

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository: <https://orca.cardiff.ac.uk/id/eprint/169354/>

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Ding, Changyu, Pan, Xiaoli, Gow, Isla E., Wu, Xia, Cao, Hongchen, Yu, Zhounan, Liu, Xiaoyan, Yang, Xiaofeng, Liu, Qinggang and Huang, Yanqiang 2024. Regeneration of copper catalysts mediated by molybdenum-based oxides. *Journal of Energy Chemistry* 95 , pp. 618-625. 10.1016/j.jechem.2024.04.007

Publishers page: <http://dx.doi.org/10.1016/j.jechem.2024.04.007>

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See <http://orca.cf.ac.uk/policies.html> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



Regeneration of copper catalysts mediated by molybdenum-based oxides

Changyu Ding ^{a,b}, Xiaoli Pan ^a, Isla E. Gow ^c, Xia Wu ^{a,d}, Hongchen Cao ^a, Zhounan Yu ^a, Xiaoyan Liu ^a, Xiaofeng Yang ^a, Qinggang Liu ^{a,†}, Yanqiang Huang ^a

^aCAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

^cCardiff Catalysis Institute, School of Chemistry, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, United Kingdom

^dCollege of Chemistry, Chemical Engineering and Resource Utilization, Northeast Forestry University, Harbin 150040, Heilongjiang, China

article info

Keywords:

Cu-based catalysts

Aggregation

Regeneration

Oxidation

CO₂ hydrogenation

abstract

Cu catalysts, known for their unparalleled catalytic capabilities due to their unique electronic structure, have faced inherent challenges in maintaining long-term effectiveness under harsh hydrogenation conditions. Here, we demonstrate a molybdenum-mediated redispersion behavior of Cu under high-temperature oxidation conditions. The oxidized Cu nanoparticles with rich metal-support interfaces tend to dissolve into the MoO₃ support upon heating to 600 °C, which facilitates the subsequent regeneration in a reducing atmosphere. A similar redispersion phenomenon is observed for Cu nanoparticles supported on ZnO-modified MoO₃. The modification of ZnO significantly improves the performance of the Cu catalyst for CO₂ hydrogenation to methanol, with the high activity being well maintained after four repeated oxidation-reduction cycles. In situ spectroscopic and theoretical analyses suggest that the interaction involved in the formation of the copper molybdate-like compound is the driving force for the redispersion of Cu. This method is applicable to various Mo-based oxide supports, offering a practical strategy for the regeneration of sintered Cu particles in hydrogenation applications.

1. Introduction

Copper (Cu) exhibits tunable electronic states capable of participating in reactions via both one- and two-electron pathways [1], a property that has propelled the use of Cu-based catalysts across a variety of chemical reactions [2–4]. Notably, the distinctive hydrogenation selectivity of Cu has established its prominence in the synthesis of methanol from synthesis gas (CO₂/CO/H₂), achieving an annual output of approximately 171.84 million metric tons in 2022 [5,6]. However, the low reduction potential of Cu makes the copper-support interface vulnerable to damage in harsh hydrogen environments, which induces the migration and aggregation of Cu nanoparticles, posing a significant obstacle to the durability of copper-based nano-catalysts in hydrogenation reactions [7–10]. This agglomeration results in the loss of catalytic active sites and

leads to irreversible catalyst deactivation, requiring replacement of the catalyst through production shutdowns [11,12].

In order to regenerate the active sites of the nano-catalysts after metal sintering, it's necessary to break down the big particles into smaller clusters. Several studies have shown that Cu nanoparticles (NPs) can be redispersed by appropriate treatments [13,14]. Upon heating, various compounds, such as N₂, NO, and O₂, can weaken the bonds between surface atoms and the bulk through electron transfer, promoting the redispersion of Cu NPs into smaller clusters [15–18]. In addition to the redispersion caused by the effects of these environments, there are also reactant-mediated redispersion strategies. The latest research has highlighted the effectiveness of methanol in breaking bonds within Cu NPs. Specifically, on the surface of dealuminated Beta zeolite, Cu atoms mobilized by methanol are captured by silanol nests, serving as novel nucleation sites to form smaller clusters [19]. However, treatments aimed at initiating such redispersion behaviors often need supports with defects to anchor the mobile metal atoms [16,20]. These anchoring sites may reconstruct or deactivate during the reaction process, bringing

† Corresponding author.

E-mail address: liuqg@dicp.ac.cn (Q. Liu).

challenges for the application of these catalysts in repeated regeneration cycles.

Here, we report a molybdenum-mediated redispersion strategy for regenerating sintered Cu catalysts, which can disrupt the large Cu NPs under high-temperature oxidation conditions and ultimately dissolve them into the molybdenum-based oxide support. Upon subsequent reduction of these samples, Cu NPs reappear on the MoO₃ support, resulting in a high Cu surface area comparable to that of the fresh catalyst. In situ X-ray diffraction (XRD) results provide clear evidence of the redispersion process of Cu on various molybdenum-based supports, accompanied by the formation of copper molybdate-like compounds. Density functional theory (DFT) calculations suggest that the formation of copper molybdate-like compounds is thermodynamically favored under high-temperature oxidation conditions, which provides a sufficient thermodynamic driving force to disrupt the metal lattice. Notably, doping other oxides into MoO₃ will not quench the driving force required for Cu redispersion. This featuring advantage allows the Mo-mediated redispersion strategy to be applicable to a range of Mo-based oxide supports, thus offering a pragmatic strategy for the regeneration of sintered Cu catalysts for a variety of applications.

2. Experimental

2.1. Sample preparation

The MoO₃-supported Cu catalysts (CuMo) were synthesized via a co-precipitation method. For instance, the CuMo catalyst with a Cu metal loading of 37 wt% was prepared as follows. Initially, 14.25 g of Cu(NO₃)₂·3H₂O and 8.60 g of (NH₄)₆Mo₇O₂₄·4H₂O were dissolved in 150 mL of deionized water. Subsequently, a freshly prepared solution of N(CH₂CH₃)₃ (16.5 mL in a mixture of 250 mL ethanol and 50 mL deionized water) was rapidly introduced into the aforementioned solution at room temperature (RT). The mixture was then stirred continuously for 30 min. The filtered solid was washed multiple times with water and ethanol, followed by drying at 100 °C. This dried precursor was calcined at 600 °C for 2 h. The resulting orange catalyst (CuMo^{1st}) underwent

further treatment under an H₂ atmosphere (20 mL/min) at 250 °C for 30 min, producing CuMo^{1st}-H₂. The CuMo^{1st}-H₂ catalyst was then subjected to a further calcination procedure at 600 °C for 2 h, to produce the CuMo^{2nd} catalyst. Following an additional reduction treatment at 250 °C for 30 min, the CuMo^{2nd}-H₂ catalyst was produced. By repeating this cycle using the same catalyst, CuMo^{3rd}, CuMo^{3rd}-H₂, CuMo^{4th}, and CuMo^{4th}-H₂ were obtained.

