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Review

Electronic and geometric structure of the copper-ceria interface on Cu/CeO₂ catalysts

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ABSTRACT

The atomic structure of the active sites in Cu/CeO₂ catalysts is intimately associated with the copper-ceria interaction. Both the shape of ceria and the loading of copper affect the chemical bonding of copper species on ceria surfaces and the electronic and geometric character of the relevant interfaces. Nanostructured ceria, including particles (polyhedra), rods, and cubes, provides anchoring sites for the copper species. The atomic arrangements and chemical properties of the (111), (110) and (100) facets, preferentially exposed depending on the shape of ceria, govern the copper-ceria interactions and in turn determine their catalytic properties. Also, the metal loading significantly influences the dispersion of copper species on ceria with a specific shape, forming copper layers, clusters, and nanoparticles. Lower copper contents result in copper monolayers and/or bilayers while higher copper loadings lead to multi-layered clusters and faceted particles. The active sites are usually generated via interactions between the copper atoms in the metal species and the oxygen vacancies on ceria, which is closely linked to the number and density of surface oxygen vacancies dominated by the shape of ceria.

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1. Introduction

Copper species, dispersed on ceria, constitute a new catalyst system for several chemical reactions that are closely related to energy and environmental applications. In the oxidized form (CuO/CeO₂), it catalyzes CO oxidation [1–7], N₂O decomposition [8–10], NO reduction by CO [11–13], and preferential oxidation of CO in excess H₂ [14–18], showing comparable and even superior performance to noble metal catalysts. In the reduced form (Cu/CeO₂), it efficiently catalyzes reactions in syn-gas chemistry such as the low-temperature water-gas-shift [19–21], CO/CO₂ hydrogenation to methanol [22–24], and methanol steam reforming [25–27]. For these applications, the copper-ceria interaction is generally viewed to be responsible for the activity, selectivity, and stability. Experimental studies

on both model CeO₂/Cu systems (CeO₂ inlands on large, crystalline copper) [28–31] and real Cu/CeO₂ catalysts (Cu species deposited on ceria) [32,33], using mainly spectroscopic techniques [34,35] and theoretical calculations on the interfacial bonding patterns of copper on ceria [36–38], have concluded that the copper-ceria interface, where the reaction occurs, plays a vital role in determining the catalytic performance.

The shape of ceria is of great importance for dispersing and stabilizing CuO and/or Cu species as well as forming the copper-ceria interfaces, governing the chemical nature of the interfacial structure [5,6,11,18,33,39]. Ceria is expected to exhibit unique catalytic activities largely due to its specific electronic properties, i.e. the highly localized 4f orbitals. When an electron is localized on Ce-4f state, a Ce³⁺ ion forms. The formation of oxygen-defect is generally accompanied by localization of the

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electrons left behind in Ce 4f state. For forming one oxygen vacancy in ceria, two electrons localize on two cerium ions, generating two Ce³⁺ ions with a Ce 4f¹ configuration [40]. Usually, the formation of Ce³⁺ ion is relatively easier on ceria surface than in the bulk, and the formation energy of oxygen vacancy is facet-dependent, following the order of (110) < (100) < (111) [41]. Therefore, the chemical nature of shape effect for ceria is linked to the variations in the number and density of surface defects and/or oxygen vacancies on different facets of ceria. This would affect the electronic and geometric interaction between copper species and ceria, and consequently the structure of the active sites at their interfaces [21,31]. The copper-ceria interaction proceeds via a synergistic effect; ceria stabilizes the reactive copper species while the migration of copper cations into ceria lattice promotes the redox behavior of ceria, involving electronic perturbations between copper and ceria, interplay between Cu²⁺/Cu⁺/Cu⁰ and Ce³⁺/Ce⁴⁺ redox couples, and formation and mobility of oxygen vacancies.

By far, the structure-activity relationship on the Cu/CeO₂ system is still under strong debate, primarily because of the difficulties in unambiguously identifying and quantitatively describing the atomic structure of copper-ceria interface. First, the copper-ceria system may present in two forms in catalysis, CuO/CeO₂ and Cu/CeO₂; their interconversion requires oxygen and hydrogen treatments at elevated temperatures, which is accompanied with the redox cycles of Cu²⁺/Cu⁺/Cu⁰ and Ce⁴⁺/Ce³⁺. Second, the co-existence of several types of copper species, with respect to size and chemical state, results in diverse interfacial structures with weakly or strongly interacting manners. Third, the lack of in situ microscopic and spectroscopic techniques that are sensitive to probe both surface and bulk copper species under or close to reaction conditions. In this review article, we summarized the dispersion of copper species on ceria with variable shapes, the construction of copper-ceria interfaces, the structural characters and redox properties, fundamentally involving copper-ceria interactions. We further discussed the catalytic role of the copper-ceria interfaces with respect to the electronic and geometric structure over ceria in the forms of particles, rods and cubes.

