Construction of stabilized bulk-nano interfaces for highly promoted inverse CeO$_2$/Cu catalyst

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As the water-gas shift (WGS) reaction serves as a crucial industrial process, strategies for developing robust WGS catalysts are highly desiderated. Here we report the construction of stabilized bulk-nano interfaces to fabricate highly efficient copper-ceria catalyst for the WGS reaction. With an in-situ structural transformation, small CeO$_2$ nanoparticles (2–3 nm) are stabilized on bulk Cu to form abundant CeO$_2$-Cu interfaces, which maintain well-dispersed under reaction conditions. This inverse CeO$_2$/Cu catalyst shows excellent WGS performances, of which the activity is 5 times higher than other reported Cu catalysts. Long-term stability is also very solid under harsh conditions. Mechanistic study illustrates that for the inverse CeO$_2$/Cu catalyst, superb capability of H$_2$O dissociation and CO oxidation facilitates WGS process via the combination of associative and redox mechanisms. This work paves a way to fabricate robust catalysts by combining the advantages of bulk and nano-sized catalysts. Catalysts with such inverse configurations show great potential in practical WGS applications.
Bulk catalysts with stable structure have been applied to many industrial procedures, such as fused Fe for ammonia synthesis and Cu-Zn-Al for water–gas shift (WGS) reaction. In recent years, the introduction of nanotechnology has brought valuable insights into heterogeneous catalysis. Remarkable catalytic performances in many reactions have been discovered for supported nanoparticles, clusters, and single atoms, of which defects and vacancies on the oxide supports are often considered as important anchoring sites. One major shortcoming of these supported catalysts is the vulnerability against sintering. The highly dispersed active sites tend to aggregate and deactivate under reaction conditions. Thus, combining the advantages of bulk and nano-sized catalysts is of great significance, though it seems tough, since the bulk structure contradicts the high dispersion.

WGS (CO + H2O = CO2 + H2) reaction is a crucial process in H2 production industry, to which Cu-based catalysts have been applied for decades. Cu–CeO2 has been considered as a promising alternative to Cu–Zn–Al catalyst, while it still suffers from low activity caused by Cu sintering. It has been known that the metal–oxide interface plays a critical role in catalyzing WGS reaction, of which the key is the adsorption and activation of reactants. To deeply understand the interface effect, catalysts with inverse configuration have been designed. Different to commonly supported catalysts, for which active metals are loaded onto the oxide supports, active metals serve as the support for oxides nanoparticles in inverse catalysts. Model inverse CeO2/Cu(111) has shown superior WGS activity to normal Cu/CeO2(111), owing to enhanced reducibility of CeO2. Meanwhile, the CeO2–Cu interface could be highly stable, since bulk Cu has grown well and CeO2 nanoparticles are anti-sintering under WGS conditions, which is very beneficial to the catalyst stability. Thus, prominent activity and stability promotion of Cu–CeO2 catalyst is expected by applying inverse configuration. However, the assumed high WGS activity has never been found on real CeO2/Cu catalyst, due to severe separation of bulk Cu and CeO2 nanoparticles. Therefore, strategies to fabricate inverse CeO2/Cu catalyst with sufficient bulk–nano interfaces are in great need.

Herein, we have constructed stabilized bulk–nano interfaces to fabricate inverse CeO2/Cu catalyst, through which the advantages of bulk and nano-sized catalysts are perfectly combined. With an in situ structural transformation, CeO2 nanoparticles (2–3 nm) are dispersed on bulk Cu, forming sufficient CeO2–Cu interfaces with great stability. Enrichment of stable bulk–nano interfaces results in great promotion of WGS activity and stability. The inverse CeO2/Cu catalyst achieves a remarkable WGS reaction rate of 47.3 μmol g−1 s−1 (300 °C), which is at least five times that of other Cu catalysts. Mechanistic study demonstrates the CeO2/Cu catalyst possesses superb capability of H2O dissociation and CO oxidation, which facilitates WGS reaction via the combination of associative and redox mechanism. Development of such inverse catalyst is very likely to make huge breakthrough in the exploration of other robust catalysts.

**Results**

**Catalytic performances of the inverse CeO2/Cu catalyst.** A series of catalysts with different Cu/Ce ratio was prepared via an aerosol-spray method. As shown in Supplementary Fig. b and c, the inverse CeO2/Cu catalyst with Cu/Ce ratio of 9:1 showed the highest and repeatable WGS activity. Increased or decreased proportion of Cu led to lower CO conversion (Supplementary Fig. 1b). The physical and chemical properties of the catalysts are listed in Supplementary Table 1. Fresh CeO2/Cu catalyst contained 61.5 wt% of Cu, and the Cu content elevated to 82.9 wt% after WGS reaction, due to the reduction of CuO to Cu. The 17.1 wt% CeO2 loading corresponded well to the finding of Rodriguez et al., illustrating the optimal CeO2 coverage on Cu surface was around 20%. For supported Cu2CeO2 catalyst, 10 wt% of Ce has often been applied to obtain an effective catalyst. Therefore, normal Cu/ CeO2 catalyst, with 10.7 wt% of Cu, was chosen for comparison.

