Ti³⁺ Tuning the Ratio of Cu⁺/Cu⁰ in the Ultrafine Cu Nanoparticles for Boosting the Hydrogenation Reaction

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Hydrogenation of diesters to diols is a vital process for chemical industry. The inexpensive Cu⁺/Cu⁰-based catalysts are highly active for the hydrogenation of esters, however, how to efficiently tune the ratio of Cu⁺/Cu⁰ and stabilize the Cu⁺ is a great challenge. In this work, it is demonstrated that doped Ti ions can tune the ratio of Cu⁺/Cu⁰ and stabilize the Cu⁺ by the Ti-O-Cu bonds in Ti-doped SiO₂ supported Cu nanoparticle (Cu/Ti-SiO₂) catalysts for the high conversion of dimethyl adipate to 1,6-hexanediol. In the synthesis of the catalysts, the Ti⁴⁺-O-Cu²⁺ bonds promote the reduction of Cu²⁺ to Cu⁺ by forming $Ti^{3+}-O_v-Cu^+$ (O_v: oxygen vacancy) bonds and the amount of Ti doping can tune the ratio of Cu⁺/Cu⁰. In the catalytic reaction, the O vacancy activates C=O in the ester by forming new Ti^{3+ δ}-O_R-Cu^{1+ δ} bonds (O_R: reactant oxygen), and Cu⁰ activates hydrogen. After the products are desorbed, the $Ti^{3+\delta} - O_R - Cu^{1+\delta}$ bonds return to the initial state of $Ti^{3+}-O_v-Cu^+$ bonds. The reversible Ti-O-Cu bonds greatly improve the activity and stability of the Cu/Ti-SiO₂ catalysts. When the content of Ti is controlled at 0.4 wt%, the conversion and selectivity can reach 100% and 98.8%, respectively, and remain stable for 260 h without performance degradation.

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1. Introduction

Diols are high value industrial raw material, such as ethylene glycol (EG), 1,6-hexanediol (HDO). Especially, HDO is widely used in pharmaceuticals, adhesives, dyes, and plasticizers.^[1-6] At present, diols are produced by hydrogenating carboxylic acids or their esters.^[1] However, the hydrogenation reaction of the carboxylic acids usually involves harsh operating conditions (T = 523-623 K and $P(H_2) = 10-20$ MPa) and severe corrosion of the reactors. In contrast, the reaction of ester is relatively easier than acid, so hydrogenation of dimethyl adipate (DMA) has received researchers' attention. To achieve high yield of HDO from hydrogenation of DMA, noble metallic-based (Pt, Pd, Rh, and Rh) catalysts supported on different supports (Al₂O₃, La₂O₃, TiO₂, SiO₂, and Nb₂O₅) were studied in this catalytic process and various Co, Sn, and Zn metal elements are doped into the noble metals to improve the activities of these

catalysts.^[1–4,7] Specifically, it demonstrated that the presence of Sn⁴⁺ species acting as Lewis acid sites are responsible for the carbonyl activation and the addition of cobalt could stabilize Sn⁴⁺ species. Based on this hypothesis, Li and co-workers^[8] reported a Ru–Sn–Co/Al–O(OH) catalyst for hydrogenation of DMA. The DMA conversion and the selectivity to HDO were as high as 98% and 95%, respectively, under 5 MPa of H₂ at 493 K for 10 h. They also found that the synergistic effect between cobalt and tin species could promote the reduction of ruthenium oxide. However, the high cost of noble metal catalysts and the harsh operation condition limited the further development for DMA hydrogenation.

The inexpensive Cu-based catalysts have been reported to exhibit high activities for hydrogenation of esters to alcohols.^[9–13] The Cu sites can selectively activate C=O bond without catalyzing the hydrogenation of C–C bond, thus avoiding the breaking of C–C bond.^[14] The synergistic effect between Cu⁰ and Cu⁺ active sites, in which Cu⁰ species activate hydrogen and Cu⁺ species activate C=O, are widely applied to enhance the catalytic performance toward hydrogenation of esters.^[15–17] Therefore, it is crucial to tune the right ratio of Cu⁺/Cu⁰ and maintain it in the whole reaction process for improving the activity of catalyst. Ma and co-workers^[15]



reported that when the accessible metallic Cu surface area is below a certain value, the catalytic activity of hydrogenation linearly increases with increasing Cu⁰ surface area. While the amount of Cu⁰ species is sufficient, the catalytic performance increases with Cu⁺ surface area. Tuning of the surface copper species of Cu/SiO₂ and increasing the amount of Cu⁺ can enable catalysts with high hydrogenation performance.[11] Ge and co-workers^[18] reported that the Cu⁰ can be oxidized to Cu⁺ by the ester and the obtained Cu⁺ can be reduced back to Cu⁰ by H₂ under reaction conditions. It is a dynamic redox cycle between Cu⁺ and Cu⁰, but the balance of copper species cannot be maintained. In order to obtain high activity and stability of Cu-based catalysts, doping trace metal or nonmetallic elements such as B,^[19,20] La,^[21] In,^[12] and Zn^[9,22-24] into SiO₂ support or mixed oxide support are used to control the valence state of Cu. Although some progress has been made, it is still a challenge to realize the controllable adjustment and maintain the ratio of Cu⁺/Cu⁰ and prevent the aggregation of Cu nanoparticles in the Cu-based catalysts.