CuZnMo catalysts were synthesized using methods similar to those detailed for CuMo. Catalysts such as Cu/ZnMoO₄, Cu/MoO₃ and Cu/M_x(MoO₄)_y (where M = Ce, Al, Zr, and Fe), were produced by impregnating Cu(NO₃)₂ onto the respective carriers, achieving a Cu content of 5 wt%. The control catalyst Cu/ZnO was obtained by co-precipitation method. For a comprehensive description of these methods, refer to the [supplementary material](#).

2.2. Catalysis and structure characterization

The catalytic efficiency of the synthesized materials was assessed using a methanol synthesis reaction via CO₂ hydrogenation in a fixed-bed reactor. Experiments utilized 0.5 g of CuMo and CuZnMo at 240 °C and 5 MPa, with a gas hourly space velocity (GHSV) of 1500 h⁻¹ and a gas ratio of n(CO₂)/n(H₂)/n(Ar) = 23/69/8. Prior to the reaction, the CuMo and CuZnMo precursors were pre-reduced in H₂ flow (30 mL/min) at 250 °C for 0.5 h. The gaseous products were analyzed by gas chromatography.

The content of elements in the catalysts was detected by an inductively coupled plasma optical emission spectrometer (ICP-OES, 7300DV). XRD was used to identify the phase composition of the catalysts on an Empyrean diffractometer with Cu-Kα (40 kV, 40 mA) radiation. The structural details of the Cu-based catalysts and the elemental distribution were analyzed by combining high-angle annular dark-field (HAADF) imaging in the scanning transmission electron microscope (STEM, JEM-2100F) with energy dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM, JSM-7800F). 5 mg of CuZnMo^{1st}-H₂ was placed inside the thermogravimetric analyzer (TG, NETZSCH). The thermogravimetric weight curve (TGA) and the weight derivative curve (DTG) were recorded during the process of heat-ing at a rate of 10 °C/min to 600 °C under an air atmosphere. The chemical states of Cu, Zn, Mo, and O were investigated through X-ray photoelectron spectroscopy (XPS, Thermofisher Escalab 250 Xi+). The X-ray absorption spectra (XAS), encompassing X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at the K-edge of Cu, at the beamline 11B of the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Advanced Research Institute, China. A double Si(111)-crystal monochromator was employed to select the X-ray energy, which was calibrated against a Cu foil. The XAS data were processed and analyzed via the Athena software package. The k³-weighted EXAFS functions (V(k)) underwent Fourier transformation over a k-range of 3–11.5 Å⁻¹. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were carried out using a Bruker Vertex V70 equipped with a mercury cadmium telluride (MCT) detector.

3. Results and discussion

3.1. Regeneration of CuMo catalysts with repeated oxidation-reduction cycles

Redispersion of the MoO₃-supported Cu NPs was achieved by calcining the catalysts at 600 °C in static air. The CuMo catalysts exhibit thermochromic characteristics. The following regeneration of the catalyst can be discerned via the alteration in color ([Fig. 1a](#)). The CuMo^{1st} exhibit a yellow color after calcination. Upon exposure to a reducing atmosphere, the Cu species is reduced to its metallic state, leading to the material transforming into a black powder. Alvarez-Fregoso et al. reported that within CuMoO_x compounds, an increase in Mo content leads to a color transition from black to golden yellow [\[21\]](#). Such color variations are important in the production of colored composite Cu thin films, as these changes in color are closely associated with the amount and distribution of Cu-metal bonds [\[22–24\]](#).

The cyclic regeneration capacity of Cu was further confirmed by the XRD measurements. The XRD results show that the yellow CuMo^{1st} catalyst is composed of Cu₃Mo₂O₉ and CuMoO₄ ([Fig. 1b](#)) [\[25\]](#). In the reduced CuMo^{1st}-H₂ catalyst, metallic Cu emerges as the dominant phase ([Fig. 1c](#)). According to the Scherrer formula, the particle size of Cu after each reduction is calculated to be around 33 nm ([Fig. 1c](#)). Extraction of Cu from the copper molybdates leaves the molybdenum oxides a defective and amorphous structure. In situ DRIFTS experiments show the same CO adsorption bands across the CuMo^x-H₂ catalysts ([Fig. 1d](#)), providing evidence of the consistency of Cu electronic states in these catalysts [\[26\]](#). XRD analysis also reveals the recovery of the CuMo^x structure after each calcination cycle ([Fig. 1b](#)). Interestingly, no CuO phase is observed in these CuMo^x catalysts, which indicates that the oxidized Cu is dissolved in and reacts with the support to form Cu₃Mo₂O₉ and CuMoO₄.

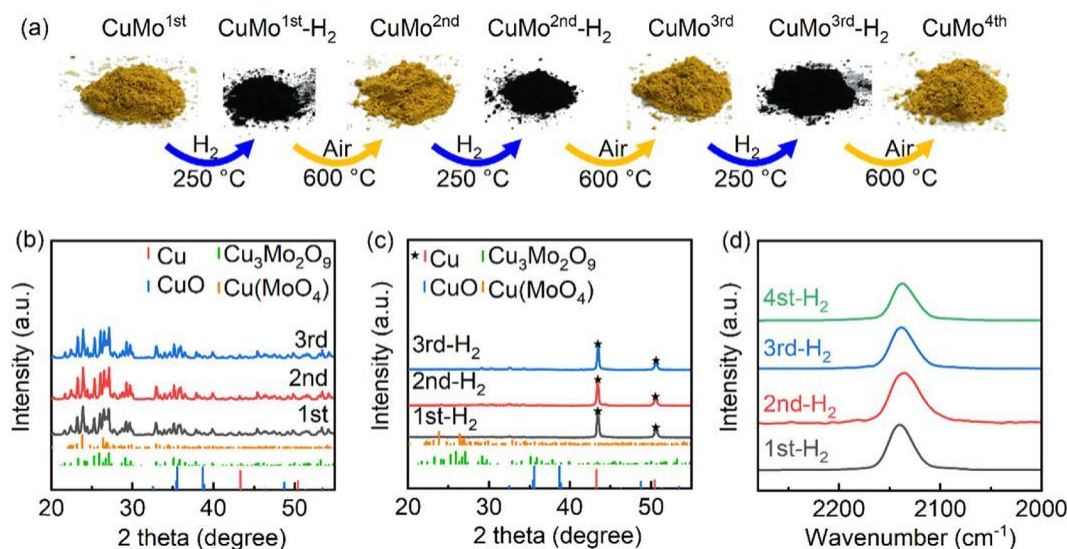


Fig. 1. (a) Structure and color changes in the CuMo^x (x = 1st, 2nd, 3rd, and 4th) and CuMo^x-H₂ catalysts. XRD patterns of CuMo^x (b) and CuMo^x-H₂ (c). In situ DRIFTS results of CO adsorption over the reduced CuMo^x-H₂ catalyst after four repeated oxidation–reduction cycles (d).

