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## ARTICLE

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Activated carbon aerogels supported copper catalysts for the hydrogenation of methyl acetate to ethanol: Effect of KOH activation

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Methyl acetate (MA) hydrogenation is crucial in the indirect ethanol synthesis through syngas ( $CO+H_2$ ). In our work, activated carbon aerogels supported copper (Cu-ACAs) catalysts have been prepared by a conventional impregnation method. The surface area and functional groups of the ACA soared after KOH activation. The highest surface area of the ACA achieved was 2562 m<sup>2</sup>g<sup>-1</sup>. The anchoring effect of micropores and external oxygen-containing groups (OCGs) significantly enhanced the metal-support interaction in catalysts, facilitating the high dispersion of Cu and an enhancement in surface Cu<sup>+</sup> species, both of which improved catalytic activity of catalysts. Cu-ACAs-A4 showed the most outstanding catalytic performance, with a MA conversion of 95.2% and an ethanol selectivity of 62.2%, close to the carbon equilibrium selectivity of 66.7%.

## Introduction

The production of ethanol has become a hot topic around the world because it can be widely used as an alternative energy source, a hydrogen carrier, and a chemical feedstock. In particular, ethanol can also simultaneously be blended with gasoline and holds great promise due to its environmentally friendly nature<sup>1-6</sup>. Currently, two main methods have been developed for the production of ethanol: fermentation and ethylene hydration. However, fermentation of edible grain crops and ethylene hydration face great challenges owing to the negative effect on global food supplies and the shrinking worldwide oil resource crisis, respectively<sup>2, 7</sup>. As a result, it is critical to explore alternative processes for ethanol production. It is known that synthetic gas (syngas) can be produced from extensive ingredients, such as biomass and coal, and has a wide range of applications in producing quantities of chemicals, including ethanol<sup>8, 9</sup>. However, the direct ethanol production by syngas is hampered by difficulties, such as low conversion and low selectivity, abundant byproducts, high

investment cost, and high energy consumption<sup>10–12</sup>. In recent years, the indirect ethanol synthesis by two successive processes, dimethyl ether (DME) carbonylation and methyl acetate (MA) hydrogenation, have been proposed<sup>3,13–17</sup>. As Compared with the hydrogenation of acetic acid, the hydrogenation of MA has outstanding advantages in terms of the cost of catalysts, the conversion rate, and the equipment requirement<sup>18, 19</sup>.

Copper catalysts supported on silica are well-suited for the hydrogenation of esters, showing high activation in the hydrogenolysis of C-O or C=O bonds, but much lower stimulation for C-C cleavage<sup>20–23</sup>. In a previous study, the catalytic mechanism that synergistic effect of Cu<sup>0</sup> and Cu<sup>+</sup> has been shown to improve the catalytic hydrogenation activity, whereby Cu<sup>0</sup> promotes H<sub>2</sub> splitting and Cu<sup>+</sup> adsorbs and stimulates CH<sub>3</sub>O- or CH<sub>3</sub>CO-<sup>24</sup>. However, Cu<sup>0</sup> nanoparticles toward to transfer and agglomerate and Cu<sup>+</sup> species are apt to reduce during the reaction. Therefore, it is crucial to develop copper catalysts with high stability and high dispersion for the hydrogenation of MA.

It is noted that carbon nanotubes (CNTs) had been used to prepare supported copper catalysts for gas-phase catalytic hydrogenation of MA<sup>25, 26</sup>. However, only a relatively low MA conversion (22.5%) and low ethanol selectivity (27.6%) were thereby acquired. Owing to its particular superiorities, such as, low density, high surface area, fine pore size, threedimensional nano-networks, and outstanding electrical conductivity<sup>27–29</sup>, carbon aerogel is considered to be a prospective support for catalysts. By virtue of its unique properties and surface chemistry, carbon aerogels represent a promising materials for performance in catalyst support<sup>30</sup>.