In Table 1, the two fresh catalysts exhibited similar specific BET surface areas (S BET, 46–48 m² g−1). After catalysis, the S BET of CeO2/Cu catalyst (16.2 m² g−1) apparently decreased, while that of Ce/CuO2 catalyst (42.8 m² g−1) was well preserved. Cu surface area (S Cu) was also calculated for both catalysts (see Supplementary Methods for detail). The S Cu of CeO2/Cu (71.7 m² g−1) was also higher than that of CeO2/Cu (50.7 m² g−1). However, the inverse CeO2/Cu catalyst exhibited much higher WGS conversion than that of CeO2/Cu catalyst (Fig. 1a). Within the tested temperature range, the reaction rate (r) of CeO2/Cu catalyst measured under kinetics conditions was 4–5 times higher than that of Cu/CeO2 catalyst. Under the industrial WGS atmosphere, as illustrated in Fig. 1b, the activity of inverse CeO2/Cu catalyst was very close to that of commercial Cu/Zn–Al, approaching the equilibrium in harsh reaction conditions. To further demonstrate the promotion of WGS activity, r values at 300 °C for different catalysts were illustrated in Fig. 1c. Normal Cu/ CeO2 gave r of 10.2 μmol g−1 s−1, slightly higher than that of reported Cu–Ce(Al)Ox (9.0 μmol g−1 s−1). The similar r values here reflected the general WGS activity of supported Cu/ CeO2 catalysts. Meanwhile, the inverse CeO2/Cu gave a very high r value of 47.3 μmol g−1 s−1, which was five times that of normal Cu/ CeO2 catalyst. Compared to former inverse CeO2/Cu catalyst (9.8 μmol g−1 s−1), the r of inverse CeO2/Cu was also much higher. The activities of some efficient WGS catalysts are listed in Supplementary Table 2. The inverse CeO2/Cu catalyst exhibited the highest r among the Cu-based catalysts, and its activity was even close to supported Pt catalysts. Thus, we believe that the inverse CeO2/Cu catalyst with tremendous WGS activity has been successively developed. Arrhenius plots for the catalysts were constructed by using the ln of r (Supplementary Fig. 2). In the repeated experiments, the WGS on inverse CeO2/Cu catalyst gave an apparent energy (Ea) of ca. 37 kJ mol−1, which was a little lower than that (ca. 40 kJ mol−1) found on normal Cu/ CeO2.

For WGS catalysts, sintering is often considered as the main reason for deactivation. The well-dispersed active species may aggregate and deactivate rapidly under reaction conditions. Figure 1d present the results of time-on-stream stability tests. Normal Cu/ CeO2 gave very low r (3 μmol g−1 s−1), while the inverse CeO2/Cu exhibited surprisingly high stability. With the temperature of 250 °C and very high space velocity of 600,000 cm³ g−1 h−1, the WGS r of the inverse CeO2/Cu maintained at 17 μmol g−1 s−1, showing negligible decrease in the test up to 50 h. The long-term stability of commercial Cu/Zn–Al was measured as well. The initial r of Cu–Zn–Al was slightly higher than that of inverse CeO2/Cu. After 50 h test, the r dropped from 19.5 to 14.8 μmol g−1 s−1. Thus, the CeO2/Cu catalyst gave very solid performance in the time-on-stream test, which showed superior stability under very high space velocity (600,000 cm³ g−1 h−1).

**Construction of bulk–nano interfaces.** The catalytic performances were largely determined by the structure of the catalysts. CeO2 has been well known as suitable support for Cu catalysts, since the strong interaction between CuO and CeO2 could achieve homogeneous Cu dispersion. For the fresh CeO2/Cu catalyst, such interaction could be confirmed by temperature-programmed reduction by H2 (H2-TPR), with the fact that reducibility for CuO was enhanced after CeO2 addition.
Moreover, the strong CuO–CeO2 interaction was convinced by the X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 4a) and ultraviolet–visible spectroscopy (UV–vis) analysis (Supplementary Fig. 5a), showing peak shifting and broadening with increased CeO2 content. The strong CuO–CeO2 interaction enhanced the redox properties of the catalysts, and improved the dispersion of both Cu and CeO2.

