Formation and Activity Enhancement of Surface Hydrides by the Metal-Oxide Interface

Beibei Wang

ShanghaiTech University

Lunjia Zhang

ShanghaiTech University

Jun Cai

ShanghaiTech University

Zheng Peng

ShanghaiTech University

Peihong Cheng

ShanghaiTech University

Xiaobao Li

Shanghai Institute of microsystem and information Technology

Hui Zhang (✉ huizhang@mail.sim.ac.cn)

Shanghai Institute of microsystem and information Technology

Fan Yang (✉ fyang@shanghaitech.edu.cn)

ShanghaiTech University

Zhi Liu (✉ liuzhi@shanghaitech.edu.cn)

ShanghaiTech University

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Abstract

The observation of hydride species in reduced ceria has triggered recent interest, because the formation of hydrides in solid catalysts has been limited although hydrides are widely explored in homogeneous catalysis as active species for hydrogenation reactions. Here, we proposed a strategy to enhance the formation and activity of surface hydrides on oxide-based catalysts via the construction of metal-oxide interface. Specifically, during the reaction with H_2 , Cu supported on CeO_2 nano-rods (NRs) were found to enhance the formation of hydride species, with the capacity more than an order of magnitude higher than that of CeO_2 NRs. Moreover, sub-nanometer clusters (sub-NCs) of Cu supported on CeO_2 NRs could enhance the formation and activity of surface hydrides, much more superior than that of Cu nanoparticles (NPs) on CeO_2 NRs. A combination of ambient pressure photoelectron spectroscopy (AP-PES) techniques has enabled *in-situ* measurements of hydrogen interaction and as such, to correlate directly the electronic structures of solid catalysts with their activity. A strong metal-support interaction between under-saturated Cu clusters with CeO_2 was found to account for the enhanced stability and reactivity of surface hydrides at the (sub-NCs) Cu- CeO_2 interface, which provides insight for the design of highly efficient catalysts for catalytic hydrogenation reactions.

1. Introduction

Oxide-based catalysts are increasingly recognized and investigated as highly efficient and selective catalysts for hydrogenation reactions, among which ceria (CeO_2) has attracted most attention as a catalyst or a support for various hydrogenation reactions, including CO/ CO_2 hydrogenation, partial hydrogenation of alkynes, etc.^[1, 2] The interaction between H_2 and ceria is thus a center issue to understand and control these selective hydrogenation reactions.^[3] Particularly, recent studies have suggested that oxygen vacancies (V_o) on ceria could facilitate the formation of hydrides (H^-),^[2, 4-6] despite the homolytic dissociation of H_2 to form two hydroxyl groups is thermodynamically favored on stoichiometric ceria.^[2, 7] The catalytic properties of hydride species in ceria-based catalysts have since attracted increasing attention for hydrogenation reactions, including the hydrogenation of CO_2 and N_2 molecules under moderate conditions.^[7, 8, 9] Yet, a major challenge remains on how to enhance the formation and activity of surface hydride species over ceria-based catalysts,^[10] as such they could be utilized for a wide range of hydrogenation reactions.

Hereby, we propose a strategy to enhance the formation and activity of surface hydride species with the metal-oxide interface. Although surface hydrides are usually difficult to form over late-transition metals,^[7] we expect that supported clusters could serve as a viable approach to combine the advantages of heterogeneous catalysis with those of homogeneous catalysis, as molecular transition-metal hydrides have often been observed and widely explored for homogeneous catalytic hydrogenation reactions.^[11, 12]

For instance, CuH has been intensively studied for C-H bond formation,^[13] and becoming an integral part of modern organic synthesis. Thus, we synthesized a series of ceria-supported Cu catalysts and studied their interactions with H₂.

