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Efficient Cu catalyst for 5-hydroxymethylfurfural hydrogenolysis by forming Cu-O-Si bond

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Selective hydrogenolysis of C-O bonds of biomass derived precursors has been identified as a promising and essential way to produce fuel additives. Supported transition metals were explored to give efficient reactivity commonly based on bifunctionality strategy. Here we report that covalent bonding between SiO₂ and Cu features a homologous bifunctional catalyst with metallic Cu and Lewis acidic Cu cations. The catalyst gave superior reactivity for 5-hydroxymethylfurfural to 2,5-dimethylfuran. Lewis acidic cations contributed more predominant roles than metallic sites for C-O hydrogenolysis by stretching and dissociating C-O bonds, whereas they remained inactive for C=C bonds. The results rationalize the valence-state-sensitive catalysis for chemistry involving C-O cleavage. The covalent metal-O-Si bonding provides an alternative for developing efficient catalysts since silicates with such feature are versatile in nature.

Introduction

Hydrogenolysis of C-O bond is an essential way to remove oxygen from biomass precursors for biofuels production. For example, C-O hydrogenolysis of 5-hydroxymethylfurfural (HMF) can afford 2,5-dimethylfuran (DMF), which is an alternative and sustainable fuel with high energy density (30 kJ/cm³) and octane number (RON=119).¹⁻³ Supported transition metals have been widely explored for C-O hydrogenolysis based on bifunctionality strategy, including (1) modification of metals by alloying and (2) utilization of the support by introduction of oxygen vacancy or acid sites.⁴⁻⁷

Yet, the achievement of selective C-O activation by more active, low temperature and cheap catalysts are still needed. SiO₂ is a cheap and widely used support. The inertness of its Si-O-Si framework generally leads to the minimal interaction with guest species, where the metal mainly interacts with SiO₂ by secondary bonds, such as Van der Vaals and electrostatic interactions. The catalytic performance was not sufficient due to the poorly dispersed/modulated metal species. SiO₂ is also considered to be ineffective in cleavage and hydrogenolysis of C-O bonds, due to the absence of acidic and basic sites.⁸⁻⁹ The modulation of chemical bonding of oxide and metal is a feasible way for regulating the structures and states of catalytically active centers, preparing effective metal catalysts.¹⁰⁻¹³ Recently, some works reported that Cu phyllosilicate formed during the preparation of Cu/SiO₂ catalyst, which can promote the hydrogenation ability.¹⁴⁻¹⁶ Copper phyllosilicate has lamellar structure composed of alternate layers of SiO₄ tetrahedra and discontinuous layers of CuO₆ octahedra, in which Cu-O-SiO_x moieties are readily available. Copper phyllosilicate derived Cu⁰/Cu₂O-SiO₂ catalyst show good activity in furfural hydrogenation and a yield of 2-methylfuran (90%) was obtained.¹⁷ Moreover, Wang et al. found that the formation of copper phyllosilicate was more kinetically favored over silica sol with high hydroxyl groups in the preparation of Cu/SiO₂ catalyst.¹⁸ The interaction between Cu and Si in Cu-O-Si bond is proposed to play important role to modulate the Cu⁰ and Cu⁺ sites, stabilize Cu sites and improve hydrogenation ability.

Herein, the strong covalent bonding between SiO₂ and Cu is identified, and the catalysis efficiency for C-O hydrogenolysis is effectively boosted. This work rationalizes the valence-statesensitive catalysis for chemistry involving C-O cleavage. The electrons in the hybridized orbital of Cu-O-Si bond shift from Cu to Si-O moiety for the calcined catalyst. In contrast, because of the changing orbital hybridization of Cu, Cu atoms show higher affinity to electrons for the reduced catalysts. The bonding resulted in substantial amounts of homologous $Cu^{\delta+}$ proximal to well-dispersed Cu⁰ sites on the reduced catalysts. The $Cu^{\delta+}$ sites are Lewis acidic because of the high electron affinity. The mechanistic studies revealed that $Cu^{\delta+}$ sites play more predominant roles in weakening and dissociating C-O bonds, collaborating with Cu⁰ sites for hydrogenolysis. As a result, the efficiency for the hydrogenolysis of HMF to DMF has been significantly enhanced. The covalent metal-O-Si bonding is expected to be a facile strategy for designing efficient metal-Lewis acid centers that does not require the addition of promoters and increase of structural complexity.