2. Copper dispersion on ceria

Cu/CeO₂ catalysts are usually prepared by aqueous-phase impregnation, co-precipitation and deposition-precipitation, and they often present as the as-calcined form (CuO/CeO₂). In most cases, the CuO/CeO₂ precursor is further reduced by hydrogen at elevated temperatures (usually 200–400 °C) into the Cu/CeO₂ catalyst, prior to the chemical reactions. Therefore, microscopic and spectroscopic characterizations and chemical titrations involve the two forms (CuO/CeO₂ and Cu/CeO₂) for revealing the copper-ceria interaction mechanism and identifying the active sites, mostly located at the copper-ceria interfaces. Since the activity of the Cu/CeO₂ catalysts could be promoted by maximizing the length of the copper-ceria interfacial perimeter, shrinking the size of the copper particles as much as possible and exposing more O_v site on ceria by tuning its size/shape, both for enhancing the copper-ceria contact area

and chemical bonding strength, have been popularly adapted to enhance the catalytic efficiency [42–44].

The structure of copper-ceria interfaces largely depends on the shape of ceria. Traditionally, increasing the surface area of ceria, i.e. decreasing the size of ceria particles, was the priority strategy to achieve a higher dispersion of copper species. Recently, mediating the shape of ceria, enabling a preferential exposure of the reactive facets, is employed to promote copper dispersion on ceria [32,45]. The shape of ceria includes mainly spherical nanoparticles or nanopolyhedra, nanorods and nanocubes [46–49]. Generally, the surface area of ceria nanorods, nanoparticles and nanocubes is around 100, 120, and 30 m²/g, respectively. From a crystalline point of view, the shape of ceria determines the population of the (100), (110) and (111) facets. CeO₂ nanorods preferentially expose the {100} and {110} facets [50] or {100} and {111} facets [51,52]. Ceria nanocubes dominantly expose the {100} facets while the nanoparticles exposing both the {111} and {100} facets [50]. The reactivity of these facets follows an order (100) > (110) > (111) while the formation energies of oxygen vacancies decreases as {110} < {100} < {111} [41,53,54].

Copper species may appear at both the surface and the bulk of ceria, depending on the shape of ceria and the loading of copper [55]. The dispersion of copper species on ceria is characterized by microscopic and spectroscopic techniques and predicted by theoretical calculations. It was early proposed that oxygen vacancies facilitated the incorporation of Cu²⁺ into ceria lattice [56], while the theoretical value of Cu²⁺ on CeO₂ was 1.22 × 10⁻² mmol/m² according to an incorporation monolayer dispersion model which considers that all the cation vacancies on the CeO₂ {111} plane are occupied by Cu²⁺ [57]. The site geometry and coordination environment of the dispersed copper oxide depend on the exposed facets of ceria, which are in a five-coordinated structure on the {111} and {110} facets while in a symmetrical eight-coordination environment on the {100} plane (Fig. 1) [11]. This means that the surface property of ce-

Fig. 1. Coordinating environments of copper oxides on the (111), (110), and (100) planes of ceria. Re-printed with permission from Ref. [11]. Copyright 2011, WILEY VCH Verlag GmbH & Co. KGaA, Weinheim.

ria, especially the number and density of oxygen vacancies that are commonly viewed as the sites to anchor copper species, is the crucial parameter for determining the interfacial structure in the CuO/CeO₂ catalysts.

The dispersion of copper on ceria, with a specific shape, strongly depends on the amount of copper. Copper oxide (4 wt%) on CeO₂ particles (115 m²/g) mainly presented as densely populated clusters containing one or several copper atoms on ceria, together with particles of 1.5–4.5 nm (Fig. 2) [9]. Ceria octahedra (100 m²/g), with the main exposure of the (111) facets, showed similar feature on dispersing CuO species of 5–20 wt% loadings; clusters were formed at 5–10 wt% whereas particles appeared at 20 wt% [44]. Copper species could be dispersed mainly as clusters on ceria nanorods (75–100 m²/g) as the copper loading is no more than 10 wt% [18,58–60]. Lower contents (< 2–6 wt% Cu) resulted in monolayer and/or bilayer copper clusters while higher loadings (>8 wt%) led to multi-layered copper clusters and a small fraction of faceted nanoparticles [60]. Copper dispersion on cubic ceria is somewhat different from the cases on ceria particles and rods. Ceria cubes have smaller surface areas (usually less than 30 m²/g) and dominantly expose the polar (100) facet, which complicate the dispersion of copper species. At copper loading of less than 4 wt%, small copper species were populated on ceria surface; whereas copper oxide particles ranging from 3 to 15 nm, with a nonuniform distribution pattern, were detected as the copper loading was above 4 wt% [9,19,33,39].