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In the present work, ACAs was synthesized by a sol-gel method and then subjected to KOH activation at various concentrations. The obtained materials were then used to prepare supported copper catalysts through a wet impregnation method, and these were tested for their efficacy in the hydrogenation of MA. The influence of KOH activation on the hydrogenation activity had been studied in terms of structural properties, surface chemical groups, and dispersion and valence state of copper of the Cu-ACAs catalysts. Our results may encourage readers to design and investigate other related carbon material-based catalysts with favorable performances for the hydrogenation of methyl acetate.

## Experiment

## Catalysts preparation

**Preparation of carbon-silica aerogel (CSA).** Carbon-silica aerogel was synthesized by a sol–gel process through resorcinol, formaldehyde and TEOS. Resorcinol (1.5 g) was dissolved in a mixture of acetone (8.5 mL), TEOS (5.5 mL), and APTES (640  $\mu$ L). After the addition of formaldehyde (37%, 3.2 g), the mixed solution was transferred to a polypropylene container and left undisturbed at 50°C for 6 h. The container was tightly packed to avoid solvent loss. The polymer was then washed thoroughly using acetone and kept at 60 °C for 10 h in a hot dryer. This established material was carbonized at 900 °C for 60-minutes in nitrogen. The as-synthesized sample was designated as CSA.

**Etching of silica templates.** To etch silica, the obtained CSA was immersed in NaOH liquor (1 M) at 80 °C for 12 h and then collected by filtration. The step was repeated every 12 hours to ensure the total removal of silica. The obtained aerogel was rinsed thoroughly, and then dried overnight in 80 °C oven. This material was carbon aerogel, designated as CAs.

Activation of CAs with KOH. Activated carbon aerogels (ACAs) was obtained by the following procedure. CAs was pre-treated with 0.5 m aqueous  $HNO_3$  at 80 °C for 6 h then flushed out, and dried overnight at 100 °C. Subsequently, the pre-treated CAs was activated by mixing with solid KOH in various proportions (2/1, 4/1, and 6/1, w/w), and carbonizing at 750 °C (3 °C/min) in N<sub>2</sub> atmosphere. The resulting materials were flushed out with HCl solution (1 M) and deionized water for several times. The achieved materials were designated as ACAs-A2, ACAs-A4, and ACAs-A6, respectively.

Cu-ACAs preparation. The Cu-ACAs catalysts with Cu loading of 30 % were synthesized through a conventional impregnation method. In brief, ACAs or CAs (1 g) was immersed in copper (II) nitrate solution (40 mL) at a certain concentration, and the mixture was ultrasonicated for several minutes and then vigorously stirred under ambient temperature for 8 h. Thereafter, each precursor was reduced in H<sub>2</sub> atmosphere at 350 °C for 2 h. The catalysts are defined as Cu-CAs, Cu-ACAs–A2, Cu-ACAs-A4, and Cu-ACAs-A6.

## Catalytic activity evaluation.

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The catalytic performance was checked through a micro reaction device. Samples (0.5 g in all cases) were placed between plugs of quartz wool in the reactor. For each catalyst, tests were performed with fresh samples, heating from ambient temperature to 330 °C. After pre-heating, MA was blended with hydrogen, then fed into the reactor to initiate the reaction. The products were tested on a gas chromatograph (GC-950, Shanghai Haixin, China) fitted with a flame-ionization detector (FID).

Conversions and products selectivity were acquired by the following equations:

Conversion (%) = $(1 - 1)$	$\frac{amount of MA after reaction(mol)}{total amount of MA in the feed(mol)} \Big)$	× 100%	(1)
Selectivity $(\%) =$	Amount of carbon of ethanol (mol)	— v 100%	(2)

Selectivity  $(\%) = \frac{1}{Total amount of carbon of MA converted (mol)} \times 100\%$  (2) Characterization of the catalysts