In this work, we demonstrate that doped Ti ions can tune the ratio of Cu⁺/Cu⁰ and stabilize the Cu⁺ by the reversible Ti-O-Cu bonds in the Ti-doped SiO₂ supported Cu nanoparticles (Cu/Ti-SiO₂) catalysts for the high conversion of DMA to HDO. The dual-template hydrothermal method is applied to synthesize the Ti-SiO₂ supports with macro-mesoporous structure, in which macropores can increase the diffusion of reactants and products,^[25-29] and mesopores are used to anchor catalyst nanoparticles.^[1,30] And then, the Cu nanoparticles are loaded on the support by the ammonia evaporation method, in which copper salt reacts with Ti-SiO₂ to form copper silicate as the precursor of Cu⁺/Cu⁰. A series of characterizations show that doped Ti ions can tune the ratio of Cu⁺/Cu⁰ and stabilize the Cu⁺ by the reversible Ti-O-Cu bonds in Cu nanoparticles. In the synthesis of the catalysts, the Ti^{4+} –O–Cu²⁺ bonds promote the reduction of Cu²⁺ to Cu^+ by the formation of $Ti^{3+}-O_V-Cu^+$ (O_V : oxygen vacancy) bonds and the amount of Ti doping can tune the ratio of Cu⁺/Cu⁰. In the catalytic reaction, the O vacancy activates C=O in the ester by forming a new $Ti^{3+\delta}-O_{R}-Cu^{1+\delta}$ (O_R: reactant oxygen) bond, and Cu⁰ activates hydrogen. After the products are desorbed, the Ti^{3+ δ}-O_R-Cu^{1+ δ} bonds return to the initial state of $Ti^{3+}-O_V-Cu^+$ bonds. The reversible Ti-O-Cu bonds greatly improve the activity and stability of the Cu/Ti-SiO₂ catalysts, with conversion of 100% and selectivity of 98.8% during 260 h hydrogenation for the optimized 0.4 wt% Ti sample.

2. Results and Discussion

2.1. Synthesis of Cu/Ti(x)–SiO₂ Catalysts

As shown in Figure 1, the synthesis process mainly includes two parts: the first part is the synthesis of Ti-doped SiO₂ support, and the second part is the loading of Cu catalyst. The Ti-doped SiO₂ supports are synthesized by dual-template hydrothermal method. Polystyrene spheres (PSs) with diameter of 160 nm and F127 triblock copolymers are used as templates and dispersed in the HCl solution, and then tetrabutyl titanate (TBOT) predissolved in alcohol and tetraethyl orthosilicate (TEOS) are injected into above acid solution (Figure S1a, Supporting Information). The mixture solution reacts for 96 h at 80 °C in a sealed beaker. The solid product is obtained by filtering and washing three times with deionized water. After drying at 120 °C and calcining at 550 °C of the solid product, the porous Ti-doped SiO₂ support with pore size of ≈140 nm was obtained (Figures S1b-d and S2, Supporting Information). And then, the Ti-doped SiO₂ support is added into the aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ and ammonia. The derived [Cu(NH₃)₄](OH)₂ will react with Ti-SiO₂ during the ammonia evaporation (AE) process at 90 °C and the copper phyllosilicate phase is formed after the further calcination in air at 450 °C, in which the copper phyllosilicate phase is demonstrated by the X-ray diffraction (XRD) patterns and Fourier-transform infrared (FT-IR) spectra (Figures S3 and S4, Supporting Information), and the calcined Cu/Ti(x)-SiO₂-C (C represents calcination) catalysts are obtained. Finally, the Cu²⁺ ions trapped in the cupric silicate are gradually reduced to Cu⁺/Cu⁰ under H₂ flow at 300 °C. The reduced catalyst is denoted as Cu/Ti(x)-SiO₂ (x refers to the wt% dopant of Ti, x = 0%, 0.2%, 0.4%, and 0.6%).

2.2. Texture Properties of Cu/Ti(x)-SiO₂ Catalysts

The morphology and structure of the reduced catalysts Cu/Ti(x)–SiO₂ are characterized by transmission electron microscopy (TEM). The porous structure of Cu/Ti(0.4)–SiO₂ catalyst can be observed with the average pore size of 140 nm (**Figure 2**a). Compared to the Ti–SiO₂ support (Figures S1 and S2, Supporting Information), the surface of Cu/Ti(0.4)–SiO₂ catalyst becomes rough due to the reaction of Cu salts with Ti–SiO₂ during the AE process. In the high-magnification TEM image (Figure 2b,c), small Cu nanoparticles with average size of 4.6 nm are observed on the surface of support. The



Figure 1. The synthesis process of Cu/Ti(x)–SiO₂ catalysts.







Figure 2. Morphology of reduced Cu/Ti(0.4)–SiO₂ catalysts. a) The macroporous of Cu/Ti(0.4)–SiO₂ catalysts, b) TEM image of Cu/Ti(0.4)–SiO₂ catalyst, c) particle size distribution, d) HRTEM of copper species, e) HAADF-STEM image of Cu/Ti(0.4)–SiO₂ catalyst, and f–i) EDX-mapping of reduced catalyst.

high-resolution TEM (HRTEM) image (Figure 2d) shows the lattice fringes of the Cu metal and Cu₂O nanoparticles. The distribution of Cu and Ti species are characterized by highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM) combined with an energy dispersive X-ray (EDX) spectroscopy (Figure 2e-i; Figure S5, Supporting Information). The mapping images of Cu and Ti elements in the Cu/Ti(0.4)-SiO₂ catalyst overlap each other, demonstrating that Cu and Ti species are highly distributed on the support. Other samples without or with different Ti doping amounts are also characterized by TEM. As shown in Figure S6 in the Supporting Information, the Cu particles size of Ti-doped catalysts (about 5 nm) is smaller and distribution is narrower, compared to that of Ti free sample (about 6 nm). However, the specific surface areas and pore volumes of the catalysts significantly decrease relative to the supports (Table 1; Figure S7 and Table S1, Supporting Information), suggesting that Cu nanoparticles occupy mesopores, and interestingly, the sizes of mesopore and nanoparticles are similar. So, as expected, mesopores play a role in anchoring nanoparticles with the controllable sizes. The Cu⁰ dispersion and surface area of Ti-doped samples measured by N₂O titration exhibit larger values than that of Ti-free samples (Table 1), suggesting that the Ti doping slightly increase the dispersion of Cu nanoparticles. The Cu and Ti contents of the Cu/Ti(x)–SiO₂ catalysts are detected by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Table 1), which are close to the designed values.

