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Synergistic effect of boron-doped carbon nanotubes supported Cu catalyst for selective hydrogenation of dimethyl oxalate to ethanol

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Abstract: Heteroatom doping is a promising approach to improve the properties of carbon material for customized applications. Herein, a series of boron-doped carbon nanotubes supported Cu catalysts (Cu/xB-CNTs) were prepared for the hydrogenation of dimethyl oxalate to ethanol. The structure and chemical properties of boron doped catalysts were characterized by XRD, TEM, N₂O pulse adsorption, CO chemisorption, H₂-TPR and NH₃-TPD, which revealed that doping boron into CNTs support improved the Cu dispersion, strengthened the interaction of Cu species with CNTs support, introduced more surface acid sites and elevated surface area of both Cu⁰ and Cu⁺ sites, especially the surface area of Cu⁺ sites. Consequently, the catalytic activity and stability of the catalysts were greatly enhanced with boron doping. 100% DMO conversion and 78.1% ethanol selectivity could be achieved over the Cu/1B-CNTs catalyst, whose ethanol selectivity was almost 1.7 times higher than that of the catalyst without boron doping. These results suggest that doping CNTs with boron is an efficient approach to improve the catalytic performance of CNTs based catalysts for hydrogenation of DMO. The boron-doped CNTs based catalyst with improved ethanol selectivity and catalytic stability will be helpful in the development of efficient non-silica materials supported Cu catalysts for selective hydrogenation of DMO to ethanol.

Introduction

With dwindling petroleum resources and deteriorating global environment, searching for clean and renewable energy is a top priority for social sustainable development. Ethanol, as a form of alcohol that is combustible and can power engines easily, has been pushed to the center stage of clean and renewable

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energy.^[1] Currently, ethanol is principally produced from microbial fermentation of agricultural feedstock and ethylene hydration over solid acidic catalysts, which are limited by the expensive biological process and shrinking oil resource.^[2, 3] As an alternative route, the efficient production of ethanol from syngas (the mixture of CO and H₂) with dimethyl oxalate (DMO) as the intermediate has gained increasing attention in recent years.^[4] The successful industrialization of DMO produced from syngas makes the ethanol synthesis from hydrogenation of DMO to ethanol is known to consist of several sequential reactions (Scheme 1): DMO reacting with hydrogen to methyl glycolate (MG), hydrogenation of EG to ethanol.^[6]



Scheme 1. Alternative synthesis approach for ethanol from DMO hydrogenation.

Versatile Cu-based catalysts have been known to afford excellent activity for DMO hydrogenation, as Cu active sites account for the selective hydrogenation of C-O bond and are relatively inactive for the hydrogenolysis of C-C bond.[7-8] Support materials, as an important component of Cu-based catalyst, have attracted increasing attention, because the Cu dispersion and the interaction between Cu species with support are strongly affected by the surface property and structure of the support material.^[9-11] Currently, the silica supported Cu catalysts have been widely investigated for hydrogenation of DMO due to their high catalytic activity for DMO hydrogenation to ethanol.^[12] Nevertheless, the usage of silica support could be a fatal flaw in the DMO hydrogenation process because of the leaching of the silica under the gas phase reaction condition containing methanol.^[13] The severe silica loss would not only result in the agglomeration of copper nanoparticles, but also degrade the quality of ethanol product.^[14] Therefore, the development of nonsilica support material is critical for obtaining highly active and stable Cu-based catalyst for DMO hydrogenation to ethanol from commercial application prospect.

As one of the burgeoning and promising materials, carbon nanotubes (CNTs) have attracted considerable attention in the field of nanoscience and nanotechnology. In previous works,

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carbon nanotubes (CNTs) have been found to be outstanding catalyst support because of their unique features, including welldefined nano-channel, graphene-like tube wall and sp² hybridized carbon framework.^[15, 16] Moreover, heteroatom doped CNTs usually exhibit outstanding performance for specific purposes. In this contribution, the boron-doped carbon nanotubes (B-CNTs) were prepared and utilized as support for Cu-based catalyst. Boron (B), a heteroatom neighbouring carbon in the Periodic Table, differs only by one in its number of valence electrons compared to carbon atoms and hence doping boron into the graphitic lattice of CNTs is possible.^[3] Doping boron atoms into the CNTs would significantly change the surface properties of CNTs and further introduce defect sites into CNTs lattice, which could act as the anchoring sites to support metal nanoparticles.^[17, 18] Wang et al.^[19] had reported that doping boron into CNTs created defect sites, resulting in the uniform deposition of Pt nanoparticles on B-CNTs. A theoretical study by Wang at al.^[20] also indicated that the strong orbital hybridization between d orbitals of platinum atoms and p orbitals of boron atoms was believed to account for their enhanced chemical bonding. Accordingly, doping boron into CNTs may lead to tremendous improvements in Cu dispersion and interaction between Cu species and CNTs support, which are vital for the high activity and stability in hydrogenation of DMO to ethanol. Moreover, boron atoms enter the carbon lattice by substituting the carbon atoms at the trigonal sites.^[21] Because boron has three valence electrons, it can act as electron acceptor (Lewis acid) and tune the acid-base properties of B-CNTs supported Cu catalyst.^[22] The acid sites over catalyst surface could be expected to catalyze the dehydration of hydroxyl groups and then metal sites could hydrogenate the unsaturated intermediates into ethanol.^[23] One can envision that boron-doped CNTs as support can be a promising option to obtain highly active and stable non-silica Cu-based catalyst for DMO hydrogenation to ethanol. However, the CNTs, especially boron-doped CNTs, have been rarely reported as support of Cubased catalyst for DMO hydrogenation to ethanol.

