (Supplementary Fig. 9). In contrast, Cu/ZnO and Cu/TiO₂ give a low CO conversion of 20.3% and 5.86% at 250 °C, respectively. In order to satisfy the work requirement of fuel cells for potential practical application, it is very critical to maintain a high activity within reaction temperature up and down. As shown in Fig. 5B, the Cu/ZnTi-MMO(H350) catalyst gives a drop (~8%) of CO conversion after five successive start-up/shut-down cycles, indicating a good repeatability.

The turnover frequency (TOF) values for various catalysts were calculated with the CO conversion below 15% (250 °C), which decreases in the following order: Cu/ZnTi-MMO (H350) > Cu/ZnTi-MMO (H300) > Cu/ZnTi-MMO (H400) > Cu/ZnO > Cu/TiO₂ (Fig. 5C, Supplementary Table 4), in accordance with the tendency of CO conversion (Fig. 5A). The optimal catalyst Cu/ZnTi-MMO(H350) displays the maximum TOF value ($5.7 \times 10^{-2} \text{ s}^{-1}$, Supplementary Table 5) with the lowest active energy (38.2 kJ mol⁻¹, Fig. 5D). In addition, the TOF value as a function of either surface concentration of Cu^{δ+} species or Ti³⁺/(Ti³⁺+Ti⁴⁺) ratio is illustrated in Fig. 5E and F, from which a positive correlation is obtained. This demonstrates that Cu^{δ+}-O_v-Ti³⁺ interface sites serve as active center toward LT-WGSR.

Fig. 5 Catalytic performance. (A) CO conversion as a function of reaction temperature over various samples (WGS conditions: 6% CO, 24% H₂O, 70% Ar; WHSV of 13200 ml g_{cat}⁻¹ h⁻¹). (B) CO conversion for five successive start-up/shut-down cycles over the Cu/ZnTi-MMO(H350) catalyst. (C) TOF value at 250 °C and (D) Arrhenius plots of WGS for the five catalysts. TOF value as a function of (E) surface Cu^{δ+} concentration and (F) Ti³⁺/(Ti³⁺ + Ti⁴⁺) ratio, respectively.

Studies on intrinsic active sites and catalytic mechanism

In situ time-resolved DRIFTS was carried out to explore the catalytic properties over the Cu^{δ+}–O_v–Ti³⁺ interfacial sites. As shown in Fig. 6A, after reduction at 350 °C for 2 h in a 5% H₂/He stream, the obtained Cu/ZnTi-MMO(H350) catalyst was cooled to 200 °C. Afterwards,

H₂O vapor is introduced in the *in situ* reaction cell; and two weak IR bands at 3727 and 3676 cm⁻¹ are observed, which are attributed to the stretching vibration of Ti³⁺-OH and Ti⁴⁺-OH, respectively.³⁶ This indicates that O_v-Ti³⁺ and O_{lattice}-Ti⁴⁺ sites directly take part in the H₂O dissociation to generate surface hydroxyls species. Then, after a switch to 5% CO/He atmosphere, the two bands of surface hydroxyl decrease gradually (Fig. 6B). Simultaneously, a new band at 2108 cm⁻¹ due to adsorbed CO on Cu^{δ+} sites is observed and enhances gradually, and another two bands at 2363 and 2337 cm⁻¹ ascribed to adsorbed CO₂ appear (Fig. 6C).³⁷ Accordingly, as shown in Fig. 6B, the band intensity at 2933 and 2876 cm⁻¹ increases gradually, attributed to the stretching vibration of C-H bond of formate species;^{38,39} moreover, three bands at ~1590, 1390 and 1365 cm⁻¹ are observed, which are assigned to O-C-O bending vibrations of HCOO species (Fig. 6D).³⁸⁻⁴⁰ Meanwhile, IR bands at ~1543 and 1290 cm⁻¹ ascribed to chemisorbed carboxylate species (CO₂^{δ-}) appear progressively.³⁶ Thus, the results above indicate the occurrence of associative mechanism in the WGS over Cu/ZnTi-MMO(H350) catalyst.

Fig. 6 *In situ* infrared spectroscopy studies on Cu/ZnTi-MMO(H350) catalyst. *In situ* time-resolved DRIFTS spectra of Cu/ZnTi-MMO(H350) catalyst at 200 °C upon exposure to H₂O atmosphere for 10 min recorded in (A) 3780–3630 cm⁻¹, followed by a switch to CO flow recorded in (B) 3780–3630 cm⁻¹ and 2950–2800 cm⁻¹, (C) 2450–2000 cm⁻¹ and (D) 1650–1250 cm⁻¹ as a function of reaction time.