Table 1. The texture and physicochemical properties of synthesized $\mbox{Cu/Ti}(x)\mbox{-SiO}_2$ catalysts.

Catalysts	Cu loading ^{a)} [%]	Ti loading ^{a)} [%]	S _{BET} ^{b)} [m ² g ⁻¹]	$V_{\rm P}^{\rm c)}$ [cm ³ g ⁻¹]	D _P c) [nm]	SA _{Cu} ^{d)} [m ²]	Cu Disp ^{d)} [%]	D _{Cu} ^{e)} [nm]
Cu/SiO ₂	19.94	0	112	0.317	3.76	32.5	25.1	5.8
Cu/ Ti(0.2)–SiO ₂	19.81	0.15	193	0.410	3.68	38.4	31.1	4.9
Cu/ Ti(0.4)–SiO ₂	20.52	0.35	191	0.372	3.42	38.9	29.9	4.6
Cu/ Ti(0.6)–SiO ₂	20.61	0.56	160	0.271	3.79	37.8	28.3	5.1

^{a)}Determined by ICP-OES analysis; ^{b)}Specific surface area measured by BET method; ^{c)}Mesopore volume determined by BJH method; ^{d)}Cu dispersion is detected by N₂O titration; ^{e)}Copper nanoparticle size is calculated by Scherrer equation.



2.3. Chemical Compositions of Cu/Ti(x)-SiO₂ Catalysts

The chemical compositions of the reduced Cu/Ti(x)-SiO₂ catalysts are characterized by the XRD patterns. As shown in **Figure 3**a, the broad diffraction peaks centered at $2\theta = 36.73^{\circ}$ and 61.50° are ascribed to the Cu₂O phase (JCPDS 34-1354) or the 6CuO·Cu₂O phase (JCPDS 03-0879).^[31] The characteristic diffraction peaks at $2\theta = 43.30^\circ$, 50.43° , and 74.13° are assigned to the Cu⁰ (JCPDS 04-0836). In the sample of Cu/SiO₂ without Ti doping, the diffraction peaks intensity of Cu oxides is slightly stronger than that of Cu⁰. In contrast, for the Ti-doped samples, the phenomenon is reverse and the peaks of Cu⁰ is obviously stronger than that of Cu oxides, indicating the Ti doping enhances the reducibility of cupric silicate. Moreover, with the increase of Ti content, the peak of Cu⁰ gradually becomes sharp, indicating the enhancement of crystallinity. The absence of TiO₂ diffraction peaks in the XRD patterns, no lattice fringe of TiO₂ in the HRTEM images, and uniform Ti element distribution in the EDX mapping indicate that the Ti⁴⁺ ions are uniformly doped in the SiO₂ matrix.^[32,33]

To study the reducibility of calcined samples, the H₂ temperature program reduction (H₂-TPR) is conducted. As shown in Figure 3b, the Ti(0.4)–SiO₂ support shows no reduction peaks and the Cu-based catalysts of temperature-programmed reduction (TPR) profiles exhibit a main and nearly symmetric reduction peak centered at 265 °C belongs to the reduction of Cu²⁺ to Cu⁰ and/or Cu⁺ species.^[34] Although there is no obvious difference among the Cu/SiO₂-C, Cu/Ti(0.2)–SiO₂-C, and Cu/Ti(0.4)– SiO₂-C, a shoulder peak centered at 228 °C can be clearly observed in the Cu/Ti(0.6)–SiO₂-C and further increasing Ti content to 3.0 wt%, the intensity of this lower temperature peak increases significantly (Figure S8, Supporting Information). There are two reduction peaks in Ti-doped samples indicating that part of the Cu²⁺ ions is preferentially reduced at low temperature under the activation of Ti ions.^[35] Obviously, there is an interaction between Cu²⁺ and Ti⁴⁺ ions. As discussed above, Ti ions are uniformly doped in the SiO₂ matrix. Therefore, the interaction between Cu and Ti ions can only be realized by the Ti⁴⁺–O–Cu²⁺ bond at the interface between Cu and Ti–SiO₂ matrix. The oxygen atoms at the interface may be easier to lose than those in the lattice due to the asymmetric structure, which leads to the preferential reduction of Ti⁴⁺–O–Cu²⁺ bonds into Ti³⁺–O_V–Cu⁺ bonds. Accordingly, the Ti⁴⁺–O–Cu²⁺ bonds promote the reducibility of partial Cu²⁺ to Cu⁺ at low temperature (Figure S9, Supporting Information).^[35–37]

The surface chemical states of the reduced Cu/Ti(x)-SiO₂ catalysts are further characterized by X-ray photoelectron spectra (XPS). The high-resolution Cu 2p spectra display two peaks at 932.8 and 952.6 eV (Figure S10a, Supporting Information), which are assigned to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively.^[1] In the Ti-doped samples, the whole peaks can be assigned to the Cu⁺ and/or Cu⁰ species, but in the Cu/SiO₂ sample, except the main peak at 932.8 eV, an additional peak at 934.8 eV can be fitted and there is also a satellite peak at 943.3 eV, and both of two peaks are attribute to the Cu^{2+} species. Obviously, the Ti species promoted the reduction of Cu²⁺ species to lower valence states under the applied reduction condition, which is consistent with the H2-TPR results. Figure 3c shows the Ti 2p XPS spectra in the Ti-doped samples. After fitting, one set of peaks at 459.1 and 464.5 eV can be assigned to Ti³⁺ ions and another set of peaks at 459.9 and 465.9 eV are assigned to Ti⁴⁺ ions.^[38] The coexistence of Ti³⁺ and Cu⁺ from the XPS of reduced



Figure 3. The characterization of calcined and reduced Cu/Ti(x)–SiO₂ catalysts. a) XRD patterns of reduced catalysts, b) H₂-TPR profiles of calcined Cu/Ti(x)–SiO₂-C catalysts, c) Ti 2p XPS spectra of reduced catalysts, and d) Cu LMM XAES spectra of the reduced catalysts.