In this work, a series of Cu/xB-CNTs catalysts were designed and prepared by thermal treating CNTs in the presence of boric acid followed by post impregnation with Cu species, and their catalytic performances were comprehensively evaluated in the hydrogenation of DMO to ethanol. In combination with systematic characterizations, the effect of boron doping on the Cu dispersion, interaction between Cu species and CNTs support, Cu^0 and Cu^+ distribution, as well as surface acidity of Cu/xB-CNTs catalysts were elucidated. Significant improvements in catalytic activity and stability could be achieved by boron-doped Cu/xB-CNTs catalysts.

Results and Discussion

Structure and surface properties of boron-doped CNTs support

The boron-doped CNTs were prepared by thermal annealing of a mixture of CNTs and boric acid at 1000 °C. In the thermal annealing process, the boric acid molecules first melted and then decomposed to yield boron oxide with increasing temperature in the tubular furnace. At the same time, a part of oxygen-containing groups linked to the surface of CNTs were removed at high temperature. The defect and removal process of oxygen-containing groups provided active sites for boron doping into carbon lattice of CNTs.^[24] Due to the excellent thermal stability, CNTs could remain its unique physical structure even treated by elevated temperature under inert gas.^[25, 26] The FE-SEM images were taken to examine the morphologies of CNTs, CNTs-T and xB-CNTs, as shown in Figure 1(a-e). The CNTs-T and xB-CNTs exhibited similar tube structure with CNTs, indicating that the structure of CNTs did not be damaged during the thermal treatment and boron doping process. The similar result could be also obtained by XRD characterization in Figure 1f. For all samples, several characteristic diffraction peaks for graphite structure of CNTs were presented in the XRD patterns. These peaks at 20 of around 26, 43.1, 53.8 and 78.2° corresponded to the planes (002), (100), (004) and (110) of CNTs, respectively,^[27] demonstrating that CNTs-T and xB-CNTs maintained the same crystal structure as the original CNTs even after thermal treatment and boron doping.



Figure 1. FE-SEM images of (a) CNTs, (b) CNTs-T, (c) 0.05B-CNTs, (d) 0.1B-CNTs, (e) 1B-CNTs and (f) XRD patterns of all samples.

Raman spectrum is a very efficient and non-destructive tool to catch information about the presence of sp²-sp³ hybridization, doping and other crystal disorder of CNTs. As in Figure 2, the spectra of CNTs, CNTs-T and xB-CNTs showed two characteristic peaks located at around 1343 cm⁻¹ (D band) and 1568 cm⁻¹ (G band), which corresponded to the disordered carbon and in-phase vibration of the graphite lattice, respectively.^[28, 29] The CNTs structure was retained after thermal treatment and boron doping, because there was no obvious shift or line broadening of Raman spectra, which was in accordance with the results of FE-SEM and XRD. The defect level in CNTs can be clearly reflected by the relative peak intensity ratio of the D band to G band (I_D/I_G). After calcined at 1000 $^\circ C$ for 4 h without doping boron, the I_D/I_G ratio of CNTs-T decreased from 0.726 of CNTs to 0.682. The decrease could be attributed to the fact that the thermal treatment removed a part of surface oxygen-containing functional groups and thus increased the order degree. Nevertheless, it is noticed that the I_D/I_G ratios for xB-CNTs were larger than that of CNTs, indicating the introduction of more defects and imperfections into xB-CNTs after boron doping. From the Raman spectra of xB-CNTs, the I_D/I_G ratios exhibited the following order: 1B-CNTs>0.1B-CNTs>0.05B-CNTs, indicating that the defects increased with the enhanced weight ratio of boric acid to CNTs. Furthermore, compared with other CNTs analogues, the G band of 1B-CNTs

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exhibited a 13 cm⁻¹ blue-shift, which might be due to the weaker B-C bonds and lighter boron atoms.^[30]



Figure 2. Raman spectra of (a) CNTs, (b) CNTs-T, (c) 0.05B-CNTs, (d) 0.1B-CNTs and (e) 1B-CNTs.



Figure 3. XPS survey spectra of (a) all samples and high-resolution B 1s spectra of (b) 0.05B-CNTs, (c) 0.1B-CNTs and (d) 1B-CNTs.