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Cu

(%)^c

62.7

61.5

48.4

34.8

32.2

19.9

dispersion

 S_{Cu}

Cu²⁺

(%)^b

73.8

75.6

81.7

75.6

68.2

19.3

dispersion

Cu content

(wt. %)^a

5.0

10.1

19.4

29.4

37.7

24.6

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Catalysts

CuSi-PS-5

CuSi-PS-10

CuSi-PS-20

CuSi-PS-30

CuSi-PS-40

CuSi-IM-30

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Results and discussion

Table 1 The physiochemical properties of catalysts.

S_{BET} (m²/g)

256.3

305.0

391.7

481.2

484.2

81.7

S _{Cu} (mmol/g) ^d	S _{Cu0} (mmol/g) ^e	S _{Cuδ+} (mmol/g) ^e
0.49	0.1	0.39
0.97	0.22	0.75
1.48	0.44	1.04
1.61	0.51	1.10
1.91	0.94	0.97
0.77	0.45	0.32
calculated from XPS data of reduced sample		

^a determined by ICP experiments; ^b calculated from XPS data of calcined samples; ^c calculat es; ^d determined by ICP results and Cu dispersions; ^e determined by analysis of Cu LMM spectra and Cu dispersions ot reduced catalysts.

2.1 Cu/SiO₂ catalysts with covalent Cu-O-Si features

We prepared the Cu/SiO₂ composites (CuSi-PS-x, x indicates the Cu weight loading, x= 5, 10, 20, 30, 40) by an ammonia evaporation method (Table 1). At a base condition, the disiloxy Si-O-Si bond would undergo nucleophilic attack by OH⁻ anions, producing silanol Si-OH groups and then Si-O⁻ anions.¹⁹⁻²¹ In the meantime, ammonia was used as the ligand to keep Cu2+ cations as the soluble species, which can be facilely removed by thermal evaporation. The cupric ammonia complexes under basic conditions are expected to coordinate with and assembly to the surface anions of SiO_2^{21} , and eventually form the lamellar copper phyllosilicate by selective removal of ammonia ligand (Figure 1A). The phyllosilicate structure was proved by XRD results and characteristics (670 and 1034 cm⁻¹)¹⁴ in infrared (IR) spectra (Figure S1 and S2). This phyllosilicate is assembled by the [CuO₆] octahedron and [SiO₄] tetrahedron units through Cu-O-Si bonding with H atoms saturate the uncoordinated sites.²²



Figure 1. (A) Assembly of CuO₆ octahedron and SiO₄ tetrahedron gives the lamellar copper phyllosilicate. (B) CBC model (L refers to Lewis base bonding with the empty orbital of metals and donating two electrons. Z is Lewis acid bonding with the electron-rich species. X donates one electron to the surface sites). (C) Illustrations for the polar covalent Cu-O-Si bonding for calcined and reduced CuSi-PS-x catalysts. (D) Cu2p, O1s and Si2p spectra of calcined CuSi-PS-30 and CuSi-IM-30. (E) Cu2p, O1s and Si2p spectra of reduced CuSi-PS-30 and CuSi-IM-30.

The impregnated Cu/SiO₂ was taken as a reference with a nominal Cu loading of 30 wt. %, namely CuSi-IM-30, followed by the similar drying and calcination procedures. Structural characterizations revealed the presence of monoclinic CuO nanoparticles and amorphous SiO₂ for the calcined CuSi-IM-30 (Figure S3). As shown in Table 1, the formation of layered phyllosilicate also contributes the increase of surface areas ranging from 256.3 to 484.2 m²/g, while the CuSi-IM-30 only has a surface area of $81.7 \text{ m}^2/\text{g}$.