The temperature-programmed surface reaction (TPSR) experiments were also carried out to investigate the catalytic mechanism over the Cu/ZnTi-MMO(H350) catalyst. Supplementary Fig. 10 shows CO+H₂O TPSR recorded from 100 to 350 °C (heating rate: ~5 °C/min). Due to the reaction between CO and the original surface O* of catalyst, CO₂ product appears slightly earlier and stronger than H₂ between 100 and 150 °C.⁴¹ Subsequently, CO₂ and H₂ signals simultaneously appear with close intensity at above 150 °C, indicating two products originate from a common surface reaction intermediate. This points to an

associative mechanism in WGSR, in accordance with the results from *in situ* DRIFTS. Additionally, for the Cu/ZnTi-MMO(H350) catalyst under water vapor treatment, H₂ signal is absent at 150 °C whilst a strong one is detected at 250 °C (Supplementary Fig. 11), which verifies that surface H₂O molecules dissociate to generate H₂ in the absence of CO at high temperature (250 °C).⁴² Moreover, after a 15 min water vapor treatment at 250 °C to enhance the surface hydroxyl concentration (surface active oxygen species), CO-TPSR spectra (Supplementary Fig. 12) were collected to further study the above catalytic process. After the subsequent introduction of CO, an obvious CO₂ signal is observed accompanied with the production of hydrogen. This demonstrates that CO molecules react with surface hydroxyl species at 250 °C *via* redox mechanism. As the temperature rises above 250 °C, CO₂ curve still remain a high level with decreased H₂ formation, indicating that CO molecule reacts with surface active oxygen species to produce CO₂ *via* redox mechanism. Therefore, WGSR follows an associative pathway at low temperature (150 °C) whilst obeys a redox one at high temperature (above 250 °C).

In situ/operando EXAFS was carried out at Cu and Ti *K*-edge to monitor the dynamic structural evolution of active Cu^{δ+}-O_v-Ti³⁺ interfacial sites for Cu/ZnTi-MMO(H350) catalyst in different reaction atmospheres. As shown in Fig. 7A₁, the white line of Cu *K*-edge XANES spectra displays a slight shift (inset: from blue line to orange line) toward higher photo energy upon exposure to H₂O, indicating the oxidation of Cu^{δ₁+} to Cu^{δ₂+} during the dissociation of H₂O molecule. Subsequently, 5% CO/He atmosphere is switched into this reaction system for another 30 min, and the absorption edge (inset: magenta line) moves back to its initial state, indicating a recovery of Cu^{δ₂+} to Cu^{δ₁+}. In the case of Fourier-transform Cu

K-edge EXAFS spectra (Fig. 7A₂), no obvious change in Cu–Cu bonding length and coordination number is observed after the introduction of H₂O and/or CO at certain temperature. This demonstrates that Cu^{δ+} species directly participates in the H₂O dissociation during WGS without change in Cu particle size. Meanwhile, the A₂ peak of Ti *K*-edge XANES spectra (Fig. 7A₃) weakens and slightly shifts to higher energy in the pre-edge region (inset: orange line) upon exposure to H₂O vapor, indicating the increase of Ti coordination number (from 5 to 6), ascribed to the occupation of surface hydroxyl species and active oxygen species at the O_v–Ti³⁺ site. The phenomena above demonstrate a transformation from O_v–Ti³⁺ to O–Ti⁴⁺. After the introduction of CO, a reverse situation occurs to the Ti *K*-edge XANES spectra (inset: magenta line), indicating a recovery of O_v–Ti³⁺. The aforementioned process demonstrates that Cu^{δ+}–O_v–Ti³⁺ interfacial sites serve as active center and participate in LT-WGSR at 250 °C. In addition, *operando* EXAFS was also executed to investigate the electronic and geometric structure of Cu/ZnTi-MMO(H350) catalyst under realistic reaction conditions (Fig. 7B₁–B₃), and the results showed that the active interfacial sites (Cu^{δ+}–O_v–Ti³⁺) in Cu/ZnTi-MMO(H350) remained stable during the WGS reaction process. The *in situ/operando* EXAFS results strongly demonstrate a dynamic structural evolution process: water dissociation process results in the oxidation of the interface site (from Cu^{δ₁+}–O_v–Ti³⁺ to Cu^{δ₂+}–OH–Ti⁴⁺ or Cu^{δ₂+}–O–Ti⁴⁺); subsequently, chemisorbed CO molecule captures surface hydroxyl species and active oxygen species to produce H₂ and CO₂, along with the reduction of interface site to its original state (Cu^{δ₁+}–O_v–Ti³⁺) at 250 °C.