A combination of synchrotron radiation-based ambient pressure photoelectron spectroscopy (AP-PES) techniques has enabled *in-situ* measurements of hydrogen interaction with tunable incident photon energy and as such, to correlate directly the electronic structures of solid catalysts with their activity.^[14, 15] Our study showed that sub-NCs of Cu supported on thermally reduced CeO₂ NRs with strong metal-support interaction (SMSI) could significantly enhance the formation and activity of hydrides species in both Cu and ceria, as compared to those of CeO₂ NRs and Cu NPs on CeO₂ NRs. Our study has thus provided a guide for the optimum design for heterogeneous catalysts for selective hydrogenation reactions, including the hydrogenation of CO and CO₂.

2. Results And Discussion

The synthesis of CeO₂ NRs and Cu/CeO₂ NRs catalysts with 2 wt % and 5 wt % Cu loadings (xCuCe, x=2, 5) was described in the experimental section. **Figure 1** showed the structures and morphologies of CeO₂ and xCuCe catalysts. EDX elemental mapping showed that Cu species were well-dispersed on CeO₂ for both 2CuCe and 5CuCe catalysts (Figure 1a-b). However, PXRD spectra showed weak diffraction peaks of metallic Cu on 5CuCe, indicating the presence of Cu NPs (Figure 1c).

The average size of Cu clusters or NPs in xCuCe catalysts were estimated from *in-situ* XAFS experiments.^[16] Upon the reaction in 1 bar H₂ at 260 °C, *in-situ* X-ray absorption near-edge structure (XANES, Figure S1a-b) suggested the increase of metallic Cu for both 2CuCe and 5CuCe catalysts, which was also exemplified by the nearest neighbor Cu-Cu peak in Fourier transform of *k*³-weighted Cu *K*-edge EXAFS spectra (Figure 1d). The H₂-treated xCuCe catalysts, termed as xCuCe-H₂, gave a Cu-Cu coordination number of 3.1 for 2CuCe-H₂ and 7.9 for 5CuCe-H₂ (Figure S1c-d and Table S1). Thus, Cu species in 2CuCe-H₂ were highly under-coordinated, with an estimated average size at sub-nanometer scale (< 1 nm), whereas Cu NPs in 5CuCe-H₂ should exhibit an average size of several nanometers.^[16, 17]

In-situ AP-XPS were employed to study the reaction between CeO₂, xCuCe catalysts and H₂. **Figure 2a-c** showed sequential Ce 3d spectra of CeO₂ and xCuCe catalysts, when they were annealed in UHV or H₂ at 260 °C and above. Quantitative analysis on the surface concentrations of Ce³⁺ (Ce³⁺/Ce, C[Ce³⁺]) could be acquired from Ce 3d spectra for CeO₂, 2CuCe and 5CuCe catalysts, respectively. Interestingly, the exposure to 0.3 mbar H₂ at 260 °C led to the decreases of C[Ce³⁺], which decreased from 39% to 23% for CeO₂, from 52% to 8% for 2CuCe and from 50% to 11% for 5CuCe, respectively. Li et al. showed recently that H₂ dissociation on reduced ceria at 300 K led to the formation of hydride species, causing the oxidation of Ce³⁺ into the Ce⁴⁺-H⁻ complex.^[4] Apparently, the presence of Cu-CeO₂ interfaces resulted in more significant formation of hydride species, where ~85% and ~78% of surface Ce³⁺ were oxidized to

Ce⁴⁺ in 2CuCe and 5CuCe, respectively. Note that, the exposure to 0.3 mbar O₂ could also cause a significant decrease in C[Ce³⁺], although a severe charging phenomenon was observed by AP-XPS (Figure S2), indicating that the infiltration of hydrogen and oxygen affected differently the electronic properties of ceria.^[18]

