Subnanometric Cu Clusters on Atomically Fe-doped MoO₂ for Furfural Upgrading to Aviation Biofuels

Xin Zhao

South China University of Technology

Fengliang Wang

South China University of Technology

Xiangpeng Kong

Harbin Institute of Technology

Ruiqi Fang

South China University of Technology

Yingwei Li (✉ liyw@scut.edu.cn)

South China University of Technology

Article

Keywords:

Posted Date: December 3rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1103878/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Version of Record: A version of this preprint was published at Nature Communications on May 11th, 2022. See the published version at <https://doi.org/10.1038/s41467-022-30345-0>.

Abstract

Single cluster catalysts (SCCs) are considered as versatile boosters in heterogeneous catalysis due to their modifiable single cluster sites and supports. In this work, we report subnanometric Cu clusters dispersed on Fe-doped MoO₂ support for biomass-derived furfural upgrading. Systematical characterizations suggest uniform Cu clusters (composing four Cu atoms in average) are homogeneously immobilized on the atomically Fe-doped ultrafine MoO₂ nanocrystals (Cu₄/Fe_{0.3}Mo_{0.7}O₂@C). The atomic doping of Fe into MoO₂ leads to significantly modified electronic structure and consequently charge redistribution inside the supported Cu clusters. The as-prepared Cu₄/Fe_{0.3}Mo_{0.7}O₂@C shows superior catalytic performance in the oxidative coupling of furfural with C₃~C₁₀ primary/secondary alcohols to produce C₈~C₁₅ aldehydes/ketones (aviation biofuel intermediates), outperforming the conventionally prepared counterparts. DFT calculations and control experiments are further carried out to interpret the structural and compositional merits of Cu₄/Fe_{0.3}Mo_{0.7}O₂@C in the oxidative coupling reaction, and elucidate the reaction pathway and related intermediates.

Introduction

Downsizing metal active sites into several atoms scale is demonstrated effective in boosting their catalytic performances.^[1–3] Compared with conventional metal nanoparticles/bulks, atomic site catalysts combine the advantages of both homogeneous and heterogeneous ones, such as extremely high atom utilization, well-defined active sites, and reliable durability, thus showing remarkably enhanced catalytic activities.^[4–6] Consequently, single cluster catalysts (SCCs) are emerging, which compose of a certain number of metal atoms as active sites (M_x, where M and x represent metal and atom number, respectively).^[7, 8] Apart from the above-mentioned common merits of atomic site catalysts, the tunable composition and geometry of M_x may endow SCCs with other distinctive properties. Thus, a rational decoration of M_x could correspondingly modify its charge distributions and consequently affect the catalytic processes.^[9, 10]

Recently, numerous efforts have been devoted to the synthesis of novel SCCs with unique electronic structures. For instance, tailoring the metal type and atom number of M_x could effectively modify its geometrical topology. The distinctively spatial distribution of the metal atoms in M_x leads to unexpected size effect and polarized charge distribution, achieving remarkable catalytic performances in various reactions.^[11–14] This protocol is highly dependent on the physicochemical natures of the metals employed (e.g., coordination number, chemical state, and geometry topology), which could only qualitatively change the electronic structure of SCCs. Alternatively, decorating the support of SCCs may modify the electronic structure of M_x in a more precise and selective way, i.e., altering the metal-support interactions.^[15–20] In theory, the even introduction of different dopants into SCC supports could generally and uniformly modulate the electronic property of M_x, which however, is still scarcely investigated in spite

of the significance in the pursuing of highly efficient single cluster catalysts for advanced catalytic applications.

In this work, subnanometric Cu clusters immobilized on Fe-doped MoO₂ nanocrystals are fabricated via a cation exchange-diffusion strategy and subsequent pyrolysis procedure. The obtained nanocomposite features a multi-shelled hollow hierarchical porous octahedron (SHHPO) morphology. Spherical aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) and X-ray absorption spectroscopy (XAS) results uncover the homogeneous immobilization of Cu clusters composing four Cu atoms in average (Cu₄) upon the atomically Fe-doped ultrafine MoO₂ nanocrystals in the obtained Cu₄/Fe_{0.3}Mo_{0.7}O₂@C. The atomic doping of Fe into MoO₂ leads to significantly modified electronic structure and consequently charge redistribution inside the Cu clusters. Moreover, the as-prepared Cu₄/Fe_{0.3}Mo_{0.7}O₂@C shows superior catalytic performance in the oxidative coupling of furfural (FFA) with C₃~C₁₀ primary/secondary alcohols (e.g., isopropanol) to produce the corresponding C₈~C₁₅ aldehydes/ketones (e.g., 4-(2-furyl)-buten-2-one, FBO) as aviation biofuel intermediates. The structural and compositional relationship of Cu₄/Fe_{0.3}Mo_{0.7}O₂@C in the oxidative coupling reaction and the possible reaction pathway are also investigated.

Results And Discussion

The synthesis of Cu₄/Fe_{0.3}Mo_{0.7}O₂@C SHHPO is illustrated in Scheme 1. First, NENU-5 is assembled by using a reported method.^[21] Powder X-ray diffraction (XRD) patterns (Figure S1) and scanning electron microscopy (SEM) images (Figure S2) reveal the successful synthesis of monodispersed NENU-5 octahedrons in size of 800-900 nm with smooth external surfaces. N₂ adsorption-desorption isotherms indicate the microporous nature of NENU-5 (Figures S3B, S3C). Subsequently, the obtained NENU-5 is immersed into a Fe³⁺-contained aqueous solution to substitute partial Cu ions with Fe species to yield Fe-NENU-5. Meanwhile, the Fe³⁺-contained aqueous solution could also facilitate the structural evolution of the solid NENU-5 octahedrons through cation exchanging to fabricate multi-shelled nanostructures. The XRD patterns of Fe-NENU-5 match well with those of the parent NENU-5 (Figure S3A), suggesting the well-retained crystalline phase of NENU-5 upon Fe³⁺ substitution. The as-prepared Fe-NENU-5 features typical type IV N₂ adsorption-desorption isotherms with an obvious N₂-uptake increment at high relative pressures (0.9-1.0) (Figure S3B), revealing the generation of meso- and macro-pores. Correspondingly, the formation of hierarchical pores in Fe-NENU-5 is also confirmed by the significantly reduced specific surface area (from 615.2 to 399.3 m² g⁻¹, Table S1) and enlarged pore-size distribution range (Figure S3C) in comparison with NENU-5.

