



ChemComm

**High-area alumina supported Cu-Ce atomic species for
water-gas shift reaction**

Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-03-2024-001023.R1
Article Type:	Communication

SCHOLARONE™
Manuscripts

COMMUNICATION

High-area alumina supported Cu-Ce atomic species for water-gas shift reaction†

Yiwei Yu,^a Tie Wang,^{b,c} Ning Yan^b and Jingyue Liu^{*d}Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Atomically dispersed cerium species, anchored to high-area alumina by unsaturated penta-coordinated aluminum, strongly interact with atomically dispersed Cu species to provide active centers for water-gas shift reaction (WGSR). The alumina-anchored Ce³⁺ species stabilize atomically dispersed Cu⁺ to form Cu⁺-Ce³⁺ active complexes and they work synergistically to enhance low-temperature WGSR activity. This work offers alternative approaches to developing low-cost catalysts for the WGSR process.

The water-gas shift reaction (WGSR) is a highly valuable industrial process for manufacturing hydrogen, ammonia, methanol, and hydrocarbons. For example, WGSR plays an important role in the production of hydrogen via steam reforming of methane or other types of hydrocarbons.¹ The copper-ceria catalytic system has exhibited remarkable efficiency in low-temperature WGSR.^{2,3} The strong interaction between copper species and the ceria support, leading to modifications of the copper chemical state at the copper-ceria interfaces, is considered to be key to the notable catalytic performance.^{4,5} The perimetric boundaries between copper particles and crystalline ceria support surfaces are proposed to be the active centers for WGSR.^{5,6}

Anchored metal atoms, due to their strong interaction with support, function as effective active centers for a variety of catalytic reactions⁷ including WGSR.⁸ Recently, atomically dispersed Cu species, supported on crystalline CeO₂, demonstrated higher activity than the copper clusters/particles

for WGSR, primarily due to strong interactions between atomic copper and selected facets of crystalline ceria.⁹ Specifically, the CeO₂ {111} facets stabilize more atomically dispersed copper species, and therefore increase the number of active sites for low-temperature WGSR.⁹ Such strong electronic interactions between Cu atoms/clusters and surface Ce³⁺ species on crystalline CeO₂ maintain stable Cu⁺ species during the WGSR.⁵ The interfacial Cu⁺-O_v-Ce³⁺ complexes are considered to serve as active sites, where the Cu⁺ adsorbs an CO molecule and the neighboring O_v-Ce³⁺ site dissociatively activates H₂O.⁵ The adsorbed CO is either oxidized by a reactive oxygen on the CeO₂ surface to form a CO₂ or it reacts with surface OH groups to form an intermediate which subsequently decomposes to H₂ and CO₂.^{10–12} Abundant surface OH groups from water dissociation and their intimate contacts with adsorbed CO molecules at the copper-ceria interfaces are critical to high WGSR activity.¹³ It is not clear whether crystalline CeO₂ is required for developing highly active Cu-based catalysts for low-temperature WGSR.

In this work, we demonstrate that atomically dispersed Ce species not only stabilize atomically dispersed Cu but also modify their electronic structure to form stable Cu⁺-Ce³⁺ active centers that significantly enhance the activity of low-temperature WGSR. Commercially available, high-area γ -Al₂O₃ was used to support the atomically dispersed metal species. Experimental results showed that atomically dispersed Ce atoms have a major effect on the catalytic behavior of atomically dispersed Cu species: the grafting of Ce atoms onto γ -Al₂O₃ surfaces increased the WGSR rate of Cu atoms by nine times at a reaction temperature of 200 °C. The WGSR activity of the atomically dispersed Cu-Ce/ γ -Al₂O₃ catalyst, with a Cu and Ce loading levels of only 1.2 wt% and 2.2 wt%, respectively, is comparable to that of the Cu/CeO₂ catalysts reported in literature.^{9,14} We propose that the intimate contact between Cu and Ce atoms induces strong electronic interaction and the Cu-Ce species act synergistically to provide enhanced WGSR activity: the Ce³⁺ adsorbs and dissociates H₂O whereas the

^a School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona 85287, USA.

^b Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117585, Singapore.