To understand the possibility of strong covalent bonding between metals and SiO₂, covalent bond classification (CBC) gave an appropriate framework for metal oxides, for which defined as L, Z and X types (Figure 1B).23 This depends on the numbers of electrons (0, 1, and 2) of ligand species contributed to the covalent bonds. During the assembly, cupric ammonia complex evolved into a [CuO₆] octahedral coordination with sp³d² hybridization, for example $[Cu(NH_3)_x(H_2O)_{4-x}(OH)_2]$. If the self-polymerization to give Cu(OH)₂ is prevented, Cu atoms mainly give orbitals for O atoms of ligands, such as [SiO₄], and thus gave a L type feature for Cu-O bonding. Similarly, the O atoms of [CuO₆] donate another lone pair for the sp³ hybrid orbitals of Si atoms and O-Si bonds.

The polar covalent Cu-O-Si bonding (Figure 1C and 1D) for calcined CuSi-PS-x is evidenced by comparing XPS spectra of CuSi-PS-30 with CuSi-IM-30. Cu2p features of CuSi-PS-30 significantly shifted to ~1.8 eV higher binding energy (B. E.) than that of CuSi-IM-30. The opposite downward tendencies (~0.8 eV) were observed for O1s and Si2p. The above cases also fit for CuSi-PS-x samples with various Cu loadings (Figure S4, S5, and S6). The polar Cu-O-Si bonding is rationalized by hybrid orbital theory for which the energy of hybrid orbitals is determined by the atomic orbitals. Four-coordinated Si tetrahedron of phyllosilicate is hybridized in sp³ and sixcoordinated Cu octahedron is hybridized in sp³d². Each sp³ hybrid orbital has 25% s character while sp³d² has 17% s character. With the increase of s character, the energy of orbitals decreases and its affinity for electrons increases.²⁴ Therefore, the electron density of Cu atoms is decreased with

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the bonding electrons excited more difficult. The electrons shift towards Si-O moieties, by causing the shifts of XPS spectra. This Cu-O-Si bonding is quite stable upon drying and calcination as evidenced by the almost identical XRD patterns for CuSi-PS-x catalysts (Figure S7), facilitating the dispersion of Cu species for calcined CuSi-PS-x catalysts. Quantitative elemental analysis of surface species by XPS shows that Cu dispersions of calcined CuSi-PS-x catalysts are greatly higher than CuSi-IM-30 by the factors of 3.5-4.2 (Table 1). Note that CuSi-PS-x catalysts with low Cu loadings (e.g., CuSi-PS-5) have slightly decreased Cu dispersions. This is because the excessive amounts of amorphous SiO₂ partially confined the Cu species into the bulk and thereby decreased the dispersion. This is supported by the increase of reduction temperature (CuSi-PS-5) due to the limitation of H₂ diffusion by SiO₂ coverage²⁵, as compared to the CuSi-PS-x with high loadings (Figure S8). The TPR results also demonstrated that the Cu-O-Si bond will benefit the Cu dispersion and make the Cu species to be reduced more easily compared with CuSi-IM-30 catalyst.

Moreover, the covalent Cu-O-Si bonding is preserved and evolved upon reduction of the CuSi-PS-x catalysts by H₂ at 250 °C, as evidenced by the XPS results (Figure 1C and 1E). The satellite peaks of both reduced CuSi-IM-30 and CuSi-PS-30 at 940-950 eV disappeared, indicating the reduction of Cu²⁺ species into Cu^0 and $Cu^{\delta+}$. Reduced CuSi-IM-30 gave the $Cu2p_{3/2}$ and $Cu2p_{1/2}$ peaks at 932.0 and 952.0 eV respectively, revealing a typical feature of Cu⁰ species. This is supported by the XRD results of reduced CuSi-IM-30 catalyst (metallic Cu nanoparticles, ~16 nm, Figure S9). The XRD diffractions of reduced CuSi-PS-x catalysts are rather broad, indicating the well-dispersed surface Cu species instead of Cu crystallites. The B. E. of Cu2p of reduced CuSi-PS-30 is 0.9 eV higher than reduced CuSi-IM-30, which is because that Cu species are composed of Cu^0 and substantial amount of $Cu^{\delta+}$ for reduced CuSi-PS-30. In compared to reduced CuSi-IM-30, the O 1s and Si 2p both shifted to higher B. E. for CuSi-PS-30, indicating the electron density for O and Si atoms decreased. The shifts of XPS peaks are also observed for reduced CuSi-PS-x catalysts (Figure S10, S11, and S12). The phenomena can also be interpreted by the hybridization of orbitals. Cuprous cation was taken as a simplified and stable model for the reduced CuSi-PS-x, since Chen et al. have observed the formation of slight intermediate Cu₂O when the copper phyllosilicate is reduced¹⁴. The cuprous cation is hybridized in sp model in oxide, i.e. Cu₂O. The sp hybrid orbitals have 50% s characters, indicating the more affinity for electrons than that of sp³ of Si atoms. Therefore, the electrons shifted from Si and O atoms towards Cu atoms for reduced catalysts, which gave the different electronic features from the calcined catalysts. The generation of substantial amount of $Cu^{\delta+}$ species is related to the chemical bonding between Cu and SiO₂. We here successfully observed the covalent bonding between Cu and an irreducible oxide i.e. SiO₂, leading to the greatly modified electronic and structural properties of the as-prepared catalysts and reduced catalysts.