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Ti-doped samples further suggest the formation of Ti³⁺-O_V-Cu⁺ bonds during the reduction of Ti⁴⁺-O-Cu²⁺ bonds.^[39-41] Moreover, the ratio of Ti³⁺/(Ti⁴⁺+Ti³⁺) in the three Ti-doped samples are similar, 41.2%, 39.6%, and 40.4% for Cu/ Ti(0.2)-SiO₂, Cu/Ti(0.4)-SiO₂, and Cu/Ti(0.6)-SiO₂, respectively (Table S2, Supporting Information). Due to the similar sizes and dispersion of Cu nanoparticles among the three samples, the contact areas between Cu nanoparticles and the supports are similar, which leads to the similar proportion of Ti⁴⁺-O-Cu²⁺ bonds to be reduced. Additionally, the O 1s XPS is shown in Figure S10b in the Supporting Information. The observed OH peak at 531.4 eV in O 1s can be assigned to oxygen vacancies induced by hydrogenation, and the variation trend of intensity is similar to that of Ti³⁺ species.^[42,43] The peak of 532.5 eV attribute to the O 1s of supports.^[44]

Due to the overlapping of XPS peaks of Cu⁺ and Cu⁰, it is difficult to distinguish them. So, the X-ray-induced Cu LMM Auger electron spectra (XAES) of the reduced Cu/Ti(*x*)–SiO₂ catalysts are carried out (Figure 3d). The Cu LMM XAES spectra exhibit a broad and asymmetrical peak, suggesting that Cu⁺ and Cu⁰ species coexist on the surface of catalysts. The peak is deconvoluted into two peaks located at 916.0 and 913.2 eV, which can be assigned to Cu⁰ and Cu⁺, respectively.^[10] In addition, the Cu⁰ and Cu²⁺ coexist in Cu/SiO₂ catalyst at 915.9 eV.^[45] Interestingly, the ratio of Cu⁺/(Cu⁰+Cu⁺) first increases from 36.0% to 48.8% as the Ti content raises from Cu/SiO₂ to Cu/Ti(0.4)–SiO₂ and then decreases to 43.4% for the Cu/Ti(0.6)–SiO₂ (Table S2, Supporting Information). According to the analysis of H₂-TPR and Ti XPS spectra, the proportion of Cu⁺ should increase with the increase of Ti content, but the Cu LMM XAES results show

that when the amount of Cu⁺ increases to a certain extent, it will begin to decrease, which indicates that the excessive Ti species promote the reduction of Cu⁺ to Cu⁰.^[35,37]

2.4. Catalytic Performance in DMA Hydrogenation

The gas-phase DMA hydrogenation is conducted in a fixed bed reactor to study the catalytic performance of Cu/Ti(x)-SiO₂ catalysts. The reaction condition is T = 210-235 °C, $P(H_2) = 3.0$ MPa, $H_2/DMA = 170$, and $WHSV_{DMA} = 0.53 h^{-1}$. Figure 4a,b shows the catalytic performance for hydrogenation of DMA as a function of reaction temperature and each temperature maintained for 12 h (Figure S11, Supporting Information). It can be seen that the conversions of DMA over Cu/Ti(0.2)-SiO₂ and Cu/Ti(0.4)-SiO₂ are almost 100% in the whole temperature range (Figure 4a). However, for the Cu/SiO₂ catalyst without Ti doping, the DMA conversion is very low, only 78% at 210 °C, while for the Cu/Ti(0.6)–SiO₂ catalyst with the high Ti content, the conversion is also below the Cu/Ti(0.2)-SiO₂ and Cu/Ti(0.4)-SiO₂. For the selectivity of HDO over Cu/Ti(x)-SiO₂ catalysts (Figure 4b), they change obviously with the Ti doping amount. All the samples exhibit a volcanic curve and the maximum of 98.8% was achieved at 220 °C over the Cu/Ti(0.4)–SiO₂ catalyst. From Cu/SiO_2 to Cu/Ti(0.6)-SiO₂, the maximum of selectivity for each sample first increase and decrease, depending on the Ti doping amount. The HDO yields of all samples also exhibit similar variation trend (Figure S12a, Supporting Information). We also calculated the turnover frequency (TOF) value of 31.5 h^{-1} for the Cu/Ti(0.4)-SiO2 catalyst, which are higher than the



Figure 4. DMA hydrogenation over Cu/Ti(x)–SiO₂ catalysts as a function of temperature. a) Conversion of DMA; b) selectivity of HDO; c) correlation between surface area of Cu⁺ species and the STY of HDO; d) DMA hydrogenation over Cu/Ti(0.4)–SiO₂ and Cu/SiO₂ catalysts as a function of time on stream. Reaction condition: T = 220 °C, $P(H_2) = 3.0$ MPa, $H_2/DMA = 170$, and WHSV_{DMA} = 0.53 h⁻¹.

reported TOF value of 15.1 h^{-1} for CuZn catalyst.^[46] The H_2/DMA ratio affects the selectivity of the product and varying the H_2/DMA ratio can produce the product with one ester group hydrogenated (Figure S13, Supporting Information). Moreover, except DMA, the Cu/Ti(0.4)–SiO₂ can also catalyze the dimethyl oxalate (DMO) hydrogenation to EG (Figure S14, Supporting Information).