^c Joint School of NUS and TJU, International Campus of Tianjin University, Fuzhou 350207, China

^d Department of Physics, Arizona State University, Tempe, Arizona 85287, USA.
E-mail: jingyue.liu@asu.edu

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

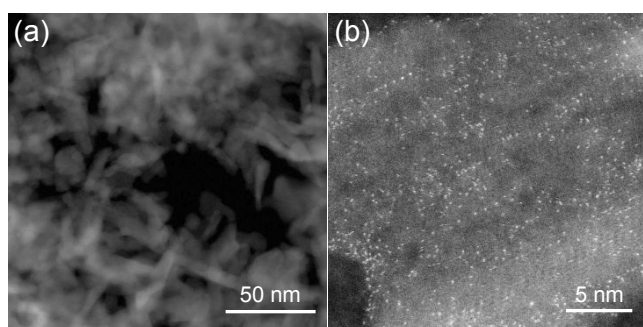


Fig. 1 (a) Representative low-magnification HAADF-STEM image of Cu-Ce/ γ -Al₂O₃ shows absence of metal clusters/particles. (b) Representative atomic resolution HAADF-STEM image displays atomically dispersed metal species uniformly distributed on the γ -Al₂O₃ support. Atomically dispersed Cu atoms could not be reliably distinguished from the Ce single atoms.

adjacent Cu⁺ adsorbs CO. The activated OH species react with the CO molecules on the Cu⁺ sites, which are stabilized by neighboring Ce³⁺, forming intermediate species and subsequently decomposing to CO₂ and H₂.

An electrostatic-adsorption-assisted deposition method was used to disperse the Ce and Cu species onto high-area γ -Al₂O₃ (see ESI for details). The content of the Cu and Ce in the as-synthesized Cu-Ce/ γ -Al₂O₃ catalyst was measured to be 1.2 wt% and 2.2 wt%, respectively. Catalysts with lower Cu content were synthesized and evaluated as well (Table S1, ESI[†]). A Cu/ γ -Al₂O₃, containing 1.4 wt% of atomically dispersed Cu species, was synthesized as a control catalyst. The XRD patterns of the Cu/ γ -Al₂O₃ and Cu-Ce/ γ -Al₂O₃ catalysts (Fig. S1, ESI[†]) did not provide recognizable diffraction peaks of Ce- or Cu-related crystalline phases. Although low levels of metal loading complicate the interpretation of the XRD patterns these catalysts did not contain large crystals of Ce and Cu compounds as evidenced by SEM and STEM examinations.

Because of its high sensitivity to particles of heavy elements, the backscattered electron (BSE) imaging method was used to screen the catalyst samples to optimize our synthesis processes (Fig. S2, ESI[†]). BSE images of the Cu-Ce/ γ -Al₂O₃ (Fig. S2(c, d), ESI[†]) and Cu/ γ -Al₂O₃ (Fig. S3(a, b), ESI[†]) catalysts show absence of large particles/agglomerates of Cu- or Ce-containing species.

High-angle annular dark-field (HAADF) images, which provide atomic number (Z) contrast, of the Cu/ γ -Al₂O₃ catalyst show absence of Cu particles/clusters (Fig. S4a, ESI[†]) and presence of atomically dispersed Cu species (Fig. S4b and S4c, ESI[†]). A representative HAADF image of the Cu-Ce/ γ -Al₂O₃ catalyst (Fig. 1a) confirms absence of detectable Cu-/Ce-related particles. The atomic-resolution HAADF image (Fig. 1b) unambiguously shows the spatial distribution of the atomically dispersed Ce and Cu atoms on the γ -Al₂O₃ support. Reliable information on the elemental mapping of individual Ce and Cu atoms is beyond the current instrumentation limit.¹⁵