Fig. 7 Dynamic structural evolution of $\text{Cu}^{\delta_1+}\text{-O}_v\text{-Ti}^{3+}$ interfacial sites. (A₁) Normalized XANES spectra at Cu *K*-edge, (A₂) corresponding Fourier-transform Cu *K*-edge EXAFS spectra (*R*-space), and (A₃) normalized Ti *K*-edge XANES collected at 250 °C for the Cu/ZnTi-MMO(H350) sample: H₂O vapor was firstly introduced for 15 min (orange line), followed by flowing CO for another 15 min (magenta line). (B₁) Normalized XANES spectra at Cu *K*-edge, (B₂) corresponding Fourier-transform Cu *K*-edge EXAFS spectra (*R*-space), and (B₃) normalized Ti *K*-edge XANES collected at 250 °C for the Cu/ZnTi-MMO(H350) sample under *operando* conditions (6% CO, 25% H₂O, and 69% He). The inset in A₁ and B₁ displays the enlarged image of the absorption edge region.

It has been reported that H₂O dissociation serves as the rate-determining step during WGS reaction;^{43,44} therefore, DFT calculations were carried out to explore the adsorption and activation energies of H₂O molecule. As shown in Supplementary Fig. 13, we calculated the activation energy barrier of H₂O dissociation over the Cu/ZnO(101) interface, Cu/TiO_{2-x}(101) interface and Cu/ZnO/TiO_{2-x}(101) interface, respectively, and summarized the energy profile for H₂O dissociation. The interfacial sites plays a key role for H₂O dissociation: the

dissociated H atom is located nearly at the interfacial Cu site, and OH species stays on the O_v site (transition state).^{45,46} The energy barrier (E_a) of H₂O dissociation increases in the sequence: Cu/ZnO/TiO_{2-x}(101) < Cu/TiO_{2-x}(101) < Cu/ZnO(101) (0.36 eV, 0.67 eV, and 0.90 eV, respectively). Cu/ZnO/TiO_{2-x}(101) system presents the lowest activation energy for H₂O dissociation; Moreover, the bond length of activated H–O in H₂O are 0.99 Å, 1.02 Å and 1.03 Å at Cu/ZnO(101), Cu/TiO_{2-x}(101) and Cu/ZnO/TiO_{2-x}(101) interface, respectively. The results above indicate the most favorable process of H₂O dissociation on Cu/ZnO/TiO_{2-x}(101).

Fig. 8 Density functional theory results. Initial state (IS), the corresponding transition state (TS) and final state (FS) structures and energies barrier (E_a) of (A) redox pathway, (B) carboxyl pathway and (C) formate pathway of WGSR at the Cu/ZnO/TiO_{2-x}(101) interface. (D) Energy profiles of the three reaction pathways at the Cu/ZnO/TiO_{2-x}(101) interface. The numbers are the values of energy barrier (in eV) of individual step (Cu: rose red; Zn: blue; Ti: gray; lattice O: red; H: white; C: dark gray; OH₂O: pink).

DFT calculations were also performed to further investigate the reaction mechanism at Cu/ZnO/TiO_{2-x}(101) interface, including redox pathway, carboxyl pathway and formate pathway. In the case of redox pathway, H₂O dissociation ($H_2O^* \rightleftharpoons OH^* + H^*$) could generate surface OH* which further dissociates to produce surface active oxygen species (O*) located

at the interface (Fig. 8A). Subsequently, CO^* adsorbed at the $\text{Cu}^{\delta+}$ site reacts with O^* species to generate CO_2 ($\text{CO} + \text{O} \rightarrow \text{CO}_2$), which needs to overcome an activation energy of 0.85 eV *via* redox pathway (Fig. 8A and D). As for the carboxyl pathway, CO^* could react with surface OH^* to yield COOH^* species, with a high energy barrier (TS6) of 1.16 eV (Fig. 8B and D), which is thermodynamically unfavorable. In terms of formate pathway, however, CHO generation (TS8) *via* $\text{CO} + \text{H} \rightarrow \text{CHO}$ (rate determining step) is more reasonable with a lower energy barrier of 0.75 eV than redox pathway and carboxyl pathway (Fig. 8C and D), and the formation of HCOO^* intermediates requires an energy barrier of 0.64 eV (TS9). The results above demonstrate that both redox and associative mechanism would occur over $\text{Cu/ZnO/TiO}_{2-x}(101)$ system, and formate (HCOO^*) is the most favorable active intermediate species in the latter one, which is in accordance with *in situ* time-resolved DRIFTS results described above. In order to deeply explore the correlation between catalytic mechanism and reaction temperature, the ΔG was elaborately calculated for the critical elemental step. As shown in Supplementary Fig. 14, the step $\text{CO}^* + \text{H}^*$ gives a lower free energy ($\Delta G < 0.84$ eV) below 473 K, so the formate path is dominant. Moreover, the ΔG increases from 0.84 eV to 0.88 eV as the temperature rises from 473 K to 723 K. While above 523 K, redox pathway is predominant since the ΔG of $\text{CO}^* + \text{O}^*$ decreases from 0.84 eV to 0.83 eV with the increase of temperature from 473 K to 723 K. This is consistent with the results from experimental investigations mentioned above.

