


## Article

# Copper Supported on $\text{MgAlO}_x$ and $\text{ZnAlO}_x$ Porous Mixed-Oxides for Conversion of Bioethanol via Guerbet Coupling Reaction

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**Abstract:** The direct conversion of biomass-derived ethanol to high-valued-added chemicals has attracted widespread attention recently due to the great economic and environmental advantages. In the present study, the conversion of bioethanol through the Guerbet coupling process was studied in a fixed-bed reactor for  $\text{MgAlO}_x$  and  $\text{ZnAlO}_x$  mixed-oxides supported Cu catalysts. From the results, Cu adding into the system greatly enhance the dehydrogenation of ethanol and increase the H-transfer in the course of Guerbet coupling process. Simultaneously, the porous mixed-oxides provide the acid-base property of the catalysts for intermediate transformation. Notably, for Cu/ $\text{MgAlO}_x$ , the main product of ethanol conversion is butanol, but for Cu/ $\text{ZnAlO}_x$ , the primary product is ethyl acetate. Characterizations such as X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and  $\text{CO}_2$  temperature programmed desorption (TPD) were carried out to evaluate the structure and property of the catalysts. In combination with the catalytic performances with the characterization results, the synergistic catalytic effect between metal sites and acid-base sites were elaborated.

**Keywords:** Cu catalyst; mixed-oxide; bioethanol; Guerbet coupling; butanol



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## 1. Introduction

Over the past decades, due to the increased depletion of fossil feedstock, the demand for alternate and renewable energy is continuously growing [1,2]. Ethanol is a versatile and sustainable raw material which can be produced from the fermentation of renewable biomass such as sugars and corns [3,4]. Currently, bioethanol is widely used as a fuel additive, blending with gasoline for partly replacing traditional fossil fuels [5,6]. However, when compared with gasoline, ethanol has some major drawbacks, such as low energy density ( $19.6 \text{ MJ} \cdot \text{L}^{-1}$ ), high water solubility, and corrosion compared to the current technology of engines and fuel infrastructure [7–10]. Compared to ethanol, butanol has larger energy density ( $29.2 \text{ MJ} \cdot \text{L}^{-1}$ ) and lower miscibility in water. Thus, it is considered as a potential gasoline fuel additive and “advanced biofuel” with good environmental benefits [8,9]. In addition to use as a biofuel, butanol can be also utilized as an important raw bulk material in the manufacture of paints, solvents, and plasticizers [11,12].

Traditionally, *n*-butanol is produced through fossil-based oxo process or the fermentation of sugar-containing crops (ABE process) [13,14]. Alternatively, with the increased availability of ethanol from biomass, the direct conversion of ethanol into butanol has been proposed to be an economical and sustainable route for butanol production [15–18]. The Guerbet coupling reaction, corresponding to the catalytic conversion of light alcohols

into higher ones, have recently attracted widespread attention [19,20]. Several heterogeneous catalysts such as hydroxyapatites (HAP) [21,22], metal oxides [8,12,23], activated carbon [17,24,25], and molecular sieves [26] were utilized to convert ethanol into higher alcohols through the Guerbet coupling process. However, under the present catalytic systems, the reaction condition needs to be performed at high temperatures (generally above 623 K) [12,21,26]. Thus, many researchers have tried their best to decrease the operating temperature and increase the activity of catalysts by adding metal species [14,27–30].

Hydrotalcite (HT) derived mixed oxides supported copper catalysts have been found to be a good candidate for the Guerbet coupling process due to the synergistic effect between metal species and mixed oxides by coupling dehydrogenation/hydrogenation process and condensation reactions for ethanol transformation [23,27,28]. For example, Cu/Mg<sub>x</sub>AlO<sub>y</sub> catalysts with low Cu loadings (0.1–0.6 wt.%) exhibited high selectivity (49–63%) to linear chain C<sub>4</sub>+ alcohols [28]. Cu has been proven to have a promotional effect on the reaction rates of H-transfers, accelerating acid-base-catalyzed deprotonation and hydrogenation/dehydrogenation steps. Cu modified NiMgAlO catalysts were reported to improve ethanol conversion and butanol selectivity at moderate reaction conditions (523 K) [27]. The presence of Cu species was supposed to create Lewis acid-base pairs and CuNi alloy sites, thus increasing H-transfer and condensation reactions, resulting in elevated ethanol conversion (30%) and butanol selectivity (64.2%). Recently, our group found that Cu supported on NiAlO<sub>x</sub> exhibited good performance and stability in the Guerbet coupling process [31]. An optimal compromise between the ethanol conversion (~35%) and butanol selectivity (~45%) has to be sustained for the 0.75%Cu/NiAlO<sub>x</sub> catalyst for 1000 h at 523 K [31]. However, for the above catalysts, the effect of support was seldomly elaborated, which in most cases, influencing the property and performances of the catalysts [32–35]. Additionally, the product distribution of the Guerbet coupling process was highly related with the support effect when synthesized with other valuable chemicals such as acetaldehyde, ethyl acetate, ether, butadiene, etc. [32,35].

This research aims to investigate the MgAlO<sub>x</sub> and ZnAlO<sub>x</sub> porous mixed-oxides supported Cu catalysts for ethanol conversion to butanol via Guerbet coupling reaction. With similar synthesis process and Cu contents, the catalytic performance and stability of both catalysts were studied systematically. N<sub>2</sub>-physical adsorption-desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) were carried out to evaluate the geometric structure and electronic property of the catalysts. Additionally, CO<sub>2</sub> temperature programmed desorption (TPD), pyridine adsorbed Fourier-transformed infrared absorption spectra (FT-IR), and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were employed to test the acid-base property and adsorptive property of the catalysts, from which the relationship between the property and catalytic performances were accordingly revealed.