The shape of ceria alters the chemical bonding of copper species, even if with a similar copper loading. For a series of 5 wt% CuO/CeO₂ samples, using ceria nanorods (72 m²/g), nanosphere (78 m²/g) and nanocubes (29 m²/g), the average coordination number of the Cu–Cu shell varied remarkably: 3.0 on nanosphere, 2.2 on nanorod and 5.0 on nanocube, indicating

smaller size of CuO on rod-shaped ceria [19]. When these CuO/CeO₂ samples were converted into Cu/CeO₂ catalysts, via hydrogen reduction at 400 °C, the Cu–Cu coordination number on ceria nanorods and nanospheres was almost the same (6.7), around 1.5 nm in size by assuming a hemispherical model, whereas a much higher Cu–Cu coordination number (10.3), corresponding to copper particle over 4.0 nm, was detected on ceria nanocubes [33]. Therefore, it is highly likely that the copper species present monolayers and/or submonolayers at lower copper contents, following the monolayer model (copper on ceria surface) and/or the incorporation model (copper cations incorporated into ceria lattice); while bilayers, multilayers and faceted particles appear with increasing copper loading. The threshold loading level of copper for a monolayer dispersion should be associated with the number and density of the oxygen vacancies on ceria. Moreover, the shape of ceria has tremendous impact on stabilizing these copper species.

3. Theoretical simulations of copper species on ceria

Cu/CeO₂ catalysts possess unique properties in both oxidative and reductive reactions, where the copper-ceria interaction occurs via redox circles between Cu²⁺/Cu⁺/Cu⁰ and Ce³⁺/Ce⁴⁺, requiring the participation of oxygen vacancies that are intrinsically related to the exposed facets governed by the shape of ceria. Theoretical studies on the growth of Cu species on the (111), (110) and (100) facets of ceria and the electronic and geometric property of the formed Cu–CeO₂ interfaces elaborated the copper-ceria interaction mechanism. Density functional theory (DFT) calculations have illustrated the copper-ceria interactions on stoichiometric and reduced ceria surfaces [37]. Cu adatoms on stoichiometric surfaces are more stable than on reduced surfaces, suggesting that Cu species do not nucleate at surface oxygen vacancies. Moreover, the substitution of Ce⁴⁺ by Cu²⁺, forming solid solutions, is more stable under oxidizing conditions. Supported Cu adatoms and particles, presented under reductive conditions, lie above a subsurface layer of Ce³⁺ ions that extends up to the perimeter of the metal-oxide interface. The extensive charge transfer at their interfaces leads to ceria reduction, forming interfacial Ce³⁺ and Cu⁺ or Cu^δ (Fig. 3). Cu adsorption on the regular terrace sites of CeO₂ (111) surface involves a 3-fold coordination, and its stabilization on the ceria surface is accompanied by a charge transfer between Cu⁰ and the neighboring Ce⁴⁺: ceria is partially reduced into Ce³⁺ while Cu⁰ is oxidized to Cu⁺ [36].

Theoretical calculations and experimental measurements on the adhesion energy of copper on ceria detailed the dispersion mechanism of copper on ceria. The chemical potential of isolated Cu adatoms on stoichiometric terrace sites of ceria is ~110 kJ/mol higher than that for Cu particles larger than 2.5 nm [61]. Cu monomers and dimers are representative species on the stoichiometric CeO₂ (111) surfaces. The adhesion energy of Cu to CeO_{1.95} (111) is 3.52 J/m² for 2.2 nm copper particles, decreasing slightly with the extent of ceria reduction [62]; while the Ce³⁺/Ce⁴⁺ ratio increases with Cu coverage, evidenced by Ce 3d XPS, corresponding to donation of at most ~0.17 and 0.06 electrons per Cu atom to CeO_{1.95} (111) and CeO_{1.8} (111),

Fig. 2. Copper species over ceria. (a) STEM images and EDX mappings for 4 wt% CuO on ceria nanocubes, nanorods and nanoparticles; the green and red color represent Cu and Ce element, respectively. Re-printed with permission from Ref. [9]. Copyright 2015, American Chemical Society. (b) TEM images of copper species on ceria nanorods as varying the loading of copper in the range of 2–12 wt%. Re-printed with permission from Ref. [60]. Copyright 2019, Elsevier B. V.