The XPS characterization was carried out to confirm the presence and chemical states of the doped boron. The XPS survey spectra of CNTs, CNTs-T and xB-CNTs were illustrated in Figure 3a. For CNTs and CNTs-T, no B1s peak was detected due to the absence of boron source. Besides the peaks of C 1s and O 1s, a small peak of B 1s was detected in the spectra of xB-CNTs, demonstrated the successful doping of boron. In addition, surface characterization by nanoscale elemental STEM-EDX mapping (Figure 4) was also used to determine the distribution of B species in the 1B-CNTs support. The distribution domain of B species was clearly located on the wall of CNTs, demonstrating that the B species were successfully doped into the outer and inner wall of 1B-CNTs support. More details of the doped boron could be achieved from the deconvoluted B 1s spectrum as compared in Figure 3(b-d). The B 1s spectrum was accordingly deconvoluted into three peaks with the binding energies of 190.2 (magenta line), 190.8 (olive line) and 191.8 eV (blue line). The peak at 190.2 eV corresponded to the B-C bonds in BC₃ structure,^[31] and the highenergy peaks at 190.8 and 191.8 eV could be ascribed to the B- O band in BC₂O and BCO₂ structure, respectively.^[27, 32] The boron doped in CNTs could break the hexagonal lattice of graphitic shell and introduce more defects, and thus led to the increased I_D/I_G ratio in Raman spectrum (Figure 2).



Figure 4. STEM-EDX images of 1B-CNTs support.

Table 1. Content of C, B and O of CNTs, CNTs-T and xB-CNTs.

Sample	C (at%)	B (at%)	O (at%)	
CNTs	91.2		8.8	
CNTs-T	98.1		1.9	
0.05B-CNTs	95.9	0.8	3.3	
0.1B-CNTs	95.3	1.1	3.6	
1B-CNTs	93.9	1.8	4.3	

The content of each element calculated from the XPS survey spectra was summarized in Table 1. The boron contents of 0.05B-CNTs, 0.1B-CNTs and 1B-CNTs obeyed the following order: 1B-CNTs>0.1B-CNTs>0.05B-CNTs, demonstrating that tunable boron content could be obtained by thermal annealing boric acid and CNTs with the varied weight ratio. Furthermore, the decrease of oxygen content on CNTs-T strongly suggested that most of surface oxygen-containing functional groups were removed by thermal treatment. This is in agreement with the result of Raman spectrum in Figure 2. Interestingly, the oxygen content increased steadily with increasing boron content. This phenomenon was considered to be induced by the strong interaction of boron with oxygen-containing species, which had a relatively high affinity for electrons. The possible effects from this interaction on the chemical properties of boron-doped Cu/xB-CNTs catalysts will be discussed in detail at the following part.

Structure and surface properties of boron-doped CNTs supported Cu catalysts

As mentioned above, doping boron into CNTs introduced defect sites into CNTs lattice, and further significantly changed the surface properties of CNTs. Accordingly, doping boron into CNTs may realize remarkable improvements in the structure and chemical properties of boron-doped CNTs supported Cu catalyst. To investigate the effect of boron doping on copper species of catalysts, XRD patterns of boron-free and boron-doped CNTs supported Cu catalysts thermally treated in argon atmosphere at 500 °C were collected and presented in Figure 5.

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Figure 5. XRD patterns of (a) Cu/CNTs, (b) Cu/CNTs-T, (c) Cu/0.05B-CNTs, (d) Cu/0.1B-CNTs and (e) Cu/1B-CNTs.

The strong diffraction peak around 26° could be attributed to the graphite-like structure of CNTs.^[33] For Cu/CNTs catalyst, the appearance of peaks from Cu₂O and metallic Cu diffraction could be distinguished easily. The obvious Cu₂O and metallic Cu peaks indicated that the facile reduction of copper species by CNTs support took place even in the absence of hydrogen.^[34, 35] In contrast, the intensity of metallic Cu peaks of Cu/CNTs-T decreased sharply, because thermal treatment removed most surface oxvgen-containing functional groups of CNTs. leading to the decrease of the reducibility of CNTs.^[34] For Cu/xB-CNTs catalysts, due to the strong interaction of boron with oxygencontaining species, part of oxygen-containing functional groups were retained on the surface of xB-CNTs (Figure 3 and Table 1). Therefore, the reducibility of xB-CNTs was enhanced and the metallic Cu peaks were more obvious than those of Cu/CNTs-T catalyst. It is worth noting that, with increasing amount of doped boron, the intensity of metallic Cu peaks of Cu/1B-CNTs decreased, probably because the electron-deficient boron doped in CNTs hindered the reduction of Cu₂O to Cu. Theoretical calculations indicated that boron doping enhanced the interaction of positive-valence Cu species with CNTs support, which thus resulted in a relatively difficult reduction of Cu₂O.^[31, 36] Therefore, from XRD results, it is reasonable to conclude that boron doping could affect the reduction of Cu species by changing the interaction of copper species with CNTs support. The influence of boron doping on the interaction of Cu species with CNTs support could be further investigated by H2-TPR as in Figure 6.