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Generally, Cu⁺ ions are considered to be the primary sites for activation of C=O bonds by polarizing the electron lone pair in oxygen atoms and Cu⁰ acts as adsorption sites of activating H_2 .^[11] The ratio of Cu⁺/(Cu⁰+Cu⁺) and the synergistic effect between Cu⁰ and Cu⁺ play a key role in the ester hydrogenation process.^[14] Assuming that the Cu⁺ ions and Cu⁰ atoms occupy identical area, and have identical atomic sensitivity factors, the Cu⁺ surface areas can be estimated according to the Cu⁰ surface areas from the N₂O titration and the ratios of $Cu^+/(Cu^++Cu^0)$ from the Cu LMM XAES.^[1] These values are calculated and are given in Table S2 in the Supporting Information. Interestingly, the space time yield (STY) of HDO is linearly related to both surface areas of Cu⁺ and Cu⁰ (Figure 4c; Figure S12b, Supporting Information),^[16] indicating that Cu⁺ and Cu⁰ are almost equally important in the DMA hydrogenation reaction. Coincidentally, the ratio of Cu⁺/Cu⁰ in the best catalyst of Cu/ Ti(0.4)-SiO₂ is close to 1:1. Therefore, appropriate Ti doping amount can optimize the ratio of Cu⁺/Cu⁰, thus improve the performance of the catalyst. In addition to the high activity, the Cu/Ti(0.4)-SiO₂ catalyst also shows excellent stability, as shown in Figure 4d. The DMA conversion and HDO selectivity of Cu/ Ti(0.4)-SiO₂ catalyst have no obvious decline during hydrogenation for 260 h. In sharp contrast, for the Cu/SiO₂ catalyst without Ti doping, the DMA conversion drops to 84% and the HDO selectivity drops to 76% after 260 h. This demonstrates that the appropriate Ti species also enhance the stability of the catalyst by the strong interaction between Cu and Ti species.

2.5. Chemical Properties of Cu/Ti(x)–SiO₂ Catalysts after Performance Test

To further gain insight into the interaction between Cu and Ti species, the structure and composition of the catalysts are characterized after the performance tests. According to the TEM images, the Cu nanoparticles in the Cu/Ti(0.4)-SiO₂ catalyst have no obvious change compared with the reduced catalyst (Figure S15, Supporting Information), and the HRTEM image of Cu/Ti(0.4)-SiO₂ also shows the lattice fringes of Cu₂O(111) and Cu(111) as shown in Figure S16a in the Supporting Information. But for the Cu/SiO₂ catalyst, the average sizes of Cu particles increase from 5.8 to 6.9 nm (Figure S15a, Supporting Information) and for the Cu/Ti(0.6)-SiO2 catalyst, the Cu particle sizes also increase slightly from 5.1 to 5.9 nm and the size distribution becomes wide (Figure S15d, Supporting Information). The chemical component is further detected by XRD patterns. Figure S16b in the Supporting Information shows that diffraction peaks at 36.42° and 43.30 ° are ascribed to Cu_2O and Cu⁰ species, respectively. The copper species of Cu/Ti(0.4)-SiO₂ catalyst show almost no change during the reaction process, which indicates the Ti species stabilize Cu⁺ species in Cu/Ti(0.4)-SiO₂, while the diffraction peak intensity of Cu oxides in the Cu/SiO₂ catalyst increases obviously, compared with that of reduced catalyst. In the Cu XPS spectrum of Cu/ SiO₂ catalyst (Figure S17a, Supporting Information), the characteristic peak of Cu²⁺ disappeared after the performance test, implying that Cu²⁺ species was reduced to Cu⁺ or Cu⁰.

The Ti XPS and Cu LMM XAES spectra of Cu/Ti(x)-SiO₂ catalysts after the performance tests are fitted and analyzed quantitatively (Figure S16c,d and Table S4, Supporting Information). An interesting discovery is that the contents of Ti³⁺ and Cu⁺ almost remain unchanged in the Cu/Ti(0.4)-SiO₂ catalyst, while the changes are obvious in Cu/SiO₂ catalyst without Ti or Cu/Ti(0.6)-SiO₂ catalyst with high Ti content. For the Cu/ SiO₂ catalyst, due to the weak reducibility of Si⁴⁺-O-Cu²⁺ bonds, the reduction process is long (Cu^{2+} to Cu^{+} to Cu^{0}), so the composition has been changing. For the Cu/Ti(0.6)-SiO₂ catalyst, with high Ti content, too many Ti⁴⁺-O-Cu²⁺ bonds lead to a large amount of Cu+, which promotes the transition to Cu⁰, leading to the strong Cu⁰ diffraction peak (Figure S16b, Supporting Information). However, for the Cu/Ti(0.4)-SiO₂ catalyst, the content of Ti³⁺ and Cu⁺ can be maintained, which means that the formed $Ti^{3+}-O_V-Cu^+$ bonds are stable in the reaction process.^[47] The O 1s XPS spectra were also carried out as shown in Figure S17b in the Supporting Information. It is well-known that the oxygen vacancy is highly active sites for catalytic reactions.