## 2. Results and Discussion

### 2.1. Catalytic Performances

The catalytic performance of MgAlO<sub>x</sub> and ZnAlO<sub>x</sub> porous mixed-oxides supported Cu catalysts for ethanol conversion were carried out in a continuous fixed-bed reactor at 553 K and 2 MPa of N<sub>2</sub>. For comparison, pure mixed-oxides without addition of Cu were carried out for this reaction under the identical reaction conditions. From Table 1, MgAlO<sub>x</sub> and ZnAlO<sub>x</sub> (entries 1 and 2) showed very low activity for ethanol, with values of 4.4% and 8.5%, respectively. In addition, the selectivity of butanol was very low for the above mixed-oxides. Nevertheless, when Cu was added into the mixed-oxides, ethanol conversion was greatly enhanced to 43.1% for Cu/MgAlO<sub>x</sub> (Table 1, entry 3) and 33.9% for Cu/ZnAlO<sub>x</sub> (Table 1, entry 4). Simultaneously, the selectivity of butanol for Cu/MgAlO<sub>x</sub> greatly increased to 33.2%, accomplished by major byproducts of ethyl acetate (Sel. 11.8%), butaldehyde (Sel. 8.6%), ethyl butyrate (Sel. 5.0%), and hexanol (Sel. 8.0%). Such results are comparable or better than the previous results, in which a good compromise between ethanol conversion and butanol selectivity was pursued [23,31,34]. In contrast, the main

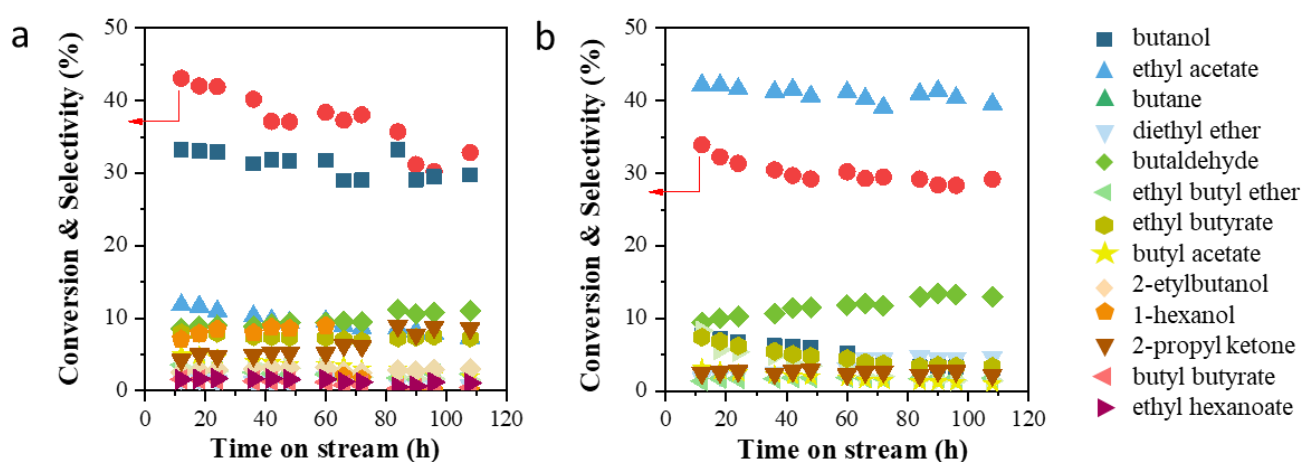
product on the Cu/ZnAlO<sub>x</sub> was ethyl acetate, with the selectivity of 42.2%, which is widely used in paints, coatings, inks, and adhesives. Other byproducts, such as butanol (Sel. 7.7%), ether (Sel. 1.8%), butaldehyde (Sel. 9.4%) and ethyl butyrate (Sel. 8.3%), can be also detected. Thus, the results suggested Cu species could facilitate the transformation of ethanol in the Guerbet coupling process, both in the Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalytic systems. However, the support effect also makes a big difference on the distribution of products, implying a synergistic effect between Cu and mixed-oxides on the Guerbet coupling process.

**Table 1.** Catalytic activities of mixed oxides and supported Cu catalysts for ethanol conversion.

Entry	Catalysts	Conversion (%)	Selectivity (%)					
			Butanol	Ethyl Acetate	Ether	Butaldehyde	Ethyl Butyrate	Hexanol
1	MgAlO <sub>x</sub>	4.4	0	0.7	1.5	1.5	0	0
2	ZnAlO <sub>x</sub>	8.5	0.2	38.6	0	2.1	1.5	0
3	Cu/MgAlO <sub>x</sub>	43.1	33.2	11.8	0	8.6	5.0	8.0
4	Cu/ZnAlO <sub>x</sub>	33.9	7.7	42.2	1.8	9.4	8.3	0

Reaction conditions: Catalyst: 1 g, T = 553 K, P<sub>N2</sub> = 2 MPa, GHSV = 692 h<sup>−1</sup>, LHSV = 4.8 h<sup>−1</sup>.

To further evaluate the products distribution and stability of above catalysts, a time on stream (TOS) of above 100 h was performed for the Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts for the Guerbet coupling process. The results are displayed in Figure 1. From Figure 1a, the major product of Cu/MgAlO<sub>x</sub> is butanol, with selectivity preserving in the range of 30~33%. Other byproducts including ethyl acetate, butane, butaldehyde, hexanol, ethyl butyrate, etc. can be also detected. However, the selectivities were all below 10%. Undetectable gas byproducts or liquid products might also be formed in the process, which account for 20% of the carbon mass loss. In addition, Cu/MgAlO<sub>x</sub> catalyst exhibited an obvious deactivation feature, with ethanol conversion decreased from 43% to 33% after a TOS of 108 h. Unlike the Cu/MgAlO<sub>x</sub>, the main product of the Cu/ZnAlO<sub>x</sub> is ethyl acetate, with the selectivity maintained at 40~42% (Figure 1b). Butane, butanol, ethyl butyrate, etc. appeared as the main byproducts. Except for a slight decrease in initial 24 h, the conversion of ethanol for Cu/ZnAlO<sub>x</sub> is preserved in the range of 29~33%, implying an excellent stability of Cu/ZnAlO<sub>x</sub> catalyst for ethanol conversion.



**Figure 1.** The products distributions of reaction with time courses for the (a) Cu/MgAlO<sub>x</sub> and (b) Cu/ZnAlO<sub>x</sub> catalysts. Reaction conditions: amounts of catalyst: 1 g; pressure of N<sub>2</sub>: 2 MPa; temperature: 553K; GHSV: 692 h<sup>−1</sup>, LHSV: 4.8 h<sup>−1</sup>.