#### Characterization of the cataly

The texture properties of each sample was observed by transmission electron microscopy (TEM, JEOL, JEM-2100F, Tokyo, Japan) operating at 200 keV. The catalysts were ultrasonically dispersed in ethanol solvent and this suspension was then dropped on a Cu grid and was allowed to dry before measurement. Actual loading of Cu obtained by atomic absorption spectrometer (AAS, AA240FS, VARIAN). XRD was performed through a D/max 2500 diffractometer employing Cu- $K_{\alpha}$  radiation in a region of 10–80°. The specific surface areas were tested by  $N_2$  adsorption-desorption data obtained at  $P/P_0 = 0.04-0.32$  using the Brunauer-Emmett-Teller (BET) method (Micromeritics Instrument Co., GA, USA). The nitrogen at  $P/P_0 = 0.99$  was used to evaluate the gross pore volume. To characterize the functional species in the samples, Fouriertransform infrared (FTIR) measurement was performed in the range from 650 to 4000 cm<sup>-1</sup> with a KBr beam splitter. The content of the surface OCGs on the surface of the ACA was equipped by the Boehm's titration method. N<sub>2</sub>O chemisorption on the catalysts was determined to reckon the copper dispersion (D<sub>Cu</sub> %) and copper surface area (S<sub>Cu</sub>, m<sup>2</sup>g<sup>-1</sup>Cu). XPS was measured on a 250Xi electron spectrometer (Al- $K_{\alpha}$  X-ray).

## Table 1 Hydrogenation of MA over Cu-ACAs catalysts.

Samples	MA Conversion	Selectivity (%)					
	(%)	EtOH	MeOH	EAC	Else		
Cu-CAs	77.4	61.1	32.9	0.4	5.6		
Cu-ACAs-A2	89.5	61.5	30.2	3.5	4.8		
Cu-ACAs-A4	96.7	62.2	30.5	2.6	4.7		
Cu-ACAs-A6	79.5	59.5	34.1	0.4	6.0		
Cu-CNTs <sup>31</sup>	19.5	26.6	57.1	16.3	-		
Cu-inside-CNTs <sup>32</sup>	35.0	32.5	54.7	11.9	0.9		

Reaction conditions: T = 330 °C, P = 2.0 MPa, H<sub>2</sub>/MA = 60, m<sub>cat</sub> = 0.5 g, LHSV = 2.5 h<sup>-1</sup>, reaction time was 10 h.

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Figure 1 N₂ adsorption-desorption isotherms and pore size distribution of supports (a, b) and Cu-ACAs catalysts (c, d). TPR test was actualized on an AutoChenFinsore-3010 The catalytic performances of Cu-CAs an apparatus (Zhejiang FINETEC). catalysts in the hydrogenation of MA were evalu

## **Results and discussion**

**Catalytic activity** 

supports and Cu-ACAs catalysts.										
Samples	KOH/ CAs	S <sup>a</sup> <sub>BET</sub> (m <sup>2</sup> * g <sup>-1</sup> )	S <sup>b</sup> micr o (m <sup>2</sup> * g-1)	V <sup>c</sup> <sub>total</sub> (cm <sup>3</sup> *g <sup>-</sup> <sup>1</sup> )	V <sup>d</sup> <sub>micro</sub> (cm <sup>3</sup> *g <sup>.</sup> 1)	D <sup>e</sup> (nm)				
CAs	0	1279	979	1.47	0.57	1.82				
Cu-CAs	0	516	335	0.91	0.23	1.92				
ACAs-A2	2	1849	1570	1.79	0.80	1.82				
Cu-ACAs- A2	2	716	518	1.00	0.33	1.92				
ACAs-A4	4	2562	2193	2.33	0.96	1.76				
Cu-ACAs- A4	4	695	553	0.86	0.30	1.84				
ACAs-A6	6	2497	2186	2.29	0.94	1.80				
Cu-ACAs-	6	1358	936	1.73	0.60	1.84				