To explore more detailed structural information, the catalysts are further investigated by the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies of the Cu K-edge and Ti K-edge. As shown in the XANES spectra of the Cu K-edge (Figure 5a), the absorption edges of the Cu/Ti(0.4)-SiO₂ and Cu/SiO_2 located between those of pristine Cu foil and Cu₂O, suggesting the averaged valence state of both Cu species is between 0 and +1, indicating the coexistence of Cu⁰ and Cu⁺. But the curve of Cu/Ti(0.4)-SiO₂ slightly shifts to higher energy compared to that of Cu/SiO₂, indicating the higher Cu⁺ content in Cu/ Ti(0.4)-SiO₂. However, the absorption edge of Cu/Ti(0.6)-SiO₂. with high Ti content shift back to lower energy, close to that of Cu/SiO₂, indicating that excessive Ti species enhance the reduction of Cu⁺ to Cu⁰ (Figure S18a, Supporting Information). The bonding environments of Cu atoms are analyzed by the EXAFS spectra (Figure 5b). The peaks at ≈1.55 Å (uncorrected) are assigned to the Cu–O path, and the peaks at ≈2.25 Å (uncorrected) are attributed to the Cu-Cu path. The fitted data are shown in Table S3 in the Supporting Information, and interestingly, the Cu-O coordination numbers of Cu/Ti(0.4)-SiO₂ and Cu/SiO₂ are ≈1.2 and 0.46, respectively. Obviously, compared to the Cu/SiO₂, the existence of Ti in Cu/Ti(0.4)-SiO₂ induces the formation one-coordinated Cu-O-Ti bonds. From the Ti K-edge absorption curves (Figure S18b, Supporting Information), the averaged valence state of Ti species is between 0 and +4 and close to +4, suggesting the possible existence of Ti³⁺ species due to the formation of Cu-O-Ti bonds. Therefore, the results of XAFS are consistent with other experimental data such as XAES and XPS, and further demonstrate the Cu-O-Ti bonds.

The strong interaction between Ti^{3+} and Cu^+ is further verified through the different characteristics of Cu/SiO₂ and Cu/Ti(0.4)–SiO₂ catalysts after the stability test. The performance



Figure 5. a) XANES spectra and b) Fourier transformed EXAFS spectra of the Cu K-edge for the Cu/Ti(0.4)-SiO₂ and Cu/SiO_2 catalysts after performance test.

test lasted only 60 h, while the stability test lasted 260 h. As shown in Figure S19 in the Supporting Information, the severe aggregation of Cu nanoparticles is observed in the Cu/SiO₂ catalyst. The particle size increases from 5.8 nm of reduced catalyst to 9.6 nm of the catalyst after stability test. By contrast, the Cu nanoparticles in the Cu/Ti(0.4)-SiO2 catalyst only increased from 4.6 to 6.1 nm. The almost disappeared diffraction peak of Cu₂O species at 36.42° and the sharp peak of Cu⁰ species at 43.30° in the XRD pattern of Cu/SiO₂ imply the Cu⁺ species are reduced to Cu⁰ species, as well as confirming the sintering of Cu nanoparticles (Figure S20a, Supporting Information). For the Cu/Ti(0.4)-SiO₂ catalyst, although the two diffraction peaks of Cu₂O and Cu⁰ species are stronger than the reduced sample, the intensity of the peaks still keeps a certain proportion, similar to that of Ti³⁺/Ti⁴⁺ species (Figure S20b,S21a,b, Supporting Information). The Cu LMM XAES spectra (Figure S21c, Supporting Information) show that the reduction of Cu⁺ to Cu⁰ species results to the decreased $Cu^+/(Cu^0+Cu^+)$ ratio by about 10% in Cu/SiO2 during the stability test process, compared to that of after performance test. Whereas, the Cu⁺/(Cu⁰+Cu⁺) ratio of Cu/Ti(0.4)-SiO2 merely decreased by 2% (Figure S21c and Table S4, Supporting Information). Additionally, the O 1s XPS of Cu/Ti(0.4)-SiO₂ catalyst also shows no significant change after stability test (Figure S21d, Supporting Information). These results confirm that Ti³⁺ stabilize Cu⁺ and prevent the aggregation of Cu nanoparticles by the Ti-O-Cu bonds.

2.6. Discussion of the Reaction Mechanism

Based on above experimental results, we can reasonably speculate the reaction process of DMA hydrogenation to HDO over Cu/Ti(0.4)–SiO₂ catalyst and provide the most likely reaction model. As shown in **Figure 6**: I) The precursor of the catalyst is reduced under H₂ flow at 300 °C for 3 h. The Cu²⁺ on the surface of Cu nanoparticles are reduced to Cu⁰, and the Ti⁴⁺–O–Cu²⁺ bonds are reduced to Ti³⁺–O_V–Cu⁺ bonds (site A) by H atoms that spill over from Cu⁰. II) H₂ and DMA gas flow is introduced to the reaction system. H₂ is activated by Cu⁰ species, meanwhile, the C=O group in DMA is absorbed by Cu⁺ species, and the oxygen in C=O group occupy the oxygen vacancy between Cu⁺ and Ti³⁺ species. III) The synergistic effect between Cu⁺ and Ti³⁺ species enhance the activation

of C=O group by polarizing the lone pair electron on oxygen atoms. The $Ti^{3+\delta} - O_R - Cu^{1+\delta}$ bonds (site B) are formed under reaction conditions. IV) The active H that spilled over from Cu⁰ directly attack the nearby C-O bond, followed by formation of CH₃OH and acyl intermediate that absorb on Ti³⁺-O_V-Cu⁺ bond. V) The acyl intermediate reacts with other H atoms and complete the hydrogenation of C=O bond. VI) The C=O group is reduced completely and the products are desorbed, as well as, the $Ti^{3+}-O_V-Cu^+$ bond is exposed again and the next circle starts again. There are two main reaction paths for diester hydrogenation to synthesize alcohol.^[48,49] One is that methoxy group is preferentially hydrogenated to produce methanol, then carbonyl group, in which C and O are hydrogenated in turn; the other is that carbonyl group is hydrogenated first, and then the methoxy group. Density functional theory (DFT) calculations show that the activation energy barriers (ΔG^{\ddagger}) of the first and second ester groups of the former pathway are 19.2 and 24.7 kcal mol⁻¹, respectively, which are lower than those of the latter pathway ($\Delta G^{\ddagger} = 19.9$ and 26.2 kcal mol⁻¹, respectively), indicating that the former reaction path is more likely to occur.^[48] Interestingly, the reaction mechanism based on our experimental results is consistent with the former one. Methoxy group is hydrogenated first and then carbonyl group. Moreover, the formation of $Ti^{3+\delta} - O_R - Cu^{1+\delta}$ bond activates methoxy and carbonyl groups at the same time and accelerates the hydrogenation reaction.

