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

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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 MoO$_2$ 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 MoO$_2$ nanocrystals (Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C). The atomic doping of Fe into MoO$_2$ leads to significantly modified electronic structure and consequently charge redistribution inside the supported Cu clusters. The as-prepared Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C shows superior catalytic performance in the oxidative coupling of furfural with C$_3$~C$_{10}$ primary/secondary alcohols to produce C$_8$~C$_{15}$ 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 Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@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 MoO$_2$ 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 (Cu$_4$) upon the atomically Fe-doped ultrafine MoO$_2$ nanocrystals in the obtained Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C. The atomic doping of Fe into MoO$_2$ leads to significantly modified electronic structure and consequently charge redistribution inside the Cu clusters. Moreover, the as-prepared Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C shows superior catalytic performance in the oxidative coupling of furfural (FFA) with C$_3$~C$_{10}$ primary/secondary alcohols (e.g., isopropanol) to produce the corresponding C$_8$~C$_{15}$ aldehydes/ketones (e.g., 4-(2-furyl)-buten-2-one, FBO) as aviation biofuel intermediates. The structural and compositional relationship of Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C in the oxidative coupling reaction and the possible reaction pathway are also investigated.

Results And Discussion

The synthesis of Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@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. N$_2$ adsorption-desorption isotherms indicate the microporous nature of NENU-5 (Figures S3B, S3C). Subsequently, the obtained NENU-5 is immersed into a Fe$^{3+}$-contained aqueous solution to substitute partial Cu ions with Fe species to yield Fe-NENU-5. Meanwhile, the Fe$^{3+}$-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 Fe$^{3+}$ substitution. The as-prepared Fe-NENU-5 features typical type IV N$_2$ adsorption-desorption isotherms with an obvious N$_2$-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 m$^2$ 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 immerged 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 FeCl\(_3\)\(\cdot\)6H\(_2\)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 FeCl\(_3\)\(\cdot\)6H\(_2\)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 FeCl\(_3\)\(\cdot\)6H\(_2\)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 FeCl\(_3\)\(\cdot\)6H\(_2\)O usage of 0.10 g (Figure S8C). When the FeCl\(_3\)\(\cdot\)6H\(_2\)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 FeCl\(_3\)\(\cdot\)6H\(_2\)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 Cu\(_4\)/Fe\(_{0.3}\)Mo\(_{0.7}\)O\(_2\)@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 Cu\(_4\)/Fe\(_{0.3}\)Mo\(_{0.7}\)O\(_2\)@C SHHPO inherits the octahedral morphology from Fe-NENU-5 but exhibits a shrunken size of ca. 500 nm (Figures 1F and 1G). Cu\(_4\)/Fe\(_{0.3}\)Mo\(_{0.7}\)O\(_2\)@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 Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C SHHPO is reduced to 169.7 m$^2$ g$^{-1}$ with a pore volume of 0.41 cm$^3$ g$^{-1}$ (Table S1). In comparison, Cu$_x$/MoO$_2$@C prepared via the direct pyrolysis of NENU-5 has a slightly larger BET specific surface area (182.9 m$^2$ g$^{-1}$) with smaller pore volume (0.24 cm$^3$ g$^{-1}$) due to the more micropores and fewer mesopores.

The multi-shelled hollow hierarchical nanostructure of Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@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 Fe$_{0.3}$Mo$_{0.7}$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 Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@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 Cu$_x$/MoO$_2$@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 Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C SHHPO are shown in Figure 2A (with Fe foil, FeO, Fe$_2$O$_3$, and Fe$_3$O$_4$ as references). The K-edge of Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C is located between Fe$_2$O$_3$ and Fe$_3$O$_4$, revealing the valent state of Fe species is between Fe(II) and Fe(III). Besides, a prominent peak at ca. 1.5 Å in the Fourier transform (FT) $k^3$-weighted extended X-ray absorption fine structure (EXAFS) spectrum of Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C contributes similarly to Fe$_2$O$_3$ and Fe$_3$O$_4$ (Figure 2B), which is attributed to the scattering of Fe-O (Table S2). Moreover, no apparent peak at ca. 2.2 Å is observed in Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@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 Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C, quantitative EXAFS fitting was carried out (Figures 2C, S11-S13, and Table S2). Considering the possibility of H$_2$O (in air) adsorption upon the atomic Fe sites, the fitting curves imply that each Fe atom is coordinated to four O atoms in Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C with a Fe-O bonding length of 1.98 Å. Besides, the wavelet transforms (WT) analysis was performed to verify the above findings (Figures 2D-2H). As compared with the Fe foil, FeO, Fe$_2$O$_3$, and Fe$_3$O$_4$ references, the WT maximum at approximately 4.2 Å$^{-1}$ is assigned to the Fe-O bonds in Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@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 MoO₂.