3.2. Regeneration of CuZnMo catalysts with repeated oxidation–reduction cycles

To investigate the effects of doping with other oxides on the redispersion behavior of Cu NPs, subsequent studies were conducted on CuZnMo catalysts. Similar to the CuMo catalysts, the CuZnMo catalysts also exhibit inherent thermochromic properties. After calcination, the CuZnMo^{1st} catalyst appears dark green, which transitions to black after reduction (CuZnMo^{1st}-H₂), and reverts to dark green after a subsequent high-temperature calcination (CuZnMo^{2nd}). This color-change cycle provides evidence of the regenerative capability of the CuZnMo catalysts (Fig. 2a). XRD results indicate that the Cu species in the CuZnMo catalysts mainly exist in the form of CuZn₂(MoO₄)₂O (Fig. 2b and c). Interestingly, the introduction of ZnO into CuMo catalysts does not suppress the redispersion behavior of Cu NPs. This inference could be confirmed by XPS and in situ DRIFTS measurements, as the CuZnMo catalyst exhibits consistent valence states (Fig. S1) and similar

CO adsorption behavior after four repeated oxidation–reduction cycles (Fig. 3a) [27,28].

The identical structure of the CuZnMo^x-H₂ catalyst can be further confirmed by the Cu K-edge XANES. The CuZnMo^x-H₂ catalysts display XANES spectra similarly with that of Cu foil (Fig. 3b). EXAFS analysis about CuZnMo^x-H₂ reveals a consistent coordination number (CN) for the Cu-Cu shell (10.6 to 11.1) (Fig. 3c). These results indicated that the reduced CuZnMo^x-H₂ catalysts are primarily in the metallic state and have the similar average particle sizes [29]. Moreover, the first derivative maxima of the XANES spectra for CuZnMo^{2nd} and CuO appear at the same energies, indicating a Cu²⁺ dominance in the CuZnMo^{2nd}. Notably, the pre-edge peak shape is very sensitive to changes in the coordination environments. The difference in the shape of XANES spectra between the CuZnMo^{2nd} and CuO clearly indicates that the Cu species in CuZnMo^{2nd} is not present as CuO [30]. Combining the results of XRD findings, CuZn₂(MoO₄)₂O phase appearing in the CuZnMo^{2nd} catalyst could be the reason for the difference between the XANES

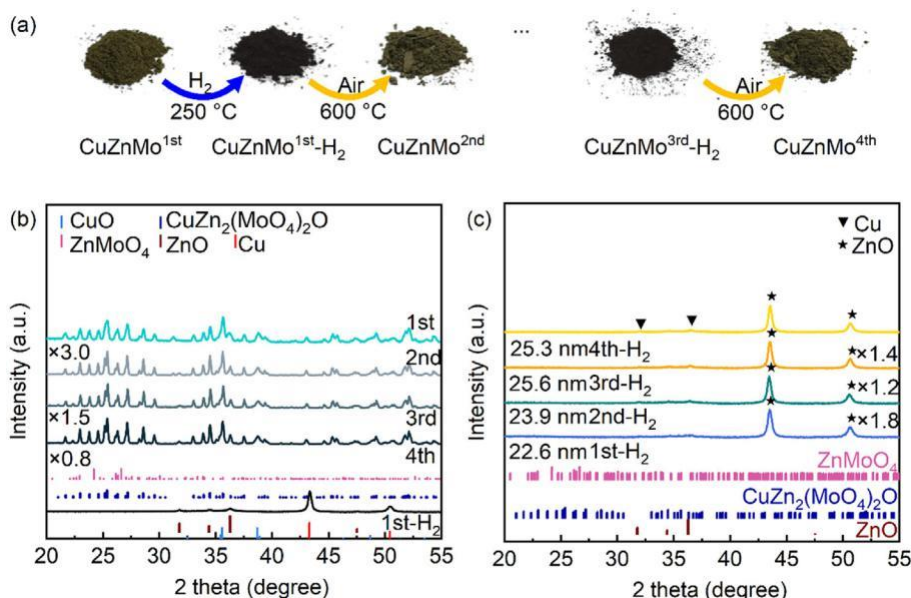


Fig. 2. (a) Structure and color changes in the CuZnMo^x (x = 1st, 2nd, 3rd, and 4th) and CuZnMo^x-H₂ catalysts. XRD patterns of CuZnMo^x (b) and CuZnMo^x-H₂ (c).