Fig. 3. Electronic interactions between copper and ceria over (a) stoichiometric and (b) reduced ceria surfaces. Re-printed with permission from Ref. [37]. Copyright 2010, AIP Publishing.

respectively.

DFT calculations also demonstrated that the shape of ceria has a significant impact on the electronic structure of copper-ceria interface, allowing to tailor the dispersion of copper species. In principle, the competition between the Cu–O bond at the interface and the Cu–Cu bond in Cu species determines the morphology of Cu on CeO₂. It was predicted that the copper-oxygen interaction at Cu₄/CeO₂ interface is comparable to the copper-copper intra-cluster interaction [63]. Cu_x ($x = 1-4$) clusters tend to bond with the surface oxygen of CeO₂ (111) and their interaction induces a charge transfer from copper to ceria, resulting in positively-charged copper species. Calculations on the nucleation of Cu_x ($x = 1-5$) clusters on ceria surfaces showed that the atomic Cu prefers to aggregate into large clusters on the CeO₂ (111) surface, but is thermodynamically and kinetically unfavorable on both CeO₂ (110) and CeO₂ (100) surfaces [38]. Therefore, the strong Cu–O bonding on CeO₂ (110) and CeO₂ (100) results in more flattened Cu particles while the relatively weaker Cu–O bonding on CeO₂ (111) forms more 3D-like Cu particles.

4. CO oxidation

CuO/CeO₂ catalysts are highly active for CO oxidation. Only a small amount of copper (0.7 wt%) essentially promoted the activity of CeO₂, while excess of copper species formed bulk CuO particles that contributed to the activity marginally [1]. The copper oxides existed in three forms: isolated ions (Cu²⁺), CuO_x clusters and CuO particles. The isolated ions had strong tendency to the surface of CeO₂ and aggregated to CuO_x cluster upon calcination at higher temperatures. Cu⁺ species originated from the interaction between CuO cluster and CeO₂, and their interface activated oxygen molecules, which is largely responsible for the activity [64]. EPR and IR studies on a 1 wt% CuO/CeO₂ catalyst confirmed that the copper presented in at least two configurations: isolated Cu²⁺ ions and clustered Cu²⁺, while the latter representing the largest fraction of the observed Cu species [34]. The redox behavior of both copper and ceria was observed even at room temperature, which related to

the remarkably high activity for CO oxidation.

The shape of ceria obviously affected the activity of CuO/CeO₂ catalysts. CuO/CeO₂-rod (48 m²/g) was more active for CO oxidation than CuO/CeO₂-particle (64 m²/g), which was ascribed to the preferential exposure of the more reactive {001} and {110} planes on CeO₂ nanorods [2]. A combined XANES and DRIFTS study revealed that surface Cu⁺ species had a strong correlation with the activity toward CO oxidation [4]; the positively-charged copper species were formed on ceria nanorods *via* the redox cycle between Cu²⁺/Cu⁺ and Ce⁴⁺/Ce³⁺. Another comparative study, by XAFS, TPR and IR, over CuO/CeO₂-sphere with a {111}/{100}-terminated surface and CuO/CeO₂-rod exposed {110}/{100} facets identified that copper oxides were uniformly dispersed as subnanometer clusters on CeO₂ nanosphere while existed in both CuO_x clusters and Cu-[O_x]-Ce species on ceria nanorods [5]. The CeO₂ {110} facet induced a strongly bound Cu-[O_x]-Ce structure that was adverse to the formation of Cu⁺ sites, resulting in low activity. In contrast, CuO_x clusters on the {111} face of ceria spheres was easily reduced to Cu⁺ species when they were subjected to interaction with CO. The reaction rate for CO oxidation was 5.7×10^{-6} mol_{CO} g_{cat}⁻¹ s⁻¹ on ceria spheres (104 °C) but 1.8×10^{-6} mol_{CO} g_{cat}⁻¹ s⁻¹ (118 °C) on ceria nanorods. The activity of CuO/CeO₂ catalysts for CO oxidation followed the sequence: nanorods > nanopolyhedra > nanocubes [6]. With an identical copper loading (8.5 wt%), CeO₂ nanorods exhibited the highest activity, over which CO was eliminated at 150 °C while it was achieved only at 250 °C on CeO₂ cubes (Fig. 4). The copper-ceria interactions on ceria nanorods greatly facilitated the regeneration of active sites, favoring CO adsorption on Cu⁺ species and O₂ activation over oxygen vacancies. A proper pre-treatment of the CuO/CeO₂ catalyst verified such a catalytic mechanism for CO oxidation; hydrogen reduction of the CuO/CeO₂-rod redispered the copper species into highly isolated copper clusters or surface Cu-[O_x]-Ce species, further enhancing the activity for CO oxidation [7]. Quite recently, calcination of a CuO/CeO₂-rod sample at 800 °C in air is reported to yield atomically dispersed Cu²⁺ on CeO₂ (111); these copper atoms had unsaturated coordination environment (coordina-