Compared with Cu/CNTs catalyst, Cu/CNTs-T catalyst displayed a higher reduction temperature (218 °C) than that of Cu/CNTs (145 °C), indicating that the reducibility of Cu species supported on CNTs-T support was lower. This difference should have the following reasons: the average size of Cu species increased from 16.1 nm of Cu/CNTs catalyst to 19.2 nm of Cu/CNTs-T catalyst as in Table 3, which caused the Cu species to be reduced more difficultly.^[34] The Cu/xB-CNTs catalysts with boron doping showed much higher reduction temperature and the reduction peak gradually shifted to higher temperature with increased boron amount. As an electron-deficient element, boron doped in the graphitic structure of CNTs could strengthen the interaction of positive-valence Cu species with CNTs support.^[37] Therefore, boron doping hindered the transformation of the positive-valence Cu species to metallic Cu to some extent,

and the positive-valence Cu species increased with increasing boron amount for the Cu/xB-CNTs catalysts. The higher reduction temperature also demonstrated the strong interaction between Cu species and CNTs support, which could improve the stability of Cu species on the catalyst during reaction.



Figure 6. H_2 -TPR patterns of (a) Cu/CNTs, (b) Cu/CNTs-T, (c) Cu/0.05B-CNTs, (d) Cu/0.1B-CNTs and (e) Cu/1B-CNTs.

Furthermore, dual peaks appeared in the H₂-TPR patterns of Cu/xB-CNTs catalysts with high boron content, indicated that at least two different Cu⁺ species existed. Highly dispersed Cu species on supports were well documented to be more readily reduced than bulk Cu species.^[38] Thus, the dual reduction peaks should be attributed to the reduction of highly dispersed Cu⁺ (left peak) and bulk Cu⁺ (right peak), respectively. With increasing boron content, the amount of highly dispersed Cu⁺ species increased gradually based on the proportions of the two peaks. These findings confirmed that boron doping could not only enhance the interaction of Cu species with CNTs support, but also control the valence distribution of copper species. In addition, the H₂ consumption peak at around 650 °C was attributed to the gasification of oxygen-containing functional group on the surface of CNTs support due to the reduction action of H₂ at high temperature.^[39, 40]



Figure 7. $\rm NH_3-TPD$ of (a) Cu/CNTs, (b) Cu/CNTs-T, (c) Cu/0.05B-CNTs, (d) Cu/0.1B-CNTs and (e) Cu/1B-CNTs.

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Furthermore, the boron atoms entered the carbon lattice by substituting carbon atoms at the trigonal sites, which could act as electron acceptor, Lewis acid, in catalysts. Because the acidic sites were beneficial to deep hydrogenation of EG to ethanol, surface acidity played a critical role on ethanol selectivity in DMO hydrogenation. The NH₃-TPD measurement was taken to evaluate the strength and quantity of acidic sites on Cu/CNTs, Cu/CNTs-T and Cu/xB-CNTs catalysts and the obtained profiles were compared in Figure 7. In order to eliminate the interference of other gaseous products, the TPD-MASS was used to monitor the desorption of NH₃ with MS signals at m/e =17. No obvious NH₃ desorption peak could be observed on Cu/CNTs and Cu/CNTs-T catalysts, whereas Cu/xB-CNTs catalysts exhibited multiple peaks corresponded to acid sites of weak and medium strength, indicating that the doped boron was responsible for the surface acidity of Cu/xB-CNTs catalysts. The variation of surface acidity, induced by boron doping with varied amount, could exert great influence on ethanol selectivity of Cu/xB-CNTs catalysts for DMO hydrogenation to ethanol.

Boron-doped CNTs supported Cu catalysts for DMO hydrogenation

Table 2. DMO hydrogenation to ethanol over Cu/CNTs, Cu/CNTs-T and Cu/xB-CNTs catalysts.

Cataly at ^[a]	Conv. (%)	Sel.(%) ^[b]				
Calalysi		Ethanol	MG	EG	Others	
Cu/CNTs	99.8	46.4	4.6	47.7	1.3	
Cu/CNTs-T	97.8	44.8	14.1	37.3	3.8	
Cu/0.05B-CNTs	99.9	62.7	6.0	25.0	6.3	
Cu/0.1B-CNTs	100.0	68.2	5.7	18.3	7.8	
Cu/1B-CNTs	100.0	78.1	3.7	13.6	4.6	

[a] Reaction conditions: 300 $^{\circ}$ C, 2.5 MPa, LHSV = 0.4 h⁻¹, H₂/DMO = 200, reaction time= 6 h, 15 wt% DMO/1, 4-dioxane as feed. [b] MG: methyl glycolate, EG: ethylene glycol, Others mainly consist of methyl methoxyacetate, methyl acetate, 1, 2-propanediol and 1, 2-butanediol.