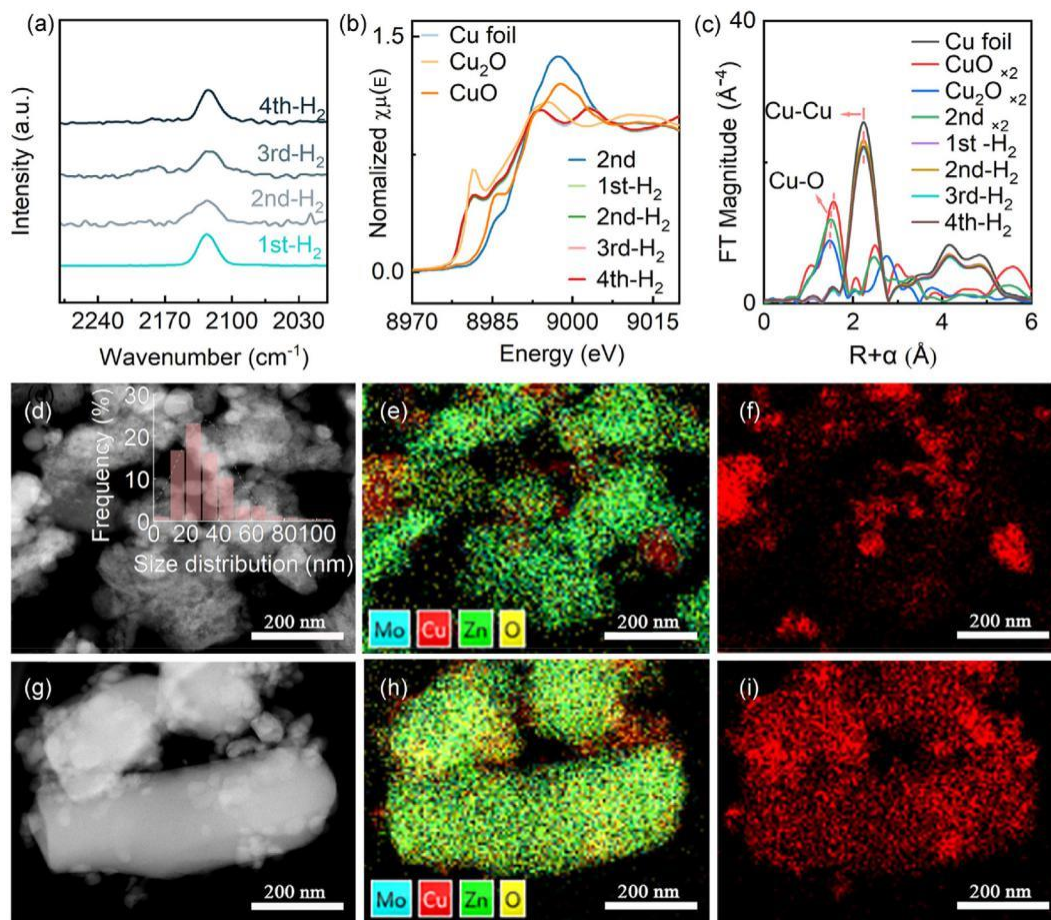


Fig. 3. (a) In situ DRIFTS results of CO adsorption over the $\text{CuZnMo}^x\text{-H}_2$ catalysts. Normalized XANES (b) and EXAFS (c) spectra of $\text{CuZnMo}^x\text{-H}_2$ ($x = 1\text{st}, 2\text{nd}, 3\text{rd}, \text{and } 4\text{th}$), $\text{CuZnMo}^{2\text{nd}}$, Cu_2O , CuO , and Cu foil. HAADF-STEM and the corresponding EDS images of $\text{CuZnMo}^{1\text{st-H}_2}$ (d–f) and $\text{CuZnMo}^{2\text{nd}}$ (g–i). The red color shows the distributions of Cu elements in $\text{CuZnMo}^{1\text{st-H}_2}$ (f) and $\text{CuZnMo}^{2\text{nd}}$ (i), respectively. Inset in (d): the particle size distribution of Cu NPs.

spectra, which may change the spatial symmetry of Cu. Hence, the analysis confirms that the sintered Cu NPs have integrated into the Mo-based oxide.

The structure changes of the CuZnMo catalysts during the oxidation-reduction cycles were subsequently monitored by HAADF-STEM (Fig. 3d–i and Figs. S2–S7). The images show that high-temperature reduction results in the formation of metallic Cu NPs. The Cu NPs are generally well dispersed ranging in size from 30–50 nm, with occasional formation of large agglomerates exceeding 100 nm. The distribution map of Cu element depicted in red offers an overview of the Cu aggregation state (Fig. 3f). In contrast, Zn and Mo elements in the reduced catalysts appear uniformly dispersed, indicating that the reduction conditions do not adversely affect the carrier material (Fig. 3e). Interestingly, sup-ported Cu NPs exhibit size-dependent redispersion behavior upon heating to 600 LC under oxidation conditions (Fig. 3i). The separated Cu NPs exceeding 100 nm show a tendency to further segregate. Conversely, Cu NPs within the 30–50 nm range featuring a rich Cu-ZnMoO_x interface are prone to dissolution into the support. These findings imply that the Cu-ZnMoO_x interface could serve as a crucial atomic transport pathway, facilitating the diffusion of Cu atoms from the Cu NPs into the support. Notably, the redispersion behavior of Cu NPs consistently persists across repeated oxidation-reduction treatments, with the $\text{CuZnMo}^{3\text{rd}}$ and $\text{CuZnMo}^{4\text{th}}$ catalysts showing uniformly dispersed Cu species (Figs. S4–S6).

The redispersion behavior of Cu NPs was further confirmed by depositing Cu NPs on the ZnMoO_4 support using the impregnation

method. To maximize the metal-support interface, the Cu loading was lowered to 5 wt%. XRD results show that Cu is highly dispersed on the surface of ZnMoO_4 , with no peaks corresponding to metallic Cu species being detected (Fig. S8). Interestingly, after oxidation treatment at 600 LC, distinct $\text{CuZn}_2(\text{MoO}_4)_2\text{O}$ diffraction peaks are observed by XRD, indicating that Cu NPs undergo dispersion and integrate into the lattice of ZnMoO_4 .

3.3. Performance of Cu-based catalyst in CO₂ hydrogenation to methanol

Cu-based heterogeneous catalysts are widely used to catalyze the CO₂ hydrogenation to methanol [31], but questions remain about the catalytic efficiency. Subsequent investigations into the capacity of the Cu catalysts to perform selective catalytic hydrogenation of CO₂ were performed. Cu NPs supported on the MoO_3 surface exhibit very low performance (Fig. 4a). Interestingly, the addition of ZnO to CuMo-H_2 significantly enhances the catalytic activity and stability for methanol synthesis. Under reaction conditions at 240 LC, the conversion rate of CO₂ reaches 14%, with a methanol selectivity of over 54% (Fig. 4b). The cycle performance of the CuZnMo-H_2 catalyst was investigated, revealing that the catalyst regains 90% of its initial activity. This finding is supported by the XRD results, which demonstrate a consistent particle size throughout the oxidation-reduction cycles (Fig. 4b). The gradual loss of the cycle performance may be attributed to the agglomeration of segregated large Cu particles during high-temperature

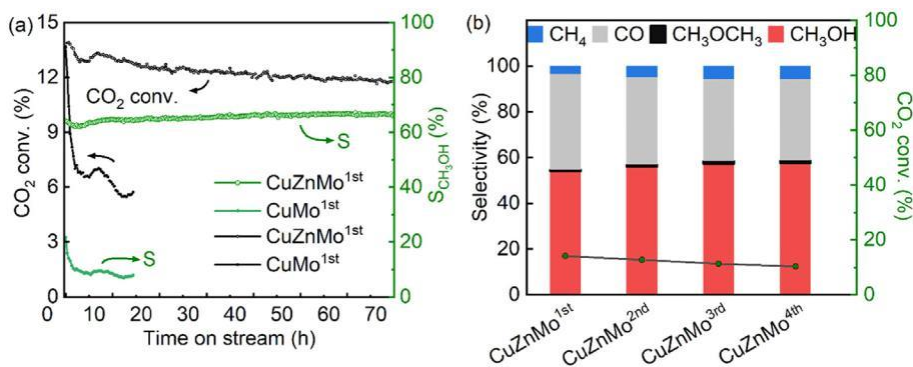


Fig. 4. (a) Long-term catalytic performance of CuMo^{1st} and CuZnMo^{1st}. (b) Catalytic performances of the CuZnMo^x-H₂ (x = 1st, 2nd, 3rd, and 4th) catalysts in CO₂ hydrogenation. Reaction conditions: 240 LC, 5 MPa, GHSV of 1500 h⁻¹, and n(CO₂)/n(H₂)/n(Ar) = 23/69/8.