A combination study based on *quasi in situ* XPS, *in situ* DRIFTS, TPSR experiments, *in situ/operando* EXAFS and DFT calculations substantiate that the $\text{Cu}^{\delta+}-\text{O}_v-\text{Ti}^{3+}$ interfacial sites serve as the dual-active-site toward WGS. A dynamic structural evolution of

$\text{Cu}^{\delta+}-\text{O}_v-\text{Ti}^{3+}$ interfacial sites is demonstrated as follows: (i) H_2O molecule undergoes dissociation at the interface site ($\text{O}_v-\text{Ti}^{3+}$) to generate surface hydroxyl species (Eqa. 1) or active oxygen species (Eqa. 5); (ii) subsequently, chemisorbed CO at $\text{Cu}^{\delta+}$ site reacts with the surface hydroxyl species or active oxygen species to produce CO_2 and H_2 (Eqa. 2, 3, 4, 6 and 7). The corresponding interfacial synergistic catalysis based on associative mechanism (low temperature) and redox mechanism (high temperature) are described as following two reactive paths.

Path one: associative pathway:

Path two: redox pathway:

In summary, the interfacial structure ($\text{Cu}^{\delta+}-\text{O}_v-\text{Ti}^{3+}$) derived from strong SMSI between metallic Cu and ZnTi-MMO support was clearly identified, which serve as active sites for WGSR verified by *in situ* electron microscope and spectroscopy characterizations. The $\text{Cu}^{\delta+}$ species promotes the CO chemisorption while $\text{O}_v-\text{Ti}^{3+}$ sites accelerate the H_2O dissociation, accounting for the excellent catalytic performance of Cu/ZnTi-MMO(H350) catalyst toward WGSR. By coupling *in situ/operando* characterization techniques and DFT calculations, it is

concluded that formate species serve as the critical intermediates *via* associative mechanism at the low temperatures (below 200 °C); whilst redox pathway is predominant at high temperatures (above 250 °C) over Cu/ZnTi-MMO(H350) catalyst. This work provides a strategy on the modulation of interfacial active sites *via* SMSI, which can be extended to the design of high-performance structure-sensitive heterogeneous catalysts.

Methods

Materials. Analytical grade chemicals including $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, TiCl_4 and urea were purchased from Sigma-Aldrich. The commercial ZnO and TiO_2 (anatase) was purchased from Aladdin Co and used without further purification. Deionized water was used in the whole experimental process.

Synthesis of Cu/ZnTi-MMO. The CuZnTi-LDHs precursor with a molar ratio of $[\text{Cu}^{2+}][\text{Zn}^{2+}]/[\text{Ti}^{4+}]=1/2/1$ was prepared by a urea decomposition method as follows. A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.01mol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.02 mol) and TiCl_4 solution (1.09 ml) was dissolved in deionized H_2O (200 ml), then 18 g of urea was added the solution, followed by incubation at 95 °C for 24 h with vigorous stirring. Subsequently, the resulting precipitate was separated by centrifugation, washing thoroughly and drying at 60 °C for 24 h. The obtained CuZnTi-LDHs was reduced in a H_2/N_2 (4:6, v/v) stream for 2 h at 300, 350 and 400 °C, respectively, with a heating rate of 5 °C min^{-1} . The resulting products were slowly cooled to room temperature in N_2 atmosphere, which were denoted as Cu/ZnTi-MMO(300), Cu/ZnTi-MMO(350) and Cu/ZnTi-MMO(400), respectively.