The effects of atomic Fe doping on the charge distributions over the as-synthesized Fe₀.₃Mo₀.₇O₂ 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 Cu₄/Fe₀.₃Mo₀.₇O₂@C and Cu₄/MoO₂@C (Figures S14A, S14C) reveal the +4 valence state of Mo species. After the doping of atomic Fe, an obvious up-shift of ca. 1.0 eV for the characteristic XPS peaks of Mo in Cu₄/Fe₀.₃Mo₀.₇O₂@C is observed (Figures S14A, S15A), which may be due to the electron transferring from Mo to Fe and the resultant charge polarization. Similarly, the O 1s peak of Cu₄/Fe₀.₃Mo₀.₇O₂@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 Cu₄/Fe₀.₃Mo₀.₇O₂@C and Cu₄/MoO₂@C are also studied by XPS, and the details can be seen in the Supporting Information (Figures S14-S17). In pristine MoO₂, 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).

The Cu K-edge XANES and EXAFS spectra were also collected to study the electronic structure and coordination environment of Cu species in the Cu₄/Fe₀.₃Mo₀.₇O₂@C (Figures 2l-2O, Figures S18-19, and Table S3). The Cu K-edge XANES spectrum of Cu₄/Fe₀.₃Mo₀.₇O₂@C is located slightly higher than that of Cu foil (Figure 2l), revealing the metallic state of Cu species. A prominent peak at ca. 2.2 Å in the FT k³-weighted EXAFS spectrum of Cu₄/Fe₀.₃Mo₀.₇O₂@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 Cu₄/Fe₀.₃Mo₀.₇O₂@C (Figure 2k). Besides, the intensity maximum at 7 Å⁻¹ in the WT contour plots of Cu₄/Fe₀.₃Mo₀.₇O₂@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 2l) suggests the Cu species is lacking of long-range orders. Additionally, the sharply reduced first-shell intensity in Cu₄/Fe₀.₃Mo₀.₇O₂@C (Figure 2M) indicates a much lower coordination number of Cu in Cu₄/Fe₀.₃Mo₀.₇O₂@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 Cu₄/Fe₀.₃Mo₀.₇O₂@C are present in the form of subnanometric clusters with six Cu-Cu bonds, i.e., Cu₄, 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 Cu₄/Fe₀.₃Mo₀.₇O₂@C consisting of Cu subnanometric clusters (four Cu atoms in average) dispersed on ultrafine Fe-doped MoO₂ nanocrystals (Fe₀.₃Mo₀.₇O₂). As expected, the atomic doping of Fe
into MoO$_2$ leads to significantly modified electronic structure of Fe$_{0.3}$Mo$_{0.7}$O$_2$ and the consequent charge redistribution inside the obtained Cu$_4$ species.

The distinctive structure and properties of the Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@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. 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 $\alpha,\beta$-unsaturated aldehydes/ketones, which are well-known as critical intermediates for the production of aviation biofuels (C$_8$~C$_{15}$ alkanes) via a hydrodeoxygenation process. 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 $\alpha,\beta$-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, Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@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., H-Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C, Cu$_x$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C, Cu-Fe-MoO$_2$, Cu@C, Fe-Cu@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). H-Cu$_4$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@C and Cu$_x$/Fe$_{0.3}$Mo$_{0.7}$O$_2$@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),\cite{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 Cu\textsubscript{4}/Fe\textsubscript{0.3}Mo\textsubscript{0.7}O\textsubscript{2}@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\textsubscript{2} to N\textsubscript{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 Cu\textsubscript{4}/Fe\textsubscript{0.3}Mo\textsubscript{0.7}O\textsubscript{2}@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\textsubscript{4}/MoO\textsubscript{2} (Figures 3C and 3G) and Cu\textsubscript{4}/Fe\textsubscript{0.3}Mo\textsubscript{0.7}O\textsubscript{2} (Figures 3D and 3H) are simulated and optimized. In Cu\textsubscript{4}/MoO\textsubscript{2}, uniform electron transferring from Cu\textsubscript{4} subnanometric clusters to MoO\textsubscript{2} support is observed (averagely ca. 0.175 e for each Cu atom). Interestingly, after Fe doping, the electron transferring between Cu\textsubscript{4} subnanometric clusters and Fe\textsubscript{0.3}Mo\textsubscript{0.7}O\textsubscript{2} is modified, each Cu atom at the bottom of Cu\textsubscript{4} cluster donates ca. 0.2 e towards the Fe\textsubscript{0.3}Mo\textsubscript{0.7}O\textsubscript{2}. In terms of the top Cu atom in Cu\textsubscript{4} (denoted as Cu\textsuperscript{0}), the electron transferring is negligible (verified by Bader charge analysis in Table S8). As a result, the symmetric charge distribution inside Cu\textsubscript{4} clusters is redistributed after the atomic doping of Fe upon MoO\textsubscript{2}, which is believed largely contributing to the observed outstanding catalytic performance of Cu\textsubscript{4}/Fe\textsubscript{0.3}Mo\textsubscript{0.7}O\textsubscript{2}@C in the FFA oxidative coupling reaction.