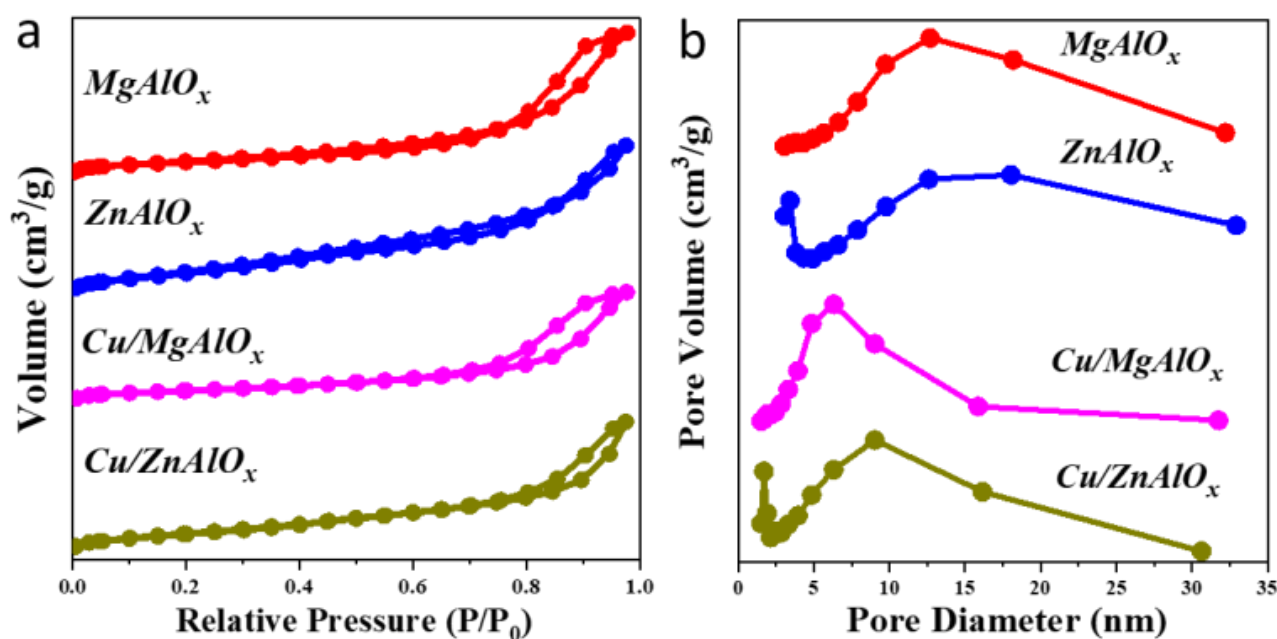
## 2.2. Structure of the Catalysts

N<sub>2</sub>-physical adsorption-desorption was evaluated to test the pore structure of catalysts such as the specific surface area (S<sub>BET</sub>), pore volume, and pore width (as displayed in

Table 2). The isotherms and BJH pore size distribution curves are displayed in Figure 2. From the results,  $\text{MgAlO}_x$  and  $\text{ZnAlO}_x$  showed  $S_{\text{BET}}$  of 119.7 and 155.9  $\text{m}^2/\text{g}$ , respectively. However, as Cu species was added, a decrease in  $S_{\text{BET}}$  and pore volume were observed in  $\text{Cu}/\text{MgAlO}_x$  and  $\text{Cu}/\text{ZnAlO}_x$  catalysts, which could be attributed to the deposition of Cu species inside the pores of mixed oxides. Furthermore, the isothermal curves of above samples show obvious type IV hysteresis loops according to IUPAC classification, indicating the presence of porous structure in the above samples [36,37]. Additionally, the contents of Cu for the  $\text{Cu}/\text{MgAlO}_x$  and  $\text{Cu}/\text{ZnAlO}_x$  catalysts were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), with the similar values of 1.11 wt.% and 1.35 wt.%, which also agreed well with the nominal values.

**Table 2.** Textural properties of mixed oxides and supported Cu catalysts.

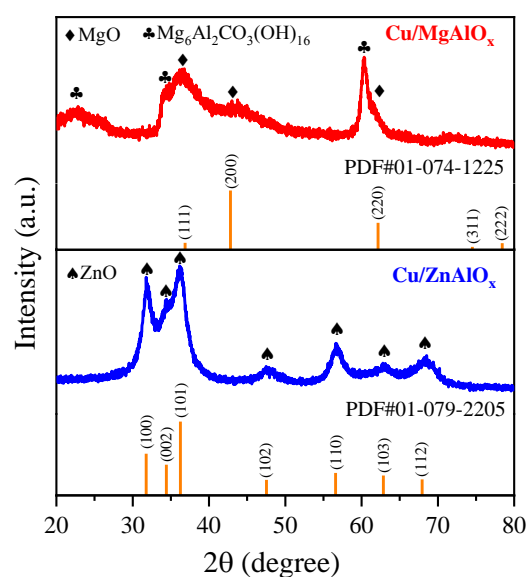
Entry	Catalyst	Loadings of Cu (%)	Surface Area ( $\text{m}^2/\text{g}$ )	Pore Volume ( $\text{cm}^3/\text{g}$ )	Half Pore Width (nm)
1	$\text{MgAlO}_x$	-	119.7	0.44	12.69
2	$\text{ZnAlO}_x$	-	155.9	0.30	3.43
3	$\text{Cu}/\text{MgAlO}_x$	1.11	101.5	0.36	4.87
4	$\text{Cu}/\text{ZnAlO}_x$	1.35	115.7	0.25	1.71



**Figure 2.** (a)  $\text{N}_2$  physical adsorption-desorption isotherms and (b) BJH-pore size distributions of mixed oxides and supported Cu catalysts.