X-ray photon spectroscopy (XPS) method was used to characterize atomically dispersed Cu/Ce species in the reduced (300 °C for 1 h in 5 vol% H₂/He) Cu/ γ -Al₂O₃ and Cu-Ce/ γ -Al₂O₃. The wide-scan spectra of Cu/ γ -Al₂O₃ and Cu-Ce/ γ -Al₂O₃ (Fig. S5, ESI[†]) indicate presence of Cu, O, C and Al in both catalysts and Ce in the Cu-Ce/ γ -Al₂O₃ catalyst. The Ce 3d XPS spectrum of the Cu-Ce/ γ -Al₂O₃ (Fig. 2a) shows all the characteristic peaks (v_0 , v' , u_0 , and u') of Ce³⁺ species and absence of the peaks representing Ce⁴⁺ species¹⁶, in agreement with literature reports.^{17–19} The Cu 2p XPS spectra of the Cu/ γ -Al₂O₃ and Cu-Ce/ γ -Al₂O₃ catalysts (Fig. 2b) show peaks at 932.7 eV and 952.4 eV, corresponding to the Cu 2p_{3/2} and Cu 2p_{1/2}, respectively.²⁰ The Cu 2p_{3/2} peak can be deconvoluted into two distinct peaks: Cu²⁺ at 933.8 eV and Cu⁰/Cu⁺ at 932.4 eV.²⁰ The Cu Auger LMM region (Fig. S6, ESI[†]) suggests characteristic peaks of Cu⁺ and Cu²⁺ but not the characteristic peaks of the Cu⁰ species.²⁰ The percentage of the Cu⁺ to the total Cu species (Cu⁺+Cu²⁺) was estimated to be ~57% in the Cu/ γ -Al₂O₃ and ~82% in the Cu-Ce/ γ -Al₂O₃.

We conducted *in-situ* diffuse reflectance infrared Fourier transform (DRIFT) experiments to study the dynamic behaviour of CO adsorption on the metal species. All catalysts were first pre-treated in H₂ at 300 °C for 1h, then CO molecules were allowed to adsorb on the metal species at 25 °C to saturation, and finally the CO desorption experiment was carried out with flowing argon (Figure S7, ESI). Figure 2c displays the CO absorption spectra after argon purging: no detectable CO adsorption on Ce/ γ -Al₂O₃ and a distinct IR band at 2108 cm⁻¹ on

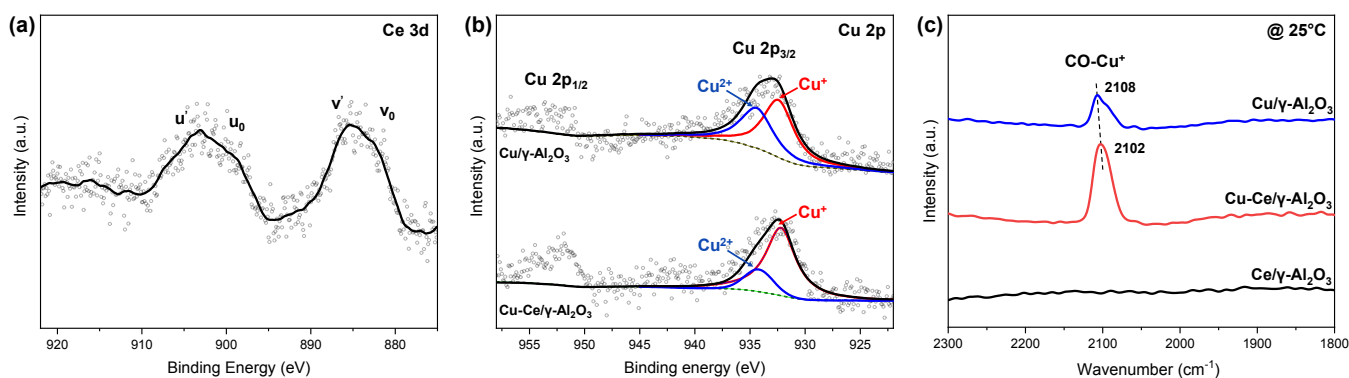


Fig. 2 XPS spectrum of the Ce 3d region of Cu-Ce/ γ -Al₂O₃ (a) clearly reveals characteristic peaks of the Ce³⁺ species and XPS spectra of the Cu 2p region of Cu/ γ -Al₂O₃ and Cu-Ce/ γ -Al₂O₃ (b) show higher Cu⁺ content in Cu-Ce/ γ -Al₂O₃. Catalysts were reduced at 300 °C in 5 vol% H₂/He for 1 h prior to the acquisition of the XPS spectra. *In-situ* DRIFT spectra of CO adsorption at 25 °C on Ce/ γ -Al₂O₃, Cu/ γ -Al₂O₃, and Cu-Ce/ γ -Al₂O₃ (c) show no CO adsorption on Ce/ γ -Al₂O₃ and CO adsorption on the Cu⁺ sites in Cu/ γ -Al₂O₃ and Cu-Ce/ γ -Al₂O₃. Prior to CO adsorption-desorption experiment, all catalysts were reduced by 5% H₂ at 300 °C for 1h. The spectra were collected after 60 min purging with Ar for Cu/ γ -Al₂O₃ and Cu-Ce/ γ -Al₂O₃, and 20 min purging with Ar for Ce/ γ -Al₂O₃.