In order to investigate the effect of boron doping on the catalytic performances, DMO hydrogenation reactions catalyzed by boron-free and boron-doped catalysts were conducted under identical reaction conditions. DMO conversion and product selectivity over the series of catalysts were listed in Table 2. DMO conversion was close for all catalysts, while the best ethanol selectivity of 78.1% was obtained over the Cu/1B-CNTs catalyst. The catalytic activity for DMO hydrogenation versus Cu/xB-CNTs with different boron content was plotted in Figure 8. Under the given reaction conditions, although the DMO conversions of Cu/CNTs catalyst (99.8%) and Cu/1B-CNTs catalyst (100%) were so close, the selectivity of ethanol increased obviously from 46.4 to 78.1%. This result indicated that boron doping on Cu/xB-CNT catalysts had remarkable influence on the enhanced ethanol selectivity of DMO

hydrogenation reaction. Furthermore, the catalytic performance of Cu/1B-CNTs catalyst was evaluated at different LHSV and shown in Figure S1. As the LHSV increasing from 0.2 h⁻¹ to 1.0 h⁻¹, the DMO conversion was still stable, with no significant changes, and the ethanol selectivity was gradually decreased from 88.8% to 65.2%. The XRD and TPR of spent catalysts have conducted and displayed in Figure S2. The results indicate that the Cu⁺ species can partly be reduced under reaction conditions.



Figure 8. The correlation of catalytic activity with Cu/xB-CNTs with different boron content.

It is worth noting that although the catalytic activity of Cu/xB-CNTs catalysts could be gradually enhanced with weight ratio of boric acid with CNTs increased from 0.05 to 1, this trend could not proceed when the weight ratio greater than 1. As shown in Table S1, DMO conversion and ethanol selectivity of Cu/2B-CNTs catalyst were 100.0% and 75.8% respectively, which were very close to that of Cu/1B-CNTs catalyst (DMO conversion of 100.0%, ethanol selectivity of 78.1%). This result could be attributed to the fact that the content of boron doped into CNTs by thermal annealing did not increase constantly with weight ratio of boric acid to CNTs, and had a maximum value.^[27] To confirm this reason, XRD and XPS were carried out to investigate the crystal structure and doped boron of 2B-CNTs support. From XRD patterns (Figure S3), the characteristic diffraction peaks of 2B-CNTs support were the same with those of CNTs, indicating that thermal treatment of CNTs with elevated boric acid amount did not affect the crystal structure of CNTs. Subsequently, the presence and chemical states of the doped boron were confirmed by XPS (Figure S4), and the content of doped boron was summarized in Table S2. Apparently, the boron content of 2B-CNTs support prepared with higher weight ratio of boric acid to CNTs was same as that of 1B-CNTs support (Table 1). This finding disclosed that although tunable boron content could be obtained by thermal annealing CNTs and boric acid with varied weight ratio, it was more difficult to implant more doped boron atoms into the framework of CNTs. Therefore, Cu/2B-CNTs catalyst exhibited the similar catalytic performance with Cu/1B-CNTs catalyst.

To further clarify the effect of boron doping on long-term catalytic performance, the catalytic activity as a function of time on stream over the boron-free Cu/CNTs and boron-doped catalysts was investigated as in Figure 9. The catalytic activity was measured first at 300 $^\circ C$ for 120 h and then raised the

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Table 3. Physicochemical properties of Cu/CNTs, Cu/CNTs-T and Cu/xB-CNTs catalysts.

Catalyst	Cu loading (wt%) ^[a]	S _{BET} (m²/g) ^[b]	$S_{Cu}^{0} (m^{2}/g)^{[c]}$	$S_{Cu}^{+} (m^2/g)^{[d]}$	acid amount (mmol/g) ^[e]	d _{Cu} ⁰ (nm) ^[f]	d _{cu} ⁺ (nm) ^[ſ]	d _{Cu} (nm) ^[g]	Cu ⁺ /(Cu ⁰ +Cu ⁺)
Cu/CNTs	15.3	126.9	18.8	3.4		19.1	23.6	16.1	0.15
Cu/CNTs-T	14.3	124.6	13.3	2.3		20.2	25.7	19.2	0.15
Cu/0.05B-CNTs	14.7	129.6	23.4	9.5	0.3	15.5	18.2	15.0	0.29
Cu/0.1B-CNTs	14.6	134.2	28.4	16.7	0.6	13.9	16.6	12.3	0.37
Cu/1B-CNTs	14.5	141.2	32.5	23.4	1.0	11.9	13.8	10.9	0.42

[a] Cu loading determined by ICP-OES analysis. [b] BET specific surface area. [c] Cu metal surface area determined by N₂O pulse adsorption. [d] Cu⁺ surface area determined by CO chemisorption. [e] Amount of acid sites estimated by NH₃-TPD. [f] Average diameter of particle size calculated from the XRD data based on Scherrer equation. [g] Average diameter of particle size calculated based on statistical results of TEM images.