Fig. 4. CO oxidation over CuO/CeO₂ catalysts. (a) CO conversion as a function of reaction temperature; (b) Schematic illustration of the reaction mechanism. Re-printed with permission from Ref. [6]. Copyright 2018, Elsevier B. V.

tion number of 3.3) in the form of Cu₁O₃ and were identified to be the sole active sites for the activation of both CO and O₂ molecules in CO oxidation [65].

5. Preferential oxidation of CO in excess hydrogen

Preferential oxidation of CO in excess hydrogen (CO-PROX) is used to eliminate traceable CO (0.5–2 vol%) in hydrogen-rich streams to an acceptable level (below 100 ppm) for fuel cell application. The outstanding performance of CuO/CeO₂ catalysts for this highly selective reaction was attributed to the synergistic redox properties [16]. That is, the dispersion of copper species on ceria determines both the activity and the selectivity. Varying the loading of copper is routinely adapted to mediate the dispersion of copper species and examine the size effect of copper particles on the catalytic property. Generally, faceted CuO particles on ceria are much less active and can be viewed as spectator, while CuO clusters and surface Cu-O-Ce species (copper ions strongly interacting with ceria) [66] or copper-enriched oxides [55] are more frequently ascribed to be the active phases. Operando DRIFT and XANES experiments demonstrated that CO oxidation under rich hydrogen occurred at the interfacial Cu⁺ sites, by correlating the intensity of Cu⁺-carbonyls formed under reaction conditions and the conversion rate of CO (Fig. 5) [14,16]. The critical role of the interfacial Cu⁺ sites was further supported by a comprehensive study on a reversed CeO_{2-x}/Cu catalyst under CO-PROX conditions (Fig. 6).

The shape of ceria dramatically affects the formation of the active sites. Equal amount of copper (1 wt%) was dispersed on CeO₂ spheres (115 m²/g), rods (75 m²/g) and cubes (14 m²/g); ceria sphere- and rod-supported copper catalysts composed of small CuO particles and showed higher activities but lower selectivities, whereas the CuO/CeO₂-cube catalyst, containing relatively large CuO particles, exhibited a lower CO conversion but a higher CO₂ selectivity [15]. The lower reduction level of large copper oxide particles under the reaction conditions enhanced CO₂ selectivity. Near-ambient XPS measurements, together with DFT calculations, verified that the lower reducibil-

Fig. 5. Preferential oxidation of CO in excess hydrogen over a CuO/CeO₂ catalyst. (a) TEM images of the Ce_{0.8}Cu_{0.2}O₂ catalyst. Re-printed with permission from Ref. [55]. Copyright 2007, American Chemical Society. (b) Variations in the chemical states of copper species and the gases detected in the course of Operando XANES test under CO-H₂-O₂ mixture over the Ce_{0.8}Cu_{0.2}O₂ catalyst. Re-printed with permission from Ref. [14]. Copyright 2009, Elsevier B.V.

Fig. 6. Schematic illustration of CO oxidation in excess hydrogen over a reversed $\text{CeO}_{2-x}/\text{Cu}$ catalyst. Re-printed with permission from Ref. [31]. Copyright 2015, American Chemical Society.

ity of CuO particles on the {100} facets of ceria cubes was caused by the extensive electron transfer from CuO to CeO_2 [17,67]. CuO (5 wt%) on CeO_2 -rod (76.7 m^2/g) and CeO_2 -polyhedra (67.6 m^2/g) had a higher activity for CO-PROX at low temperatures, coupled with a broader operating temperature window (CO conversion > 99.0%, 90–125 $^\circ\text{C}$) than that on CeO_2 nanocubes (17.2 m^2/g). This was linked to the smaller copper oxide clusters and the rich oxygen vacancies on the surfaces of ceria rods [18]. However, highly dispersed CuO clusters on ceria nanorods, rather than $\text{Cu}-[\text{O}_v]-\text{Ce}$, were also viewed as the more crucial active species, based on the identification of the dominant Cu^{2+} species, by XANES, in the spent catalysts [58].