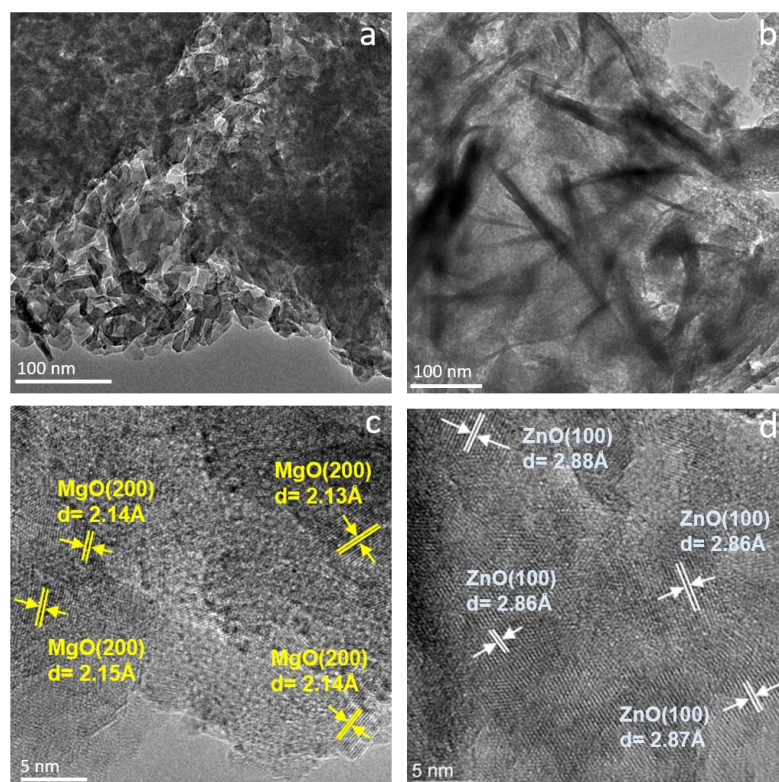
The powder XRD patterns of  $\text{Cu}/\text{MgAlO}_x$  and  $\text{Cu}/\text{ZnAlO}_x$  catalysts are displayed in Figure 3. From the results, both catalysts show characteristic peaks of corresponding oxides (MgO or ZnO), which derived from the collapse of layered hydroxalite structure. The absence of  $\text{Al}_2\text{O}_3$  phase in the two catalysts indicated an amorphous state of  $\text{Al}_2\text{O}_3$  or homogeneous dispersion of  $\text{Al}_2\text{O}_3$  inside the mixed oxides. In addition, in the  $\text{Cu}/\text{MgAlO}_x$  and  $\text{Cu}/\text{ZnAlO}_x$  catalysts, no diffraction peaks ascribed to Cu nanoparticles could be observed, indicating a uniform dispersed Cu species or low concentration of Cu on the surface.





**Figure 3.** XRD patterns of different supported Cu catalysts.

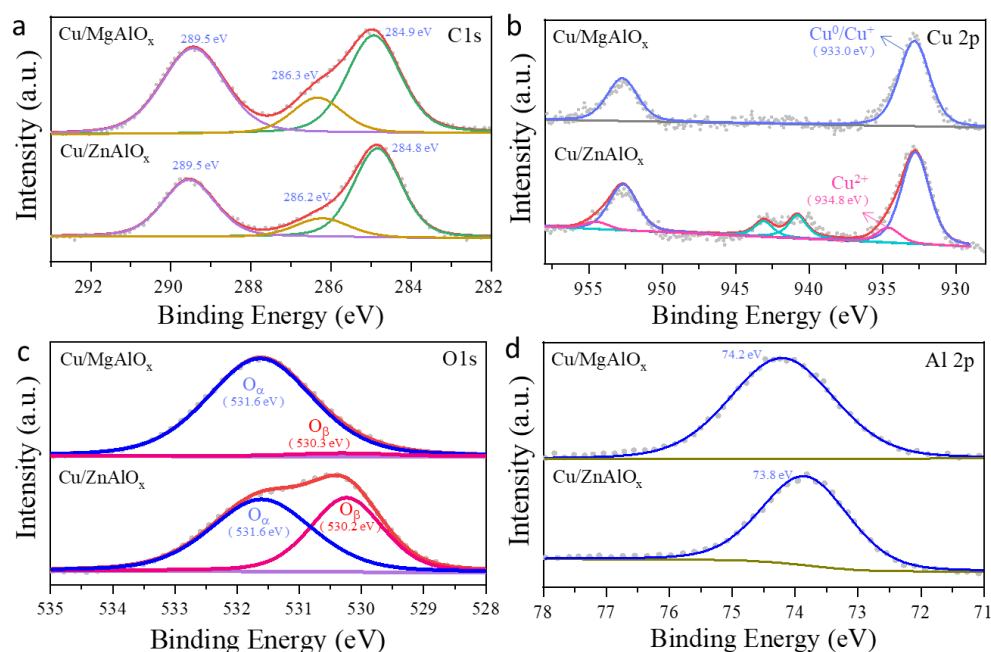
In order to get the structural information and lattice parameters of above catalysts, TEM and HRTEM were performed on the Cu/MgAlO<sub>x</sub> (Figure 4a,c) and Cu/ZnAlO<sub>x</sub> (Figure 4b,d) catalysts. From TEM images (Figure 4a,b), no obvious particles could be observed in the above samples, implying Cu species were highly dispersed on the surface of the catalysts. In addition, the interplanar spacing of  $\sim 2.14$  Å and  $\sim 2.86$  Å corresponding to MgO (200) and ZnO (100) lattice fringes could be discerned for Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> (Figure 4d), implying the major phase of above catalysts is corresponding oxides, which was consistent with the XRD results.



**Figure 4.** TEM and HRTEM images of different supported Cu catalysts: (a,c) Cu/MgAlO<sub>x</sub>; (b,d) Cu/ZnAlO<sub>x</sub>.

### 2.3. Electronic Property of the Catalyst

The surface composition of Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts were measured by X-ray photoelectron spectroscopy (XPS). The C 1s, Cu 2p, O 1s, and Al 2p XPS spectra are shown in Figure 5. The binding energies (B.E.) of the above elements were referenced; the B.E. of C 1s core level at 284.8 eV (Figure 5a) [38]. Figure 5b shows the Cu 2p XPS spectra of Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts. A couple of peaks located at 933.0 eV and 952.8 eV were ascribed to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub>, respectively [27,39]. The Cu 2p<sub>3/2</sub> at 933.0 eV and 934.8 eV should be assigned to Cu<sup>+</sup>/Cu<sup>0</sup> and Cu<sup>2+</sup> species [31,39]. Noteworthy, the Cu species of the Cu/MgAlO<sub>x</sub> are almost Cu<sup>+</sup>/Cu<sup>0</sup>, whereas for the Cu/ZnAlO<sub>x</sub>, except for Cu<sup>+</sup>/Cu<sup>0</sup>, Cu<sup>2+</sup> species also existed on the surface, as proved by the coexistence of satellite peaks at 940~945 eV [39,40]. Figure 5c shows the O 1s XPS spectra of the two catalysts. From the results, two distinct peaks at 531.6 eV and 530.2 eV were observed and should be ascribed to the existence of adsorbed oxygen (O<sub>α</sub>) and lattice oxygen (O<sub>β</sub>) [27,41]. The relative amounts of O<sub>α</sub> and O<sub>β</sub> changed with the composition of supports, suggesting that the chemical form of surface oxygen depends heavily on the chemical composition. Obviously, the Cu/MgAlO<sub>x</sub> has more O<sub>α</sub> than that of the Cu/ZnAlO<sub>x</sub>, indicating that oxygen molecules prefer to accumulate on the surface of the Cu/MgAlO<sub>x</sub> in the form of a hydroxyl group, which might provide some basic sites to the catalysts [27]. In contrast, for the Cu/ZnAlO<sub>x</sub> catalyst, more O<sub>β</sub> were present on the surface, suggesting that oxygen appears in the form of metal oxides, i.e., ZnO or Al<sub>2</sub>O<sub>3</sub>. In addition, in the Al 2p XPS spectra (Figure 5d), the binding energy at 73.8–74.2 eV could be assigned to Al<sup>3+</sup>, which corresponded to the Zn-O-Al and Mg-O-Al, respectively [41].