2.2 Cu-O-Si bonding introduces the well-dispersed metallic Cu^0 and Lewis acidic $Cu^{\delta +}$ sites



Figure 2. High-resolution TEM images of the reduced CuSi-IM-30 (A, B) and CuSi-PS-30 (C, D) catalysts.



Figure 3. (A) Deconvolution of Cu XAES spectra of reduced catalysts reveals the diverse surface Cu species with both metallic and cationic features. (B) Proportions of surface Cu⁰ and Cu^{δ +} species as the functions of catalyst compositions and methods.

The dispersion of Cu species was greatly enhanced for the reduced CuSi-PS-x catalysts by the Cu-O-Si bonding, which is in consistent with improvement of Cu dispersion for calcined catalysts (Table 1). Quantitative analysis by XPS showed the high surface Cu dispersion and concentrations for reduced CuSi-PS-x, which detects all the surface Cu species with different valence states. The reduced CuSi-PS-x catalysts gave the 1.6-3.2 times of surface Cu dispersions in compared with the CuSi-IM-30. Considering the different Cu loadings of CuSi-PS-x catalysts, reduced CuSi-PS-30 showed the highest surface Cu concentration among the catalysts. In consistent with the XPS results, the broad peaks of XRD results and high-resolution TEM results confirmed the well dispersed Cu species on the reduced CuSi-PS-x catalysts (Figure S9 and Figure 2). It was also found that the Cu dispersion determined by quantitative XPS is linearly correlated with N₂O titration (Figure S13). Because N_2O titration cannot differentiate the Cu⁰ and Cu^{$\delta+$} species, we employed quantitative XPS to determine the concentrations of Cu species with different valence states.

To determine the surface contents of Cu species with different valence states, we turned to Cu X-ray Auger electron spectra (XAES, **Figure 3A**). The metallic Cu⁰ and cationic Cu^{δ +}

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Figure 4. (A) NH₃-TPD of reduced CuSi-PS-x and CuSi-IM-30. (B) Pyridine-adsorbed IR spectra of dried, calcined, reduced CuSi-PS-30 and calcined, reduced CuSi-IM-30. (C) Schematic representation of nature of Lewis acids over reduced CuSi-PS-x catalysts. (D) Correlations between surface concentrations of Cu^{$\delta+$} species and acidity measured by XPS and NH₃-TPD respectively.

species located at ~917.8 eV and ~915.8 eV at Cu XAES spectra respectively, which were quantitatively differentiated by deconvolution of the peaks. The proportions of surface $Cu^{\delta+}$ species of reduced CuSi-PS-x decreased gradually from 78.9% to 50.5% with the increase of Cu contents from 5 wt. % to 40 wt. % (Figure 3B). In contrast, reduced CuSi-IM-30 gave the minimal proportion of $Cu^{\delta +}$ species. The existence of large amount of $Cu^{\delta+}$ sites is related to the interfacial Cu-O-Si bonding that altering the Cu properties to cationic, as illustrated by the structural evolutions observed in XPS analysis. The heterogeneous distributions of surface species (e.g., Cu⁰ and $Cu^{\delta+}$) would alter the surface and adsorption properties, which may therefore influence the catalysis performance. Based on the measured Cu dispersions and distributions of Cu species of reduced catalysts, the surface concentrations of Cu⁰ and $Cu^{\delta+}$ species were determined (**Table 1**).