treatment. The lack of sufficient Cu-ZnMoO_x interfaces will largely hinder the redispersion of Cu into the support. However, such regeneration of Cu NPs mediated by MoO_x remains of significant importance for the application of Cu-based catalysts in hydrogenation reactions. Additionally, there are slight differences in the catalytic performance of CuZnMo^{1st}-H₂ reduced at different temperatures (Fig. S9). Overall, reduction at lower temperatures (220 LC) results in higher CO₂ conversion rates. However, the methanol selectivity does not show a monotonic trend, which may be related to the particle size distribution and partial reduction of Cu species.

3.4. Mechanistic study on the regeneration mechanism of the Mo-based catalysts

To understand the mechanism of Cu regeneration on the MoO₃ support, in situ XRD measurements were performed (Fig. 5). The results suggest that the CuMo catalyst is primarily composed of a mixture of CuMoO₄ and Cu₃Mo₂O₉ phases after calcination at 600 LC (Fig. 5a). The reduction exsolution of the Cu species from the CuMoO₄ and Cu₃Mo₂O₉ lattice leaves the MoO₃ support amorphous. Upon exposure to air and heating to 300 LC, the metallic Cu NPs are oxidized and react with the amorphous MoO_x to form CuMoO₄, implying the initiation of Cu dispersion. At 400 LC, the dispersion of Cu is notably enhanced, as indicated by stronger CuMoO₄ peaks. The accumulation of Cu atoms on the MoO₃ surface to a critical threshold induced a surface strain-related phase transition. Consequently, a new Cu₃Mo₂O₉ phase emerges at 500 LC. It is important to note that high-temperature treatment at 600 LC is essential for achieving complete dispersion of Cu species. With the continued growth of the Cu₃Mo₂O₉ phase, the CuMo catalyst ultimately reverts to its initial composition.

Mechanistic investigations using in situ XRD were also carried out for the CuZnMo catalyst (Fig. 5b). In the calcined CuZnMo catalyst, the Cu species predominantly exists in the CuZn₂(MoO₄)₂O phase. Metallic Cu forms upon reduction at 250 LC, leading to the dissolution of the CuZn₂(MoO₄)₂O structure (Fig. 5c). Transitioning to an air atmosphere and elevating the temperature facilitates the crystallization of the ZnMoO_x, as shown by an increase of the ZnMoO₄ peak. Different from the MoO₃ support, the dispersion of Cu on the ZnMoO_x takes place only upon 600 LC. At this temperature, the ZnMoO₄ phase disappears and gives way to a CuZn₂(-MoO₄)₂O structure (Fig. 5b), meaning the integration of Cu into the ZnMoO₄ lattice. During the subsequent two hours at 600 LC, no notable changes in the composition of the catalyst are detected (Fig. 5d).

The variations in the oxidation state of Cu during high-temperature oxidation treatment were tracked using XPS (Fig. 6a and b). Interestingly, the oxidation treatment of the CuMo-H₂ and CuZnMo-H₂ catalysts reveals a similar pattern of valence state changes in Cu. The CuMo-H₂ catalyst is primarily composed of metallic Cu⁰ initially (Fig. 6a). Trace amounts of Cu²⁺ likely comes from the exposure to the air in the preparation of XPS. An elevation in Cu²⁺ levels is recorded as temperature increases, marked by the intensification of satellite peaks in the Cu 2p spectra. Note that the shape of these satellite peaks also depends on the coordination environment of the Cu²⁺ species [32,33]. The spectral changes observed in CuMo-H₂-600 compared to CuMo-H₂-300 clearly indicate the integration of Cu into the MoO_x matrix.

To elucidate the role of ZnO in the dispersion process, Cu nano-catalysts loaded on ZnO were prepared using the impregnation method, and their structural changes during the reduction-oxidation cycle were monitored (Figs. S10 and S11). XRD analysis reveals that metallic Cu NPs can be transformed into CuO NPs under oxidizing conditions but fail to disperse into the ZnO lattice (Fig. S11). The irreversible regeneration of the Cu/ZnO clearly indicates that the dispersion of Cu is primarily dictated by the presence of Mo species in the support, rather than by ZnO.

The research findings above indicate that the Mo-mediated Cu dispersion can only occur in an oxidizing atmosphere, but questions remain about the role of O₂ molecular in the dispersion process. TGA result shows that the reduced CuZnMo-H₂ catalyst experiences a slight mass loss below 100 LC in an air atmosphere (Fig. 6c). This may be attributed to minor dehydration. Between 100 and 425 LC, the mass of the catalyst continues to increase due to the oxidation of Cu, resulting in a 7.7% increase in mass. Note that with further temperature increases, no significant mass change has occurred. These results indicate that, prior to dispersion, the metallic Cu NPs have been fully oxidized to CuO. Besides, despite the significant structural alterations induced by Cu dispersion, the morphology of the catalyst remains a floral shape throughout the treatment cycles (Fig. 6d and Fig. S12).

In order to reveal the role of molecular O₂ in the dispersion process, the treatment atmosphere was studied. The XRD results reveal that the reduced CuZnMo-H₂ catalyst tends to agglomerate at 600 LC in an Ar atmosphere (Fig. 6e). By subjecting the CuZnMo-H₂ catalyst to air at 250 LC and subsequently exposing it to 600 LC in an Ar environment, the dispersion of Cu is triggered, associated with the generation of CuZn₂(MoO₄)₂O (Fig. 6f). This implies that O₂ does not directly participate in the dispersion process of Cu. In combination with the in situ XRD results, the interface reconstruction leading to CuZn₂(MoO₄)₂O phase formation at 600 LC, could be the primary driving force for the dispersion of the CuO.