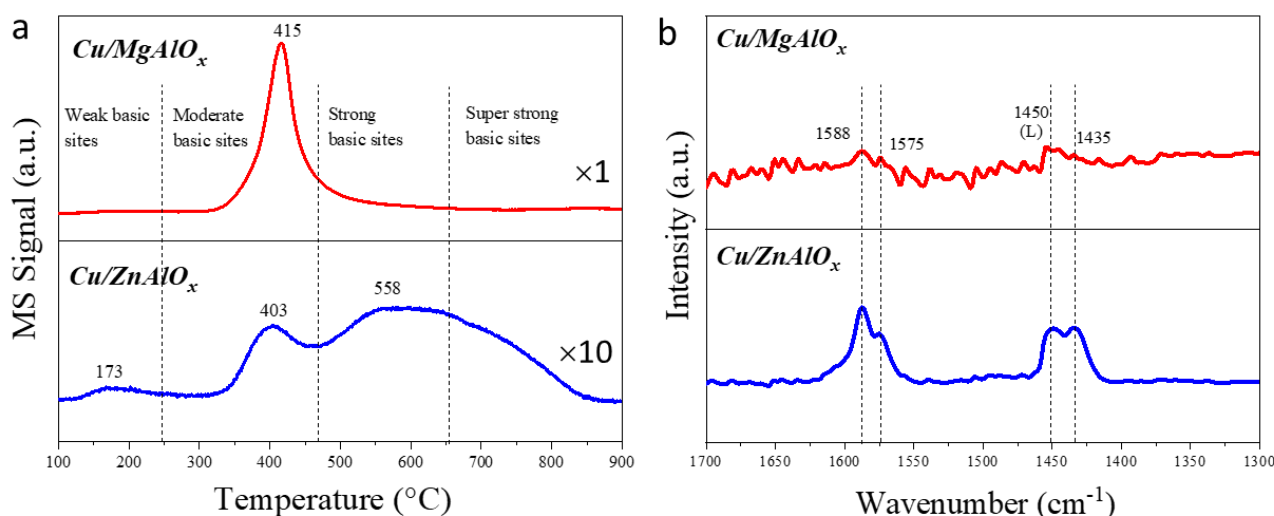


**Figure 5.** XPS spectra of different supported Cu catalysts: (a) C 1s; (b) O 1s; (c) Cu 2p; and (d) Al 2p.

### 2.4. The Acid-Basic Property of the Catalyst

Figure 6 shows the CO<sub>2</sub> temperature-programmed desorption (TPD) profiles and pyridine adsorbed FT-IR spectra of the supported Cu catalysts. From the results, the acid-basic property of the Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts were thereby compared. In Figure 6a, the surface basicity has been determined by CO<sub>2</sub>-TPD. In the range of 100~900 °C, the CO<sub>2</sub> desorption peaks can be deconvoluted into four contributions, which could be assigned to the weak (<250 °C), moderate (250~470 °C), strong (470~650 °C), and super strong basic sites (>650 °C), respectively [42,43]. For Cu/MgAlO<sub>x</sub>, a large amount of moderate basic sites can be observed in CO<sub>2</sub>-TPD profiles, and the intensity is 10 times higher than that

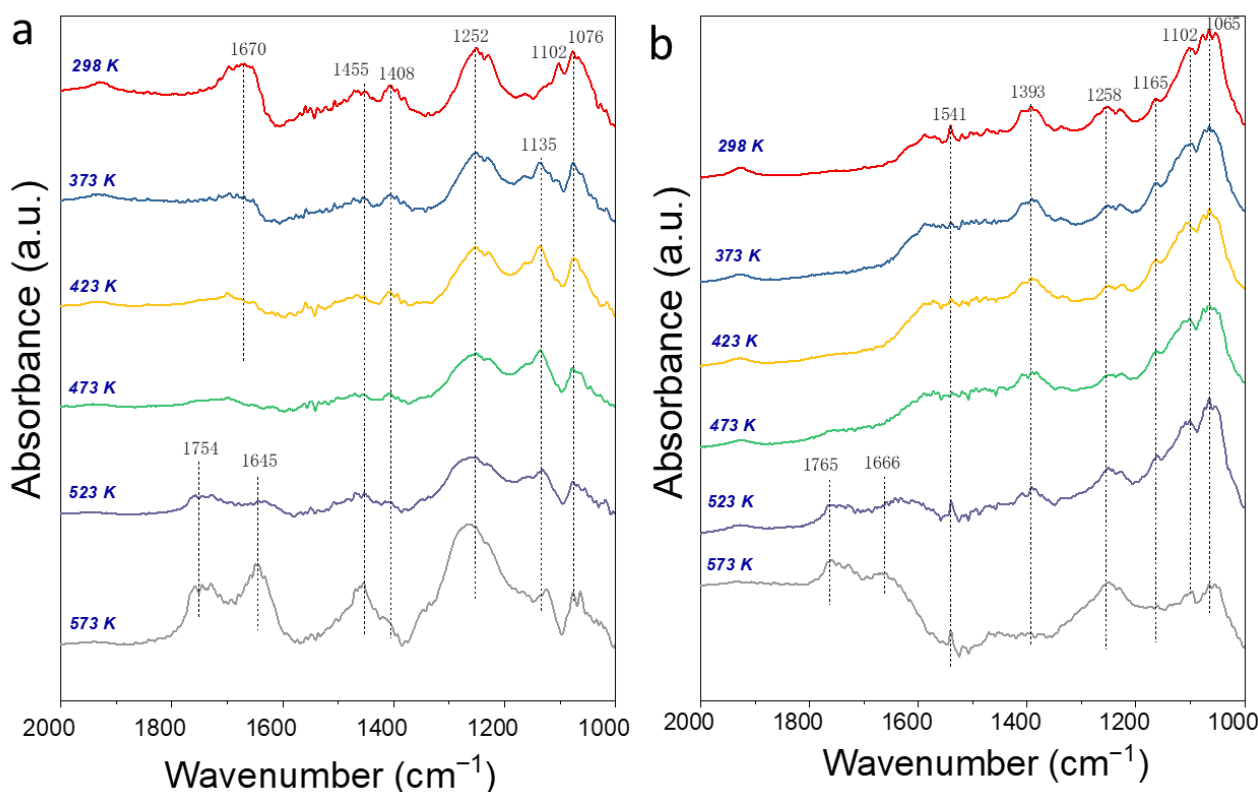
of Cu/ZnAlO<sub>x</sub>. Based on O 1s XPS spectra (Figure 5b), the moderate basic sites might derive from the surface hydroxyl group [33,43], whereas for the Cu/ZnAlO<sub>x</sub>, more lattice oxygen contributes to the strong and super strong basic sites [33,43]. In order to determine surface acidity, in situ FT-IR of pyridine adsorbed on Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> were measured separately. The distribution of Brønsted and Lewis acid sites were determined in the range of 1300–1700 cm<sup>−1</sup>. As seen in Figure 6b, the absence of a band positioned at 1540 cm<sup>−1</sup> in Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> reflects the lack of Brønsted acid sites (B), whereas the band at 1450 cm<sup>−1</sup> corresponding to pyridine chemisorbed on Lewis acid sites (L) could be clearly observed, indicating that only Lewis acidity is present [35,44]. Notably, the relative intensity of adsorption band at 1450 cm<sup>−1</sup> is stronger on Cu/ZnAlO<sub>x</sub> than that of Cu/MgAlO<sub>x</sub>, suggesting that higher acidity is observed for the Cu/ZnAlO<sub>x</sub> catalyst.