Synthesis of Cu/ZnO and Cu/TiO₂. Cu/ZnO was synthesized by a conventional urea deposition-precipitation method. In detail, ZnO (3.0 g) was dispersed in deionized water (60 mL) in a three-neck flask with ultrasonication and vigorous stirring. 2.28 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was completely dissolved in deionized water (20 mL), which defined as solution A. Meanwhile, solution B was prepared by diluting 10 ml of ammonia water to 100 mL water. Solution A and B were simultaneously added dropwise into the three-necked flask with magnetic stirring, with a constant pH value of 9.0. Afterwards, the suspension was stirred vigorously for 6 h at room temperature, followed by washing and drying at 60 °C for 24 h. Finally, the obtained sample was calcinated in a muffle furnace at 300 °C for 4 h, and then

reduced in a H₂/N₂ (4:6, v/v) at 300 °C for 2 h with a heating rate of 5 °C min⁻¹, to obtain the final Cu/ZnO sample. Cu/ TiO₂ was prepared *via* a similar deposition-precipitation method described above.

Characterizations. Powder X-ray diffraction (XRD) patterns were measured on a Rigaku XRD-6000 diffractometer at 40 kv and 30 mA using a Cu-K α (λ = 0.15418 nm) radiation source, with a 2θ angle ranging from 3° to 80° with a scanning rate of 10° min⁻¹. Morphological features were observed using a Zeiss Supra 55 scanning electron microscope (SEM; accelerating voltage: 20 kV) and a JEM-3010 High resolution transmission electron microscopy (HRTEM; accelerating voltage: 200 kV). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (ac-HAADF-STEM) images, element energy dispersive spectroscopy (EDS) mapping and electron energy loss spectroscopy (EELS) were obtained on a JEOL JEM-ARM200F instrument. Elemental analysis was determined by a Shimadzu ICPS-7500 inductively coupled plasma–atomic emission spectrometer (ICP–AES). H₂ temperature-programmed reduction (H₂-TPR) was conducted on a Micromeritics ChemiSorb 2070 equipped with a thermal conductivity detector (TCD). Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method on a Quantachrome Autosorb-1C-VP analyzer.

Hydrogen pulse reduction (N₂O titration) that provides dispersion and specific surface area of Cu species, was performed on a Micromeritics Autochem II 2920 instrument equipped with a TCD detector. *In situ* EXAFS at Cu and Ti K-edge was measured on the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS), operated at 2.5 GeV at the typical energy of the storage ring with a constant current of 250 mA. *Quasi in situ* X-ray photoelectron spectra (XPS) and X-ray excited Auger electron spectra (XAES) were carried out on an AXIS SUPRA X-ray photoelectron spectrometer equipped with Al K α radiation (1486.6 eV) operated at a pressure of 2×10^{-9} Torr. *In situ* DRIFTS was performed in a home-made *in situ* reaction cell on a Bruker TENSOR II spectrometer equipped with an MCT narrow-band detector.

Catalyst Evaluations. LT-WGSR was performed by a continuous flow fixed-bed with a quartz reactor (8 mm inner diameter) at atmospheric pressure and the gas products were measured on an online gas chromatograph (GC-2014C Shimadzu) equipped with a thermal conductivity detector (TCD). After an *in situ* reduction treatment (40.0 volume % H₂/N₂ mixture, 100 ml min⁻¹, 350 °C, 2 h) for the Cu/ZnTi-MMO precursor (0.5 g), a feed gas of 6%CO, 25%H₂O, 69%Ar (total gas flow: 110 mL min⁻¹) was introduced into the reactor within 120–350 °C and weight hourly space velocity (WHSV) was maintained at 13200

mL g_{cat}⁻¹ h⁻¹. At each temperature, the evaluation was repeated for 3 times to obtain accurate catalyst performance. The reaction rate and turnover frequency (TOF) were measured with CO conversion below 15%. The stability evaluation was performed under the same reaction conditions and exposed to the mixed gas at 250 °C for 60 h and a start/stop cycles test was carried out for five cycles.

Computational methods. First-principle calculations based on spin polarized DFT+U were performed using the Vienna ab-initio simulation package (VASP). The electronic exchange and correlation potential is described by the Perdew–Burke–Ernzerhof (PBE) function of the generalized gradient approximation (GGA). The projector augmented wave (PAW) method is employed to describe the interaction between the atomic cores and electrons. 3×3×1 *k*-point sampling in the surface Brillouin zone is used in the calculations. Spin polarization is considered for the calculations of all the models. An energy cutoff of 400 eV, and the converge criteria of the force on each relaxed atom below 0.05 eV/ Å were used. In this work, the value of Hubbard-U parameter was set to 3.5 eV for Ti atom. Transition state (TS) searches are performed at the same theoretical level with the CI-NEB method.