Accompanying the oxidation of Ce³⁺ by H₂, hydrogen-induced oxidation of Cu species could also be observed for xCuCe catalysts (Figure 2d-e). The binding energies of Cu 2p 3/2 shifted from 932.5 eV to 933.9 eV for 2CuCe, while a shoulder peak at 933.9 eV was observed for 5CuCe, along with the appearance of Cu²⁺ satellite peaks.^[19, 20] Consistently, the shift of Cu LMM Auger peak from 916.4 eV (Cu⁺) to 917.8 eV (Cu²⁺) could be observed for both 2CuCe and 5CuCe, suggesting the unchanged peak in Cu 2p 3/2 spectra for 5CuCe could be attributed to Cu⁰.^[19, 21] That means, Cu⁺ cations at the Cu-CeO₂ (Figure S1a-b and Figure 2d-e) interface could account for the formation of hydrides species, which could be CuH₂, through an oxidative addition process during the exposure to H₂.^[11, 22] For 5CuCe, Cu⁰ species in Cu NPs did not react with hydrogen to form hydrides at elevated temperature, similar to the behavior of bulk Cu. In 0.3 mbar H₂ at 260 °C, the interfacial cuprous centers between Cu sub-NCs and ceria resulted from the SMSI effect facilitated the dissociation of H₂ and the formation of copper hydrides as well as the formation of Ce⁴⁺-H⁻ complex in ceria. As a comparison, we have also evaluated the reaction between H₂ and Cu supported on carbon black. No reaction of Cu was obvious from AP-XPS measurements (Figure S3), suggesting the importance of the Cu-CeO₂ interface for the formation of copper hydride species.

The surface molar ratio of CuH₂ species could be derived from the molar ratio of Cu²⁺/Ce based on Cu 2p and Ce 3d spectra (Figure 3, and Figure S4). 2CuCe possessed more Cu-CeO₂ interfacial sites and gave the proportion of Cu²⁺ at M(Cu²⁺/Ce) = ~5.5, which corresponded to ~56% H⁻/Ce ratio (Ce-H⁻: ~45% and Cu-H⁻: ~11%). Yet, 5CuCe contained less CuH₂ (Cu²⁺/Ce = ~3) and exhibited ~45% H⁻/Ce (Ce-H⁻: ~39% and Cu-H⁻: ~6%), and bare CeO₂ only exhibited ~16% H⁻/Ce.

To further examine the influence of electronic structure by hydride formation, *in-situ* valence band (VB) spectra were taken at hν = 200 eV (**Figure 3a**). It is clear that, accompanying H₂ dissociation and the formation of hydride species, the intensity of Ce 4f band at ~1 eV below Fermi level (E_F) decreased significantly, owing to the removal of 4f electrons and the oxidation of Ce³⁺ into Ce⁴⁺.^[23] Density of states in VB further away from E_F, which originated from predominantly O 2p states, did not show much change, which again confirmed the oxidation of Ce³⁺ by hydrogen, rather than oxygen. Upon the evacuation of H₂, the intensity of Ce 4f band increased significantly for CeO₂ at 300 °C owing to the re-combinative desorption of H₂, as is the case for 5CuCe. In contrast, the intensity of Ce 4f band increased only slightly

for 2CuCe at 300 °C in UHV, indicating the stability of $\text{Ce}^{4+}\text{-H}^-$ species are much higher on 2CuCe than on either CeO_2 or 5CuCe.

Further, *in-situ* AP-RPES, sensitive to the Ce 4d-4f transition, was employed to compare the evolution of Ce^{3+} on 2CuCe and 5CuCe during their reaction with H_2 . In Figure 3b, the two resonance peaks resulted from the incident photon energies at 121.4 eV ($4f^1$) and 124.8 eV ($4f^0$) correspond to the resonance adsorption of Ce^{3+} and Ce^{4+} , respectively. The spectra taken with incident photon energy at 115 eV have no resonance adsorption for ceria and provided a spectral background for quantitative analysis of $\text{C}[\text{Ce}^{3+}]$ ($\text{DCe}^{3+}/\text{DCe}^{3+}+\text{DCe}^{4+}$).^[24] Consistently, AP-RPES spectra showed that $\text{Ce}^{4+}\text{-H}^-$ species on 2CuCe were more stable at 300 °C than those on 5CuCe.