**Figure 6.** (a) CO<sub>2</sub> TPD profile and (b) pyridine adsorbed FT-IR spectra of the supported Cu catalysts.

### 2.5. In Situ Drift Spectra of Ethanol Adsorption and Transformation

In situ DRIFT spectra of ethanol adsorption and transformation for the Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts were performed and are displayed in Figure 7. With the temperature increasing from 298 K to 573 K, ethanol gradually converted into different intermediates and products for the above catalysts, directly reflecting the reaction of the Guerbet coupling process. For Cu/MgAlO<sub>x</sub> (Figure 7a), the bands at 1252 cm<sup>−1</sup> are observed at 298 K, which is assigned to the δ(C-OH) of adsorbed 3-hydroxybutanal [45], whereas for Cu/ZnAlO<sub>x</sub> (Figure 7b), the vibration at 1393 cm<sup>−1</sup> could be discerned, indicating the presence of ethyl-acetate species [46]. In addition, the bands at 1076 and 1102 cm<sup>−1</sup> were presented in both Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts, corresponding to C-O stretching vibrations in adsorbed ethoxide [27,41]. The Cu/ZnAlO<sub>x</sub> catalyst has higher intensity of adsorbed ethoxide at the elevated temperatures, implying that it is more difficult for ethanol transformation for Cu/ZnAlO<sub>x</sub> than for Cu/MgAlO<sub>x</sub>. The results were in accordance with the catalytic performance (Table 1 and Figure 1). Additionally, as the test temperature increased from 298 K to 523 K, two new bands positioned at 1645 and 1754 cm<sup>−1</sup> were produced, which is due to the stretching vibrations of C=C group and C=O group in adsorbed crotonaldehyde [27,47]. Furthermore, with the reaction temperature further increased to 573 K, the peaks at 1645 and 1754 cm<sup>−1</sup> become more prominent for Cu/MgAlO<sub>x</sub>, implying the intermediate of crotonaldehyde is easier to produce on Cu/MgAlO<sub>x</sub> on Cu/ZnAlO<sub>x</sub>, and probably leads to higher yields of a major product such as butanol (Table 1).



**Figure 7.** In situ drift spectra of ethanol adsorption and transformation on (a) Cu/MgAlO<sub>x</sub> and (b) Cu/ZnAlO<sub>x</sub> catalysts.

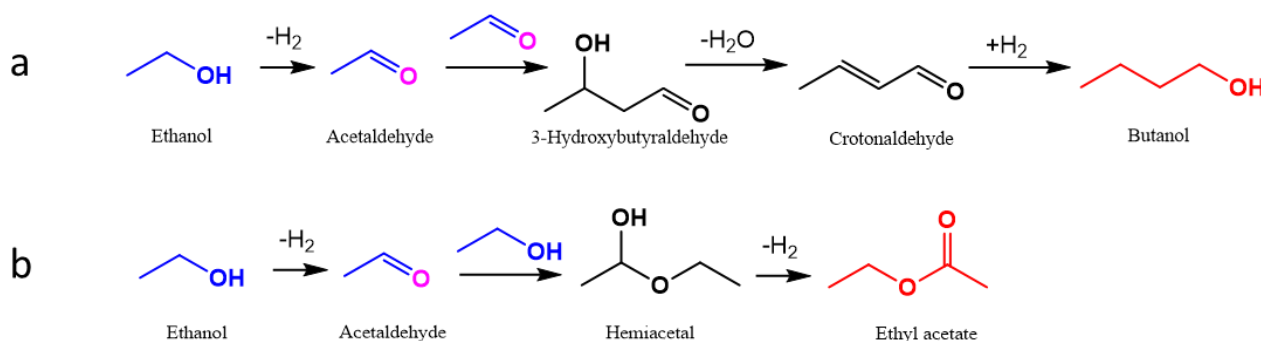
## 2.6. Insight into the Catalytic Performances

According to the catalytic performances on the MgAlO<sub>x</sub> and ZnAlO<sub>x</sub> supported Cu catalysts and the corresponding mixed oxides for ethanol transformation (Table 1 and Figure 1), the active sites were supposed to relate with the Cu species and the supports. Firstly, the structure of Cu species was evaluated by XRD (Figure 3) and TEM (Figure 4) techniques. From the results, Cu species were found highly dispersed on the MgAlO<sub>x</sub> and ZnAlO<sub>x</sub> supports before catalytic performance. After the catalytic test, Cu particles aggregated to larger ones, with the average particle sizes of 6.4 nm for Cu/MgAlO<sub>x</sub> and 4.8 nm for Cu/ZnAlO<sub>x</sub>, respectively (Figure S1). The increased metal particles might account for the decreased activity of both catalysts, especially for Cu/MgAlO<sub>x</sub>. EDX-mapping (Figure S2) and XRD results (Figure S3) indicated the Cu species were still highly dispersed on the catalysts, despite the increased particle sizes.