The adsorption energy (E_{ads}) is calculated as

$$E_{\text{ads}} = E_{\text{total}} - (E_{\text{slab}} + E_{\text{g}}) \quad (8)$$

where E_{total} is the total energy after adsorption; E_{slab} is the energy of the clean slab before adsorption; and E_{g} is the energy of the free adsorbate in the gas phase.

The energy barrier (E_{a}) is obtained from the electronic energy difference between the transition state (E_{TS}) and its corresponding initial state (E_{IS}), which is calculated by

$$E_{\text{a}} = E_{\text{TS}} - E_{\text{IS}} \quad (9)$$

The free energy (G) is calculated by

$$G = E_{\text{elec}} + E_{\text{ZPE}} - TS \quad (10)$$

wherein E_{elec} is the total electronic energy of the interface at 0 K; E_{ZPE} is the zero-point vibrational energy, and only the vibration entropy (S_{vib}) is taken into account.

Entropy of adsorbed species is obtained from the standard vibrational entropy (S_{vib}°) by

$$S_{\text{vib}}^{\circ} = R \sum_i \left\{ \frac{h c \nu_i / k_{\text{B}} T}{e^{h c \nu_i / k_{\text{B}} T} - 1} - \ln \left(1 - e^{-h c \nu_i / k_{\text{B}} T} \right) \right\} \quad (11)$$

where R is gas molar constant; k_{B} is the Boltzmann constant; h is the Planck constant; c is the light speed, and ν_i is the wavenumber.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper or its Supplementary Information files and from the corresponding author upon reasonable request.

References

1. Yao, S. et al. Atomic-Layered Au Clusters on α -MoC as Catalysts for the Low-Temperature Water-Gas Shift Reaction. *Science* **357** (3), 389–393 (2017).
2. Chen, A. L. et al. Structure of the catalytically active copper–ceria interfacial perimeter. *Nat Catal.* **2** (4), 334–341 (2019).
3. Zhai, Y. et al. Alkali-Stabilized Pt-OH_x Species Catalyze Low-Temperature Water-Gas Shift Reactions. *Science* **329** (5999), 1633–1636 (2010).
4. Figueiredo, R. T., Santos, M. S., Andrade, H. M. C. & Fierro, J. L. G. Effect of Alkali Cations on the CuZnOAl₂O₃ Low Temperature Water Gas-Shift Catalyst. *Catal. Today* **172** (1), 166–170 (2011).
5. Si, R. et al. Structure Sensitivity of the Low-Temperature Water-Gas Shift Reaction on Cu–CeO₂ Catalysts. *Catal. Today* **180** (1), 68–80 (2012).
6. Yao, S. Y. et al. Morphological Effects of the Nanostructured Ceria Support on the Activity and Stability of CuO/CeO₂ Catalysts for the Water-Gas Shift Reaction. *Phys. Chem. Chem. Phys.* **16** (32), 17183–17195 (2014).
7. Chen, C. S., Lin, J. H., Lai, T. W. & Li, B. H. Active Sites on Cu/SiO₂ Prepared Using the Atomic Layer Epitaxy Technique for a Low-Temperature Water–Gas Shift Reaction. *J. Catal.* **263** (1), 155–166 (2009).
8. Liu, X. et al. Effect of Cu Loading on Cu/ZnO Water–Gas Shift Catalysts for Shut-Down/Start-up Operation. *Int. J. Hydrog. Energy* **37** (8), 6381–6388 (2012).
9. Price, C., Pastor-Pérez, L., le Saché, E., Sepúlveda-Escribano, A. & Reina, T. R. Highly Active Cu–ZnO Catalysts for the WGS Reaction at Medium–High Space Velocities: Effect of the Support Composition. *Int. J. Hydrog. Energy* **42** (16), 10747–10751 (2017).