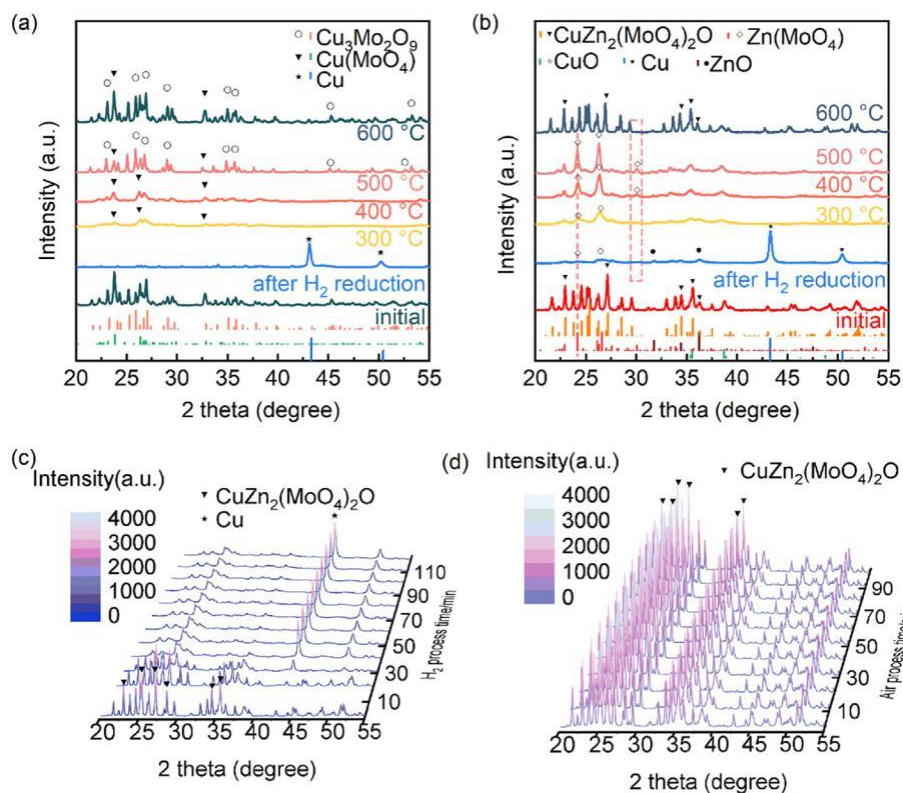


Fig. 5. In situ XRD patterns of CuMo (a) and CuZnMo (b). This figure shows the structural changes in CuMo and CuZnMo catalysts. Initial XRD spectra were taken at 25 LC, followed by a hydrogen reduction at 250 LC, cooling, and then gradual heating to 600 LC in air. In situ XRD patterns of CuZnMo^{1st} during 250 LC reduction (c) and subsequent 2 h isothermal treatment at 600 LC in air (d).

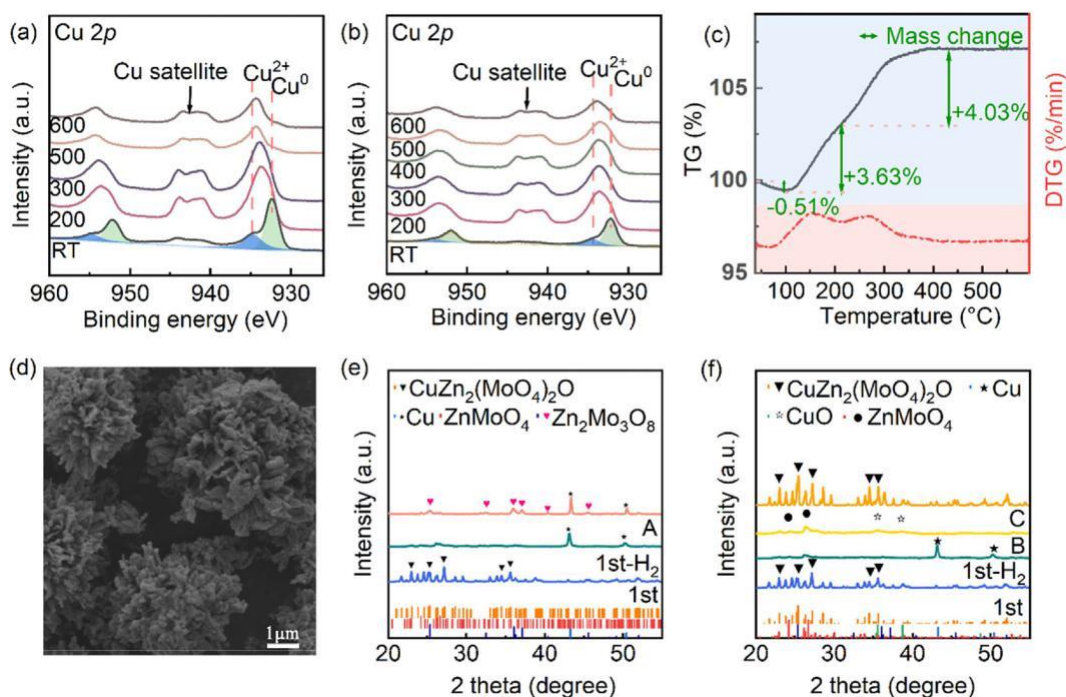


Fig. 6. Cu 2p XPS results from CuMo-H₂-x (a) and CuZnMo-H₂-x (b), (where x indicates the calcination temperature). (c) TGA curve for CuZnMo-H₂ under an air atmosphere during the process of heating to 600 LC and the derivative of the curve. (d) SEM image of the CuZnMo-H₂ after re-calcination at 450 LC. The XRD results in the process: CuZnMo^{1st} were reduced with H₂, then heated to 600 LC in Ar (marked as A in the figure) without air exposure (e). In contrast, in experiments involving oxygen (f), CuZnMo^{1st}-H₂ was firstly subjected to thorough oxidation at a lower temperature of 250 LC in air (marked as B). After oxidation treatment, the catalysts were heated to 600 LC in an Ar atmosphere (marked as C).

3.5. DFT calculations

To elucidate the regeneration of Cu NPs at the atomic-level, DFT calculations were performed. The initial step is the desorption of a Cu atom from the Cu₁₃ cluster (comprising 13 atoms). The Cu₁₃ cluster with high cohesive energy tends to be spherical on the MoO₃(0 1 0) surface (Fig. 7a). A significant energy requirement (0.45 eV) indicates that the direct detachment of a Cu atom from the Cu₁₃ cluster to adjacent oxygen sites is hindered by the strong Cu–Cu bonding. Interestingly, under oxidizing atmospheres, surface oxidation of the Cu₁₃ cluster will disrupt the metal lattice, leading to the detachment and migration of Cu atom energetically favorable. This is consistent with the experimental observations that the dispersion is initiated only when the Cu NPs are oxidized.