Figure 9. The catalytic activity as a function of time on stream over Cu/CNTs and Cu/1B-CNTs catalysts.

temperature to 450 °C under N₂ for 12 h. Subsequently, the catalytic activity was evaluated at 300 °C after heat treatment. At the initial stage, there was no obvious change of the DMO conversion and ethanol selectivity for both catalysts. However, the catalytic performances of two catalysts after a 12 h thermal treatment were different. The ethanol selectivity of Cu/CNTs catalyst decreased from 46.4 to 26.3%, whereas that of Cu/1B-CNTs catalyst decreased slightly from 78.1 to 69.2%. This result suggested that boron-doped Cu/1B-CNTs catalyst exhibited a higher stability than boron-free Cu/CNTs catalyst. The improved stability could be attributed to the enhanced interaction between Cu species and CNTs support by the doped boron, which might reduce the sintering of Cu to some extent. The XRD characterization of spent Cu/CNTs and Cu/1B-CNTs catalysts was conducted and displayed in Figure S5. After long-term test, the particles size of Cu/1B-CNTs catalyst increased from 11.9 to 16.4 nm, whereas that of Cu/CNTs catalyst increased obviously from 19.1 to 33.7 nm. This result demonstrated the stabilizing effect of the doped boron on the particles size of Cu via strong interaction.

In view of above characterizations, boron doping could tune the surface properties of CNTs support, thus alter the structure and chemical properties of boron-doped catalysts. Firstly, the doping of boron was beneficial for improving the dispersion of Cu species and enhancing the interaction between Cu species and CNTs support. In general, as for hydrogenation reaction catalyzed by Cu species, the particle size, dispersion and interaction of Cu species with CNTs support were always considered vital parameters that greatly promoted the catalytic performance.^[41, 42] Calculated by the Scherrer formula based on the (111) diffraction of XRD patterns (Figure 5), the average sizes of metallic Cu particles and monovalent Cu particles were listed in the Table 3. As expected, the size of copper nanoparticles followed the order Cu/CNTs-T > Cu/CNTs > Cu/0.05B-CNTs > Cu/0.1B-CNTs > Cu/1B-CNTs. The TEM images also displayed the similar result and the average size of Cu nanoparticles was about 19.2 nm on Cu/CNTs-T, 16.1 nm on Cu/CNTs, 15.0 nm on Cu/0.05B-CNTs, 12.3 nm on Cu/0.1B-CNTs and 10.9 nm on Cu/1B-CNTs, as shown in Table 3 and Figure S6. Moreover, from XRD results, it had been deduced that boron doping could affect the reducibility of Cu species by changing the interaction of copper species with CNTs support. Subsequently, the enhanced interaction between Cu species and CNTs support had been demonstrated by H2-TPR results (Figure 6). These results indicated that doping boron into CNTs support played a very important role in promoting the dispersion of copper species and enhancing the interaction between Cu species and CNTs support. Secondly, the high surface area of Cu⁰ and Cu⁺ sites and synergy between Cu⁰ and Cu⁺ of Cubased catalyst both played a key role on the extent of hydrogenation proposed by Gong et al.^[4] In relation to the role of Cu⁰ and Cu⁺ in DMO hydrogenation, a reasonable interpretation suggested that the Cu⁰ species activated H₂ and adsorbed intermediates (methoxy and acyl species), and the Cu⁺ species acted as the stabilizer.^[23] Accordingly, the activity of DMO hydrogenation to ethanol greatly depended on the surface area of Cu⁰ and Cu⁺ sites, and synergy between Cu⁰ and Cu⁺ sites. Here, to distinguish the surface Cu^0 and $\text{Cu}^{\scriptscriptstyle +}$ site, N_2O pulse adsorption and CO chemisorption were conducted, respectively. As shown in Table 3, both the Cu⁰ surface area and Cu⁺ surface

area increased gradually with increased boron content. This phenomenon could be attributed to the following reasons: 1) the boron doping into the CNTs could improve the dispersion of supported Cu species, resulted in large Cu exposed surface area; 2) the doped boron could strongly interact with positive-valence Cu species, keeping highly dispersed Cu⁺ sites simultaneously. Furthermore, the boron-doped catalysts exhibited different Cu⁺/(Cu⁰+Cu⁺) ratios. The Cu⁺/(Cu⁰+Cu⁺) ratio increased gradually from 0.15 over Cu/CNTs catalyst to 0.42 over Cu/1B-CNTs catalyst. Meanwhile, the selectivity of ethanol was enhanced steadily with Cu⁺/(Cu⁰+Cu⁺) ratio, from 46.4% over Cu/CNTs to 78.1% over Cu/1B-CNTs catalyst. Therefore, the optimal ethanol selectivity over Cu/1B-CNTs catalyst was attributed to the high surface area of both Cu⁰ and Cu⁺ sites, as well as appropriate Cu⁰ and Cu⁺ distribution.

Otherwise, the synthesis of ethanol from DMO hydrogenation also lies in the cooperative effect of metal and acid sites, which can be explained by the acid sites catalyzing the dehydration while metal sites acting as an active phase for hydrogenation process.^[43, 44] Therefore, variation of the surface acidity on the Cu/xB-CNTs catalysts, induced by different boron doping amount, was responsible for the high ethanol selectivity.^[45] The quantitative estimation of acid sites according to their desorbed amount of ammonia from NH₃-TPD results was summarized in Table 3. It was easy to find that the total acid amount of Cu/xB-CNTs catalysts increased along with increasing boron doping amount, suggesting that boron doping was responsible for the increased surface acidity of Cu/xB-CNTs catalysts. Surface acidity was beneficial to deep hydrogenation of EG to ethanol, demonstrated by the decreased EG selectivity as shown in Figure 8 and Table 2. Thus, the observed notable increase of ethanol selectivity could also be partially attributed to the presence of surface acidity in the Cu/xB-CNTs catalysts.