10. Rodríguez, J. A. et al. High Water-Gas Shift Activity in TiO₂(110) Supported Cu and Au Nanoparticles: Role of the Oxide and Metal Particle Size. *J. Phys. Chem. C* **113** (17), 7364–7370 (2009).
11. Peng, S. F. & Ho, J. J. The Mechanism of the Water-Gas Shift Reaction on Cu/TiO₂(110) Elucidated from Application of Density-Functional Theory. *Phys. Chem. Chem. Phys.* **13** (45), 20393–20400 (2011).
12. Yan, H. et al. Construction of Stabilized Bulk-Nano Interfaces for Highly Promoted Inverse CeO₂/Cu Catalyst. *Nat Commun.* **10** (1), 3470 (2019).
13. Li, D. et al. Characterization and Catalytic Performance of Cu/ZnO/Al₂O₃ Water–Gas Shift Catalysts Derived from Cu–Zn–Al Layered Double Hydroxides. *Ind. Eng. Chem. Res.* **56** (12), 3175–3183 (2017).
14. Yan, H. et al. Promoted Cu-Fe₃O₄ Catalysts for Low-Temperature Water Gas Shift Reaction: Optimization of Cu Content. *Appl. Catal., B* **226**, 182–193 (2018).
15. Zhu, M. et al. Strong Metal-Support Interactions between Copper and Iron Oxide during the High-Temperature Water-Gas Shift Reaction. *Angew. Chem., Int. Ed.* **58** (27), 9083–9087 (2019).
16. Lu, J. et al. Unravelling the Nature of the Active Species as Well as the Doping Effect over Cu/Ce-Based Catalyst for Carbon Monoxide Preferential Oxidation. *ACS Catal.* **9** (3), 2177–2195 (2019).
17. Rodriguez, J. A. et al. Water-Gas Shift Reaction on a Highly Active Inverse CeO_x/Cu(111) Catalyst: Unique Role of Ceria Nanoparticles. *Angew. Chem., Int. Ed.* **48** (43), 8047–8050 (2009).
18. Zhang, J. et al. Wet-Chemistry Strong Metal-Support Interactions in Titania-Supported Au Catalysts. *J. Am. Chem. Soc.* **141** (7), 2975–2983 (2019).
19. Zhang, J. et al. Sinter-Resistant Metal Nanoparticle Catalysts Achieved by Immobilization within Zeolite Crystals Via Seed-Directed Growth. *Nat Catal.* **1** (7), 540–546 (2018).
20. Schumann, J. et al. Promoting Strong Metal Support Interaction: Doping ZnO for Enhanced Activity of Cu/ZnO:M (M = Al, Ga, Mg) Catalysts. *ACS Catal.* **5** (6), 3260–3270 (2015).
21. Chen, C. S. et al. Effect of Ti³⁺ on TiO₂-Supported Cu Catalysts Used for CO Oxidation. *Langmuir* **28** (26), 9996–10006 (2012).
22. Laffont, L. et al. High Resolution EELS of Cu-V Oxides: Application to Batteries Materials. *Micron* **37** (5), 459–464 (2006).

23. Tang, H. et al. Classical Strong Metal-Support Interactions between Gold Nanoparticles and Titanium Dioxide. *Sci. Adv.* **3** (10), No. e1700231 (2017).
24. Wang, W. W. et al. Highly Dispersed Copper Oxide Clusters as Active Species in Copper-Ceria Catalyst for Preferential Oxidation of Carbon Monoxide. *ACS Catal.* **5** (4), 2088–2099 (2015).
25. Ma, K. et al. Achieving Efficient and Robust Catalytic Reforming on Dual-Sites of Cu Species. *Chem. Sci.* **10** (9), 2578–2584 (2019).
26. Schwartz, V. et al. Structural Investigation of Au Catalysts on TiO₂-SiO₂ Supports: Nature of the Local Structure of Ti and Au Atoms by EXAFS and XANES. *J. Phys. Chem. C* **111** (46), 17322–17332 (2007).
27. Farges, F. O., Brown, G. E. & Rehr, J. J. Ti K-Edge Xanes Studies of Ti Coordination and Disorder in Oxide Compounds: Comparison between Theory and Experiment. *J. Phys. Rev. B* **56** (4), 1809–1819 (1997).
28. Angelomé, P. C. et al. Mesoporous Anatase TiO₂ Films: Use of Ti K XANES for the Quantification of the Nanocrystalline Character and Substrate Effects in the Photocatalysis Behavior. *J. Phys. Chem. C* **111** (29), 10886–10893 (2007).
29. Gao, Z., Liu, F., Wang, L. & Luo, F. Highly Efficient Transfer Hydrodeoxygenation of Vanillin over Sn⁴⁺-Induced Highly Dispersed Cu-Based Catalyst. *Appl. Surf. Sci.* **480** (30), 548–556 (2019).
30. Cui, G. et al. Low-Temperature Hydrogenation of Dimethyl Oxalate to Ethylene Glycol Via Ternary Synergistic Catalysis of Cu and Acid-Base Sites. *Appl. Catal., B* **248**, 394–404 (2019).
31. Yuan, L. et al. Dynamic Evolution of Atomically Dispersed Cu Species for CO₂ Photoreduction to Solar Fuels. *ACS Catal.* **9** (6), 4824–4833 (2019).
32. Hammer, B. & Norskov, J. K. Theoretical surface science and catalysis-calculations and concepts. *Adv. Catal.* **45**, 71–129 (2000).
33. Schott, V. et al. Chemical Activity of Thin Oxide Layers: Strong Interactions with the Support Yield a New Thin-Film Phase of ZnO. *Angew. Chem., Int. Ed.* **52** (45), 11925–11929 (2013).
34. Berkó, A., Balázs, N., Kassab, G. & Óvári, L. Segregation of K and Its Effects on the Growth, Decoration, and Adsorption Properties of Rh Nanoparticles on TiO₂(110). *J. Catal.* **289**, 179–189 (2012).
35. Xu, M. et al. TiO_{2-x}-Modified Ni Nanocatalyst with Tunable Metal-Support Interaction for Water-Gas Shift Reaction. *ACS Catal.* **7** (11), 7600–7609 (2017).