Raman spectra of the catalysts depicted in Supplementary Fig. 5b exhibited a tiny peak of Raman mode \( A_g \), which belonged to cupric oxide. Thus, it seemed difficult to tell whether CeO2 was doped into CuO lattice.

The structural and chemical information of inverse CeO2/Cu catalyst is given in Fig. 2. The transmission electron microscopy (TEM) image (Fig. 2a) of fresh inverse CeO2/Cu catalysts present morphology of microspheres with diameters ranging from 200 to 500 nm. These microspheres were stacked of CuO and CeO2 nanoparticles. After WGS reaction, the microspheres became condensed and formed bulk particles (Fig. 2b). Catalysts with other Cu–Ce ratios exhibited similar size and morphology (Supplementary Fig. 6). Powder X-ray diffraction (XRD) results (Supplementary Fig. 7) showed that monoclinic CuO and fluorite CeO2 served as dominate phase for the fresh catalyst. In Fig. 2c, the XRD pattern of Cu/CeO2 had no observable change after WGS test, indicating the Cu-species remained well-dispersed. This observation correlated well with the stable nature of Cu/CeO2 (Fig. 1d). For inverse CeO2/Cu

### Table 1 Physicochemical properties of fresh and used catalysts

| Catalyst          | Cu (wt%\( \text{a} \)) | \( d_{\text{CuO}_2} \) (nm)\( \text{b} \) | \( d_{\text{Cu}} \) (nm)\( \text{b} \) | \( S_{\text{REy}} \) (m\(^2\) g\(^{-1}\)) | \( S_{\text{Cu}} \) (m\(^2\) g\(^{-1}\)) | TOF (s\(^{-1}\))\( \text{c} \) | Interface sites\( \text{d} \) |
|------------------|----------------------|---------------------------|---------------------------|-----------------|-----------------|-----------------|-----------------|
| CeO\(_2\)/Cu     | 61.5\( \text{d} \)   | 82.9\( \text{e} \)        | 2.6\( \text{d} \)        | 2.7\( \text{e} \) | 8.0\( \text{d} \) | 101.2\( \text{e} \) | 47.2\( \text{d} \) | 16.2\( \text{e} \) | 50.7            | 0.058           | 4.9 \( \times 10^2 \) |
| Cu/CeO\(_2\)     | 10.7                 | 13.4                      | 3.6                       | 4.7             | —               | —               | 46.2            | 42.8            | 71.7            | 0.056           | 1.1 \( \times 10^2 \) |

\( \text{a} \)Weight ratio of fresh catalysts determined by EDS

\( \text{b} \)CuO for fresh samples. Cu for used samples. Determined by the XRD patterns and Scherrer formula

\( \text{c} \)See detailed calculation process in Supplementary Methods

\( \text{d} \)Data acquired from fresh catalysts

\( \text{e} \)Data acquired from used catalysts

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**Fig. 1** Catalytic performances of the inverse CeO\(_2\)/Cu catalyst. **a** Water–gas shift (WGS) activities of the inverse CeO\(_2\)/Cu and normal Cu/CeO\(_2\) catalysts. **b** WGS activities of the inverse CeO\(_2\)/Cu catalyst and commercial Cu–Zn–Al under industrial atmosphere. **c** Comparison of WGS reaction rates for different catalysts at 300 °C. **d** Time-on-stream tests of the inverse CeO\(_2\)/Cu, normal Cu/CeO\(_2\) catalysts, and commercial Cu–Zn–Al.
catalyst, sharp metallic Cu peaks emerged after WGS test, and the crystalline size of Cu reached 101.2 nm (Table 1). The XRD results were consistent with the trend of dispersity for Cu (Supplementary Table 1), though CeO2 has been found to participate in N2O chemisorption, causing higher measured dispersion44. The XRD data demonstrated that the CeO2/Cu catalyst underwent severe sintering and bulk Cu was formed during WGS reaction. However, even though formation of bulk Cu was observed, the WGS activity and long-term stability of inverse CeO2/Cu were surprisingly excellent (Fig. 1). This finding was contrary to former knowledge that WGS was favored with smaller Cu-species38,45. The unusual phenomenon could be well explained by the fact that WGS reaction occurred at CeO2–Cu interfaces of inverse CeO2/Cu. As the bulk Cu was present, sufficient interfaces could be created if CeO2 was well dispersed. Small CeO2 nanoparticles supported on CuO were confirmed by high-resolution TEM (HR-TEM) images in Fig. 2e and Supplementary Fig. 8. After WGS reaction, small-sized CeO2 (2–3 nm) was still well-dispersed on bulk Cu (Fig. 2f and Supplementary Fig. 8). The element mapping results (Fig. 2g) further demonstrated the high dispersion of CeO2, with Ce signal appearing uniformly on the surface of used CeO2/Cu catalyst. XPS profiles of Ce 3d were recorded in Fig. 2d. For both inverse and normal catalysts, Ce4+ present as the dominating chemical state before and after WGS reaction. The other prepared Cu–CeO2 catalysts also exhibited only Ce4+ (Supplementary Fig. 4b). Combining with the fact that no shift for the CeO2 XRD peaks were observed (Fig. 2c), we believed that the CeO2 nanoparticles were supported on CuO, rather than incorporated into the CuO lattice. Therefore, enriched CeO2–Cu interfaces were present in the inverse CeO2/Cu catalyst.