Fe-NENU-5 retains octahedral morphology of NENU-5 and uniform particle size (Figures 1A and 1B) whereas possesses rougher external surfaces. Transmission electron microscopy (TEM) images (Figure 1C) clearly disclose the triple-shelled hollow nanostructure of Fe-NENU-5 with even shell thickness (50 nm), intershell spacings (40 nm) and hollow cavities (120 nm). Further, HAADF-STEM and the corresponding elemental mappings (Figures 1D-E) show the homogeneous distribution of Cu, Mo, Fe, C,

O, and P elements throughout the Fe-NENU-5. Notably, no obvious Cu or Fe aggregations are observed, excluding their residue or adsorption within the nanostructure. These results indicate that the cation exchange-diffusion process leads to a partial substitution of Fe to Cu, and simultaneously an evolution of the solid NENU-5 octahedron into multi-shelled hollow hierarchical structure with the generation of meso- and macro-pores inside.

The morphology evolution of NENU-5 nanocrystals is tracked and characterized by TEM and SEM at different periods of the cation exchange-diffusion process (Figure S4). At the very beginning, the Fe^{3+} cations adsorb on the external surfaces of NENU-5 and in-situ substitute some Cu nodes, leading to partial decomposition of NENU-5 nanostructure and the resultant rough external surfaces. With time goes by, the Fe^{3+} cations are immersed into the bulk NENU-5 nanocrystals for continuous substitution, resulting in the structural evolution of the solid NENU-5 octahedrons into multi-shelled hollow hierarchical ones within 30 min (Figures S4A-S4C). With a further increase in etching time (i.e., 50 and 60 min), double- and even single-shelled hollow nanostructures (Figures S4D-S4E) are formed.

The content of Fe in the discarded solution decreases while that of Cu correspondingly increases in the cation exchange-diffusion process (Figure S5B), confirming the partial replacement of Cu to Fe in the material. Besides, the weakened intensity of the NENU-5 diffraction peaks in the XRD patterns of the as-prepared multi-shelled nanostructures (Figure S6) suggest the partially preserved NENU-5 topologies. Additionally, the effects of Fe^{3+} concentration on the morphology of the obtained Fe-NENU-5 are also investigated. A series of cation-exchanging solutions containing 0.05-0.30 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ are prepared for the substitution. Characteristic diffraction peaks of NENU-5 are clearly observed in the XRD patterns of the obtained counterparts (Figure S7), indicating the partially retained NENU-5 crystalline structure. When the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dosage increases from 0 to 0.30 g, the external surfaces of the as-prepared Fe-NENU-5 gradually turn from smooth to rough (Figure S8). Specifically, a low $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ loading (less than 0.05 g) leads to smooth external surfaces and solid yolk-shell nanostructures of Fe-NENU-5 (Figures S8A, S8B). Rough external surfaces and triple-shelled hollow nanostructures with irregular intershell gaps are observed at the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ usage of 0.10 g (Figure S8C). When the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ loading is higher than 0.20 g, the triple-shelled nanostructure collapses with apparent generation of defects (Figures S8D, S8E). These results suggest that a 40 min period of cation exchanging with 0.15 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ loading is appropriate for the formation of hollow triple-shelled nanostructure of Fe-NENU-5 (Figures 1A-1D).

An annealing treatment is then carried out under Ar atmosphere to convert Fe-NENU-5 into $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ SHHPO. The pyrolysis temperature is set at 600°C that is higher than the decomposition temperatures of NENU-5 and Fe-NENU-5, as determined by thermogravimetric analysis (Figure S9). The as-prepared $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ SHHPO inherits the octahedral morphology from Fe-NENU-5 but exhibits a shrunken size of ca. 500 nm (Figures 1F and 1G). $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ SHHPO also features type-IV N_2 -sorption isotherms while with a reduced N_2 uptake and an enlarged hysteresis loop (Figure S3E) as compared with Fe-NENU-5. Besides, the pore size distribution curves reveal a widened pore size distribution in 10-100 nm (Figure S3F), suggesting a large amount of micropores are

coalesced into meso- and even macropores during the pyrolysis. Correspondingly, the Brunauer-Emmett-Teller (BET) specific surface area of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ SHHPO is reduced to $169.7 \text{ m}^2 \text{ g}^{-1}$ with a pore volume of $0.41 \text{ cm}^3 \text{ g}^{-1}$ (Table S1). In comparison, $\text{Cu}_x/\text{MoO}_2@\text{C}$ prepared via the direct pyrolysis of NENU-5 has a slightly larger BET specific surface area ($182.9 \text{ m}^2 \text{ g}^{-1}$) with smaller pore volume ($0.24 \text{ cm}^3 \text{ g}^{-1}$) due to the more micropores and fewer mesopores.