Temperature-programmed desorption of ammonia (NH_3 -TPD) was used to probe the surface acid sites of reduced catalysts (**Figure 4A**). All the catalysts exhibited the desorption peaks in 150-400 °C which correspond to weak acid sites. CuSi-PS-x catalysts showed higher acid concentrations than CuSi-IM-30. The acid concentration of CuSi-PS-x varied with Cu loadings.

To elucidate the nature of surface acid, we performed pyridine-adsorbed IR experiments of the as-prepared, calcined and reduced CuSi-PS-30, and calcined and reduced CuSi-IM-30 (**Figure 4B**). The vibration at 1540 cm⁻¹ was not observed for all the samples, indicating the absence of Brønsted acid sites. The vibration (~1600 cm⁻¹) of pyridine interacting with OH groups via hydrogen bonding was also not observed for CuSi-PS-30. The vibrations at ~1450, 1490 and 1600-1620 cm⁻¹ were observed for CuSi-PS-30, attributing to vibrations of pyridine coordinating with Lewis acid.²⁶

The vibration at 1450 cm⁻¹ increased upon calcining CuSi-PS-30, whereas it decreased in intensity apphoforthereducing the catalyst. It has been revealed from XRD results that both the dried and calcined CuSi-PS-30 are composed of copper phyllosilicate. The increase of 1450 cm⁻¹ band caused by calcination is attributed to the generation of coordinatively unsaturated (CUS) Cu²⁺ species, since the calcination can partially remove the surface OH groups and create more CUS Cu2+ species27. XPS results have shown the reduction eliminated Cu²⁺ species by generating highly dispersed Cu⁰- $Cu^{\delta+}$ on SiO₂. The reduction-induced decrease of 1450 cm⁻¹ band is attributed to the elimination of Cu²⁺ species. Interestingly, the bands in 1600-1630 cm⁻¹ for CuSi-PS-30 greatly elevated in intensity after reduction, which was reported to be sensitive to the nature and strength of Lewis acids.²⁸ After the reduction, the valence states of Cu species were altered greatly whereas the concentration of surface acid was not changed greatly (Figure S14). Since SiO₂, metallic Cu⁰ and even terrace kinks or edges on Cu⁰ (species possibly exist on reduced CuSi-PS-x) have very slight acidity,^{26, 29} the surface $Cu^{\delta+}$ species are responsible for surface Lewis acids (Figure 4C). The results suggested the formation of Lewis acid on CuSi-PS-x by Cu-O-Si bonding. The vibrations of CuSi-IM-30 slightly red-shifted, indicating the decrease of Lewis acid strength or the presence of OH groups hydrogen-bonding with pyridine.²⁶ This is in accordance with weak NH₃ desorption peak of reduced CuSi-IM-30. The reduction also induced a slight decrease of 1450 cm⁻¹ band due to the elimination of Cu²⁺ species with forming Cu⁰ sites on SiO₂. The peak at 1610 cm⁻¹ was very weak over reduced CuSi-IM-30, indicating the importance of Cu-O-Si bond on the formation of large amounts of $Cu^{\delta+}$ sites. According to the above results, the acid concentration of reduced catalysts can be correlated with the surface $Cu^{\delta+}$ concentrations (Figure 4D).

2.3 Structure-performance relationship for C-O hydrogenolysis

The performance for HMF hydrogenolysis to DMF was shown in Figure 5A. The high temperatures (e.g., 220 °C) were usually needed for DMF synthesis over Cu-based catalysts to facilitate C-O cleavage.³⁰⁻³² We here chose 180 °C to investigate the efficiency of CuSi-PS-x catalysts. The main products from HMF conversions under H₂ atmosphere can be categorized into 4 types: hydrogenated-, semi-hydrogenolysis-, hydrogenolysisand decarbonylation-related compounds (Figure 5B). The overhydrogenation of C=C bonds is not observed for all the catalysts. High yields of target DMF can be achieved over CuSi-PS-x catalysts within 2 h, in particular over CuSi-PS-30 (93.4%). In contrast, CuSi-IM-30 only gave a trace amount of DMF (0.2%) and 51.7% hydrogenated product 2,5-dihydroxymethylfuran, indicating the insufficiency for C-O hydrogenolysis. Moreover, the product distributions are varied with the Cu loadings for CuSi-PS-x catalysts. The increase of Cu loadings promotes the efficiency for C-O hydrogenolysis and the production of DMF. The results further supported the categorized reaction routes for DMF synthesis via hydrogenolysis mechanism. Turnover frequencies (TOF) of DMF over different catalysts were calculated in Figure S15. The CuSi-PS-x catalysts showed much