Changing the type of CNTs support



Figure 10. Catalytic performance of Cu/xB-SCNTs catalysts in DMO hydrogenation Reaction conditions: P = 2.5 MPa, T = 300 $^{\circ}$ C, LHSV = 0.4 h⁻¹, H₂/DMO molar ratio = 200, reaction time= 8 h. Others mainly consist of methyl methoxyacetate, methyl acetate, 1, 2-propanediol and 1, 2-butanediol.

In order to verify the influence of boron doping on DMO hydrogenation to ethanol, another CNTs with small diameter (SCNTs, inner diameter: 4–10 nm; length: 0.5–2 μ m; Chengdu, China) was also used as support to prepare boron-doped SCNTs supported Cu catalysts. Primarily, the crystal structure

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and the existence of boron on xB-SCNTs supports were investigated by XRD (Figure S7) and XPS (Figure S8, Table S3) measurements, respectively. Subsequently, the XRD and TPR patterns of xB-SCNTs supported Cu-based catalysts were collected and presented in Figure S9 and Figure S10, respectively. These characterizations exhibited the similar result with Cu/xB-CNTs catalysts. The catalytic activity and selectivity for DMO hydrogenation versus Cu/xB-SCNTs catalysts with different boron content were compared in Figure 10 and Table S4. Under the given reaction conditions, the similar catalytic results were obtained over SCNTs based Cu catalysts. All catalysts exhibited high DMO conversion and the selectivity to ethanol also increased steadily from 48.4% over Cu/SCNTs catalyst to 83.1% over Cu/1B-SCNTs catalyst. These results demonstrated that boron doping was an effective approach to improve the catalytic performance of CNTs supported Cu-based catalyst for DMO hydrogenation to ethanol, regardless of the CNTs type.

Conclusions

In summary, boron-doped CNTs supported Cu catalysts exhibited superior catalytic performance in the hydrogenation of DMO to ethanol. The Cu/1B-CNTs catalyst achieved the highest ethanol selectivity and DMO conversion, which could be attributed to high copper dispersion, enhanced interaction of Cu species with CNT support, appropriate Cu⁰ and Cu⁺ distribution and suitable surface acidity. By boron doped into CNTs, the dispersion of Cu species increased and the particle size of Cu species was gradually decreased with the enhanced boron amount. A high copper dispersion of Cu-based catalyst was believed to be a prerequisite in obtaining excellent catalytic activity for DMO hydrogenation. Also, N₂O pulse adsorption and CO chemisorption revealed that surface area of Cu⁰ and Cu⁺ increased as the boron doping amount increased, and the reducibility of Cu⁺ was minimized due to the strong interaction with boron. Additionally, the suitable surface acidity induced by doped boron could further promote the deep hydrogenation of DMO to ethanol. Therefore, boron doping is an effect approach to improve the catalytic performance of CNTs based catalyst for hydrogenation of DMO.

Experimental Section

Catalysts preparation

Prior to doping, multi-walled carbon nanotubes (CNTs, inner diameter: 20–30 nm; length: 1–10 µm; Chengdu, China) were treated in a 65 wt% HNO₃ solution at 120 °C for 14 h and then washed with deionized water. The purpose of pretreatment was to eliminate the impurities and open the caps of CNTs.

xB-CNTs supports: the boron-doped CNTs supports were prepared by thermal annealing of a mixture of CNTs and boric acid. Briefly, CNTs and boric acid were mixed with different weight ratio (boric acid: CNTs = 0.05: 1, 0.1: 1, 1: 1, 2: 1, respectively) and grinded for about 30 min to obtain a uniform mixture. Subsequently, the mixture was calcined at 1000 °C for 4 h under argon atmosphere and then refluxed in 3 M KOH solution to remove the unreacted boric acid after being cooled down to room temperature. Finally, the collected sample was washed with deionized water before drying at 80 °C in vacuum. The corresponding supports

were denoted as 0.05B-CNTs, 0.1B-CNTs, 1B-CNTs and 2B-CNTs, respectively. For comparison, CNTs support was also treated by the same thermal annealing procedure of xB-CNTs without adding boric acid, named as CNTs-T.