Table 2 Physicochemical and textural properties of ACAs

a Total specific surface area

b Specific surface area of micropores

c Total pore volume

d Pore volume of micropores

e Average pore diameter calculated from adsorption branch by DFT method

The catalytic performances of Cu-CAs and Cu-ACAs catalysts in the hydrogenation of MA were evaluated under conditions of 2.0 MPa, 330 °C,  $H_2/MA = 60$ , and LHSV = 2.5  $h^{-1}$ , and the results are revealed in Table 1. The Cu-CAs catalyst displayed high MA conversion (77.4%) and ethanol selectivity (61.1%) and a methanol selectivity of about 33%. Besides, 0.4% ethyl acetate and 5.6% other hydrocarbons were obtained. After activation by KOH, crude stock conversion and ethanol selectivity were incrementally influenced by varied KOH/CAs mass ratio, reaching maximum values (96.7 and 62.2%, respectively) when the ratio was 4, beyond which a distinct decrease was observed. In general, the MA conversion and EtOH selectivity followed the order Cu-ACAs-A4 > Cu-ACAs-A2 > Cu-CAs > Cu-ACAs-A6. Apparently, the catalytic capability over the Cu-ACAs catalysts were influenced by the amount of KOH used during the activation process, and were significantly enhanced when the amount of KOH was within an appropriate range. It is worth noting that the two Cu-CNTs catalysts exhibited lower catalytic activity on the hydrogenation of MA. The MA conversion of Cu-ACAs was nearly three and five times as high as those of Cu-inside-CNTs and Cu-CNTs. The carbon aerogel has significant advantage compared with CNT support.

## Characterization of the samples

**BET.** As shown in Figure 1, the isotherms of the supports were of type I on the basis of the Brunauer–Emmett–Teller classification, without obvious hysteresis loop. The isotherms indicated a microporous structure of the samples<sup>33</sup>, as is apparent from the data in Table 2. For each support, a trimodal distribution was observed in the pore size distribution curve provided by the Horvath–Kawazoe method in Figure 1. Abundant micropores were formed upon the removal of the silica from the CSA and in calcination procedure, during which the organic components were purged at high temperature.

As indicated by the results in Figure 1 and Table 2, the  $N_2$  uptakes of the ACAs samples were significantly increased after

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It can be seen that the isotherms of All Acatalysts maintained type I on the basis of BET Classification? affer 3Cd loading. However, the specific surface areas and whole pore volumes decreased significantly for all the catalysts (shown in Table 2), compared with the corresponding supports. The highest specific surface areas of ACAs-A4 support is 4 times higher than that of Cu-ACAs-A4, indicating that part of Cu particles could reside at the opening micropore over ACAs support<sup>38</sup>.

**FTIR spectroscopy.** The Infrared optical transmittance spectra of CAs supports after treatment by KOH were exhibited in Figure 2. The broad band in v=3600–3440 cm<sup>-1</sup> can be distributed to OH stretching vibrations corresponding to free and associated hydroxyl groups, respectively, which may be associated with carboxyl, phenol groups and adsorbed water. Additionally, hydrogen bonds also offered assistance<sup>39</sup>. The absorption spectrum at v = 2850 and 2918 cm<sup>-1</sup> belonged to the stretching vibrations of methylene and methyl group, respectively, and that at v = 1614 cm<sup>-1</sup> can be apportioned to an aromatic ring stretching vibration. The band at v = 1475 cm<sup>-1</sup> can be allocated to a CH<sub>2</sub> simple harmonic vibration and CH<sub>3</sub> scissor vibration. The CH<sub>2</sub>-O-CH<sub>2</sub> vibration emerged at 1055 cm<sup>-1</sup>, indicating the formation of cross bond between aromatic rings during condensation polymerization<sup>40</sup>.

Distinct differences in stretching vibrations were observed between CAs and ACAs. The absorption peaks occurred at v=1501 and 1435 cm<sup>-1</sup> only seen for the ACA samples, due to C=C stretching vibrations of aromatic rings, suggesting the benzol rings remained intact after hightemperature carbonization. The absorption peak occurred at 2250 cm<sup>-1</sup> only seen for the ACA samples can be accredited to the =C-H telescopic vibration of R<sub>2</sub>C=CHR. The presence of these organic functional groups indicated the appearance of a gel reticulated structure during the procedure of polycondensation-polymerization. Molecules were interlinked through the bonds of  $-CH_2$  and  $-CH_2-O-CH_2^{41}$ , generating a continuous criss-cross interconnected structure when the water was eliminated, which facilitated ion transfer.