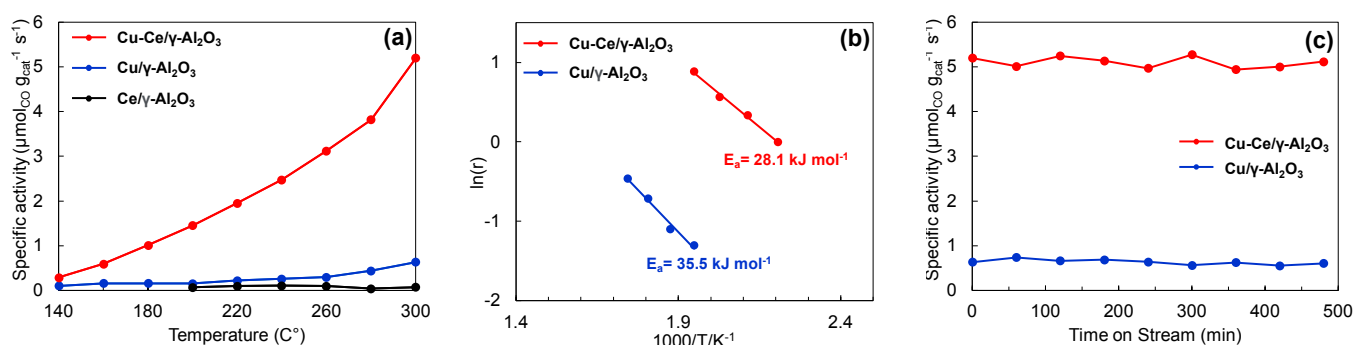


Fig. 3. Plots of WGS specific activity vs. temperature over $\text{Ce}/\gamma\text{-Al}_2\text{O}_3$, $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$, and $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalysts (a) clearly show significantly enhanced activity of the $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst. Arrhenius plots for WGS over $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ (b). Long-term stability tests over $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalysts at 300 °C (c) demonstrate the stability of both catalysts during low-temperature WGS. Reaction condition: 1% CO + 10% H_2O + He balance, $\text{SV}=74,400 \text{ ml g}^{-1} \text{ h}^{-1}$. The $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst contains 1.2 wt% Cu and 2.2 wt% Ce; the $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ catalyst contains 1.4 wt% Cu.

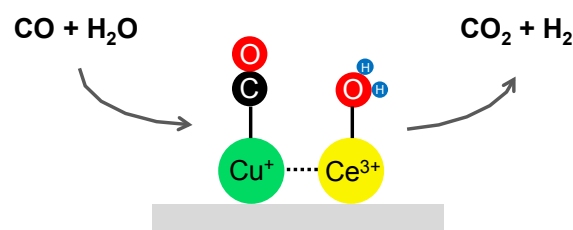
the $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$, assignable to linear CO adsorption on single Cu^+ species.^{21,22} The red-shifted, prominent band at 2102 cm^{-1} on the $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst demonstrates strong Cu^+ interaction with Ce^{3+} species.^{23,24}

It has been reported that under oxidative conditions atomically dispersed Cu species maintain a 2+ valance state while under reducing conditions some of the anchored Cu^{2+} species can be reduced to Cu^+ .²⁵ However, variations in the reducibility of copper species in the $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ catalyst have been reported.^{25,26} Previous studies showed that the atomically dispersed Cu^{2+} species in a 0.5 wt% $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst could not be reduced in H_2 at temperatures up to 700 °C.²⁶ Some of the strongly anchored Cu^{2+} species in our $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ catalyst might not have been reduced after the mild reduction treatment in H_2 at 300 °C. The increased amount of the Cu^+ species in the reduced $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst suggests that the atomically dispersed Ce^{3+} species facilitated the reduction of the Cu species, in agreement with those reported in literature.^{17,27-29} Our XPS and DRIFTS results confirmed that the presence of alumina-anchored Ce^{3+} species increased the amount of Cu^+ species after mild H_2 reduction at 300 °C. Modification of the alumina support may increase the maximum loading level of the atomic Ce species and subsequently enhances the number of active Cu^+ species in the reduced $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst.