3. Conclusion

In this work, a series of Ti-doped SiO₂ supported Cu (Cu/ Ti–SiO₂) catalysts with different Ti doping amount have been synthesized by dual-templating hydrothermal and ammonia evaporation method for the high conversion of DMA to HDO. Doped Ti ions can tune the ratio of Cu⁺/Cu⁰ and stabilize the Cu⁺ by the reversible Ti–O–Cu bonds. A series of characterizations show that in the synthesis of the catalysts, the Ti⁴⁺–O–Cu²⁺ bonds promote the reduction of Cu²⁺ to Cu⁺ by the formation of Ti³⁺–O_V–Cu⁺ bonds and the amount of Ti doping can tune the ratio of Cu⁺/Cu⁰. In the catalytic reaction, the O vacancy activates C=O in the ester by forming new Ti^{3+δ}–O_R–Cu^{1+δ} bonds, and Cu⁰ activates hydrogen. After the products are desorbed, the Ti^{3+δ}–O_R–Cu^{1+δ} bonds return







Figure 6. The mechanism of DMA hydrogenation to HDO over Cu/Ti(x)–SiO₂ catalysts.

to the initial state of $Ti^{3+}-O_V-Cu^+$ bonds, and then begin to bond new reaction molecules to achieve continuous reversible cycle. When the content of Ti is controlled at 0.4 wt%, the ratio of Cu^+/Cu^0 is close to 1:1, and the performance reached the highest value, with conversion of 100% and selectivity of 98.8%, running stably for 260 h without performance degradation. The reversible Ti-O-Cu bonds greatly improve the activity and stability of the Cu/Ti(*x*)–SiO₂ catalysts. This work provides a new strategy to highly active and inexpensive Cu-based catalysts for the hydrogenation reactions.

4. Experimental Section

Synthesis Protocol of Polystyrene Spheres: PS with a diameter of 160 nm was prepared by the surfactant-assisted emulsion anionic polymerization technique.^[50] Styrene (St) and divinylbenzene (DVB) were first washed three times with NaOH solution (0.1 M) and then washed three times with deionized water to remove polymerization inhibitors. In the detailed synthesis, deionized water (240 mL) was added to 500 mL three neck bottom flask, and nitrogen flow was injected to flush out the dissolved oxygen at least 30 min. And then, St (25 mL) and DVB (4.75 mL) were introduced in three neck bottom, and sodium dodecyl sulfate (SDS, 0.3 g) was added the above solution under the continuous nitrogen bubbling and vigorous stirring. After heating up to 80 °C, 0.187 g of potassium persulfate (KPS) predissolved in deionized water (20 mL) was injected to the reaction system and the reaction lasted 5 h. After centrifugation, washing with deionized water and drying at 80 °C for 12 h, the PS with the suitable size was obtained.

Synthesis Protocol of Hierarchical Porous Ti(x)-SiO₂ Support: Macromesoporous Ti-SiO₂ support was synthesized according to the literature.^[50] F127 (3 g) was first dissolved in alcohol (25 mL) and then the solution was injected in HCl solution (75 mL, 2 M) under stirring at 35 °C. Then, PS (4 g) was added to the above solution and the solution was stirred for 1 h to uniformly disperse PS. And then, TEOS (7 mL) was introduced into the solution. The calculated TBOT was dissolved in alcohol (15 mL), and the resulting solution is added to the above reaction solution drop by drop and stirred at 35 °C for 24 h. The obtained mixture solution was reacted at 80 °C for 96 h in a sealed beaker under static conditions. The solid products after reaction were washed for three times with deionized water, dried at 120 °C for 12 h, and calcined in air at 350 °C for 1 h and 550 °C for 6 h with heating rate of 0.5 °C min⁻¹. By varying the amount of TBOT, a series of macromesoporous supports (Ti(x)–SiO₂) were obtained with different Ti contents (x represents the Ti content in Cu/Ti(x)–SiO₂: 0, 0.2, 0.4, and 0.6 wt%).

Catalyst Preparation: Cu/Ti(x)–SiO₂ catalysts were prepared by using ammonia evaporation method as reported in ref. ^[51]. The detailed process is described as follows. Cu (NO₃)₂·3H₂O (1.236 g) was dissolved in deionized water (25 mL). And then, ammonia aqueous solution (10 mL, 25 wt%) was added to adjust the pH of the solution to 11. After the solution was stirred for 30 min, Ti(x)–SiO₂ supports (1.3 g) were added, maintaining the pH value of 11 by adding ammonia aqueous (about 2 mL). The obtained suspension was stirred under room temperature for 4 h and then ammonia evaporation process was carried out at 90 °C in air under ambient pressure. When the pH value of suspension decreased to 6–7, the evaporation process was terminated. The solid products were filtered, washed with deionized water three times, dried at 120 °C overnight, and calcined in air at 450 °C for 4 h. The obtained products were the precursor of the catalyst Cu/Ti(x)–SiO₂-catalysts were obtained.