**Boehm's titration and XPS.** Boehm titration has been used to quantify surface OCGs on carbon materials<sup>42</sup>. The concentrations of the superficial functional groups on the CAs and ACA were summarized in Table 3. The contents of surface

Table 3 Amount of OCGs of Cu-ACAs catalysts.									
Samples	Carboxyl group (mmol/g)	Lacton group (mmol/g)	Phenol group (mmol/g)	Basic group (mmol/g)	Total group (mmol/g)				
Cu-CAs	0.01	0.02	0.01	0.01	0.05				
Cu-ACAs-A2	0.10	0.06	0.12	0.10	0.38				
Cu-ACAs-A4	0.15	0.10	0.17	0.15	0.57				
Cu-ACAs-A6	0.17	0.14	0.20	0.12	0.63				





chemical activation by KOH over the full range of relative pressures. The inset in Figure 1 also showed the increased amount of micropores with an increment in mass ratio of KOH and CAs, suggesting the formation of new pores and a widening of existing pores by  $KOH^{34-36}$ . The specific surface areas and whole pore volumes (Table 2) multiplied with raised mass ratio, beyond which no obvious change was observed. The maximum surface area of ACAs-A4 reached up to 2562 m<sup>2</sup>g<sup>-1</sup>, which was twice as high as that of the original CAs (1279 m<sup>2</sup>g<sup>-1</sup>), indicating a more developed pore structure of ACAs than the primary CAs. The expansible specific surface area and incremental porosity contributed to higher dispersion of Cu nanoparticles, improving the catalytic performance compared with that of the original CAs<sup>37</sup>.

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groups increase from 0.05 to 0.63 mmol/g during increasing KOH/CAs values. This result, along with the FTIR results,



indicated that the quantity of external OCGs was greatly influenced by the KOH values.

XPS patterns of both the original and activated CA samples showed characteristic peaks in the C 1s and O 1s regions. The C 1s pattern for CAs in Figure 3(a) featured a characteristic peak at 284.6 eV, attributable to sp2 carbon atoms. Besides, peaks arose in 286.3, 287.6 and 289.4 eV were corresponding to C–O, C=O, and O=C–OH, respectively. The feature occurred at around 290.4 eV can be assigned as a p-p\* shake-up satellite peak<sup>43, 44</sup>. The three peaks at 531.2, 533.2, and 535.5 eV in the O 1s pattern in Figure 3(b) also demonstrated the existence of C–O, C=O, and O=C–OH, respectively<sup>45, 46</sup>. The O 1s/C 1s peak area ratio (Table 4) increased with increasing amounts of KOH, indicating that element content was influenced by the indirect effects from the KOH/CAs mass ratio.

**XRD.** In Figure 4, sharp diffraction peaks appeared at 43.3°, 50.5°, and 74.2° were vested in the characteristic (111), (200), and (220) facets of metallic Cu (JCPDS no. 65-9026), respectively, suggesting that  $Cu^{2+}$  was reduced to Cu0 by H<sub>2</sub>. The peak at 20=36.4° demonstrated the presence of Cu<sub>2</sub>O (JCPDS no. 05-0667), probably arising from incomplete reduction of Cu<sup>2+</sup>. This confirmed that the active species on the supports were identical. The diffraction peak in Cu-ACAs-A6 was sharper than that of the other samples, suggesting that



comparatively large Cu nanoparticles form over the catalyst. Therefore, it implied that the support with appropriate chemical activation were more beneficial to enhance



Figure 6 TEM images of Cu-CAs (a), Cu-ACAs-A2 (b), Cu-ACAs-A4 (c) and Cu-ACAs-A6 (d) catalysts.

dispersion of the active species.

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**H<sub>2</sub>-TPR.** H<sub>2</sub>-TPR figures of Cu-ACAs catalysts were exhibited in Figure 5. In every specimen, three main obvious peaks were observed. The first peak at around 150 °C corresponded to the dispersed CuO. The second reductive peak centred at 225 °C is in virtue of the reduction of crystalline CuO and the partial reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>. The last peak centred at 250 °C was caused by the reduction of Cu<sup>+</sup> to Cu<sup>0</sup>, implying a strong interaction of Cu<sup>2+</sup> species and support. Notably, KOH treatment of the CAs brought about a shift of the reduction peak of Cu species, and the reduction peak of CuO transferred to higher temperature. The results indicated that the appropriate OCGs can strengthen the copper-support interaction, thus forming smaller Cu particles.