The CO conversion (Fig. S8, ESI†) and the specific reaction rates (Fig. 3a) as a function of temperature over the $\text{Ce}/\gamma\text{-Al}_2\text{O}_3$, $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalysts show that at WGS temperatures ≤ 300 °C, the $\text{Ce}/\gamma\text{-Al}_2\text{O}_3$ (2.2 wt% Ce) did not convert much CO at all. The $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ (~1.2 wt% Cu and 2.2 wt% Ce), on the other hand, gave a reaction rate of $1.4 \mu\text{mol}_{\text{CO}} \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1}$ at 200 °C, about nine times higher than that ($1.6 \times 10^{-1} \mu\text{mol}_{\text{CO}} \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1}$) over the $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ (~1.4 wt% Cu) control catalyst. Kinetic experiments (Fig. 3b) showed an apparent activation energy (E_a) of 28.1 kJ mol^{-1} for WGS on the $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$, much lower than the 35.5 kJ mol^{-1} of the $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$. The impact of possible residue Na ions in the $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst on the WGS activity was negligible (Fig. S9, ESI†). The fact that the specific activity of WGS almost linearly increases with the total number of Cu atoms in the $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalysts (Fig. S10, ESI†) suggests that the Cu species were most probably atomically dispersed or isolated from each other. The activity of

the atomically dispersed $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst is comparable to those of the CeO_2 supported Cu catalysts (Table S2, ESI†). Our atomically dispersed $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst, however, contained only 2.2 wt% Ce and 1.2 wt% Cu, significantly lower than those of the traditional Cu/CeO_2 catalysts reported in literature. The long-term WGS tests at 300 °C (Fig. 3c) showed that both the $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalysts were stable. Atomic resolution HAADF images of the used $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ (Fig. S11, ESI†) and $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ (Fig. S12, ESI†) catalysts (after 8 hours of continuous WGS reaction) did not show sintering of the atomically dispersed Cu and Ce species.

Isolated Cu^+ sites are active for CO adsorption.^{9,25,30,31} On reducible oxides, water adsorption/dissociation are generally considered to occur on the neighboring sites of the Cu^+ species (i.e. Ti^{3+} , $\text{Ce}^{3+}\text{-O}_v$, Cu^0);^{9,30-32} competitive adsorption of both CO and H_2O molecules, and slow H_2O dissociation, on individually isolated Cu^+ sites pose limitations on the WGS on atomically dispersed $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ catalysts.³³ Experimental and computational results revealed that single Ce atoms adsorb water molecules and facilitate their dissociation process.^{34,35} Furthermore, the electronic interaction between highly active Ce species and transition metals might modulate the adsorption strength of intermediate species and expedite the reaction kinetics.²⁷ Although we could not unambiguously identify the individual atomic arrangements of the Cu and Ce atoms at this stage, our microscopy and spectroscopy characterization results strongly suggest that the Cu^+ and Ce^{3+} species are in intimate contact with each other. Therefore, we propose that the active centers of the $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst consist of $\text{Cu}^+\text{-Ce}^{3+}$ complexes and that the Cu and Ce cations work



Scheme 1. Schematic diagram illustrates the synergistic effect of the intimate contact between the Cu^+ and Ce^{3+} on the adsorption of the reactant molecules to facilitate the water-gas shift reaction.

synergistically toward the WGS (Scheme 1): the Ce^{3+} adsorbs and dissociates H_2O and the Cu^+ adsorbs CO . The close proximity of activated CO and OH species facilitates formation of intermediates (e.g., carboxyl) and their subsequent decomposition to CO_2 and H_2 . We could not rule out the presence of small amount of the $\text{Cu}_x^+-\text{Ce}_y^{3+}$ species at this stage. Further elaborate synthesis experiments and full catalyst characterizations are needed to provide a fundamental understanding of the atomically dispersed $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst systems.