36. Liu, L., Zhao, C. & Li, Y. Spontaneous Dissociation of CO₂ to CO on Defective Surface of Cu(I)/TiO_{2-x} Nanoparticles at Room Temperature. *J. Phys. Chem. C* **116** (14), 7904–7912 (2012).
37. Ang, M. L. et al. High-Temperature Water-Gas Shift Reaction over Ni/xk/CeO₂ Catalysts: Suppression of Methanation Via Formation of Bridging Carbonyls. *J. Catal.* **329**, 130–143 (2015).
38. Ribeiro, M. C. et al. Low Temperature Water Gas Shift: Evaluation of Pt/HfO₂ and Correlation between Reaction Mechanism and Periodic Trends in Tetravalent (Ti, Zr, Hf, Ce, Th) Metal Oxides. *ACS Catal.* **1** (10), 1375–1383 (2011).
39. Vecchietti, J. et al. Understanding the Role of Oxygen Vacancies in the Water Gas Shift Reaction on Ceria-Supported Platinum Catalysts. *ACS Catal.* **4** (6), 2088–2096 (2014).
40. Jacobs, G. et al. Water-Gas Shift: Comparative Screening of Metal Promoters for Metal/Ceria Systems and Role of the Metal. *Appl. Catal., A* **258** (2), 203–214 (2004).
41. Zhu, M. & Wachs, I. E. Resolving the Reaction Mechanism for H₂ Formation from High-Temperature Water–Gas Shift by Chromium–Iron Oxide Catalysts. *ACS Catal.* **6** (5), 2827–2830 (2016).
42. Xu, M. et al. Insights into Interfacial Synergistic Catalysis over Ni@TiO_{2-x} Catalyst toward Water-Gas Shift Reaction. *J. Am. Chem. Soc.* **140** (36), 11241–11251 (2018).
43. Gokhale, A. A., Dumesic, J. A. & Mavrikakis, M. On the Mechanism of Low-Temperature Water Gas Shift Reaction on Copper. *J. Am. Chem. Soc.* **130** (4), 1402–1414 (2008).
44. Wang, Y. & Wang G. A Systematic Theoretical Study of Water Gas Shift Reaction on Cu(111) and Cu(110): Potassium Effect. *ACS Catal.* **9** (3), 2261–2274 (2019).
45. Sun, K., Kohyama, M., Tanaka, S. & Takeda, S. Reaction Mechanism of the Low-Temperature Water–Gas Shift Reaction on Au/TiO₂ Catalysts. *J. Phys. Chem. C* **121** (22), 12178–12187 (2017).
46. Luo, W., Chen, Y., Du, Z. & Chen, C. Theoretical Study on PdCu/CeO₂-Catalyzed Water–Gas Shift Reaction: Crucial Role of the Metal/Ceria Interface and O₂ Enhancement Effects. *J. Phys. Chem. C* **122** (50), 28868–28883(2018).

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Author contributions

M. X. and M.W. designed the experiments. J.Z. conducted the experiment and analyzed the results. P.Y. conducted density functional theory studies. L.Z., G.C., J.Y., and N.L. contributed to the X-ray absorption fine structure spectroscopy measurements and data analysis. S.H. contributed to the ac-HAADF-STEM. This paper was written by J.Z., P.Y., and X.M. All authors contributed to discussions. M.X. and M.W. conceived the research.

Competing interests

The authors declare no competing financial interests.

Additional information

Supplementary information The online version contains supplementary material available at <http://www.nature.com/reprints>.

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