The valence states of Cu species in the Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts before catalytic tests are mainly Cu<sup>0</sup> and Cu<sup>+</sup>, as displayed by XPS (Figure 5). For Cu/ZnAlO<sub>x</sub>, except for Cu<sup>+</sup>/Cu<sup>0</sup>, Cu<sup>2+</sup> species also existed on the surface. Figure S4 shows the surface composition of Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts after stability tests. The Cu 2p XPS spectra (Figure S4c) indicated the Cu species are all Cu<sup>0</sup>/Cu<sup>+</sup> on Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub>, as the satellite peaks attributed to Cu<sup>2+</sup> disappeared after catalytic tests. Recently, many researches have reported the supported copper catalysts for the Guerbet coupling process [23,24,27–29]. Cu species in the form of Cu<sup>0</sup>/Cu<sup>+</sup> were proved to have a promotional effect on the rates of reaction steps that involve H-transfers [27,29]. Currently, our group also found that the addition of Cu to the NiAlO<sub>x</sub> could greatly enhance the activity and selectivity of ethanol coupling to butanol [31]. A small amount of Cu<sup>0</sup>/Cu<sup>+</sup> was sufficient for ethanol transformation and to improve the reaction rates of ethanol dehydrogenation [31]. In this work, Cu species with the valence state of Cu<sup>0</sup>/Cu<sup>+</sup> were also considered to be the active sites for H-transfers, because the majority of Cu species for the Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts before and after stability tests are Cu<sup>0</sup> and Cu<sup>+</sup>.



Except for Cu species, the acid-base property resulting from different mixed oxides also plays an important role on the Guerbet coupling process. Previously, large amounts of works presented the conclusions that metal active sites benefit for H-transfers, and acidic-basic sites are in favor of the aldol condensation [27–30]. In this work, based on the results of CO<sub>2</sub>-TPD and pyridine adsorbed FT-IR spectra, the Cu/MgAlO<sub>x</sub> catalyst exhibits more basic sites, whereas the Cu/ZnAlO<sub>x</sub> catalyst shows more Lewis acid sites (Figure 6). Generally, basic metal oxides were reported active for catalyzing the aldol condensation reaction [44,45], while metal cations as Lewis acid normally in conjugation with basic sites form acid-base pairs for the adsorption and activation of acetaldehyde [48]. Hence, in the Guerbet coupling process, ethanol is dehydrogenated to acetaldehyde for the metal active site, followed by a base-catalyzed aldol coupling reaction to form 3-hydroxybutyraldehyde, then 3-hydroxybutyraldehyde dehydration to crotonaldehyde, and finally hydrogenation to butanol (Scheme 1a) [28,48]. For Cu/MgAlO<sub>x</sub>, sufficient basic sites made it a good candidate for production of butanol. Nevertheless, in synthesis of ethyl acetate, ethanol is firstly dehydrogenated to form acetaldehyde, then acetaldehyde is condensed with ethanol to form hemiacetal, and finally the hemiacetal dehydrogenated to form ethyl acetate (Scheme 1b) [14,49]. As Lewis acid sites can benefit for the adsorption and activation of acetaldehyde, more ethyl acetate would be generated on the acidic Cu/ZnAlO<sub>x</sub> catalyst [14,32,48]. In situ drifts of ethanol (Figure 7) reveal the dynamic reaction process in the Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts, which is in agreement with the catalytic performance. The above results strongly suggest the synergic effect between Cu and mixed metal oxides plays an exclusive role in determining the products distribution in the Guerbet coupling reaction.



**Scheme 1.** The proposed mechanisms for synthesis of (a) butanol and (b) ethyl acetate for the Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub> catalysts.

### 3. Materials and Methods

#### 3.1. Chemicals

Copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, >99.5%), magnesium nitrate hexahydrate (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99%), zinc nitrate hydrate ((Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), 99 wt%), and aluminum nitrate hexahydrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 99%) were purchased from Sinopharm Chemical Reagent Co. LTD (Shanghai, China). Ethanol (≥99.8%), butanol (>99.5%), methanol (≥99.5%), sodium hydroxide (NaOH, ≥96.0%), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, ≥99.8%), ethyl acetate (≥99.7%), and ortho-xylene (≥99.5%) were purchased from Aladdin Industrial Corporation (Shanghai, China). All chemicals were used as received and without any purification. All glassware was washed with Aqua Regia and rinsed with ethanol and ultrapure water. Ultrapure water (18.2 MΩ) was used throughout this work.

#### 3.2. Preparation of the Supported Cu Catalysts

Hydrotalcite (HT) supports of MgAl-HT and ZnAl-HT were synthesized through coprecipitation method with Mg(Zn)/Al molar ratio of 3. In a typically synthesis, a certain amount of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.21 mol) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.07 mol) were dissolved in 200 mL of deionized water to get solution A. Then, a certain amount of

NaOH (0.438 mol) and Na<sub>2</sub>CO<sub>3</sub> (0.113 mol) were dissolved in 200 mL of deionized water to get solution B. Under vigorous stirring at 75 °C, solution A was dropwise added into solution B with a constant flow of 3 mL/min, and then the mixture was aged at 75 °C for 24 h. The obtained suspension was filtered and washed for several times with deionized water, and dried overnight at 80 °C to obtain the MgAl-HT and ZnAl-HT.

Supported copper catalysts were synthesized through hydrothermal deposition precipitation method, with the theoretical loadings of 1 wt.%. At first, 2 g of the HT supports and 100 mL of deionized water were added into a round-bottom flask. By using the 0.16 M of Na<sub>2</sub>CO<sub>3</sub>, the pH value of the solution was adjusted to about 10. Then, 75 mg of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was added into the flask and the solution was heated up to 80 °C. The mixture was stirred at 80 °C for 2 h, and the products were filtered and washed with deionized water. Before the test, the samples were dried at 80 °C overnight and calcined at 300 °C for 2 h. The obtained supported Cu catalysts were denoted as Cu/MgAlO<sub>x</sub> and Cu/ZnAlO<sub>x</sub>.