In summary, atomically dispersed Ce and Cu species were grafted onto commercially available $\gamma\text{-Al}_2\text{O}_3$ to fabricate $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalysts. The introduction of atomically dispersed Ce species led to a remarkable enhancement of WGS rate. We proposed that the intimate contact between Cu^+ and Ce^{3+} species and their synergistic effect are responsible for the experimentally observed reaction rate enhancement. Although the atomically dispersed $\text{Cu-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalyst contained very low levels of the Ce and Cu metals, its performance is comparable to those of the best Cu/CeO_2 catalysts reported in literature. These findings highlight the synergetic effects among atomically dispersed metal species and opens new route to develop low-cost WGS catalysts. The catalyst design strategy is general and can be extended to a variety of atomically dispersed catalysts for transformation of important molecules.

This work was primarily supported by the US National Science Foundation under grant number CHE-1955474 and CHE-2247571. T.W and N.Y acknowledge the Singapore Ministry of Education Tier 2 Grant (MOE-T2EP10221-0008) for the financial support. The authors acknowledge the use of facilities within the Eyring Materials Center and the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University. The authors thank Dr. Xianchun Liu for discussions.

Data availability

All data is available in the published article and its ESI.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- C. Ratnasamy and J. P. Wagner, *Catal. Rev.*, 2009, **51**, 325–440.
- Y. Li, Q. Fu and M. Flytzani-Stephanopoulos, *Appl. Catal., B*, 2000, **27**, 179–191.
- Y. Zhou, A. Chen, J. Ning and W. Shen, *Chin. J. Catal.*, 2020, **41**, 928–937.
- X. Wang, J. A. Rodriguez, J. C. Hanson, D. Gamarra, A. Martínez-Arias and M. Fernández-García, *J. Phys. Chem. B*, 2006, **110**, 428–434.
- A. Chen, X. Yu, Y. Zhou, S. Miao, Y. Li, S. Kuld, J. Sehested, J. Liu, T. Aoki, S. Hong, M. F. Camellone, S. Fabris, J. Ning, C. Jin, C. Yang, A. Nefedov, C. Wöll, Y. Wang and W. Shen, *Nat. Catal.*, 2019, **2**, 334–341.
- J. A. Rodriguez, P. Liu, X. Wang, W. Wen, J. Hanson, J. Hrbek, M. Pérez and J. Evans, *Catal. Today*, 2009, **143**, 45–50.
- J. Liu, *ACS Catal.*, 2017, **7**, 34–59.
- J. Lin, A. Wang, B. Qiao, X. Liu, X. Yang, X. Wang, J. Liang, J. Li, J. Liu and T. Zhang, *J. Am. Chem. Soc.*, 2013, **135**, 15314–15317.
- J. Ning, Y. Zhou and W. Shen, *Sci. China Chem.*, 2021, **64**, 1103–1110.
- K. Mudiyansele, S. D. Senanayake, L. Fera, S. Kundu, A. E. Baber, J. Graciani, A. B. Vidal, S. Agnoli, J. Evans, R. Chang, S. Axnanda, Z. Liu, J. F. Sanz, P. Liu, J. A. Rodriguez and D. J. Stacchiola, *Angew. Chem., Int. Ed.*, 2013, **52**, 5101–5105.
- A. L. Cámara, S. Chansai, C. Hardacre and A. Martínez-Arias, *Int. J. Hydrogen Energy*, 2014, **39**, 4095–4101.
- P. C. P. Caldas, J. M. R. Gallo, A. Lopez-Castillo, D. Zanchet and J. M. C. Bueno, *ACS Catal.*, 2017, **7**, 2419–2424.