**TEM.** The TEM images in Figure 6 showed that copper particles sizes were sized down from 40 to 11 nm, indicating Cu



uniformly dispersed on the CAs and ACAs supports. The average Cu particle size progressively decreased with increasing KOH/CAs ratios, reaching a minimum at a ratio of 4, but then increased at a ratio of 6.

On the one hand, the presence of OCGs resulted in an enhancive dispersion of Cu particles and a lessened trend in their size. Some investigator discovered the positive effect of exterior functional groups on support on the dispersity of Ru in carbon-supported Ru catalysts<sup>47</sup>. Gong et al. also observed the existence of OCGs was favorable to the 1R10<sup>3</sup>0/59875/0/149. Additionally, the presence of abundant micropores in ACAs was a further important factor for high dispersion of Cu. As indicated in Figure 1, the amount of micropores achieved the maximum at KOH/CAs of 4, which greatly contributed to decreasing the copper particle size. Kowalczyk et al. concluded that pores with diameter <3 nm, acting as anchor sites, facilitated the formation of fine Ru particles over carbon<sup>49</sup>. Hence, the synergistic effect between increased specific surface area and more abundant exterior OCGs favored the dispersion of copper species.

 $H_2-N_2O$  titration.  $N_2O$  titration examination were performed to confirm the dispersion of Cu, and the consequential data were presented in Table 5. It was notable that the dispersion of Cu increased incrementally with increasing KOH/CAs value, and



achieved a maximal value of 26.4% with a ratio of 4, beyond which a decrease was observed. This tendency was generally consistent with the TEM images. Accordingly, the calculated copper surface areas in the reduced catalysts increased incrementally, reaching a maximum at a KOH/CA ratio of 4, but decreased on further increasing the ratio to 6. Therefore, Cu-

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Table 4 Surface elemental composition of Cu-ACAs of	catalysts from XPS analysis.
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		с	1s	0/0	0 1s			
Samples	Peak 1 (284.6 eV)	Peak 2 (286.3 eV)	Peak 3 (287.6 eV)	Peak 4 (289.4 eV)	_ 0/C	Peak 1 (531.2 eV)	Peak 2 (533.2 eV)	Peak 3 (535.5 eV)
Cu-CAs	52.8	14.8	11.4	20.8	0.2	39.6	42.4	20.9
Cu-ACAs-A2	47.7	17.4	12.4	22.3	0.3	61.1	24.1	14.7
Cu-ACAs-A4	45.1	27.9	13.6	13.2	0.4	21.1	28.9	49.9
Cu-ACAs-A6	44.6	24.3	13.6	17.2	0.4	75.6	12.9	11.4

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Figure 9 TEM images of the used Cu-CAs (a) and used Cu-ACAs-A4 (b) catalysts.

ACAs-A4 displayed the optimal catalytic performance due to its greatest dispersion and largest copper specific surface area.

Stability of Cu-CAs and Cu-ACAs-A4 catalysts for MA hydrogenation. Time on stream of 100 h for catalytic

## Table 5 Physicochemical properties of Cu-ACAs catalysts.

Complex			Cu loading"		Dispersion <sup>b</sup>				Cu surface a	area <sup>b</sup>	Cu particle size <sup>c</sup> (nm)		Area of Cu LMM <sup>d</sup> (%)					
	Sam	pies			(%)	) (%) (m²/g-Cat)			Cu⁰	Cu			1+					
	Cu-	CAs			30.0			10.3	}		69.7		25		2	42.8	57	.2
	Cu-AC	As-A2			27.8			11.4	ļ		77.1 15				27.2			.8
	Cu-AC	As-A4			30.6			13.9	)		94.0 11				2	25.3	74	.7
	Cu-AC	As-A6			28.3			10.6	5		71.7	71.7 21			2	29.1	70	.9
a De	etermined by	AAS.																
b Ca	alculated from	n N₂O tit	ration.															
c Oł	oserved by Ti	EM analy	sis.															
d	Intensity	ratio	of	Cu⁺	and	Cu <sup>0</sup>	to	(Cu⁺	+	Cu <sup>0</sup> )	obtained	by	deconvolution	of	Cu	LMM	XAES	spectra.