Fig. 7(b) illustrates the energy profile for the stepwise migration of Cu atoms on the MoO₃(0 1 0) surface. Cu adatoms preferentially settle at the bridge sites between two terminal O atoms on the surface. The diffusion energy required for Cu to move from one site to the adjacent bridge site is calculated to be 0.74 eV, which can be easily overcome under operating conditions, such as at 600 LC. As the dispersion process proceeds, there is an increase in the concentration of surface Cu atoms on the MoO₃(0 1 0). Once the surface concentration of Cu exceeds the critical threshold, a surface reconstruction is initiated, leading to the formation of CuMoO₄ and Cu₃-MoO₆ phases [34,35].

Additionally, the detachment of Cu atoms from a Cu₁₃ cluster on the ZnMoO₄(0 1 0) surface was explored (Fig. 7c and d). The lower energy inputs for the Cu detachment from the partially oxidized Cu₁₃ cluster further implies that the surface oxygen species can facilitate the breaking of Cu clusters. With the formation of a copper zinc molybdate phase as the thermodynamic driving force, the Cu₁₃ cluster exhibits a similar dispersion behavior to that on the MoO₃(0 1 0) surface. The energy barrier for Cu adatom diffusion among various oxygen sites varies between 0.79 to 0.25 eV, aligning well with the 600 LC operational temperature.

Based on the above analysis, the regeneration of Cu NPs on Mo-based supports as a multi-step process involving: (i) oxygen adsorption on the Cu surface to facilitate Cu–Cu bond cleavage;

- (ii) detachment of activated Cu atoms to adjacent oxygen sites;
- (iii) migration of Cu adatoms on the oxide support; and (iv) surface reconstruction to form CuMoO₄-like compounds.

Notably, doping other oxides into MoO₃ will not quench the thermodynamic driving force required for Cu dispersion. This inference has been well confirmed by supporting Cu NPs on various Mo-based supports, including aluminium molybdate, iron molybdate, zirconium molybdate, cerium molybdate, and trioxide molybdenum (Fig. S13). After subjecting these reduced catalysts to an air atmosphere at 600 LC, the formation of CuMoO₄-like compound is observed across all supports, indicating the occurrence of the dispersion of Cu in MoO_x. This broad applicability highlights the potential of this approach in various catalytic applications, opening avenues for further exploration in catalyst design and optimization.

4. Conclusions

This study reveals a molybdenum-mediated regeneration behaviour of Cu under oxidizing conditions. The Cu NPs tend to dissolve into the Mo-based oxides upon heating to 600 LC in an oxidative atmosphere. As the dissolution of Cu progressed, a CuMoO₄-like compound could be detected. Combining in situ spectroscopy and theoretical analysis results, the interaction involved in the formation of CuMoO₄-like compounds is confirmed as the main driving force for dispersion. Notably, this driving force is little affected by the doping of other oxides. Though, the CuMo and CuZnMo catalysts do not show superior performance than other catalysts for CO₂ hydrogenation. The solid-state reaction by oxidation-reduction provides a simple and low-cost strategy to regenerate nano catalysts. These findings provide deeper insights into the potential reaction between the metallic catalyst with the support-ing material when the atmosphere is changed. By proper design the composition of the supporting oxides, promoter, and the metallic NPs, this method can be broadly applied to the optimization of efficient, recoverable catalysts for industrial applications.

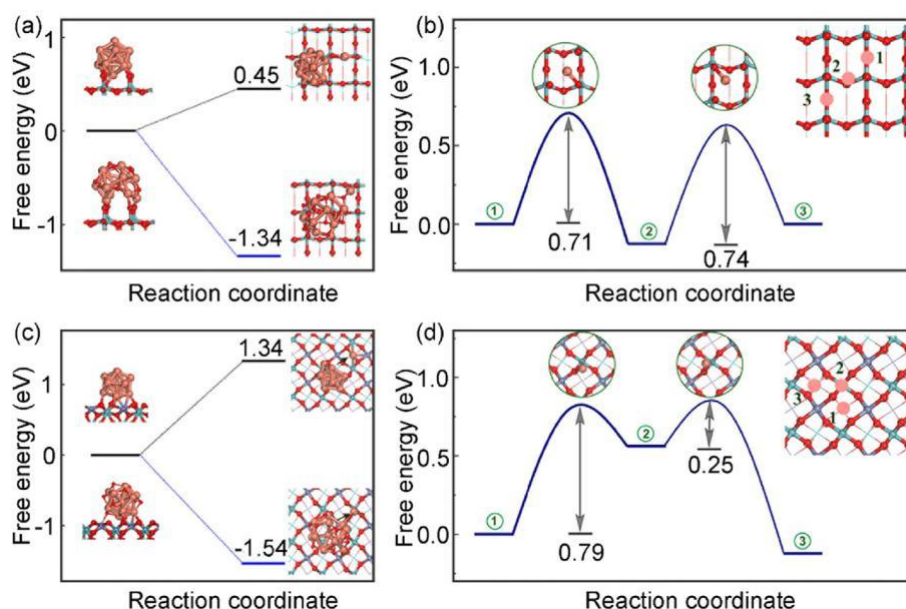


Fig. 7. (a) The DFT results showing the desorption of a Cu atom from the Cu₁₃ cluster on the MoO₃(0 1 0) surface before (top) and after (bottom) oxidation. (b) The energy profile for the stepwise migration of Cu atoms on the MoO₃(0 1 0) surface. (c) DFT studies of desorption of a Cu atom from the Cu₁₃ cluster on the ZnMoO₄(0 1 0) surface before (top) and after (bottom) oxidation. (d) The energy profile for the stepwise migration of Cu atoms on the ZnMoO₄(0 1 0) surface.

Credit authorship contribution statement

Changyu Ding: Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. Xiaoli Pan: Data curation, Formal analysis, Soft-ware. Isla E. Gow: Writing – review & editing. Xia Wu: Methodology. Hongchen Cao: Formal analysis, Visualization, Writing – original draft. Zhounan Yu: Formal analysis. Xiaoyan Liu: Data curation, Formal analysis, Supervision, Validation, Writing – review & editing. Xiaofeng Yang: Conceptualization, Resources, Writing – review & editing. Qinggang Liu: Conceptualization, Data curation, Formal analysis, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review

& editing. Yanqiang Huang: Conceptualization, Project administration, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors gratefully acknowledge the National Key Research and Development Program of China [No. 2021YFB4000700], the CAS Project for Young Scientists in Basic Research [YSBR-022], the National Natural Science Foundation of China [22008136, 21925803], and the Welsh Government funded Taith Research Mobility Programme [No. 524339].

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jechem.2024.04.007>.