The structural evolution of the inverse catalyst is depicted in Fig. 2h. With the strong interaction, CeO2 nanoparticles were well dispersed in CuO matrix of the fresh sample. After H2 reduction, CuO was reduced and sintered to form bulk Cu. Meanwhile, the CeO2 nanoparticles showed outstanding stability, holding high dispersion under WGS conditions. The aerosol-spray method enabled the inverse CeO2/Cu catalyst to give homogeneous Cu–CeO2 dispersion, which induced an in situ structural transformation, resulting in CeO2 nanoparticles (2–3 nm) stabilized on bulk Cu. The construction of bulk–nano interfaces brought stable structure of bulk materials and high dispersion of nano-sized catalysts. Tremendous promotion in WGS activity was thus achieved via creation of such bulk–nano interfaces, which was no longer at the risk of sintering deactivation.

**Simulation of sintering via in situ XRD.** In order to better simulate the sintering phenomenon during catalysis, in situ XRD measurements under 5% H2/Ar were performed towards the inverse and normal catalysts. As shown in Fig. 3a, the peaks for metallic Cu of inverse CeO2/Cu catalyst emerged at 150 °C and sharpened, indicating rapid sintering of Cu. Amplified Cu region in Fig. 3d illustrates that bulk Cu formed below 200 °C. For normal Cu/CeO2 catalyst (Fig. 3b), no obvious Cu peaks could be observed. Amplified Cu region in Fig. 3e displayed a tiny Cu peak centered at 43°. The Cu peak was absent for used Cu/CeO2

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**Fig. 2** Structure evolution of inverse CeO2/Cu catalyst during WGS reaction. a, b Transmission electron microscope (TEM) images of a fresh and b used inverse CeO2/Cu catalysts. e X-ray diffraction (XRD) patterns of the fresh and used catalysts. d Ce 3d X-ray photoelectron spectroscopy (XPS) results of the fresh and used catalysts. e, f High-resolution TEM (HR-TEM) images of fresh e and used f inverse CeO2/Cu catalyst, red circles reflect to CeO2, blue circles reflect to CuO. g Scanning transmission electron microscope (STEM) image and element mapping results of used inverse CeO2/Cu catalyst, the inset bar: 200 nm. h Scheme of structural evolution for inverse CeO2/Cu catalyst during WGS reaction, CeO2 nanoparticles are well stabilized despite Cu sintering.
catalyst (Fig. 2c), which might due to the re-oxidation and dispersion of Cu under ex situ mode. Besides, the structural evolutions of CeO$_2$ under reduction are given in Fig. 3c, e. The broad peaks suggested that CeO$_2$ nanoparticles in inverse CeO$_2$/Cu were maintained at very small size (2.1–2.9 nm, Supplementary Fig. 9), which was in accordance to the XRD data of used inverse catalyst (2.6–2.7 nm, Table 1). Figure 3e shows that the CeO$_2$ size of normal Cu/CeO$_2$ grew under H$_2$ reduction (2.8–5.3 nm, Supplementary Fig. 9). Thus, compared to depositing Cu nanoparticles on CeO$_2$ support, the dispersion of CeO$_2$ on bulk Cu created more stable CeO$_2$–Cu interfaces. This enrichment of stable interfaces for inverse CeO$_2$/Cu catalyst resulted in tremendous promotion of WGS activity, corresponding well to former report, in which Cu–CeO$_2$ interface was suggested to have great importance in WGS model catalyst$_{18}$.  