The multi-shelled hollow hierarchical nanostructure of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ SHHPO is further verified by TEM (Figure 1H), showing easily identified triple-shelled nanostructures (Figures 1I and 1M) without obvious agglomeration (Figures 1J1-J6). AC HAADF-STEM images of the ultrafine Mo oxide nanocrystals (Figures 1K and 1L) clearly demonstrate the atomic distribution of Fe and Cu species (isolated bright dots) into the MoO_2 (-111) lattice planes due to their Z-contrast differences. The support is denoted as $\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$ after Fe incorporation in which the atom ratio of Fe to Mo is determined by ICP-OES (Table S1). No obvious structural changings of MoO_2 are detected after the atomic doping of Fe. The XRD diffraction peaks of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ match well with those of MoO_2 (Figure S3D). Besides, no characteristic XRD peaks of Cu composites are observed, which is possibly related to their high dispersion and relatively small size. In contrast, the $\text{Cu}_x/\text{MoO}_2@\text{C}$ counterpart shows octahedral morphology with obvious metal agglomerations (Figure S10), indicating the proposed cation exchange-diffusion strategy is essential for the achievement of both multi-shelled hollow hierarchical nanostructure and high metal dispersion.

X-ray absorption fine structure (XAFS) measurements were performed to investigate the coordination environments of Fe and Cu at atomic level. The Fe K-edge X-ray absorption near-edge structure (XANES) spectra of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ SHHPO are shown in Figure 2A (with Fe foil, FeO, Fe_2O_3 , and Fe_3O_4 as references). The K-edge of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ is located between Fe_3O_4 and Fe_2O_3 , revealing the valent state of Fe species is between Fe(II) and Fe(III). Besides, a prominent peak at ca. $1.5 \text{ \AA}$ in the Fourier transform (FT) k^3 -weighted extended X-ray absorption fine structure (EXAFS) spectrum of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ contributes similarly to Fe_2O_3 and Fe_3O_4 (Figure 2B), which is attributed to the scattering of Fe-O (Table S2). Moreover, no apparent peak at ca. $2.2 \text{ \AA}$ is observed in $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ SHHPO, excluding the formation of Fe-Fe bonds and thus confirming the atomic doping of Fe atoms into the MoO_2 lattice planes.

To acquire the local structural parameters of Fe atom in $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$, quantitative EXAFS fitting was carried out (Figures 2C, S11-S13, and Table S2). Considering the possibility of H_2O (in air) adsorption upon the atomic Fe sites, the fitting curves imply that each Fe atom is coordinated to four O atoms in $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ with a Fe-O bonding length of $1.98 \text{ \AA}$. Besides, the wavelet transforms (WT) analysis was performed to verify the above findings (Figures 2D-2H). As compared with the Fe foil, FeO, Fe_2O_3 , and Fe_3O_4 references, the WT maximum at approximately $4.2 \text{ \AA}^{-1}$ is assigned to the Fe-O bonds in $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$, in consistent with the EXAFS results. According to the structure-sensitive XAFS test

and analysis results, the optimized structural model is established (Figure 2C inset), which suggests the successful introduction of atomic Fe species into the MoO_2 .

The effects of atomic Fe doping on the charge distributions over the as-synthesized $\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$ lattice were investigated by X-ray photoelectron spectroscopy (XPS) and density function theory (DFT) calculations. The characteristic peaks in the Mo 3d region XPS spectrum of both $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ and $\text{Cu}_x/\text{MoO}_2@\text{C}$ (Figures S14A, S14C) reveal the +4 valence state of Mo species.^[22, 23] After the doping of atomic Fe, an obvious up-shift of ca. 1.0 eV for the characteristic XPS peaks of Mo in $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ is observed (Figures S14A, S15A), which may be due to the electron transferring from Mo to Fe and the resultant charge polarization.^[24–28] Similarly, the O 1s peak of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ is also shifted to higher binding energies after Fe doping, indicating the reduced electron densities around O atoms (Figure S15B). In addition, the valence states of C, O, and P elements in $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ and $\text{Cu}_x/\text{MoO}_2@\text{C}$ are also studied by XPS, and the details can be seen in the Supporting Information (Figures S14–S17). In pristine MoO_2 , remarkable electron accumulations are observed around O atoms (verified by DFT, Figures 3A, 3E). After Fe doping, the charge density around O atoms is remarkably reduced (Figures 3B, 3F), indicating the introduction of Fe leads to a weakened electron accumulation around the neighboring O atoms, which is possibly indexing to the stronger electronegativity of Fe (1.80) than Mo (1.47).^[29, 30]

The Cu K-edge XANES and EXAFS spectra were also collected to study the electronic structure and coordination environment of Cu species in the $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Figures 2I–2O, Figures S18–19, and Table S3). The Cu K-edge XANES spectrum of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ is located slightly higher than that of Cu foil (Figure 2I), revealing the metallic state of Cu species.^[31, 32] A prominent peak at ca. 2.2 Å in the FT k^3 -weighted EXAFS spectrum of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ contributes similarly to Cu foil (Figure 2J), implying the formation of Cu–Cu bonds, in good agreement with the fitting EXAFS results of R-space spectrum of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Figure 2K).^[33–36] Besides, the intensity maximum at 7 Å^{−1} in the WT contour plots of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Figures 2M–2O) is similar to the Cu foil reference, also suggesting the existence of Cu–Cu bonds. Whereas, the dramatic attenuation of post-edge oscillations (Figure 2I) suggests the Cu species is lacking of long-range orders.^[33] Additionally, the sharply reduced first-shell intensity in $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Figure 2M) indicates a much lower coordination number of Cu in $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ than in Cu foil (6.3 to 12), in consistent with the EXAFS fitting data (Table S3). These results suggest the Cu species in $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ are present in the form of subnanometric clusters with six Cu–Cu bonds, i.e., Cu_4 , of which the topological nanostructure is illustrated in the inset of Figure 2K.

To sum up, the cation exchange-diffusion strategy demonstrated here is effective and precise for the fabrication of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ consisting of Cu subnanometric clusters (four Cu atoms in average) dispersed on ultrafine Fe-doped MoO_2 nanocrystals ($\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$). As expected, the atomic doping of Fe

into MoO_2 leads to significantly modified electronic structure of $\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$ and the consequent charge redistribution inside the obtained Cu_4 species.