According to *in-situ* AP-XPS measurements, upon the evacuation of H_2 at 260 °C, $\text{C}[\text{Ce}^{3+}]$ was recovered by ~49% and ~24% on CeO_2 and 5CuCe, respectively (Figure 2a-c, and **Figure 4a**). Yet, $\text{Ce}^{4+}\text{-H}^-$ species were much more stable on 2CuCe than those on CeO_2 and 5CuCe at 300 °C or blow. Likewise, CuH_2 species on xCuCe catalysts were also found to decompose gradually from 260 °C to 350 °C in UHV (Figure 2d-e, and Figure 4b). The stability of CuH_2 on xCuCe was in drastic contrast to the instability of CuH_2 molecule, which was reported to be unstable at room temperature and would decompose to $\text{Cu} + \text{H}_2$.^[25] The enhanced stability of CuH_2 species on xCuCe catalysts could thus enable their capability for a wide range of hydrogenation reactions.

Combining VB, RPES and XPS spectra, the interface between Cu clusters and ceria could facilitate the formation of hydride species in both ceria and Cu and in the order of $2\text{CuCe} > 5\text{CuCe} > \text{CeO}_2$. The interface between Cu sub-NCs and reduced ceria could enhance the stability of incorporated hydrogen in both copper and ceria, surpassing the capability of bare CeO_2 or the interface between Cu NPs and ceria in 5CuCe.

More interestingly, the enhanced formation of surface hydrides in 2CuCe increased also their activity for hydrogenation reactions. As a demonstration, we compared the removal of surface hydroxyl and carbon species during AP-XPS experiments for CeO_2 and xCuCe catalysts. Figure 4d-e and Figure S5-6 showed that surface hydroxyl and carbon species could be mostly removed on 2CuCe after the exposure to H_2 at 260 °C, which is in contrast to the slight decrease of those on 5CuCe. Yet, Surface hydroxyl and carbon species could be gradually removed by hydride species in 5CuCe, during the annealing from 260 °C to 350 °C. On CeO_2 , surface hydroxyl and carbon species appeared highly stable and could not be removed during the H_2 treatments and the annealing process. The C-C containing species on CeO_2 increased slightly while annealing in UHV, which could be attributed to surface segregation of carbonaceous species from the ceria bulk (Figure 4e). The reactivity could be ranked in the order of $2\text{CuCe} > 5\text{CuCe} > \text{CeO}_2$, suggesting the superior activity of interfacial sites between Cu sub-NCs and reduced CeO_2 . Such

active sites could be promising for the catalysis of CO/CO₂ hydrogenation.^[9, 26]

H₂-TPD measurements were performed on CeO₂ and xCuCe, to understand the role of (sub-NCs) Cu-CeO₂ interface in the incorporation and decomposition of H₂ (Figure 4c). Our results showed that the amount of H₂ evolved from xCuCe catalysts increased significantly than from CeO₂, with a volume ratio of 1: 56.2: 34.3 for the same weight of CeO₂, 2CuCe and 5CuCe, respectively. Meanwhile, the molar ratios of H⁻/Ce calculated from AP-XPS results above were H⁻/Ce(CeO₂): H⁻/Ce(2CuCe): H⁻/Ce(5CuCe) = 1: 3.5: 2.8. Thus, H₂ evolved from xCuCe at relatively higher temperatures should originate from the bulk Ce⁴⁺-H⁻.^[5] The contribution from hydroxyl to H₂-TPD spectra could be excluded or as a very minor factor, because surface hydroxyl species have been largely removed by the reaction with hydrogen in 2CuCe, as demonstrated in Figure 4d. Indeed, the amount of evolved H₂ from the three samples exhibited a positive correlation with the surface molar ratio of Cu sub-NCs, i.e. sub-NCs of Cu on reduced ceria can facilitate the formation of surface hydrides, as well as bulk hydride species in CeO₂ by more than an order of magnitude, as compared to those of CeO₂ (Scheme 1).