**WGS mechanism study.** For WGS reaction, two catalytic mechanisms have been proposed, namely, redox mechanism and associative mechanism$_{46–48}$. In the redox mechanism, CO reacts with surface oxygen of supports after adsorption, forming CO$_2$ and oxygen vacancy. H$_2$O dissociates at the vacancy and produces H$_2$. In the associative mechanism, CO and H$_2$O adsorb on the catalyst to form an intermediate, which decomposes to yield CO$_2$ and H$_2$. It has been proved that with associative mechanism, surface hydroxyl serves as the active species in Au/CeO$_2$ system$_{49,50}$. In this case, two CO molecules react with two surface hydroxyl groups to form 2 CO$_2$ molecules and 1 H$_2$ molecule:

$$2\text{CO} + 2\text{OH} = 2\text{CO}_2 + \text{H}_2$$

The amount of produced CO$_2$ is supposed to be double of that of H$_2$ in the outlet gas. Temperature-programmed surface reaction (TPSR) were carried out to check the reaction pathway. As shown in Fig. 4b, CO purging gave the ratio of generated CO$_2$ and H$_2$ as 2:1, corresponding very well to the above reaction. After H$_2$O was introduced, no H$_2$ signal was detected on Cu/CeO$_2$, proving the pure associative mechanism for the normal Cu/CeO$_2$ catalyst. However, for the inverse CeO$_2$/Cu catalyst (Fig. 4a), the ratio of generated CO$_2$ and H$_2$ was 3:1 after CO

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**Fig. 3** Simulation of sintering via in situ XRD. a In situ XRD patterns under 5% H$_2$–Ar for inverse CeO$_2$/Cu catalyst. b In situ XRD patterns under 5% H$_2$–Ar for normal Cu/CeO$_2$ catalyst. c Amplified CeO$_2$ region of in situ XRD patterns for inverse CeO$_2$/Cu catalyst. d Amplified Cu region of in situ XRD patterns for inverse CeO$_2$/Cu catalyst. e Amplified CeO$_2$ region of in situ XRD patterns for normal Cu/CeO$_2$ catalyst. f Amplified Cu region of in situ XRD patterns for normal Cu/CeO$_2$ catalyst.
introduction. This meant that besides the surface hydroxyls, active oxygen atoms created by the dissociation of H2O were also involved in the reaction. When H2O was injected, H2 formation could be observed immediately. These observations matched the features of redox mechanism, assuming that H2O dissociated on CeO2 oxygen vacancy to generate H2 and active surface oxygen atoms. After H2O injection, we removed the surface oxygen with H2 reduction and preserved the surface hydroxyls50, after which CO was purged into the system to conduct the TPSR test again. The subsequent CO treatment gave a CO2:H2 ratio of 2:1, showing the typical results of associative mechanism. The TPSR experiment was cycled three times in a row, and it gave very repeatable results for both catalysts. Thus, it turned out that both the redox and associative mechanism were present in the WGS reaction catalyzed by the inverse CeO2/Cu catalyst.

It has been generally believed that the redox mechanism occurs on metals46,47 and the associative mechanism dominates at the metal/oxide interface50,51. However, redox pathway has now been found on inverse CeO2/Cu catalyst. The improved redox properties of CeO2 nanoparticles on inverse CeO2/Cu played an important
role. Temperature-programmed desorption of CO (CO-TPD) was applied to detect the CO sorption on the inverse catalyst. As illustrated in Fig. 4c, after CO pre-adsorption, CO₂ was the only desorption species on CeO₂/Cu, showing easy transformation from CO to CO₂. For better study over CO adsorption, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was introduced. As shown in Fig. 4d, the in situ DRIFTS of the inverse CeO₂/Cu catalyst under WGS conditions exhibited CO₂ signal (2334, 2364 cm⁻¹) at the beginning, which indicated the ongoing of WGS reaction. Meanwhile, no signal of CO was detected during the measurement, while normal Cu/CeO₂ gave CO–Cu³⁺ adsorption (2094 cm⁻¹) (Supplementary Fig. 10b). Pure Cu showed no adsorption behavior under both WGS and CO modes, suggesting CO adsorption on bulk Cu was not favored (Supplementary Fig. 10c and d). Besides, the results of in situ DRIFTS for CO adsorption on the CeO₂/Cu also only present CO₂ signal, which showed that active surface species of the catalyst was reduced by CO (Supplementary Fig. 10a). Besides, we measured the reaction orders of CO and H₂O for different catalysts. As shown in Supplementary Fig. 11, the H₂O reaction order increased when CeO₂ content was elevated, giving the catalyst stronger capability to consume H₂O. The CO reaction order on inverse CeO₂/Cu was 0.75, which suggested CO was comparatively insufficient during WGS reaction. All the above data demonstrated the easy transformation from CO to CO₂ on inverse CeO₂/Cu, reflecting unique redox properties of the CeO₂ nanoparticles. The surface oxygen of inverse CeO₂/Cu was proved to be flexible under CO, which facilitated the formation of defect sites.