**XPS.** XPS spectrum was obtained to judge the surface chemical states of the catalysts, as revealed in Figure. 7. Two Cu 2p<sub>3/2</sub> spectra position at 934.4 and 932.3 eV were ascribed to bivalent copper and (Cu<sup>+</sup> and Cu<sup>0</sup>), respectively (Figure 7(a)). To distinguish Cu<sup>+</sup> and Cu<sup>0 50–53</sup>, Cu Auger spectra of the catalysts were obtained and revealed in Figure 7(b), in which wide and symmetric peaks centered at 914.6 and 917.5 eV were allocated to Cu<sup>+</sup> and Cu<sup>0</sup>, respectively<sup>54</sup>. It was worth noting that the proportion of Cu<sup>+</sup>/ (Cu<sup>0</sup>+Cu<sup>+</sup>) ratio increased incrementally, reaching a maximum value of 74.7% at KOH/CAs of 4, but decreased on further increasing the KOH/CAs ratio (Table 5). Thus, the distributions of superficial Cu<sup>+</sup> and Cu<sup>0</sup> were consumedly affected by the mass ratio of KOH/CAs. These results illustrated that treatment of the Cu-CAs catalyst with KOH was an effective means of controlling the distributions of surface Cu<sup>+</sup> and Cu<sup>0</sup>.

performance was performed to certify stabilities of the Cu-CAs and Cu-ACAs-A4 catalysts at 330°C, 2 MPa and H<sub>2</sub>/MA=60. Both MA conversion and ethanol selectivity were displayed in Figure 8. The Cu-CAs and Cu-ACAs-A4 catalysts exhibited decrease tendency in MA conversion and EtOH selectivity in different extents. The MA conversion and EtOH selectivity for the Cu-ACAs-A4 catalyst decreased 35.7 and 18.4%, respectively, which is only half of the corresponding values of 60.5 and 35.7% for the Cu-CAs until the reaction time of 100 h. It is demonstrated that the Cu-ACAs-A4 possessed far superior stability for MA hydrogenation than the Cu-CAs catalyst.

TEM images of the used Cu-CAs and used Cu-ACAs-A4 catalysts were displayed in Figure 9. It is obvious that there was severe agglomeration of copper particles in the used Cu-CAs catalyst after reaction for 100 h. While in the used Cu-ACAs-A4 catalyst, the average particle size was ~33 nm (far smaller than that in the used Cu-CAs), although the aggregation could be observed.

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As displayed in Figure 10 and Table 6, for both the used Cu-CAs and used Cu-ACAs-A4, the peaks at 934.4eV corresponding to  $Cu^{2+}$  species significantly weakened in comparison with those in fresh catalyst, indicating Cu species were apt to be reduced during the MA hydrogenation reaction. However, the proportion of  $Cu^+/(Cu^0+Cu^+)$  ratio in the used Cu-ACAs-A4 was higher than that in Cu-CAs. This result demonstrated the positive influence of micropores and surface OCGs on the stability of both Cu particle size and valence state of Cu species, which greatly improved the stability of catalyst.

## Discussion

As revealed in Table 1, Cu-ACAs-A4 catalyst displayed the optimal catalytic activity in the MA hydrogenation. Generally, the catalytic performances of Cu catalysts had a bearing on their Cu dispersion and Cu<sup>+</sup>/ (Cu<sup>+</sup>+Cu<sup>0</sup>) ratio<sup>55</sup>. In this work, carbon aerogels with abundant micropores and high specific surface areas were achieved through activation with KOH. The highest BET surface area of 2562 m<sup>2</sup> g<sup>-1</sup> permitted admirable dispersion of copper nanoparticles, further improved the catalytic performance<sup>35</sup>. Additionally, as anchor sites, the appearance of a crowd of micropores in support greatly enhanced the dispersion of Cu particles<sup>56</sup>, as verified by TEM analysis (Figure 6) and N<sub>2</sub>O titration (Table 5). As indicated in Table 2, accompanied with a diminution of surface areas, the micropores volumes of the ACAs supports decreased sharply after loading copper component. In particular, for Cu-ACAs-A4, the micropores volume was only one-third of that for ACAs-A4, indicating that part of Cu species could reside at the micropore opening over ACAs support<sup>38</sup>. Moreover, FTIR analysis showed a band due to organic functional groups at v=2550 cm<sup>-1</sup>, the amount of which was highly dependent on the KOH/CA ratio according to Boehm titration and XPS analyses. The increase in the amount of surface functional groups also contributed to improving Cu dispersion and further enhancing catalytic activity.