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Figure 5. (A) Catalytic performance of CuSi-PS-x and CuSi-IM-30 catalysts for HMF hydrogenolysis at 180 °C and 15 bar. (conditions: HMF 0.75 g, catalyst 0.1 g, 1,4-dioxane solvent 35 g, 2 h) (B) Reaction pathways for HMF conversions under H₂ include C=O hydrogenation (type I), hydrogenolysis (type II and III), decarbonylation (type IV), and C=C hydrogenation (undetected in our case). (C) Comparison of TOFs normalized by the surface Cu⁰ sites, Cu⁵⁺ sites and overall Cu⁰-Cu⁵⁺ sites and the relationship with surface Cu⁵⁺ concentrations.

higher TOF values than CuSi-IM-30 catalyst, demonstrating the superior hydrogenolysis ability of CuSi-PS-x catalysts for C-O bond. Moreover, CuSi-PS-30 catalyst exhibited the highest TOF for Cu⁰, indicating the promotion effect of Cu⁺ sites. The catalytic performance of CuSi-PS was compared with other reported Cu-based catalysts in **Table S1**. It can be found the alloying with Co or Ni is a commonly used strategy to lower the reaction temperature and to obtain high DMF yield. Here we created an easy way to realize the efficient conversion of HMF to DMF.

TOF of DMF, normalized by the surface Cu^0 sites, $Cu^{\delta+}$ sites and overall Cu sites (including both Cu^0 and $Cu^{\delta+}$) were summarized (Figure 5C), based on the catalytic results at DMF yield lower than 20%. Although the TOF values cannot be calculated with the same accuracy due to the indirect way for measuring the concentrations of active sites (e.g., Cu⁰ and $Cu^{\delta+}$), the difference of apparent TOF values is quite large and the trends are meaningful.³³ For the overall Cu sites, the TOF follows a volcano-type trend by firstly increasing and then decreasing with the $Cu^{\delta+}$ proportion, demonstrating the coorporation of the Cu^0 and Lewis acidic $Cu^{\delta+}$ sites. TOF for $Cu^{\delta +}$ and Cu^0 sites followed the similar trends to that of overall Cu sites while exhibited the higher values. Moreover, TOF based on the surface Cu⁰ sites increased dramatically at the topmost point, indicating that another surface center (i.e. $Cu^{\delta+}$) may contribute more to C-O hydrogenolysis under the condition. The highest intrinsic reactivity is achieved when the proportions of $Cu^{\delta+}$ and Cu^0 are 68% and 32% respectively. Dai group³⁴ and Gong group³⁵ have also experimentally observed that the performance for ester hydrogenation to ethylene glycol or ethanol is related to the ratios of $Cu^0/Cu^{\delta+}$ species.

Both TOFs on Cu⁰ and Cu^{δ +} sites correlated linearly with that of overall Cu sites (**Figure 6A**), confirming that Cu⁰ and Cu^{δ +} sites serve as the dual active sites for C-O hydrogenolysis. If the surface Cu⁰ and Lewis acidic Cu^{δ +} sites contribute equally to HMF hydrogenolysis, the reaction is valence-state-



Figure 6. (A) TOFs normalized by the surface Cu^0 and $Cu^{\delta+}$ sites as the function of TOFs for overall Cu ($Cu^0+Cu^{\delta+}$) sites (the dash lines refer to the related linear fitting functions). (B) IR spectra of gas-phase furfural and furfural-adsorbed IR spectra of reduced CuSi-PS-30.

insensitive. It means that TOFs based on either Cu⁰ or Cu^{δ +} sites would correlate with the TOFs on total surface Cu sites with the similar slopes. However, the slope of fitting functions for Cu⁰ is ~2 times that for Cu^{δ +} sites. The results clearly show that Cu^{δ +} sites contributed more predominant roles for the reaction.