Role of the surface defects in the catalysts. The formation of defect sites on inverse CeO₂/Cu were evidenced by in situ Raman measurements, since ex situ Raman and XPS results did not show pronounced Ce³⁺ signals. As shown in Fig. 5a, the Raman spectra of the inverse CeO₂/Cu after H₂ activation gave a hump at 600 cm⁻¹, which was ascribed to the intrinsic defects. When CO was filled in, surface oxygen was removed, forming two characteristic peaks located at 546 and 456 cm⁻¹, respectively. The peak centered at 546 cm⁻¹ (D peak) resulted from defects where Ce⁴⁺ was replaced by Ce³⁺, and the peak centered at 456 cm⁻¹ was typical vibration mode (F₂g) of fluorite-type structure. It is surprising that the Raman signals of the inverse CeO₂/Cu showed that the defect D peak was even more pronounced than F₂g peak. When H₂O was introduced, the intensity of the D peaks decreased apparently, which meant the Ce³⁺ defects were filled. The second cycle gave the same results. The introduction of CO induced the creation of surface defects through the reaction:

\[
\text{CO} + \text{O} \rightarrow \text{CO}_2 \\
\text{CO} + \text{OH} \rightarrow \text{CO}_2 + 1/2\text{H}_2
\]

For the normal Cu/CeO₂ catalyst (Fig. 5b), the intensity of Ce³⁺ D peaks was clearly weakened. The generation and elimination of defects with the CO/H₂O switch was also sluggish. In situ Raman under WGS conditions (Fig. 5c) showed consistent results. The inverse CeO₂/Cu also gave more pronounced signal of surface defects under the WGS conditions, with D/F₂g integral ratio of 1.8. These results were totally different from those of pure CeO₂ sample (Supplementary Fig. 12), which gave very strong F₂g peak and nearly no defect peak. The in situ Raman results have confirmed the enrichment of Ce³⁺ defect sites in inverse CeO₂/Cu under WGS conditions, which further proved the enhanced redox properties of CeO₂ on inverse CeO₂/Cu. For both catalysts, metallic Cu was the only phase detected under the WGS conditions. Supplementary Fig. 13 displayed the TPSR results of inverse CeO₂/Cu and normal Cu/CeO₂ catalysts. The WGS reaction began to occur at ~100°C. After TPSR, the following H₂-TPR measurement gave no H₂ reduction peaks, which suggested Cu remained in fully metallic state during the WGS reaction. This finding was in accordance with the former work reported by Barrio et al. However, considering the very high WGS activity of the inverse CeO₂/Cu catalyst, the active site was more likely to locate at Cu–CeO₂ interfaces rather than metallic Cu.

Discussion

The mixed oxides of Cu–Zn–Al have been applied as industrial WGS catalysts for decades. Though lots of efforts have been made, few reports have found Cu-based catalysts as effective as Cu–Zn–Al, especially under industrial atmosphere. Herein, the inverse CeO₂/Cu catalyst showed greatly promoted WGS activity, which was five times higher than that of normal Cu/CeO₂ catalyst. The WGS conversion of the inverse CeO₂/Cu was very close to that of commercial Cu–Zn–Al under industrial WGS atmosphere, approaching the equilibrium maximum. The high WGS activity for the inverse CeO₂/Cu catalyst originated from its unique structure, where bulk–nano interfaces were constructed. When Cu was loaded on CeO₂, sintering was inevitable as the aggregation of Cu species lowered the surface energy. The dynamic elimination of Cu–CeO₂ interfaces caused rapid deactivation. Thus, for normal Cu/CeO₂ catalyst, though Cu–CeO₂ interfaces were created, the elimination due to structural change would take place even in H₂ pre-treatment. This deactivation resulted in very low WGS r activity and stability tests (Fig. 1a, d). Considering its high Cu dispersion, the turnover frequency (TOF) of normal Cu/CeO₂ was calculated for single site on Cu–CeO₂ interface (see detail in Supplementary Methods). The derived TOF was 0.056 s⁻¹, as shown in Table 1. Meanwhile, for inverse CeO₂/Cu catalyst, bulk Cu formed steady structure under WGS conditions. Small CeO₂ nanoparticles were dispersed on bulk Cu and were also very stable against sintering. The maximized and stabilized bulk–nano interfaces in the inverse CeO₂/Cu catalyst gave significant WGS promotion. The high WGS activity resulted from the structural nature of the inverse CeO₂/Cu catalyst, which lied in creation and preservation of stabilized bulk–nano interfaces. A theoretical model has been built to calculate TOF for the inverse CeO₂/Cu. A 3 nm CeO₂ nanoparticle with 231 Ce atoms was loaded on metallic Cu. As shown in Supplementary Fig. 14, 16 Ce atoms were located at the periphery of Cu–CeO₂ interface. Based on this model, the TOF of the inverse CeO₂/Cu catalyst for single site on CeO₂–Cu interface was 0.058 s⁻¹ (see detail in Supplementary Methods). The similar TOF of both catalysts proved that the Cu–CeO₂ and CeO₂–Cu interfaces possessed the same intrinsic activities. As shown in Table 1, the amount of interface sites for inverse CeO₂/Cu was four times higher than that for normal Cu/CeO₂. The highly promoted WGS activity of inverse CeO₂/Cu originated from the enrichment of interface sites. Besides, owing to the strong Cu–CeO₂ interaction, the redox properties of inverse CeO₂/Cu catalyst were improved. The surface oxygen of inverse CeO₂/Cu catalyst was proved to be flexible under CO, leading to the formation of defects. H₂O dissociated at the defects, promoting the WGS activity via a combination of both the associative mechanism and redox mechanism. The discussion of reactivity and mechanism was concluded in Fig. 6.