6. Low-temperature water-gas shift reaction

The low-temperature water-gas shift reaction is industrially used to tune $\text{H}_2/\text{CO}/\text{CO}_2$ proportions in the feed gases for ammonia synthesis, methanol synthesis and Fischer-Tropsch synthesis. Cu/CeO_2 catalysts are obtained by hydrogen reduction of the CuO/CeO_2 precursors at elevated temperatures, typically 200–400 $^\circ\text{C}$. Since more oxygen vacancies are generated on ceria surface during this reduction process, the copper-ceria interaction was further enhanced. Naturally, the shape of ceria would have a more remarkable impact on the chemical feature of metallic Cu species and the copper-ceria interaction, including the re-dispersion of copper species and the stability of the newly formed Cu species. Cu particles supported on spherical CeO_2 were more active for the WGS reaction than those on nanorods and nanocubes [19]. Ceria nanospheres favored a facile dissociation of water and stabilized the active Cu species more strongly, leading to a higher activity and stability than the other two architectures. The large bonding energy of copper on ceria spheres maintained the smaller copper particles and provided more active sites at the copper-ceria interfacial perimeters, increasing the WGS activity. Simultaneously, the strong oxygen affinity on the {111} facets tightly anchored Cu particles and sustained their stability under the WGS conditions [19]. Again, Cu particles on CeO_2 octahedra exposing {111} facets showed superior WGS activity to those on ceria nanorods and nanocubes (Fig. 7). This was also attributed to the well dispersion of copper species on CeO_2 (111) planes. Spectroscopic analysis on the CuO/CeO_2 precursors indicated that the copper oxide species tend to present in Cu^{2+} -associated sites on CeO_2 (110) and

Fig. 7. Water-gas shift activity and TEM images of Cu/CeO_2 catalysts. Re-printed with permission from Ref. [44].

highly-dispersed CuO_x particles on CeO_2 (111) planes [44]. Ceria particles stabilized copper species in a finely dispersed state while ceria nanorods resulted in larger, crystalline copper particles [42].

By dispersing equal amount of copper on CeO_2 nanocubes and nanospheres, the role of ceria shape in Cu/CeO_2 catalysts for the WGS reaction was clarified. XRD and XANES analysis identified that the higher activity of Cu/CeO_2 -sphere was associated with the higher stability of metallic copper species and the larger concentration of Ce^{3+} [68]. Theoretical calculations have predicted that the chemical potential of Cu atoms over step edges of CeO_2 (111) surface is ~ 57 kJ/mol lower than that on stoichiometric terrace sites [61]. This means that the stability of Cu particles as well as the Cu- CeO_2 interaction is influenced by the coordination environment of the reduced ceria surfaces. Accordingly, the shape of ceria determines the degree of copper-ceria interaction and the generation of oxygen vacancies during hydrogen reduction and WGS. Hydrogen treatment of a CuO/CeO_2 precursor at 300 $^\circ\text{C}$ not only converted copper oxides into metallic species but also created more defect sites or oxygen vacancies on ceria, promoting the Cu- CeO_2 interaction [20]. Both metallic copper species and oxygen vacancies on ceria were involved in the generation of active sites at their interfaces; the synergistic $\text{Cu}-\text{O}_v$ interaction enhanced the chemical activity of Cu while Cu facilitated the formation of O vacancies under reaction conditions [69]. CO is adsorbed and activated on Cu while water dissociation occurs on the O_v sites or the $\text{Cu}-\text{O}_v$ interface. The superior WGS activity is thus attributed to the small-sized Cu^0 crystals and the abundance of oxygen vacancies on ceria.

The atomic structure of the copper-ceria interfacial perimeter has been identified by a combined electron microscopy and spectroscopy study on copper clusters dispersed by ceria nanorods [21]. STEM and EELS verified the location and distribution of copper bilayers of around 1.5 nm on ceria while IR and XPS identified the chemical states of these tiny copper clusters: the bottom layer was mainly Cu^+ atoms directly bonded on the oxygen vacancies of ceria, in a form of $\text{Cu}^+-\text{O}_v-\text{Ce}^{3+}$, and a top layer of Cu^0 atoms coordinated with the underlying Cu^+ atoms (Fig. 8). DFT simulations showed that 0.2–0.3 electrons per

Fig. 8. Copper bilayers on ceria nanorods. (a) A STEM image of copper species (domains, monolayers and bilayers) on ceria; the bottom shows the enlarged image of a typical copper bilayer (marked in the rectangular area) and the corresponding geometric arrangement of copper and cerium atoms at their interface. (b,c) IR spectra evidencing CO adsorption on the Cu⁺ site while water activation over the O_v site [21]. Copyright 2019, Spring Nature.