We expect that the Lewis acidic $Cu^{\delta+}$ sites promote the adsorption and activation of C-O bonds. Wang et al.³⁶ reported that $Cu^{\delta+}$ is capable of adsorption of methanol and presumed to form a $Cu^{\delta+}$ -OCH₃ configuration. Dai³⁷ and Ma³⁸ groups have also observed that the reactivity for ester hydrogenation to ethylene glycol or ethanol is related to the $Cu^0/Cu^{\delta+}$ ratio. Whether the C-O bond is stretched and activated by $Cu^{\delta+}$ species is not indicated by the experiments. Thus, in-situ diffuse reflectance IR of furfural adsorption was performed (Figure 6B). Due to the high boiling point of HMF, we used furfural to study the selective adsorption and activation of C=O bonds on reduced CuSi-PS-30. The gas-phase furfural has the vibrations of C=O and C=C bonds at 1720 and 1470 cm⁻¹ respectively. The downward shift of C=O vibration to 1670 cm⁻¹ was observed for the chemisorbed furfural, whereas the frequency of C=C vibration was slightly altered. It is reported that C=O bond is polarized by interacting with the Lewis acidic solvents via the lone pairs of O atoms.³⁹ Along with the redshift of C=O vibration, the occupancy of π (C=O) increases

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because of the electron transfer from adjacent π (C=C). A more stable resonance C⁺-O⁻ configuration with increased singlebond character was formed, leading to the partially charged C and O atoms. The C=O bond is stretched and bond length is increased for ~0.73% at an IR band shift of 40-50 cm^{-1.39} Thus, the redshift of C=O vibration can be ascribed to the withdrawal of electron density from C=O bonds by the surface Lewis acidic $Cu^{\delta +}$ sites.⁴⁰ In contrast, Lewis acids was inactive for C=C hydrogenation, as the vibration shift of C=C bond and the ringsaturated products were not observed. The above results highlight the covalent Cu-O-Si bonding drives the cooperation of metallic Cu and Lewis acidic $Cu^{\delta+}$ sites, giving the high efficiency for C-O hydrogenolysis. The mechanistic insights of metal-Lewis acid catalysis for the heterogenous Cu/SiO₂ catalyst rationlized the previous observations on the valencestate-sensitivity for both hydrogenation and hydrogenolysis reactions (e.g., Cu³⁴⁻³⁵ and Co⁴¹ catalysts).

Experimental

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Catalyst preparation

An ammonia evaporation method was employed to demonstrate the chemical bonding of metal cations and SiO₂, for which selective removal of ammonia was adopt by hydrothermal evaporation at 80 °C. Typically, the ammonia solution (25-28 wt. %) was added to and mixed with the aqueous solutions of Cu nitrate with preset contents at room temperature. The ratio of NH₃/Cu was controlled to be 6, 1.5 times than the coordination number of $Cu(NH_3)_4^{2+}$ complex. Thereafter, the SiO₂ sol gel was added to the above solution under vigorous stirring. The mixture was stirred for further 12 hours at room temperature by forming a dark-blue sol gel, which serves as the precursor for ammonia evaporation. The blue sol gel was heated to 80 °C to undergo the evaporation of ammonia until the pH value of the suspension decreased to approximate 6-7. Then, the precipitate was filtered, washed, dried overnight and annealed at 450 °C. The samples were denoted as CuSi-PS-x catalysts, of which x indicates the weight loading of Cu species over the catalysts. The actual Cu loadings were shown in Table S1. For the catalytic tests, the catalysts were pre-reduced at 250 °C under H₂ flow. The impregnated CuSi-IM-30 catalyst with a Cu loading of 30 wt. % was prepared as a reference using copper nitrate and SiO₂ sol gel as the starting materials. The SiO_2 was synthesized from the drying of SiO₂ sol gel at 80 °C, which was crushed to be a fine powder. The solution of copper nitrate was then impregnated onto the SiO₂ powder. The received material was further dried and calcined at 450 °C.