### 3.3. Catalytic Test

The catalytic conversion of ethanol into other products was carried out in a stainless steel fixed-bed reactor (inner diameter: 10 mm, length: 660 mm) equipped with a thermocouple and a mass flow controller. The reaction was performed at 280 °C with N<sub>2</sub> as the carrier gas. Prior to the test, 1 g of the catalyst was loaded into the middle of the reactor, with quartz sand to transfer mass and heat. Then, the pressure of system was increased and maintained with a back-pressure regulator, with a gas hourly space velocity (GHSV) of 692 h<sup>−1</sup>. After purging with N<sub>2</sub> for 0.5 h, the temperature was programmatically increased to 280 °C, with heating rate of 5 °C/min. Then, ethanol was introduced into the system by using a plunger pump (NP-KX-210) with liquid hourly space velocity (LHSV) of 4.8 h<sup>−1</sup>. The reaction products were analyzed offline with an Agilent 7890B chromatograph equipped with an HP-5 capillary column (30 m × 0.32 mm) and a flame ionization detector (FID). O-xylene was used as an internal standard for the quantification of the liquid products.

For the catalytic conversion of ethanol, the conversion was calculated as moles of ethanol reacted to the moles of ethanol fed to the reactor. The selectivity of each product was calculated as moles of carbon in the target product to the moles of carbon in the ethanol reacted. These calculations can be given by the following equations:

$$\text{Conversion (\%)} = \frac{\text{Moles of ethanol reacted}}{\text{Moles of ethanol fed to the reactor}} \times 100$$

$$\text{Selectivity (\%)} = \frac{\text{Moles of carbon in the target product}}{\text{Moles of carbon in ethanol reacted}} \times 100$$

### 3.4. Characterizations

The actual loadings of Cu for the catalysts were measured with an inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation, Madison, WI, USA).

N<sub>2</sub>-physical adsorption-desorption tests were measured at 77 K using an AutoSorb-1 instrument. Prior to the measurements, the catalysts were treated at vacuum for 2 h at 120 °C. The pore size distribution and the specific surface area were calculated by the BJH and BET methods.

X-ray powder diffraction (XRD) patterns were conducted on a PW3040/60 X'Pert PRO (PANalytical, Almelo, Netherlands) diffractometer, equipped with a Cu Kα radiation source (λ = 0.15432 nm) operating at 40 kV and 40 mA.

Scanning transmission electron microscopy (STEM) measurements were conducted on a JEM-2100F microscope at 200 kV equipped with an energy dispersive X-ray (EDX) spectrometer. The samples were prepared by dispersing the catalyst powder in ethanol via ultra-sonication onto a micro molybdenum TEM grid.

The X-ray photoelectron spectra (XPS) were conducted on a Thermo ESCALAB 250 X-ray spectrometer (Thermo Fisher Scientific, Madison, WI, USA) equipped with a monochromated Al K $\alpha$  anode. The binding energies were calibrated for surface charging by referencing them to the energy of the C 1s peak at 284.8 eV.

The temperature-programmed desorption of carbon dioxide (CO<sub>2</sub>-TPD) experiments were performed on an AutochemII 2920 instrument (Norcross, GA, USA) with a thermal conductivity detector and mass spectrometry. Before the test, 100 mg of the catalysts were added into a U-type quartz tube reactor. Then the samples were heated in a flow of helium at 300 °C for 30 min. After the temperature decreased to 100 °C, pulses of CO<sub>2</sub> were introduced up to saturation of the sample. Then, the CO<sub>2</sub>-TPD signal were recorded from 100 °C to 900 °C at a rate of 10 °C /min with a cold trap. The signal of the desorbed CO<sub>2</sub> was also recorded by the MS simultaneously.

Pyridine adsorbed Fourier-transformed infrared absorption spectra were conducted on a Bruker INVENIO spectrometer (Karlsruhe, Germany), equipped with a MCT detector in the range of 1000–4000 cm<sup>−1</sup>. Each spectrum was collected with a resolution of 4 cm<sup>−1</sup> and 32 scans. Self-supported catalyst wafers (~0.15 g) were pressed and placed into a in situ IR cell with a CaF<sub>2</sub> window. Before the test, the cell was vacuumed to 10<sup>−3</sup> torr, and the catalyst was treated at 200 °C for 30 min with a heating ramp of 5 °C/min. After cooling to room temperature, the background spectrum was collected under vacuum condition at 25 °C, and then the sample was exposed to pyridine vapor until adsorption saturation. Finally, the adsorbed pyridine was desorbed at 100 °C until the spectra showed no change.

In situ diffuse reflectance infrared Fourier-transformed spectroscopy (DRIFTS) was also performed on a Bruker INVENIO spectrometer (Bruker, Karlsruhe, Germany). Prior to the test, the catalyst was packed into a in situ cell with a ZnSe window and treated at 300 °C for 0.5 h. After cooling to 25 °C, the background spectrum was recorded under atmospheric pressure in helium. Then, ethanol was introduced into the cell with the assistance of helium. Finally, the reaction temperature was programmatically increased to the fixed temperatures, with a heating rate of 10 °C/min. After achieving the steady state, the spectra were collected at 100, 150, 200, 250, and 300 °C, respectively.

#### 4. Conclusions

In summary, MgAlO<sub>x</sub> and ZnAlO<sub>x</sub> mixed-oxides supported Cu catalysts were used for ethanol conversion via Guerbet coupling reaction. The two catalysts show obvious different performances under identical reaction conditions. For Cu/MgAlO<sub>x</sub>, conversion of ethanol and selectivity of butanol were 43.1% and 33.2%, respectively, whereas for Cu/ZnAlO<sub>x</sub>, the major product is ethyl acetate, with conversion and selectivity of 33.9% and 42.2%, respectively. The sole mixed-oxides were also conducted to make a comparison, from which low activity was observed in both catalysts, indicating a great influence of Cu species for ethanol transformation. The acid-base sites resulting from different mixed oxides might determine the distribution of products, from which the catalysts with appropriate basic sites were beneficial to form the condensation products such as crotonaldehyde and butanol, whereas the catalysts with more acid sites were believed to form dehydrogenation products, such as ethyl acetate. In combination the catalytic performances with the characterization results, the synergistic effect between Cu species with the acid-base sites were deduced to be the active sites. This work will provide good reference for designing supported metal catalyst for the Guerbet coupling process with good activity and high product selectivity.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/catal12101170/s1>, Figure S1: XPS spectra of supported Cu catalysts after stability test; Figure S2: XRD patterns of supported Cu catalysts after stability test; Figure S3: TEM and HRTEM images of different supported Cu catalysts after stability test; Figure S4: EDX-mapping of Cu/MgAlO<sub>x</sub> catalyst after stability test.

**Author Contributions:** Y.T. and Y.D. conceived of the study; Z.L. and J.L. performed most of the experiments; L.G. contributed with some of the characterizations. All the authors contributed to the writing of the manuscript. All authors have read and agreed to the published version of the manuscript.

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