- Y. Bu, C. J. Weststrate, J. W. Niemantsverdriet and H. O. A. Fredriksson, *ACS Catal.*, 2016, **6**, 7994–8003.
- R. Si, J. Raitano, N. Yi, L. Zhang, S.-W. Chan and M. Flytzani-Stephanopoulos, *Catal. Today*, 2012, **180**, 68–80.
- X. Li, X. I. Pereira-Hernández, Y. Chen, J. Xu, J. Zhao, C.-W. Pao, C.-Y. Fang, J. Zeng, Y. Wang, B. C. Gates and J. Liu, *Nature*, 2022, **611**, 284–288.
- J. Z. Shyu, K. Otto, W. L. H. Watkins, G. W. Graham, R. K. Belitz and H. S. Gandhi, *J. Catal.*, 1988, **114**, 23–33.
- H. C. Kwon, Y. Park, J. Y. Park, R. Ryoo, H. Shin and M. Choi, *ACS Catal.*, 2021, **11**, 10767–10777.
- O. Sodpiban, T. Kessaratikoon, J. Smith, G. Ren, S. Del Gobbo, S. Das, M. Chi, V. D'Elia and B. C. Gates, *ACS Appl. Mater. Interfaces*, 2023, **15**, 55885–55894.
- K. Khivantsev, H. Pham, M. Engelhard, H. Aleksandrov, L. Kovarik, X. Li, J. Tian, I. Koleva, I. Song, W. Hu, X. Wei, Y. Sun, P. Tran, T. Graham, D. Jiang, D. P. Dean, C. J. Breckner, J. T. Miller, G. Vayssilov, J. Szanyi, A. Datye and Y. Wang, *ChemRxiv*, 2023.
- S. Poulston, P. M. Parlett, P. Stone and M. Bowker, *Surf. Interface Anal.*, 1996, **24**, 811–820.
- H. Wan, Z. Wang, J. Zhu, X. Li, B. Liu, F. Gao, L. Dong and Y. Chen, *Applied Catalysis B: Environmental*, 2008, **79**, 254–261.
- J. Gu, M. Jian, L. Huang, Z. Sun, A. Li, Y. Pan, J. Yang, W. Wen, W. Zhou, Y. Lin, H.-J. Wang, X. Liu, L. Wang, X. Shi, X. Huang, L. Cao, S. Chen, X. Zheng, H. Pan, J. Zhu, S. Wei, W.-X. Li and J. Lu, *Nat. Nanotechnol.*, 2021, **16**, 1141–1149.
- A. Bensalem, J.-C. Muller, D. Tessier and F. Bozon-Verduraz, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3233–3237.
- W. Tan, S. Xie, X. Wang, J. Xu, Y. Yan, K. Ma, Y. Cai, K. Ye, F. Gao, L. Dong and F. Liu, *ACS Catal.*, 2022, **12**, 12643–12657.
- F. Amano, S. Suzuki, T. Yamamoto and T. Tanaka, *Appl. Catal., B*, 2006, **64**, 282–289.
- J. H. Kwak, R. Tonkyn, D. Tran, D. Mei, S. J. Cho, L. Kovarik, J. H. Lee, C. H. F. Peden and J. Szanyi, *ACS Catal.*, 2012, **2**, 1432–1440.
- B. Yang, H. Yu, X. Jia, Q. Cheng, Y. Ren, B. He and Z. Xiang, *ACS Appl. Mater. Interfaces*, 2023, **15**, 23316–23327.
- A. Martínez-Arias, R. Cataluña, J. C. Conesa and J. Soria, *J. Phys. Chem. B*, 1998, **102**, 809–817.
- M. Fernández-García, E. Gómez-Rebollo, A. Guerrero Ruiz, J. C. Conesa and J. Soria, *J. Catal.*, 1997, **172**, 146–159.
- Z. Cui, S. Song, H. Liu, Y. Zhang, F. Gao, T. Ding, Y. Tian, X. Fan and X. Li, *Appl. Catal., B*, 2022, **313**, 121468.
- N. Zhang, S. Miyazaki, Y. Qian, Y. Jing, T. Toyao and K. Shimizu, *ACS Catal.*, 2023, **13**, 8503–8515.
- E. Shaaban and G. Li, *Commun Chem*, 2022, **5**, # 32.
- C. Chen, H. Ren, Y. He, Y. Zhan, C. Au, Y. Luo, X. Lin, S. Liang and L. Jiang, *ChemCatChem*, 2020, **12**, 4672–4679.
- F. Shen, Z. Zhang, Z. Wang, H. Ren, X. Liang, Z. Cai, S. Yang, G. Sun, Y. Cao, X. Yang, M. Hu, Z. Hao and K. Zhou, *Nat. Commun.*, 2024, **15**, 448.
- R. Zhou, Y. Yang, S. Pande, B. Qu, D. Li and X. C. Zeng, *Phys. Chem. Chem. Phys.*, 2019, **21**, 4006–4014.

Data supporting this study are included within the article and/or supporting materials.