Cu/xB-CNTs catalysts: Cu/xB-CNTs catalysts were prepared by a convenient sonication-assisted impregnation method with a constant Cu loading amount of 15 wt%. In a typical procedure, a certain amount of Cu(NO₃)₂•3H₂O was dissolved in deionized water and then dripped into xB-CNTs supports, sonicated and stirred for 30 min. Subsequently, a calculated amount of deionized water was dripped, sonicated for another 30 min. All of these operations were conducted at room temperature. The resulting solid was dried overnight at 120 °C in vacuum and then calcined at 500 °C (ramping rate: 3 °C/min) under argon atmosphere for 3 h. For comparison, Cu/CNTs and Cu/CNTs-T catalysts with pristine CNTs and CNTs-T as supports were also prepared by the same synthesis procedure of Cu/xB-CNTs, respectively.

Catalysts characterization

Field emission scanning electron microscope (FE-SEM) images were recorded using a JSM-6700F (Japan) instrument at an accelerating voltage of 5 kV. X-ray powder diffraction (XRD) measurements were conducted using a Rigaku D/max-2550 V diffractometer employing Cu Kα radiation ($\lambda = 1.54056$ Å) at room temperature. Data points were acquired by scanning with a rate of 0.02°/s from 20 = 10° to 20 = 80°. Raman spectra were recorded on a Renishaw inVia 2000 Raman microscope using an Ar⁺ ion laser at 514.5 nm wavelength. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Fisher SCIENTIFIC ESCALAB 250Xi instrument equipped with an Al K α X-ray radiation source (hv = 1486.6 eV). N₂ adsorption-desorption isotherms were measured on a Quantachrome AUTOSORB-1. The specific surface area was calculated from the isotherms through the method of Brunauer-Emmett-Teller (BET).

Transmission electron microscopy (TEM) was performed on JEOL-4010T (Japan) at an acceleration voltage of 400 kV. Elemental distribution in catalysts was determined by energy-dispersive X-ray spectroscopy (EDX) mapping technique in scanning TEM (STEM) mode. Prior to the TEM measurement, sample powder was dispersed in ethanol using a sonicator and then dripped onto a copper grid.

The H₂ temperature-programmed reduction (H₂-TPR) was performed by using a catalyst analyzer BELCAT-B-TT (BEL Japan Co. Ltd.) equipped with a thermal conductivity detector (TCD). Prior to measurement, the sample was pretreated with helium gas flow at 150 °C for 1 h to remove traces of water. After cooling down to 50 °C, the H₂-TPR was conducted in a stream of 5% H₂/Ar (30 ml/min) with a heating rate of 10 °C/min to 800 °C.

The NH₃ temperature-programmed desorption (NH₃-TPD) experiments were performed on the same equipment for H₂-TPR measurement. In a typical procedure, the sample was pretreated with helium gas flow at 150 °C for 1 h to remove traces of water. After cooling down to 60 °C, a flow of NH₃ gas mixture (5% in He, 30 ml/min) was introduced for 1 h, followed by a purge of helium gas to completely remove the unabsorbed NH₃. Finally, chemisorbed NH₃ was desorbed by heating from the absorption temperature up to 850 °C at a ramping rate of 10 °C/min, being monitored with MS signals at *m*/*e* = 17.

In order to investigate the Cu⁰ and Cu⁺ sites, the surface area of Cu⁰ and Cu⁺ sites were measured by N₂O pulse adsorption and CO chemisorption independently. The metallic Cu surface area was measured by the decomposition of N₂O at 90 °C using a pulsed method with the equation: 2 Cu + N₂O = Cu₂O + N₂. The consumption of N₂O was detected by a TCD detector, and the surface area of metallic Cu was calculated from the total consumption amount of N₂O with 1.46 × 10¹⁹ copper atoms per m². CO chemisorption experiments were performed to quantify the

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surface area of Cu⁺ by using quantachrome automatic chemisorption analyzer, and the CO adsorption stoichiometry was assumed as Cu: CO = 1: 1. The CO chemisorption was conducted at room temperature (27 $^{\circ}$ C).

Catalysts evaluation

Catalytic evaluation of DMO hydrogenation was conducted in a continuous flow mode using a stainless steel fixed bed reactor. In a typical run, 0.125 g calcined catalyst mixed with 3 g quartz sand was placed in the middle of the reactor with quartz wool packed in both sides of the catalyst bed. Then, the system was heated to reaction temperature (300 °C), and the system pressure was precisely controlled at 2.5 MPa with a back-pressure regulator. Then, a 15 wt% DMO solution with 1, 4-dioxane as solvent was continuously pumped into the reactor with co-feeding H_2 at a H_2 /DMO molar ratio of 200. Finally, the products were condensed in a cold trap and then analyzed using a gas chromatography instrument (Shimadzu, GC-2014AF) equipped with a flame-ionization detector, in which 2-propanol was employed as the internal standard.

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Entry for the Table of Contents

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Doping CNTs with boron is an efficient approach to improve the catalytic performance of CNTs based catalysts for hydrogenation of DMO.



Peipei Ai, Minghui Tan, Noriyuki Yamane, Guoguo Liu, Ronggang Fan, Guohui Yang, Yoshiharu Yoneyama, Ruiqin Yang, Noritatsu Tsubaki*

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Synergistic effect of boron-doped carbon nanotubes supported Cu catalyst for selective hydrogenation of dimethyl oxalate to ethanol