As reported in the literature<sup>57, 58</sup>, for ester hydrogenation, the synergistic effect in Cu<sup>0</sup> with Cu<sup>+</sup> was of critical importance to catalytic activity in ester hydrogenation. Cu<sup>0</sup> species promoted the splitting of hydrogen, and Cu<sup>+</sup> species can adsorb and stimulate the CH<sub>3</sub>O and the acyl group<sup>59</sup>. As revealed in Table 1 and 5, the activity of Cu catalyst increased with increasing proportions of Cu<sup>+</sup>, and the highest MA conversion was achieved at a Cu<sup>+</sup>/(Cu<sup>+</sup>+Cu<sup>0</sup>) ratio of 74.7% in

Table 6. Chemical state of copper in the used Cu-ACAs-A4 and used Cu-CAs catalysts.

Samples	Area of Cu LMM <sup>a</sup> (%)					
Jampies	Cu <sup>0</sup>	Cu⁺				
Used Cu-CAs	60.5	39.5				
Used Cu-ACAs-A4	51.7	48.3				

a Intensity ratio of Cu<sup>+</sup> and Cu<sup>0</sup> to (Cu<sup>+</sup> + Cu<sup>0</sup>) obtained by deconvolution of Cu LMM XAES spectra.

Cu-ACAs–A4. From the XPS signal, the higher binding energy of Cu<sup>+</sup> than that for a bulk sample<sup>60</sup>, indicating the cristence of a strong Cu<sup>+</sup>-support interaction, which would favor formation of Cu<sup>+</sup> during catalysts reduction. TPR trace (Figure 5) also showed that the reduction peaks of copper supported on ACAs catalysts were transferred to an elevated temperature compared with that of Cu-CAs by the vigorous interaction force in Cu<sup>+</sup> and supports.

Firstly, the forceful interaction force in Cu<sup>+</sup> species and supports originated primarily from the anchoring function of micropores<sup>61</sup>, as mentioned above. Additionally, OCGs also greatly contributed to strengthening the interaction between Cu+ descriptions and activated supports. As depicted in Table 3, the total amount of OCGs increased with increasing KOH/CA ratios, as proven by Boehm's titration. Our previous study based on DFT calculation<sup>62</sup> also demonstrated that C=O groups significantly enhanced the binding energy between copper clusters and activated supports. Consequently, both abundant micropores and a high density of functional groups in ACAs-A4 can heighten the copper particles dispersity and increase the number of superficial Cu<sup>+</sup> groups, further improving the hydrogenation activity. Our results showed that adoption of chemical activation of CAs in copper-based catalysts effectively controlled dispersion of Cu and distribution of surface Cu<sup>+</sup>.

## Conclusions

Cu nanoparticles supported on activated carbon aerogels (ACAs) have been prepared by a convenient wet chemical approach and applied for ethanol preparation through gasphase MA hydrogenation. KOH activation greatly heightened the surface area, the number of micropores, and the content of functional groups on carbon aerogels supports. The highest surface area of ACAs was achieved up to 2562 m<sup>2</sup> g<sup>-1</sup> when the mass ratio of KOH/CAs was 4. Both the dispersion of Cu and proportion of Cu<sup>+</sup> were significantly enhanced in the Cu-ACAs compared with Cu-CAs owing to the strengthened interreaction between Cu species and the ACAs supports originated from micropores and functional groups. Cu-ACAs-4



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catalyst displayed the most admirable catalytic performance, giving a MA conversion (96.7%) and an ethanol selectivity (62.2%), which can be ascribed to its highest Cu dispersion of 13.9% and Cu<sup>+</sup> proportion of 74.7%. Considering the facile procedure and inexpensive materials, such chemical modification of carbon materials can develop new possibilities for the rational invention and fabrication of related catalysts showing excellent performances.

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