3. Conclusions

In this work, we proposed a strategy to enhance the formation and activity of surface hydride species on ceria-based catalysts, via the construction of Cu-CeO₂ interfaces. Specifically, we synthesized CeO₂ and CeO₂-supported Cu catalysts and studied their reaction with H₂ using the combination of *in-situ* AP-PES and H₂-TPD measurements. Our study showed that, compared to bare CeO₂, Cu supported on CeO₂ could enhance the formation of surface and bulk hydride species in CeO₂ by more than an order of magnitude. Sub-NCs of Cu on CeO₂ with strong metal-support interaction exhibited the maximum capacity in the formation of Cu hydrides species, as well as Ce⁴⁺-H⁻. Moreover, hydride species formed at interface sites between Cu sub-NCs and CeO₂ exhibited much higher activity for the removal of surface hydroxyl and carbon species than CeO₂ alone or Cu NPs on CeO₂. Our study has thus provided a guideline for the optimum design for heterogeneous catalysts for hydrogenation reactions, including the hydrogenation of CO and CO₂.

4. Experimental Section

Preparation of catalysts. CeO₂ nanorods (NRs) were prepared by dissolving 1.736 g Ce(NO₃)₃·6H₂O in 80 mL of deionized water. Then 24 g of NaOH was added under vigorous stirring. The suspension was stirred for additional 30 min and transferred into a Teflon-lined stainless steel autoclave for 24 h at 110 °C. Then the products were centrifuged at 8000 rpm for 6 min each time followed by washing with deionized water until pH ~ 7. The obtained solids were dried for 24 hours at 30 °C and calcined in air at 300 °C for 3 h.

The Cu/CeO₂ NRs composites were fabricated by impregnation method. For preparation of 2 wt % Cu/CeO₂ NRs (2CuCe), 1 wt % Cu/CeO₂ NRs (1CuCe) were first prepared. 500 mg of CeO₂ NRs was

dispersed in 25 ml of ethylene glycol, and 0.0205 of copper acetylacetonate ($\text{Cu}(\text{acac})_2$) was added. The suspension was heated to 135 °C for 1.5 h followed by centrifuged and washed with ethyl alcohol 3 times. Then the obtained 1CuCe solids were dried at 60 °C for 6 h, and used as support to load 1 wt % Cu once more. For preparation of 5 wt % Cu/ CeO_2 NRs (5CuCe), 0.1025 g of $\text{Cu}(\text{acac})_2$ was used in same procedure as preparation of 1CuCe. The Cu/carbon black (Cu/CB) sample was prepared by the same impregnation method using 0.030 g $\text{Cu}(\text{acac})_2$ and 0.110 g carbon black.

Characterization of structure and morphology. Powder X-ray diffraction (PXRD) patterns were recorded by Bruker D8 Advanced X-ray diffraction measurement system (40 kV, 40 mA) using Cu K α radiation (0.15418 nm). The powder samples were placed inside a quartz-glass holder. Scanning transmission electron microscopy (STEM) was carried out on a JEOL JEM-2000 transmission electron microscope operated at 200 KV. Energy dispersive X-ray spectroscopy (EDX) elemental mapping were recorded on an Oxford X-Max 100TLE microscope.

In-situ X-ray absorption fine structure. XAFS spectra of Cu *K*-edge (8840 eV – 9740 eV) were carried out on the beamline 17C (BL17C) of the National Synchrotron Radiation Research Center (NSRRC). A Si (111) single crystal were used to obtain a monochromatic X-ray beam. Cu *K*-edge were collected in a fluorescence mode, and the energy was calibrated using Cu foil. Fourier transformation (FT) of the k^3 -weighted extended X-ray absorption fine structure spectra (EXAFS) oscillation from the k space to the r space was performed to obtain a radial distribution function. The IFFEFIT data analysis package (Athena, Artemis) was used for data extraction and curve fitting. *In-situ* XAFS spectra (2CuCe- H_2 and 5CuCe- H_2) were conducted after reduction in flowing 1 bar H_2 (99.999 %) at 260 °C for 1 h and cooling down to room temperature.