The distinctive structure and properties of the $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ material inspired us to investigate its catalytic performance. Furfural (FFA) is a commercialized biomass platform molecule, which may be chemically converted into over 80 kinds of valuable chemicals/bio-fuels.^[37–40] One of the most promising strategies for FFA valorization is the aldol condensation of FFA with aldehydes/ketones (e.g., acetone) for the production of α,β -unsaturated aldehydes/ketones, which are well-known as critical intermediates for the production of aviation biofuels ($\text{C}_8\sim\text{C}_{15}$ alkanes) via a hydrodeoxygenation process.^[41–44] From a green, economic, and sustainable viewpoint, the direct reaction of saturated monobasic alcohols with FFA may be the most preferred and promising, due to the availability and low cost of alcohols in comparison with their oxidation products such as aldehydes and ketones.

In this work, we developed a new reaction route for the production of α,β -unsaturated ketones from FFA, i.e., the oxidative coupling of FFA with secondary alcohols. The one-pot cascade oxidative coupling of FFA with isopropanol (IPA) into 4-(2-furyl)-buten-2-one (FBO, Figure S21) is selected as the model reaction. Currently, FBO is produced from the normal aldol condensation of FFA with acetone that is known as a toxic and dangerous solvent. Typically, the reaction is carried out at 120°C under O_2 using IPA as the solvent, and the results are summarized in Figure 4A and Table S4. The FFA conversion is below the detecting limit in the absence of catalyst (Figure 4A, Table S4, entry 1), suggesting its essential role to produce FBO under the investigated reaction conditions. To our delight, $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ exhibits super catalytic performance with 100% FFA conversion and 99% FBO yield within 16 h (Figure 4A, Table S4, entry 2).

In order to verify the essential roles of the Cu_4 clusters and atomic Fe doping into the MoO_2 support, some related counterparts (e.g., $\text{H-Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$, $\text{Cu}_x/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$, Cu-Fe-MoO_2 , $\text{Cu}@\text{C}$, $\text{Fe-Cu}@\text{C}$, Fe/MoO_2 , and MoO_2) are also synthesized (Figures S22–S25 and Table S1) and employed as catalysts in this reaction. These samples afford low to moderate FFA conversions (24.8–71.9%) and FBO yields (4.7–55.5%) (Figures 4A–4B, and Table S4, entries 3–10). $\text{H-Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ and $\text{Cu}_x/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$, with atomic Cu sites or Cu nanoparticles supported on Fe doped MoO_2 , afford moderate catalytic conversions (30.0% and 71.9%, respectively, Table S4). The other catalysts all show unsatisfied catalytic activities due to the enlarged size of Cu species, weakened metal-support interactions and decomposed hollow hierarchical nanostructures.

On the basis of the intermediates detected in the reaction, the plausible reaction routes are illustrated in Figure 4C. Initially, FFA is transfer-hydrogenated by IPA into furfuryl alcohol (FFAL) with the generation of equivalent amount of acetone (route I). The obtained FFAL subsequently reacts with another IPA (greatly excessive) molecule through an oxidative-coupling process to produce FBOL (route II), which is finally oxidized into FBO. Another possible reaction route is the conventional aldol condensation of FFA with

acetone (route III),^[45] which is also investigated as a potential route in the following reaction mechanism (Figure 5B).

Some control experiments are carried out to verify the proposed reaction routes (Figure 4B and Table S5). When acetone is employed as the reactant, less than 15% FBO is obtained (Figure 4B, columns 1 and 2). Similarly, when the reaction intermediate FFAL is used as the reactant, only 31.9% FBO yield is obtained (Figure 4B, column 3). These results indicate the FFA transformation over $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ is started with the transferring hydrogenation of FFA with IPA, and FFAL could hardly react with acetone under the investigated conditions. In addition, when the reaction atmosphere is changed from O_2 to N_2 , only 5% FBO yield is detected (Figure 4B, column 4), revealing that the oxidative coupling step (route II) is the dominant route to produce FBO over the $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$.

DFT calculations were performed to deeply elucidate and bring theoretical insight to the reaction mechanism (Figures 3 and S26). The differential charge densities of Cu_4/MoO_2 (Figures 3C and 3G) and $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$ (Figures 3D and 3H) are simulated and optimized. In Cu_4/MoO_2 , uniform electron transferring from Cu_4 subnanometric clusters to MoO_2 support is observed (averagely ca. 0.175 e for each Cu atom). Interestingly, after Fe doping, the electron transferring between Cu_4 subnanometric clusters and $\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$ is modified, each Cu atom at the bottom of Cu_4 cluster donates ca. 0.2 e towards the $\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$. In terms of the top Cu atom in Cu_4 (denoted as Cu^0), the electron transferring is negligible (verified by Bader charge analysis in Table S8). As a result, the symmetric charge distribution inside Cu_4 clusters is redistributed after the atomic doping of Fe upon MoO_2 , which is believed largely contributing to the observed outstanding catalytic performance of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ in the FFA oxidative coupling reaction.