A plausible reaction mechanism is proposed for the oxidative coupling of FFA with IPA to FBO over Cu\textsubscript{4}/Fe\textsubscript{0.3}Mo\textsubscript{0.7}O\textsubscript{2}@C (Figure 5). The reaction pathway-1 consists of ten elementary steps. At the very beginning, one FFA molecule bonds with the Cu\textsuperscript{0} atom at the top of Cu\textsubscript{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-CHCH-CH(OH)-CH\textsubscript{3} (g, ph represents the furan ring). Afterwards, the *ph-CHCH-CH(OH)-CH\textsubscript{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 *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 Cu\(_4\) 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 to 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 Cu\(_4\)/Fe\(_{0.3}\)Mo\(_{0.7}\)O\(_2\)@C, C\(_3\)~C\(_{10}\) secondary and primary alcohols were also employed to synthesize the corresponding C\(_8\)~C\(_{15}\) 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 C\(_8\)~C\(_{15}\) 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 Cu\(_4\)/Fe\(_{0.3}\)Mo\(_{0.7}\)O\(_2\)@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 Cu\(_4\)/Fe\(_{0.3}\)Mo\(_{0.7}\)O\(_2\)@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 Cu\(_4\)/Fe\(_{0.3}\)Mo\(_{0.7}\)O\(_2\)@C (Figure S29). SEM, HAADF-STEM, AC HAADF-STEM images and N\(_2\) adsorption/desorption isotherms demonstrate the well retained multi-shelled hollow hierarchical nanostructure consisting of Cu\(_4\) clusters on the Fe-doped MoO\(_2\) (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 MoO\(_2\) support to fabricate the Cu\(_4\)/Fe\(_{0.3}\)Mo\(_{0.7}\)O\(_2\)@C nanocomposite. Systematical characterizations reveal the uniform Cu\(_4\) clusters, atomically Fe-doped MoO\(_2\) support and distinctive metal-support interactions between them, which eventually lead to charge redistribution inside Cu clusters. The obtained Cu\(_4\)/Fe\(_{0.3}\)Mo\(_{0.7}\)O\(_2\)@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 Cu\(_4\)/Fe\(_{0.3}\)Mo\(_{0.7}\)O\(_2\)@C is originated from the charge redistribution inside the Cu clusters. Moreover, this catalyst is also highly efficient for the preparation of C\(_8\)~C\(_{15}\) 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.

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Declarations

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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/Fe0.3Mo0.7O2@C SHHPO.

Figure 2

(A) XANES spectra at the Fe K-edge of Fe foil, FeO, Fe2O3, Fe3O4, and Cu4/Fe0.3Mo0.7O2@C (Fe). (B) Fourier transform (FT) at the Fe K-edge of Fe foil, FeO, Fe2O3, Fe3O4, and Cu4/Fe0.3Mo0.7O2@C (Fe), and (C) corresponding EXAFS fitting curves of Cu4/Fe0.3Mo0.7O2@C (Fe) in R space. Inset: model of Fe0.3Mo0.7O2 (for details, Figure S20); Fe (green), Mo (purple), and O (red). WT for the k3-weighted EXAFS signals of (D) Fe foil, (E) FeO, (F) Fe2O3, (G) Fe3O4, and (H) Cu4/Fe0.3Mo0.7O2@C (Fe). (I) XANES spectra at the Cu K-edge of Cu foil, Cu2O, CuO, and Cu4/Fe0.3Mo0.7O2@C (Cu). (J) Fourier transform (FT) at the Cu K-edge of Cu foil, Cu2O, CuO, and Cu4/Fe0.3Mo0.7O2@C (Cu), and (K) corresponding EXAFS fitting curves of Cu4/Fe0.3Mo0.7O2@C (Cu) in R space. Inset: model of Cu4 (for details, Figure S20); Cu (blue). WT for the k3-weighted EXAFS signals of (L) Cu foil, (M) Cu2O, (N) CuO, and (O) Cu4/Fe0.3Mo0.7O2@C (Cu).

Figure 3

Top view of the charge densities of (A) MoO2 and (B) Fe0.3Mo0.7O2. Top view (C, D), and side view (G, H) of the calculated charge transfer difference between subnanometric Cu4 cluster and MoO2 (C and G) or Fe0.3Mo0.7O2 (D and H). 2D charge density distributions of MoO2 (E) and Fe0.3Mo0.7O2 (F). The isosurface value is set to be 0.005 e/Å³ 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/Fe0.3Mo0.7O2@C. (C) Proposed reaction routes and possible by-products. (D) Oxidative coupling of FFA with secondary and primary alcohols (1a-7a, 8a-15b) into C8~C15 aviation biofuel intermediates over Cu4/Fe0.3Mo0.7O2@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/Fe0.3Mo0.7O2@C (the model is structure simplified as Cu4/Fe0.3Mo0.7O2, details are depicted in Figure S20). Cu (blue), Fe (green), Mo (purple), O (red), C (gray), and H (white). “TS” denotes a transition state.

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