interfacial copper atom were transferred from the metal layer to the ceria substrate, leading to a slightly positively-charged bottom layer and to a full reduction of the ceria trilayer in direct contact with the metal bilayer. In contrast, the top Cu layer in the copper cluster is little affected by the interfacial charge transfer and remains metallic. This is in line with previous theoretical works on the interaction of Cu adatoms with ceria surfaces/particles, which have addressed different ceria surfaces and predicted the similar charge transfer from the supported Cu atoms to the substrates, forming Cu⁺ [37]. In situ IR spectra evidenced the synergistic effect of the copper-ceria interfacial perimeter during the activation of CO and water by directly identifying CO-Cu⁺ at the Cu⁺ sites and hydroxyl species at the neighboring O_v sites. Accordingly, the low-temperature WGS reaction was proposed to occur at the copper-ceria interfacial perimeter *via* a site cooperation mechanism: the Cu⁺ site chemically adsorbs CO while the neighboring -O_v site dissociatively activates H₂O. Such a bilayer-dominated dispersion of copper species on ceria nanorods could be achieved at the metal loading up to 6 wt%, as evidenced by the linearly increased WGS activity that was contributed mainly by copper monolayers and/or bilayers [60]. Further increasing Cu loading up to 12 wt% enhanced the activity only slightly because of the appearance of multilayered and crystalline Cu particles. This demon-

strates that the dispersion of copper on ceria strongly depends on the loading of copper in Cu/CeO₂ catalysts, which is closely associated with the number and density of the anchoring sites on ceria.

7. CO/CO₂ hydrogenation

Cu/CeO₂ catalysts derived from CeCu₂ alloys were early reported to be active for CO hydrogenation (CO/H₂) to methanol at 150 °C [70]. It was observed that the metallic copper particles re-dispersed on the surface of ceria during the reaction, accompanying by an increase in the activity; ionic copper species, possibly Cu⁺, were presumed to be the active sites [71]. Recently, the active site was proposed to involve a combination of Cu⁺/Cu⁰ sites in close contact with oxygen vacancy on ceria; the Cu⁺ site is responsible for the activation of CO while the Cu⁰ site adsorbs and activates hydrogen [24]. Under methanol synthesis conditions, the highly dispersed copper particles contacted with the oxygen vacancy on the defective CeO_{2-x} to form the active site, and their electronic interaction resulted in a combination of Cu⁰ and Cu⁺ phases. Since the binding strength of CO on Cu⁺ is stronger than that on Cu⁰, CO activation occurs on the Cu⁺ site. CO, rather than CO₂, is the carbon source for methanol.

Cu/CeO₂ catalysts were also tested for CO₂ hydrogenation, in which the shape of ceria affected the activity and selectivity. CO₂ hydrogenation involves two routes: CO₂ hydrogenation to methanol and the reverse WGS, depending on the temperature and pressure. Under atmospheric pressure and at 250–450 °C, the reverse WGS, converting CO₂ to CO, occurred exclusively [33]. At the copper loading of 5 wt%, copper clusters on ceria rods (70 m²/g) had a higher activity than those dispersed over ceria spheres (70 m²/g) and cubes (29 m²/g). The reaction rate on Cu/CeO₂-rod was 1.8 μmol_{CO} g⁻¹ s⁻¹ at 250 °C, which is 4.3 times of that of Cu/CeO₂-sphere. XRD and XPS analysis found that the copper species were reduced into metallic and a partial Ce⁴⁺→Ce³⁺ transformation occurred under the reaction conditions for all the Cu/CeO₂ catalysts. The metallic copper favored the dissociative activation of H₂ while the (110) terminations on ceria rods provided O vacancies for the activation of CO₂ with a preferential formation of reactive bidentate carbonate and formate intermediates. Methanol synthesis became dominant over Cu/CeO₂ catalysts at high pressures. At 240 °C and 2.0 MPa, the conversion of CO₂ followed the order: rods > cubes > particles [72]. Again, Cu/CeO₂-rod acted as the most efficient system with a CO₂ conversion of 2.1% and a methanol selectivity of 89.5%. This was attributed to the stronger copper-ceria interaction on the (100) and (110) surfaces of the rod-shaped ceria. As further increasing the temperature to 300 °C, the conversion of CO₂ approached 6.8% but the selectivity of methanol dropped to only 19.8% due to the occurrence of the reverse WGS reaction.

8. Concluding remarks

The unique and interesting performance of Cu/CeO₂ catalysts is closely associated with the copper-ceria interface,

namely, the chemical bonding patterns of copper species on ceria surfaces. The copper-ceria interaction proceeds via a synergistic effect: ceria stabilizes copper species while the highly dispersed copper promotes the redox of ceria, involving the interplay between $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}^0$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$ couples.