A plausible reaction mechanism is proposed for the oxidative coupling of FFA with IPA to FBO over $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Figure 5). The reaction pathway-1 consists of ten elementary steps. At the very beginning, one FFA molecule bonds with the Cu^0 atom at the top of Cu_4 to form (a) due to a relatively low binding energy (-0.65 eV). Subsequently, the adsorbed FFA molecule reacts with one adsorbed IPA molecule, overcoming the energy barrier of 1.47 eV (TS-1) and forming FFAL radical and one acetone molecule (illustrated as c). Afterwards, the generated FFAL radical further reacts with another IPA molecule to form a (d) complex, which undergoes a dehydration process with an energy barrier of 0.92 eV (TS-2) to produce $^*ph\text{-CHCH-CH(OH)-CH}_3$ (g, *ph* represents the furan ring). Afterwards, the $^*ph\text{-CHCH-CH(OH)-CH}_3$ undergoes a dehydrogenation reaction which tends to take place on the carbon side (to form i) than at oxygen side (to form h) due to the former relatively low energy barrier (0.82 eV in comparison with 1.43 eV). Then, another dehydrogenation reaction occurs on the oxygen side overcoming an energy barrier of 0.61 eV (TS-4) to produce $^*\text{FBO}$ (j), which at last desorbs endothermically (0.46 eV) from the catalyst to yield FBO.

After the first three elementary steps of pathway-1, the generated acetone may react with the residue FFA. Therefore, the reaction mechanism of FFA and the generated acetone are additionally investigated in

pathway-2 (with the first three elementary steps listed for comparison). In the fourth elementary step, the energy barrier of the reaction between FFAL radical and acetone to produce (*k*) is much higher in comparison with that of pathway-1 (0.91 to 0.78 eV). Additionally, the subsequent dehydration reaction over Cu₄ sites (from *l* to *m*, TS-2) requires an energy barrier as high as 1.27 eV, also higher than that of the reaction pathway-1 (0.82~0.92 eV). Therefore, the reaction pathway-2 is not preferential in both thermodynamic and kinetic ways as compared with the reaction pathway-1.

To investigate the general applicability of Cu₄/Fe_{0.3}Mo_{0.7}O₂@C, C₃~C₁₀ secondary and primary alcohols were also employed to synthesize the corresponding C₈~C₁₅ ketones and aldehydes as aviation biofuel intermediates under the optimized reaction conditions (Figure 4D, Tables S6, S7). Good to excellent yields (81.7~100%) of the C₈~C₁₅ ketones and aldehydes are achieved through slightly modifying the reaction conditions (e.g., extending the reaction time or increasing the reaction temperature). These reaction results demonstrate the high practical potentials of Cu₄/Fe_{0.3}Mo_{0.7}O₂@C in the valorization of the biomass-derived FFA (and even furanic molecules) to produce biofuels.

After reaction, the catalyst was easily isolated from the reaction mixture and directly reused after washing and drying. No obvious activity loss is observed in the continuous recycling tests (Figure S27), implying the good stability and recyclability of Cu₄/Fe_{0.3}Mo_{0.7}O₂@C. Besides, the Cu, Fe and Mo contents in the reaction solution collected by hot filtration (Figure S28) are below the detecting limits of ICP-OES, indicating the loss of metals is negligible, which could account for the maintenance of catalytic activity. Furthermore, XRD and XPS results confirm the well-preserved crystallization and composition of the Cu₄/Fe_{0.3}Mo_{0.7}O₂@C (Figure S29). SEM, HAADF-STEM, AC HAADF-STEM images and N₂ adsorption/desorption isotherms demonstrate the well retained multi-shelled hollow hierarchical nanostructure consisting of Cu₄ clusters on the Fe-doped MoO₂ (Figure S29).

Conclusion

In summary, we have demonstrated that the electronic property of M_x in SCC can be efficiently modulated through atomically decorating the support. As an example, subnanometric Cu clusters are immobilized onto Fe-doped MoO₂ support to fabricate the Cu₄/Fe_{0.3}Mo_{0.7}O₂@C nanocomposite. Systematical characterizations reveal the uniform Cu₄ clusters, atomically Fe-doped MoO₂ support and distinctive metal-support interactions between them, which eventually lead to charge redistribution inside Cu clusters. The obtained Cu₄/Fe_{0.3}Mo_{0.7}O₂@C shows excellent catalytic performance in the newly developed reaction route of FFA to FBO, i.e., oxidative coupling of FFA with IPA, outperforming the conventionally prepared counterparts. DFT and control experiments uncover the reaction pathways and suggest the superior catalytic performance of Cu₄/Fe_{0.3}Mo_{0.7}O₂@C is originated from the charge redistribution inside the Cu clusters. Moreover, this catalyst is also highly efficient for the preparation of C₈~C₁₅ aviation biofuel intermediates using the corresponding secondary and even primary alcohols as feedstock. The proposed strategy of modulating the electronic structures of metal single clusters through

atom-decoration of support may present a new dimension for the development of advanced catalysts with precisely adjusted electronic properties for various frontier applications.