Measurement of Catalytic Activity and Stability: The activity test was carried out in a continuous flow unit equipped with a stainless-steel fixed-bed tubular reactor. For the activity test, the catalyst precursor was in situ reduced in pure H_2 flow (flow rate of 30 mL min⁻¹) at 300 °C under ambient pressure for 3 h and then was directly applied

to the catalytic reaction. Catalyst precursor (0.4 g, 40–60 meshes) was filled into tubular reactor with inner diameter of 8 mm. After reduction process, the reactant (1 mol L⁻¹ DMA in methanol) was injected by HPLC pump (elite HPLC P230ll) with a flow rate of 0.02 mL min⁻¹. The reaction was conducted at a system pressure of 3.0 MPa, temperature range of 210–235 °C, and a H₂/DMA molar ratio of 170. The liquid products were collected in cold trap with ice-water bath and analyzed by gas chromatograph (Agilent 7820 GC) with a DB-WAX capillary column (30 m \times 0.32 mm \times 0.25 μ m) and a TCD detector.

Catalyst Characterization: N2 physisorption analysis was carried out at -196 °C using Tristar 3000 Micromeritics instrument. The surface area of catalysts was calculated from Barrett-Joyner-Halenda (BJH) method cumulative desorption surface area. The size distribution of mesopores was calculated by BJH method based on desorption isotherms and the pore volume obtained from BJH method cumulative desorption pore volume. ICP-OES was conducted to obtain the content of Cu (W_{Cu}) and Ti (W_{Ti}) with Perkin Elmer Optima 5300DV instrument. The solid catalyst was dissolved in the HNO₃ and HF mixed acid by HBO₃ neutralizing. TPR was carried out on TP-5070 Multifunction automatic adsorber. 50 mg catalyst precursor was loaded into a quartz tube and reduced in 5% H_2/Ar (flow rate of 30 mL min⁻¹) at a temperature range of 20 to 900 °C with a heating rate of 5 °C min⁻¹. The hydrogen consumption was detected by a thermal conductivity detector (TCD). X-ray diffraction was conducted on a Bruker D8 Focus X-ray diffractometer using Cu Klpharadiation ($\lambda = 0.15$ 418 nm). The tube voltage and current were 40 kV and 40 mA, respectively. The diffraction angle of samples was recorded from 20° to 80° (2 θ) with scan rate of 8° min⁻¹ (The calcined samples were recorded from 20° to 80° (2 θ) with a scan rate of 2° min⁻¹). The FT-IR measurements were conducted on a Thermo Nicolet Nexus 470 FT-IR with a spectral resolution of 4 cm⁻¹ from 400 to 4000 cm⁻¹. The standard KBr method was used to press sample wafers. TEM images of samples were obtained by JEOL F200 system electron microscope at 200 kV. The samples were dispersed in ethanol and ultrasonic treatment for 20 min, and then dropped the samples onto the Mo grid ultrathin carbon film. XPS and XAES were conducted on the Thermo ESCALAB 250Xi instrument. X-ray radiation source was Al Ka (hv = 1486.6 eV) with X-ray power of 150 W and spot size was 500 μ m. The pass energy was 30 eV. The XPS was calibrated by C 1s binding energy of 284.8 eV. X-ray absorption spectroscopy (XAS) measurements were performed on the copper K-edges (Transsmition) and Ti K-edges (Lytle) at the hard X-ray Beamline BL11B at Shanghai Synchrotron Radiation Facility (SSRF).

The number of surface metallic copper was measured by N2O titration method using TP-5080 Multifunction automatic adsorber with TCD by N₂O chemisorption and H₂ reduction based on the reaction of $2Cu(s) + N_2O \rightarrow Cu_2O(s) + N_2$.^[1] 50 mg calcined catalyst was flushed with He flow at 200 °C for 1 h to remove the air. Catalyst was first reduced in 5% H_2/He at 300 °C for 2 h (Cu²⁺ to Cu⁰). The amount of hydrogen consumption in first reduction was detected by TCD detector and denoted as A_1 , which represents the total amount of copper species in the catalyst. And then, the catalyst bed was purged with He and cooled to 90 °C. Surface copper atoms were oxidized in 10% N₂O/N₂ (20 mL min⁻¹) at 90 °C for 1.5 h, ensuring the surface metallic copper was oxidized to Cu₂O. Finally, the sample was flushed with He flow to blow off the oxidant and cooled to room temperature to start another reduction process. The second reduction process was performed at 300 °C in 5% H₂/He flow, and the H_2 consumption was detected by TCD and denoted as A_2 that reflects the number of surface metallic copper. The dispersion of metallic copper (Disp_{Cu}) can be calculated with Equation (1)

$$Disp_{Cu} = \frac{2A_2}{A_1} \times 100\%$$
 (1)

The metallic copper surface area (S_{Cu}) was calculated by Equation (2) based on an atomic copper surface density of 1.46 \times 10¹⁹ Cu atoms m⁻²

$$S_{Cu} = \frac{2A_2N_AW_{Cu}}{1.46 \times 10^{19}A_1M_{Cu}} (m^2 g^{-1})$$
(2)

where N_A is Avogadro's constant, M_{Cu} is the relative atomic weight, and W_{Cu} is the content of copper (wt%).

The TOF calculation based on the following Equation (3)

$$TOF = \frac{n_{DMA} \times C_{DMA}}{\text{Disp}_{Cu} \times m_{Catal} \times \frac{W_{Cu}}{M_{Cu}}} (h^{-1})$$
(3)

where n_{DMA} is the number of DMA molecules fed per hour; C_{DMA} is the conversion of DMA; Disp_{Cu} is the dispersion of copper species; m_{Catal} is the dosage of catalyst (g); W_{Cu} is the content of copper (wt%); M_{Cu} is the relative atomic weight.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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