The pursuing of highly active and stable catalysts would never be out of date. A strategy to fabricate robust WGS catalyst was proposed, where the key was the construction of bulk–nano interfaces. By using aerosol-spray method, we developed the CeO₂/Cu catalysts with inverse configuration. Small CeO₂
Fig. 5 Examination of defect sites in the catalysts. a In situ Raman spectra of the inverse CeO$_2$/Cu with CO/H$_2$O switch under 200 °C. b In situ Raman spectra of the normal Cu/CeO$_2$ with CO/H$_2$O switch under 200 °C. c In situ Raman under the WGS conditions for both catalysts, the inset figure gave $D/F_{2g}$ integral ratio at different temperatures.

Transmission electron microscope (TEM). All images of TEM were taken on a JEOL JEM-2100F microscope, of which the acceleration voltage was 200 kV. The images of HR-TEM were obtained using a Philips Tecnai F20 instrument with the acceleration voltage of 200 kV. The element mapping results and EDS analysis were acquired from the same machine under STEM mode.

X-ray diffraction (XRD). For the XRD data, all experiments were performed on a PANalytical B.V. X’pert3 powder diffractometer with CuK$_{\alpha}$ radiation ($\lambda = 0.15418$ nm). Accelerating voltage and current of 40 kV and 40 mA were applied for ex situ and in situ modes. Ex situ XRD patterns were obtained by using a PIXCell detector in the 20 range of 20-80°. For the in situ XRD experiments, an Anton Paar XRR900 in situ chamber was applied. The XRD data were measured from 50 to 400 °C in 5% H$_2$/Ar mixture (3 cm$^3$ min$^{-1}$).

X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed on an Axis Ultra XPS spectrometer from Kratos, Japan. The operation was under 225 W of accelerating voltage and Al K$_\alpha$ radiation. A C 1s line located at 284.8 eV was used to calibrate each spectra for accurate binding energies.

Raman spectroscopy. Ex situ and in situ Raman spectra were obtained by excitation of the catalysts at 633 nm laser, using a LabRAM HR800 Raman spectrometer (Horiba Jobin Yvon) with the range from 200 to 800 cm$^{-1}$ in a spectral resolution of 2 cm$^{-1}$.

Temperature-programmed surface reaction (TPSR). An online mass spectrometer (Ametek LC-D200M) was used to analyze the outlet gases for TPSR, as well as CO-TPD. 100 mg of each sample were treated with 5% H$_2$/Ar (30 cm$^3$ min$^{-1}$) for 30 min at 300 °C before test. The sample was then flushed under pure He for 1 h. For CO-TPD, the samples were purged with 5% CO/Ar (30 cm$^3$ min$^{-1}$) for 0.5 h, and then flushed under pure He for another 1 h at room temperature. Afterwards, the samples were heated from room temperature to 500 °C under He flow. For TPSR, the catalysts were heated from 120 to 400 °C under 2%H$_2$O, 2% CO/Ar gas flow (30 cm$^3$ min$^{-1}$). For the examination of reaction mechanisms, the samples went through WGS reaction for 1 h at 200 °C after H$_2$ reduction. The catalysts were then purged by Ar at 200 °C, followed by the switch of 2%CO/Ar, pure Ar, 2%H$_2$O/Ar, pure Ar, 5%H$_2$/Ar, pure Ar, and 2%CO/Ar to collect the mass spectrometer signal. The heating rate for all tests was set as 10 °C min$^{-1}$.