References

1. Tyo, E. C., Vajda, S. Catalysis by clusters with precise numbers of atoms. *Nat. Nanotechnol.* **10**, 577–588 (2015).
2. Yao, Y., Gu, X.-K., He, D., Li, Z., Liu, W., Xu, Q., Yao, T., Lin, Y., Wang, H.-J., Zhao, C., Wang, X., Yin, P., Li, H., Hong, X., Wei, S., Li, W.-X., Li, Y., Wu, Y. Engineering the electronic structure of submonolayer Pt on intermetallic Pd₃Pb via charge transfer boosts the hydrogen evolution reaction. *J. Am. Chem. Soc.* **141**, 19964–19968 (2019).
3. Dong, C., Li, Y., Cheng, D., Zhang, M., Liu, J., Wang, Y.-G., Xiao, D., Ma, D. Supported metal clusters: fabrication and application in heterogeneous catalysis. *ACS Catal.* **10**, 11011–1045 (2020).
4. Chen, X., Peng, M., Cai, X., Chen, Y., Jia, Z., Deng, Y., Mei, B., Jiang, Z., Xiao, D., Wen, X., Wang, N., Liu, H., Ma, D. Regulating coordination number in atomically dispersed Pt species on defect-rich graphene for n-butane dehydrogenation reaction. *Nat. Commun.* **12**, 2664–2672 (2021).
5. Wei, Y.-S., Sun, L., Wang, M., Hong, J., Zou, Li., Liu, H., Wang, Y., Zhang, M., Liu, Z., Li, Y., Horike, S., Suenaga, K., Xu, Q. Fabricating dual-atom iron catalysts for efficient oxygen evolution reaction: a heteroatom modulator approach. *Angew. Chem. Int. Ed.* **59**, 16013–16022 (2020).
6. Shan, J., Ye, C., Chen, S., Sun, T., Jiao, Y., Liu, L., Zhu, C., Song, L., Han, Y., Jaroniec, M., Zhu, Y., Zheng, Y., Qiao, S.-Z. Short-range ordered iridium single atoms integrated into cobalt oxide spinel structure for highly efficient electrocatalytic water oxidation. *J. Am. Chem. Soc.* **143**, 5201–5211 (2021).
7. Mao, J., Yin, J., Pei, J., Wang, D., Li, Y. Single atom alloy: An emerging atomic site material for catalytic applications. *Nano Today* **34**, 100917 (2020).
8. Liu, J.-C., Ma, X.-L., Li, Y., Wang, Y.-G., Xiao, H., Li, J. Heterogeneous Fe₃ single-cluster catalyst for ammonia synthesis via an associative mechanism. *Nat. Commun.* **9**, 1610–1618 (2018).
9. Zhang, L., Fischer, J. M. T. A., Jia, Y., Yan, X., Xu, W., Wang, X., Chen, J., Yang, D., Liu, H., Zhuang, L., Hankel, M., Searles, D. J., Huang, K., Feng, S., Brown, C. L., Yao, X. Coordination of atomic Co-Pt coupling species at carbon defects as active sites for oxygen reduction reaction. *J. Am. Chem. Soc.* **140**, 10757–10763 (2018).
10. Sun, Q., Wang, N., Bing, Q., Si, R., Liu, J., Bai, R., Zhang, P., Jia, M., Yu, J. Subnanometric hybrid Pd-M(OH)₂, M=Ni, Co, clusters in zeolites as highly efficient nanocatalysts for hydrogen generation. *Chem* **3**, 477–493 (2017).
11. Ji, S., Chen, Y., Fu, Q., Chen, Y., Dong, J., Chen, W., Li, Z., Wang, Y., Gu, L., He, W., Chen, C., Peng, Q., Huang, Y., Duan, X., Wang, D., Draxl, C., Li, Y. Confined pyrolysis within metal-organic frame-works to form uniform Ru₃ clusters for efficient oxidation of alcohols. *J. Am. Chem. Soc.* **139**, 9795–9798 (2017).

12. Wan, X.-K., Wu, H. B., Guan, B. Y., Luan, D., Lou, X. W. Confining sub-nanometer Pt clusters in hollow mesoporous carbon spheres for boosting hydrogen evolution activity. *Adv. Mater.* **32**, 1901349 (2020).
13. Liu, Y., Wang, L. J., Zhang, H., Yuan, H. Y., Zhang, Q., Gu, L., Wang, H. F., Hu, P., Liu, P. F., Jiang, Z., Yang, H. G. Boosting photocatalytic water oxidation over bifunctional $\text{Rh}^0\text{-Rh}^{3+}$ sites. *Angew. Chem. Int. Ed.* **60**, 2–10 (2021).
14. Ni, B., Shi, Y., Wang, X. The sub-nanometer scale as a new focus in nanoscience. *Adv. Mater.* **30**, 1802031 (2018).
15. Guo, Y., Mei, S., Yuan, K., Wang, D. J., Liu, H. C., Yan, C. H., Zhang, Y. W. Low-temperature CO_2 methanation over CeO_2 -supported Ru single atoms, nanoclusters, and nanoparticles competitively tuned by strong metal-support interactions and H-spillover effect. *ACS Catal.* **8**, 6203–6215 (2018).
16. Fang, R., Dhakshinamoorthy, A., Li, Y., Garcia, H. Metal organic frameworks for biomass conversion. *Chem. Soc. Rev.* **49**, 3638–3687 (2020).
17. Feng, L., Pang, J., She, P., Li, J.-L., Qin, J.-S., Du, D.-Y., Zhou, H.-C. Metal-organic frameworks based on group 3 and 4 metals. *Adv. Mater.* **32**, 2004414 (2020).
18. Ma, X., Liu, H., Yang, W., Mao, G., Zheng, L., Jiang, H.-L. Modulating coordination environment of single-atom catalysts and their proximity to photosensitive units for boosting MOF photocatalysis. *J. Am. Chem. Soc.* **143**, 12220–12229 (2021).
19. Hou, C.-C., Wang, H.-F., Li, C., Xu, Q. From metal-organic frameworks to single/dual-atom and cluster metal catalysts for energy applications. *Energy Environ. Sci.* **13**, 1658–1693 (2020).
20. Zhu, M., Zhao, C., Liu, X., Wang, X., Zhou, F., Wang, J., Hu, Y., Zhao, Y., Yao, T., Yang, L.-M., Wu, Y. Single atomic cerium sites with a high coordination number for efficient oxygen reduction in proton-exchange membrane fuel cells. *ACS Catal.* **11**, 3923–3929 (2021).
21. Wu, H. B., Xia, B. Y., Yu, L., Yu, X.-Y., Lou, X. W. Porous molybdenum carbide nano-octahedrons synthesized via confined carburization in metal-organic frameworks for efficient hydrogen production. *Nat. Commun.* **6**, 6512–6519 (2015).
22. Wu, Y., Liu, X., Han, D., Song, X., Shi, L., Song, Y., Niu, S., Xie, Y., Cai, J., Wu, S., Kang, J., Zhou, J., Chen, Z., Zheng, X., Xiao, X., Wang, G. Electron density modulation of NiCo_2S_4 nanowires by nitrogen incorporation for highly efficient hydrogen evolution catalysis. *Nat. Commun.* **9**, 1425–1433 (2018).
23. Zhao, C., Yu, C., Zhang, M., Huang, H., Li, S., Han, X., Liu, Z., Yang, J., Xiao, W., Liang, J., Sun, X., Qiu, J. Ultrafine MoO_2 -carbon microstructures enable ultralong-life power-type sodium ion storage by enhanced pseudocapacitance. *Adv. Energy Mater.* **7**, 1602880 (2017).
24. Tang, Y.-J., Gao, M.-R., Liu, C.-H., Li, S.-L., Jiang, H.-L., Lan, Y.-Q., Han, M., Yu, S.-H. Porous molybdenum-based hybrid catalysts for highly efficient hydrogen evolution. *Angew. Chem. Int. Ed.* **54**, 12928–12932 (2015).
25. Yang, J., Zhang, F., Wang, X., He, D., Wu, G., Yang, Q., Hong, X., Wu, Y., Li, Y. Porous molybdenum phosphide nano-octahedrons derived from confined phosphorization in UIO-66 for efficient hydrogen