Characterizations

The BET surface area was tested via N_2 physical adsorption at -196 °C by a Micromeritics ASAP 2420 instrument. Before tests, the samples were degassed at 90 °C for 1 h and 350 °C for 8 h. The elemental compositions were measured by inductively coupled plasma-optical emission spectroscopy (ICP, Perkin Elmer Optima 2100DV). XPS analysis was conducted on an AXIS ULTRA DLD spectrometer equipped with a monochromatic AI

Kα X-ray source (1486.6 eV). For the XPS analysis of reduced catalysts, the samples were in-situ pre-reduced with PPS Mow at 250 °C. All the spectra were calibrated by the C1s spectrum. The electron flood gun was employed for charge correction. XRD patterns were analyzed by an X-ray diffractometer (MiniFlex II, Rigaku) with the Cu K α radiation (40 kV) and a rate of 4 degree per minute. The XRD patterns of reduced catalysts were recorded after the samples were reduced ex-situ in H₂ flow at 250 $^{\circ}\text{C}$ and sealed in inert medium. TPR and $N_2\text{O}$ titration experiments were performed on a Tianjin XQ TP-5080 instrument equipped with a TCD detector. The IR experiments were performed on a Nicolet Nexus 470 spectrometer in the range of 400-4000 cm⁻¹ with the resolution of 4 cm⁻¹. The pyridine adsorbed IR spectra were recorded by a Bruker VERTEX70 spectrometer equipped with a deuterium triglycine sulphate detector. TPR experiments were performed on a Tianjin XQ TP-5080 instrument equipped with a TCD detector. NH₃-TPD experiments were performed on a Micromeritics ASAP 2920 instrument with an online quadrupole mass spectrometer as the detector. The m/z=17 fragment of NH₃ would be interfered by OH fragment of H_2O . Thus, the m/z=16 fragment with an 80% intensity of m/z=17 fragment can be drawn as the characteristic of NH₃, which was barely altered by H₂O molecules.

Catalytic tests and analytic methods

The hydrogenolysis of HMF was performed on a 100 mL stainless tank reactor. For a typical procedure, the tank was fed with the reduced catalysts, HMF and 1,4-dioxane solvent, then it was sealed and purged by pure H₂ for 5 times. A prereduction of catalysts at 250 °C and H₂ atmosphere was performed. The reactor was then filled with H₂ and heated to the reaction temperature within 20 minutes. After the measurements, the tank was quenched in ice-water and the products in both liquid and gas phase were analyzed by GC-MS and GC instrument. The determination of liquid products was performed on a GC-MS equipment and the quantitative analysis of liquid products was conducted on a GC instrument equipped with DB-WAX capillary column and FID detector. The gas products was also gathered and analyzed by the GC instrument. Carbon balances were calculated for the catalysts, which was in the range of 100%±5%. Therefore, the product selectivity and HMF conversions were determined by calibrated area normalization.

Conclusions

The covalent-bonding chemistry and structural evolution upon reduction of copper and irreducible SiO₂ have been explored. An enhanced catalysis by synergistic metallic Cu and Lewis acidic Cu^{δ +} sites was demonstrated as an atomic-scale sequence of covalent Cu-O-Si bonding. The Cu-O-Si bonding of calcined catalysts was evolved upon reduction by giving substantial amounts of surface metallic Cu and Lewis acidic Cu^{δ +} sites, facilitating the efficient C-O hydrogenolysis reactivity at moderate temperature, for example hydrogenolysis of HMF to DMF. The high DMF yield of ~93.4% Journal Name

was received at 180 °C and 15 bar H₂. A relationship between surface Cu valence states and intrinsic reactivity was constructed, demonstrating the bifunctionality of metallic Cu⁰ and Lewis acidic Cu^{δ +} sites. Moreover, Lewis acidic Cu^{δ +} sites contributed more predominant roles than Cu⁰ sites for C-O hydrogenolysis. In-situ adsorption of furfural model revealed that the Cu^{δ +} sites stretch and dissociatively activate the C-O bonds while they remain inactive for C=C bonds, thus facilitating selective hydrogenolysis of C-O bonds. The work not only rationalizes the valence-state-sensitive catalysis for reactions involving C-O cleavage, but opens up an alternative for designing efficient catalysts by covalent metal-O-Si bonding.

Conflicts of interest

There are no conflicts to declare.

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Strong covalent bonding (Cu-O-Si) modulates the Cu status and boosts the C-O hydrogenolysis.