Tuning the shape of ceria varies the exposure of (111), (110) and (100) facets and alters its interaction with copper species. Ceria cubes expose dominantly the {100} facet while particles or polyhedra expose both {100} and {111} facets. For ceria rods, both {111}/{100} and {100}/{110} terminations are reported and the {110} facet is frequently adapted to correlate the catalytic performance. Contradictory results occasionally appeared in the case of cubic ceria supported copper catalysts. This might be because the metastable {100} surface is apt of refaceting. In fact, synthesizing ceria cubes and octahedra with uniform sizes and exclusive exposure the respect (100) and (111) facets remains challenging. Precise dispersion of copper species on a specific facet of these nanostructured ceria requires a priority understanding in the chemical nature of the anchoring sites. Oxygen vacancy on ceria is largely responsible for dispersing copper species, however, it remains unclear whether the chemical property of oxygen vacancies generated on the (111), (110) and (100) facets of ceria would have subtle difference upon interacting with copper species. Moreover, the metal loading, the pretreatment gas/temperature and the reaction conditions would play decisive roles in dispersing and stabilizing the copper species.

Describing the structure of the active sites require a comprehensive characterization at atomic level on the copper-ceria interface. In this regard, in situ spectroscopic techniques are sensitive to the surface and interface copper species while synchrotron-based techniques probe the coordination environment of copper species, jointly revealing the electronic feature of the copper-ceria interface. Atom-resolved electron microscopy enables to directly identify the arrangements of copper, cerium and oxygen atoms, giving the geometric structure of the copper-ceria interface. All these would essentially advance the fundamental understanding in the role of the copper-ceria interface for catalysis and shed profound insights into rational design and precise synthesis of Cu/CeO_2 catalysts.

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Graphical Abstract

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Electronic and geometric structure of the copper-ceria interface on Cu/CeO_2 catalysts

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The copper-ceria interface in Cu/CeO_2 catalysts is viewed to be the active sites; both the shape of ceria and the loading of copper alter the electronic and geometric structure of the copper-ceria interface.

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铜-氧化铈界面：几何及电子结构

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摘要: 纳米催化材料的性能主要由粒子尺寸、形貌和界面决定, 即活性位点的电子及几何结构。尺寸、形貌可控的纳米催化

材料的合成及其反应性能的研究,即催化剂的构效关系,一直是催化领域的研究热点.氧化物负载的金属催化剂广泛应用于多相催化反应过程.基于氧化铈优异的氧化还原性能,Cu/CeO₂催化剂在CO氧化、N₂O消除、水气变换、甲醇合成等反应中表现出优异性能.其中,通过铜物种与氧化铈表面化学键合形成的金属-载体界面通常被认为是催化活性中心.铜物种和氧化铈的相互作用主要体现在氧化铈固定铜物种,而铜物种促进氧化铈的氧化还原能力,涉及Cu²⁺/Cu⁺/Cu⁰和Ce³⁺/Ce⁴⁺之间电子的传输和转移.

Cu/CeO₂催化剂活性位的原子结构与金属-载体相互作用程度密切相关.氧化铈形貌和铜负载量是决定界面电子和几何结构的重要因素.常见的纳米氧化铈形貌包括纳米粒子(多面体)、纳米棒和纳米立方体,可分别选择性暴露{111}、{110}和{100}晶面;这些晶面上原子配位环境和化学性能决定了铜-氧化铈的键合方式和界面结构.与暴露{100}晶面的纳米立方体相比,主要暴露{100}/{110}晶面的氧化铈纳米棒、暴露{111}/{100}晶面的纳米粒子与铜物种具有更强的金属-载体相互作用程度,也更有利于铜物种的分散.铜的负载量也显著影响铜物种在特定氧化铈表面的分散度和化学状态;随着铜负载量的增加,可在氧化铈表面形成层状铜、铜团簇和铜纳米粒子.通常情况下,低负载量有利于单层、双层铜物种的形成,高负载量时则出现多层铜和铜纳米粒子.催化活性位通常是由铜原子与氧化铈上的氧空穴相互作用产生,与氧化铈表面氧空穴的数量和密度密切相关,即氧化铈形貌.

本文总结了Cu/CeO₂催化剂的研究进展,讨论了氧化铈形貌和铜负载量对铜物种分散度和化学状态的影响规律,总结了铜氧化铈界面结构的多维度表征结果,比较了Cu/CeO₂催化剂在CO氧化、水气变换及甲醇合成中的活性位结构和反应机制.

关键词: Cu/CeO₂; 氧化铈形貌; 铜纳米粒子; 界面结构; 活性位

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