- evolution. *Angew. Chem. Int. Ed.* **55**, 12854–12858 (2016).
26. Wang, P., Zhang, Y., Yin, Y., Fan, L., Zhang, N., Sun, K. Anchoring hollow MoO₂ spheres on graphene for superior lithium storage. *Chem. Eng. J.* **334**, 257–263 (2018).
 27. Liu, Y., Zhang, H., Ouyang, P., Chen, W., Wang, Y., Li, Z. High electrochemical performance and phase evolution of magnetron sputtered MoO₂ thin films with hierarchical structure for Li-ion battery electrodes. *J. Mater. Chem. A* **2**, 4714–4721 (2014).
 28. Liu, S., Yin, Y., Hui, K. S., Hui, K. N., Lee, S. C., Jun, S. C. High-performance flexible quasi-solid-state supercapacitors realized by molybdenum dioxide@nitrogen-doped carbon and copper cobalt sulfide tubular nanostructures. *Adv. Sci.* **5**, 1800733 (2018).
 29. Mann, J. B., Meek, T. L., Knight, E. T., Capitani, J. F., Allen, L. C. Configuration energies of the d-block elements. *J. Am. Chem. Soc.* **122**, 5132–5137 (2000).
 30. Zeng, H., Chen, S., Jin, Y. Q., Li, J., Song, J., Le, Z., Liang, G., Zhang, H., Xie, F., Chen, J., Jin, Y., Chen, X., Meng, H. Electron density modulation of metallic MoO₂ by Ni doping to produce excellent hydrogen evolution and oxidation activities in acid. *ACS Energy Lett.* **5**, 1908–1915 (2020).
 31. Lomachenko, K. A., Borfecchia, E., Negri, C., Berlier, G., Lamberti, C., Beato, P., Falsig, H., Bordiga, S. The Cu-CHA deNO_x catalyst in action: temperature-dependent NH₃-assisted selective catalytic reduction monitored by operando XAS and XES. *J. Am. Chem. Soc.* **138**, 12025–12028 (2016).
 32. Kau, L. S., Spira-Solomon, D. J., Penner-Hahn, J. E., Hodgson, K. O., Solomon, E. I. X-ray absorption edge determination of the oxidation state and coordination number of copper. Application to the type 3 site in *Rhus vernicifera* laccase and its reaction with oxygen. *J. Am. Chem. Soc.* **109**, 6433–6442 (1987).
 33. Nguyen, T.-A. D., Jones, Z. R., Goldsmith, B. R., Buratto, W. R., Wu, G., Scott, S. L., Hayton, T. W. A Cu₂₅ nanocluster with partial Cu(0) character. *J. Am. Chem. Soc.* **137**, 13319–13324 (2015).
 34. Cormary, B., Li, T., Liakakos, N., Peres, L., Fazzini, P.-F., Blon, T., Respaud, M., Kropf, A. J., Chaudret, B., Miller, J. T., Mader, E. A., Soulantica, K. Concerted growth and ordering of cobalt nanorod arrays as revealed by tandem in situ SAXS-XAS studies. *J. Am. Chem. Soc.* **138**, 8422–8431 (2016).
 35. Frenkel, A. I., Hills, C. W., Nuzzo, R. G. A view from the inside: complexity in the atomic scale ordering of supported metal nanoparticles. *J. Phys. Chem. B* **105**, 12689–12703 (2001).
 36. Liu, Y., Li, Q., Si, R., Li, G.-D., Li, W., Liu, D.-P., Wang, D., Sun, L., Zhang, Y., Zou, X. Coupling sub-nanometric copper clusters with quasi-amorphous cobalt sulfide yields efficient and robust electrocatalysts for water splitting reaction. *Adv. Mater.* **29**, 1606200 (2017).
 37. Zhao, X., Kong, X., Wang, F., Fang, R., Li, Y. Metal sub-nanoclusters confined within hierarchical porous carbons with high oxidation activity. *Angew. Chem. Int. Ed.* **60**, 10842–10849 (2021).
 38. Zhu, J., Yin, G. Catalytic transformation of the furfural platform into bifunctionalized monomers for polymer synthesis. *ACS Catal.* **11**, 10058–10083 (2021).
 39. Xu, C., Paone, E., Rodríguez-Padrón, D., Luque, R., Mauriello, F. Recent catalytic routes for the preparation and the upgrading of biomass derived furfural and 5-hydroxymethylfurfural. *Chem. Soc.*

Rev. **49**, 4273–4306 (2020).