In-situ ambient pressure X-ray photoelectron spectroscopy. *In-situ* AP-XPS experiments were performed on the beamline 02B (BL02B) AP-XPS endstation of the Shanghai Synchrotron Radiation Facility (SSRF).^[14] To minimize contamination, the gas line for H_2 was flushed three times using high-purity H_2 (99.999 %) before introducing H_2 into the chamber. Incident photon energy of 1100 eV for Ce 3d, Cu 2p, Cu LMM and C 1s, 730 eV for O 1s and C 1s, and 200 eV for valence band (VB) were used. Prior to react with H_2 , samples were thermally-reduced at 260 °C in ultrahigh vacuum (UHV) for 3 h in the AP-XPS chamber. After that, 0.3 mbar H_2 was injected at 260 °C for 1 h. The subsequent annealing experiments were performed after the main chamber was evacuated, and samples were heated from 260 °C to 300 °C and 350 °C under UHV condition. XPS spectra was collected after maintained for 20 min at each temperature. All spectra were fitted by Casa XPS software using a Shirley-type background, and the Ce 3d and Cu 2p spectra presented in Figure 2 and Figure 3 were subtracted with their Shirley backgrounds. Ce 3d and Cu 2p spectra were calibrated according to one of the Ce 3d peak attributed to Ce^{4+} and centered at 916.3 eV.

In-situ ambient pressure resonance photoelectron spectroscopy. *In-situ* AP-RPES obtained in the Ce 4d-4f photoabsorption region were acquired on the BL02B AP-XPS endstation of the SSRF as well via the same experimental steps. The photon energies of 115, 121.4 and 124.8 eV were chosen because Ce^{3+} valence

states resonate most strongly at a photon energy of about 121.4 eV whilst Ce⁴⁺ valence states are maximum for 124.8 eV. At 115 eV the system is off-resonance.

H₂-temperature program desorption (H₂-TPD). H₂-TPD profiles were performed in a high-pressure gas cell (HPGC, Fermi Corp.), which was equipped with a needle valve, a molecular pump group and a mass spectroscopy (MS, LC-D200M, TILON). 13 mg powder were placed in an inconel flag type sample holder and pretreated at 500 °C for 3 h in high vacuum (HV) condition (10⁻⁷ ~ 10⁻⁶ mbar) followed by cooled to 260 °C. Then samples were heated in flowing 0.3 mbar H₂ at 260 °C for 1 h. After evacuated hydrogen, samples were heated from 260 °C to 600 °C (2 °C/min) in HV condition, during which the H₂ signals were monitored by MS. H₂ signals tested on the same samples without H₂-treatment, and those on the sample holder (without sample) pretreated in 0.3 mbar H₂ at 260 °C for 1 h were used for background subtraction.

Declarations

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Competing interests

The authors declare no competing interests.

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Figures

Figure 1

(a), (b) STEM image of 2CuCe and 5CuCe and the corresponding EDX elemental mapping of Cu and Ce. (c) PXRD patterns for CeO₂, 2CuCe and 5CuCe, and (d) Fourier transform of k³-weighted Cu K-edge EXAFS of 2CuCe/5CuCe and 2CuCe-H₂/5CuCe-H₂. FT range: 2.5 ~ 11 Å⁻¹, in-situ condition: flowing 1 bar H₂ at 260 °C for 1 h.

Figure 2

In-situ Ce 3d XPS spectra for (a) CeO_2 , (b) 2CuCe and (c) 5CuCe. All spectra were normalized to total Ce 3d peak area. In-situ Cu 2p 3/2 XPS spectra for (d) 2CuCe and (e) 5CuCe.

Figure 3

(a) In-situ VB spectra for CeO₂, 2CuCe and 5CuCe. (b) In-situ Ce 4f level AP-RPES of 2CuCe and 5CuCe: on-resonance spectra at $h\nu = 121.4$ eV (Ce³⁺) and $h\nu = 124.8$ eV (Ce⁴⁺) are compared with off-resonance spectrum at $h\nu = 115$ eV.

Figure 4

Evolution of molar ratio of (a) Ce³⁺/Ce and (b) Cu²⁺/Cu calculated based on Ce 3d and Cu 2p spectra. (c) H₂-TPD profiles. Evolution of (d) surface hydroxyl, carbonate and (e) carbon species analyzed based on O 1s, C 1s and Ce 3d spectra for CeO₂, 2CuCe, 5CuCe catalysts, respectively.

Supplementary Files

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