References

- [1] M.B. Gawande, A. Goswami, F.-X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril, R.S. Varma, *Chem. Rev.* 116 (2016) 3722–3811.
- [2] J. Zhang, X. Sun, C. Wu, W. Hang, X. Hu, D. Qiao, B. Yan, *J. Energy Chem.* 77 (2023) 45–53.
- [3] X. Wei, Y. Liu, X. Zhu, S. Bo, L. Xiao, C. Chen, T.T.T. Nga, Y. He, M. Qiu, C. Xie, D. Wang, Q. Liu, F. Dong, C.-L. Dong, X.-Z. Fu, S. Wang, *Adv. Mater.* 35 (2023) 2300020.
- [4] Z. Zheng, Y. Yue, H. Zhuo, Q. Liu, Y. Huang, *Catal. Sci. Technol.* 14 (2024) 43–56.
- [5] F. Studt, M. Behrens, E.L. Kunkes, N. Thomas, S. Zander, A. Tarasov, J. Schumann, E. Frei, J.B. Varley, F. Abild-Pedersen, *ChemCatChem* 7 (2015) 1105–1111.
- [6] Production capacity of methanol worldwide from 2018 to 2022 <https://www.statista.com/statistics/1065891/global-methanol-production-capacity/>, 2023 (accessed 22 Feb. 2024).
- [7] J. Hao, S. Xie, Q. Huang, Z. Ding, H. Sheng, C. Zhang, J. Yao, *CCS Chem.* 5 (2023) 2046–2058.
- [8] A. Rosencwaig, G.K. Wertheim, H.J. Guggenheim, *Phys. Rev. Lett.* 27 (1971) 479.
- [9] D. Kordus, J. Jelic, M. Lopez Luna, N.J. Divins, J. Timoshenko, S.W. Chee, C. Rettenmaier, J. Kröhnert, S. Köhl, A. Trunschke, R. Schlögl, F. Studt, B. Roldan Cuenya, *J. Am. Chem. Soc.* 145 (2023) 3016–3030.
- [10] F. Jiang, T. Lan, J. Sun, G. Zhao, Y. Lu, *Nano Res.* 16 (2023) 12270–12280.
- [11] Q. Liu, X. Yang, L. Li, S. Miao, Y. Li, Y. Li, X. Wang, Y. Huang, T. Zhang, *Nat. Commun.* 8 (2017) 1407.
- [12] W.U. Khan, S.S. Chen, D.C.W. Tsang, W.Y. Teoh, X. Hu, F.L.Y. Lam, A.C.K. Yip, *Nano Res.* 13 (2020) 533–542.
- [13] D. Li, Z. Wang, S. Jin, M. Zhu, *Chem Bio Eng.* (2024), <https://doi.org/10.1021/cbe.3c00072>.
- [14] J. Yu, X. Sun, X. Tong, J. Zhang, J. Li, S. Li, Y. Liu, N. Tsubaki, T. Abe, J. Sun, *Nat. Commun.* 12 (2021) 7209.
- [15] L. Zhang, Y. Yang, Z. Zhou, J. Li, G. Chen, L. Zhou, Y. Qiu, Y. Sun, *Chem. Eng. J.* 452 (2023) 139273.
- [16] T. Kristiansen, J.A. Støvneng, M.-A. Einarsrud, D.G. Nicholson, K. Mathisen, *J. Phys. Chem. C* 116 (2012) 20368–20379.
- [17] M. Kikugawa, K. Yamazaki, H. Shinjoh, *Appl. Catal. A* 547 (2017) 199–204.
- [18] K. Faungnawakij, T. Fukunaga, R. Kikuchi, K. Eguchi, *J. Catal.* 256 (2008) 37–44.
- [19] L. Liu, J. Lu, Y. Yang, W. Ruettinger, X. Gao, M. Wang, H. Lou, Z. Wang, Y. Liu, X. Tao, *Science* 383 (2024) 94–101.
- [20] Y. Pei, Y. Quan, X. Wang, J. Zhao, R. Shi, Z. Li, J. Ren, *Appl. Catal. B* 300 (2022) 120718.
- [21] O. Alvarez-Fregoso, S. López, J.A. Juárez-Islas, M. García, E. Martínez, M.A. Alvarez-Pérez, J.C. Ramírez, S. Granados, *Phys. Status Solidi B* 220 (2000) 575–582.
- [22] H. Zhang, P. Shi, Y. Lv, H. Sun, G. Wang, *J. Vac. Sci. Technol. A* 41 (2023) 053408.
- [23] X.R. Ye, X.Q. Xin, H.N. Zhou, *Plat. Surf. Finish.* 83 (1996) 142–145.
- [24] I. Pudza, A. Anspoks, A. Cintins, A. Kalinko, E. Welter, A. Kuzmin, *Mater. Today Commun.* 28 (2021) 102607.
- [25] B. Saravanakumar, G. Ravi, R. Yuvakkumar, V. Ganesh, R.K. Guduru, *Mater. Sci. Semicond. Process.* 93 (2019) 164–172.
- [26] H. Zhou, Z. Chen, A.V. López, E.D. López, E. Lam, A. Tsoukalou, E. Willinger, D.A. Kuznetsov, D. Mance, A. Kierzkowska, F. Donat, P.M. Abdala, A. Comas-Vives, C. Copéret, A. Fedorov, C.R. Müller, *Nat. Catal.* 4 (2021) 860–871.
- [27] E. Shaaban, G. Li, *Commun. Chem.* 5 (2022) 32.
- [28] X. Yang, Y. Wei, Y. Su, L. Zhou, *Fuel Process. Technol.* 91 (2010) 1168–1173.
- [29] J. Yu, M. Yang, J. Zhang, Q. Ge, A. Zimina, T. Pruessmann, L. Zheng, J.-D. Grunwaldt, J. Sun, *ACS Catal.* 10 (2020) 14694–14706.
- [30] K.-I. Shimizu, H. Maeshima, H. Yoshida, A. Satsuma, T. Hattori, *PCCP* 3 (2001) 862–866.
- [31] M. Sadeghinia, A. Nemat Kharat Ghaziani, M. Rezaei, *Mol. Catal.* 456 (2018) 38–48.
- [32] A. Cano, I. Monroy, M. Ávila, D. Velasco-Arias, J. Rodríguez-Hernández, E. Reguera, *New J. Chem.* 43 (2019) 18384–18393.
- [33] S.J. Gerber, E. Erasmus, *Mater. Chem. Phys.* 203 (2018) 73–81.
- [34] Y.-T. Cheng, M.W. Verbrugge, *J. Appl. Phys.* 104 (2008) 083521.
- [35] S. Chu, P. Liu, Y. Zhang, X. Wang, S. Song, T. Zhu, Z. Zhang, X. Han, B. Sun, M. Chen, *Nat. Commun.* 13 (2022) 4151.