Catalytic tests and kinetics measurement. A fixed-bed reactor with diameter of 1 cm was used for the WGS reaction tests. In order to give accurate results, a thermocouple connected with a PID temperature controller was mounted on top of the catalyst bed. The catalyst powder (100 mg) was loaded and reduced with 5% H$_2$/Ar mixture for 0.5 h at 300 °C. The reaction gas contained 2% CO and 10% H$_2$O, balanced with N$_2$. The total gas hourly space velocity (GHSV) was 42,000 cm$^3$ g$^{-1}$ h$^{-1}$. In order to prevent water condensation, all pipes of the reactor were bound with heating belts. The activity results of catalysts were measured from 150 to 400 °C at 50 °C per step. Each catalyst was tested repeatedly to rule out the uncertainty. A Gasboard 3500 IR spectroscopy (WuhanSifang Company, China) was used to analyze all the outlet gases online. For the stability tests, the CO conversion data of the catalysts were continuously recorded under 250 °C for 50 h. The mass of the catalysts and the flow rate of reaction gas were tuned to keep the CO conversion under 15%. The WGS activity was measured by means of CO conversion, which was defined as the following formula:

$$X_{\text{CO}}(\%) = \left( \frac{n_{\text{CO}}^\text{in} - n_{\text{CO}}^\text{out}}{n_{\text{CO}}^\text{in}} \right) \times 100\%$$  (1)

Methods

**Catalyst preparation.** In a typical synthesis of Cu$_x$Ce$_{1-x}$O$_2$, 4 mmol of metal nitrates (99%, Tianjin Kermal Factory) were added to 60 ml of absolute ethanol (99%, Tianjin Fuyi Fine Chemical Reagent Factory). This mixture was stirred for 10 min and then put into a ultrasonic humidi fi er at 30 W, 1.5 MHz). Industrial N$_2$ served as the carrier gas to bring the spray generated through sonication into the tube furnace (pre-heated to 400 °C). The mist drop evaporated and the precursor underwent decomposition and self-assembly. The metal oxides products were spherical nanoparticles, which were collected on a piece of filter paper and dried overnight at 60 °C. Then, the obtained powder was calcined in air for 4 h ($1 \text{ °C min}^{-1}$ of ramping rate). The obtained catalysts were nominated as Cu$_x$Ce$_{1-x}$O$_2$, of which $x$ and $b$ referred to the molar ratio of corresponding element, respectively. Commercial Cu–Zn–Al catalyst (37 wt% CuO, 52 wt% ZnO, 11 wt% Al$_2$O$_3$, determined by EDS) was bought from Sichuan Shunli Chemical Engineering Company.

nanoparticles (2–3 nm) were stabilized on bulk Cu, forming stable CeO$_2$–Cu interfaces under reaction conditions. The enrichment and preservation of such interfaces resulted in significant promotion in activity. The inverse CeO$_2$/Cu catalyst exhibited great WGS activity, which was at least five times higher than other reported Cu catalysts. The improved redox properties of the inverse CeO$_2$/Cu catalyst facilitated the H$_2$O dissociation and CO oxidation, boosting WGS activity via the combination of associative and redox mechanism. Catalyst with sufficient bulk–nano interfaces has now been proved to give excellent WGS performances under realistic conditions, and show great potential in practical applications and other catalytic systems.
For the kinetic tests, 20 mg of catalysts were pre-reduced with 5% H2/Ar mixture. The apparent activation energy (Ea) of each catalyst for WGS reaction was obtained by keeping 10% equal CO conversion with the regulation of reaction temperature, catalysts mass, and stream flow rate. The calculation of reaction rate (r) for WGS followed the equation:

\[ r = \frac{F \times CO_{\text{conv}}}{W} \]  

where \( F \) is the total flow rate of the reaction stream (mol s\(^{-1}\)), \( r \) is the WGS reaction rate by means of CO (mol g\(^{-1}\) s\(^{-1}\)), \( CO_{\text{conv}} \) is the concentration of converted CO on the IR spectroscopy and \( W \) is the mass of the catalyst (g). The reaction orders of CO and H\(_2\)O for the catalysts were measured under 250°C. The WGS activity was recorded while the concentration of CO or H\(_2\)O in the reaction gas was varied on purpose.

**Data availability**

The main data supporting the findings of this study are available within the article and its Supplementary information. Extra data are available from the corresponding author upon request.

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Author contributions

C.-J.J. supervised the work; H.Y., Z.J. and C.-J.J. had the idea for and designed the experiments, analyzed the results, and wrote the manuscript; H.Y., C.Y. and W.-P.S. performed the catalyst preparation and catalytic tests; H.Y. and L.-H.C. performed the TPSR, TPD, and kinetic experiments; H.Y. and W.-W.W. performed the ex situ and in situ XRD, Raman, and DRIFTS measurements.

Additional information

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