40. Li, S., Dong, M., Yang, J., Cheng, X., Shen, X., Liu, S., Wang, Z.-Q., Gong, X.-Q., Liu, H., Han, B. Selective hydrogenation of 5-(hydroxymethyl)furfural to 5-methylfurfural over single atomic metals anchored on Nb₂O₅. *Nat. Commun.* **12**, 584–592 (2021).
41. Cho, H. J., Kim, D., Li, J., Su, D., Xu, B. Zeolite-encapsulated Pt nanoparticles for tandem catalysis. *J. Am. Chem. Soc.* **140**, 13514–13520 (2018).
42. Sutton, A. D., Waldie, F. D., Wu, R. L., Schlaf, M., Silks, L. A., Gordon, J. C. The hydrodeoxygenation of bioderived furans into alkanes. *Nat. Chem.* **5**, 428–432 (2013).
43. Huber, G. W., Chhedha, J. N., Barrett, C. J., Dumesic, J. A. Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. *Science* **308**, 1446–1450 (2005).
44. Xia, Q. N., Cuan, Q., Liu, X. H., Gong, X. Q., Lu, G. Z., Wang, Y. Q. Pd/NbOPO₄ multifunctional catalyst for the direct production of liquid alkanes from aldol adducts of furans. *Angew. Chem. Int. Ed.* **53**, 9755–9760 (2014).
45. Rojas-Buzo, S., García-García, P., Corma, A. Hf-based metal-organic frameworks as acid–base catalysts for the transformation of biomass-derived furanic compounds into chemicals. *Green Chem.* **20**, 3081–3091 (2018).

Declarations

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21825802, 21908068, 22138003), the Natural Science Foundation of Guangdong Province (2017A030312005, 2020A1515010376), and the Introduced Innovative R&D Team Leadership of Dongguan City (2020607263005).

Author contributions

Y.L. and R.F. conceived the idea and designed the experiments. R.F., X.Z., and Y.L. cowrote the manuscript. X.Z. and R.F. performed most of the experiments and characterizations. F.W. carried out the SEM and TEM characterizations. X.K. conducted the theoretical calculations. All the authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Schemes

Scheme 1 is in the supplementary files section.

Figures

Figure 1

(A, B) SEM, (C) TEM, (D) HAADF-STEM, and (E1-E6) EDX mapping images of Fe-NENU-5. (F, G) SEM, (H) TEM, (I) HAADF-STEM, (J1-J6) EDX mapping, (K, L) AC HAADF-STEM images, and (M) elemental line scan profiles of Cu₄/Fe_{0.3}Mo_{0.7}O₂@C SHHPO.

Figure 2

(A) XANES spectra at the Fe K-edge of Fe foil, FeO, Fe₂O₃, Fe₃O₄, and Cu₄/Fe_{0.3}Mo_{0.7}O₂@C (Fe). (B) Fourier transform (FT) at the Fe K-edge of Fe foil, FeO, Fe₂O₃, Fe₃O₄, and Cu₄/Fe_{0.3}Mo_{0.7}O₂@C (Fe),

and (C) corresponding EXAFS fitting curves of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Fe) in R space. Inset: model of $\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$ (for details, Figure S20); Fe (green), Mo (purple), and O (red). WT for the k^3 -weighted EXAFS signals of (D) Fe foil, (E) FeO, (F) Fe_2O_3 , (G) Fe_3O_4 , and (H) $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Fe). (I) XANES spectra at the Cu K-edge of Cu foil, Cu₂O, CuO, and $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Cu). (J) Fourier transform (FT) at the Cu K-edge of Cu K-edge of Cu foil, Cu₂O, CuO, and $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Cu), and (K) corresponding EXAFS fitting curves of $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Cu) in R space. Inset: model of Cu₄ (for details, Figure S20); Cu (blue). WT for the k^3 -weighted EXAFS signals of (L) Cu foil, (M) Cu₂O, (N) CuO, and (O) $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2@\text{C}$ (Cu).

Figure 3

Top view of the charge densities of (A) MoO_2 and (B) $\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$. Top view (C, D), and side view (G, H) of the calculated charge transfer difference between subnanometric Cu_4 cluster and MoO_2 (C and G) or $\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$ (D and H). 2D charge density distributions of MoO_2 (E) and $\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$ (F). The isosurface value is set to be $0.005 \text{ e}/\text{\AA}^3$ and the yellow and cyan areas refer to the charge accumulation and depletion, respectively. Cu (blue), Fe (green), Mo (purple), and O (red).

Figure 4

(A) Oxidative coupling of FFA with IPA into FBO over different catalysts (for details, see Table S4). Reaction conditions: FFA (0.5 mmol), catalysts (Cu, 3.6 mol%), K₂CO₃ (0.1 mmol), IPA (5 mL), O₂ (2 bar), 120 °C, 16 h. Conversion and yield were determined by GC-MS. For the control catalysts without Cu species, the catalyst usage is 0.03 g. (B) Control experiments using FFA/FFAL and/or IPA/acetone as substrates over Cu₄/Fe_{0.3}Mo_{0.7}O₂@C. (C) Proposed reaction routes and possible by-products. (D)

Oxidative coupling of FFA with secondary and primary alcohols (1a-7a, 8b-15b) into C8~C15 aviation biofuel intermediates over Cu₄/Fe_{0.3}Mo_{0.7}O₂@C (for details, Tables S6, S7).

Figure 5

(A, B) The free energy diagram for oxidative coupling of FFA with IPA, and the simplified surface structures of various reaction species along the reaction pathway on Cu₄/Fe_{0.3}Mo_{0.7}O₂@C (the model

is structure simplified as $\text{Cu}_4/\text{Fe}_{0.3}\text{Mo}_{0.7}\text{O}_2$, details are depicted in Figure S20). Cu (blue), Fe (green), Mo (purple), O (red), C (gray), and H (white). “TS” denotes a transition state.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [ESI20211122final.docx](#)
- [floatimage1.png](#)