Abstract: Bioethanol to butadiene is currently the most promising non-oil-based butadiene production route. Here, copper is introduced into the conventional bimetallic zeolite catalyst to partially substitute for zinc; the isolated tetracoordinated Cu(II) species are formed, with weak and strong basic sites transformed into medium acid sites in trimetallic CuZnY/SiBEA catalyst. A partial substitution of zinc by copper increases the dispersion of metal, reduces the formation of ZnO clusters, decreases the pore blockage, and enhances the total pore volume of catalyst. The Cu\textsubscript{1}Zn\textsubscript{2}Y\textsubscript{5}/SiBEA catalyst with an appropriate 0.33 Cu/(Cu + Zn) mass ratio, a highest medium acid sites/(weak + strong) basic sites value of 6.17, and largest total pore volume of 0.251 cm\textsuperscript{3}/g in all samples presents excellent catalytic performance in the ethanol to butadiene reaction: 99.01% ethanol conversion and 73.36% butadiene selectivity, higher than most reported ethanol to butadiene catalysts. The isolated tetracoordinated Cu(II) structure is stable, which is beneficial to the stability of trimetallic catalyst; when the reaction time is 60 h, the butadiene selectivity is 45.95%, 14% higher than corresponding bimetallic catalyst. The butadiene productivity of Cu\textsubscript{1}Zn\textsubscript{2}Y\textsubscript{5}/SiBEA catalyst reaches up to 1.68 g\textsubscript{BD}·g\textsubscript{cat}\textsuperscript{−1}·h\textsuperscript{−1} at WHSV = 6 h\textsuperscript{−1} and time-on-stream = 8 h. Increasing reaction temperature could linearly increase the ethanol conversion, while the butadiene selectivity increases first and then decreases, the suitable temperature is 375 °C for the highest butadiene yield.

Keywords: ethanol; butadiene; CuZnY/SiBEA catalyst; acid/base ratio; isolated tetracoordinated Cu(II) structure

1. Introduction

Butadiene (BD) is one of the essential raw materials for synthetic rubber and daily commodities, such as paints and adhesives, and it is mainly produced by naphtha steam-cracking processes with high energy consumption and high carbon emissions [1–3]. A valuable alternative solution is bio-ethanol to butadiene (ETB) since the commercial supply of bioethanol is already on an industrial scale. The cradle-to-gate life cycle assessment (LCA) results show that the ETB process could help to reduce CO\textsubscript{2} emissions by about 8–26% compared to the naphtha steam-cracking process [4].

The direct catalytic conversion of ethanol to butadiene was developed by Lebedev and successfully realized large-scale industrialization in the 1920s [3]. Insight into the catalytic mechanism of the ETB reaction is important for developing catalysts with excellent performance and good stability. The generally accepted reaction pathways of the Lebedev process are summarized as follows [5–7]: (1) dehydrogenation of ethanol (EtOH) to acetaldehyde (AA) and H\textsubscript{2}; (2) aldol condensation of two molecules of AA to 3-hydroxybutyraldehyde; (3) the dehydration of 3-hydroxybutyraldehyde to crotonaldehyde; (4) the Meerwein–Ponndorf–Verley (MPV) reduction of crotonaldehyde via EtOH to crotonyl alcohol and AA or the reduction of crotonaldehyde via H\textsubscript{2} to crotonyl alcohol; (5) the dehydration of crotonyl alcohol to produce butadiene. The amount and strength of acid-base sites are key
factors affecting the catalytic performance of catalysts in the ETB reaction [8,9]. Researchers have executed many experiments to modify the acid-base properties of catalysts for improving the ethanol to butadiene performance. Ivanova et al. [10] found that the content of open Zr(IV) Lewis acid sites correlates with the catalytic activity in the process of the conversion of ethanol into butadiene. The open Zr(IV) Lewis acid sites consist of isolated Zr atoms in tetrahedral positions of the zeolite crystalline structure connected to three –O–Si linkages and one OH-group. Along with the decrease of Zr acid sites from 122 to 20 µmol/g, the butadiene selectivity increases from 64% to 68%. Wang et al. [11] had found that the high dispersion of ZrO$_2$ on Ag-ZrO$_2$/SiO$_2$ catalysts generated abundant Zr–O–Si interfaces with medium and weak Lewis acidity, promoting C–C coupling of acetaldehyde. The introduction of Ag species influenced the acid sites of the catalysts, removing the minor Bronsted acid sites, and decreasing the intensity of the Lewis acid sites. The Lewis acidity played a key role in 1,3-BD production and a butadiene yield of 62.4% was achieved over the catalyst 2%Ag-4%ZrO$_2$/SiO$_2$. Dumeignil et al. [12] reported that numbers of Lewis acid sites were not directly correlated with their metal content, the larger metal oxide particles formed at higher metal contents could result in fewer acid sites. Furthermore, a linear correlation existed between the number of Lewis acid sites and the initial productivity of BD. The 3.1%Zn-1.9%Ta-TUD-1 catalyst, having a lower metal content, also showed the highest concentration of Lewis acid sites and butadiene selectivity of 68%.

The properties of catalyst carriers, such as porous volume, pore size, and specific surface area, also strongly affect catalyst activity and stability [13]. Zhang et al. [14] synthesized hierarchical ZnHf-MFI zeolite nanosheets, exhibiting a higher mesopore volume of 0.35 cm$^3$ g$^{-1}$ and a larger external surface area of 232 m$^2$ g$^{-1}$ than that of microporous ZnHf-MFI zeolite with 0.22 cm$^3$ g$^{-1}$ mesopore volume and 69 m$^2$ g$^{-1}$ external surface area. Due to the larger pore volume and specific surface area of the nanosheet structure, the dispersion of active sites was significantly improved. The butadiene yield increased from 27.3% to 40.8% over the hierarchical nanosheets’ catalyst compared to the corresponding microporous sample. Tsubaki et al. [15] reported a hierarchical ZnZr-Silicalite-1 catalyst, which has a higher total pore volume of 0.52 cm$^3$ g$^{-1}$ (vs. 0.44 cm$^3$ g$^{-1}$) than that of the conventional microporous ZnZr-Silicalite-1 catalyst. The abundant hierarchical pore structure was considered to enhance the interaction between metal oxides and zeolite framework to form more active acid sites. Moreover, the mesoporous pore could enhance the diffusion of active intermediates and products, therefore inhibit secondary reactions to form the coke. Compared with the conventional microporous ZnZr-Silicalite-1 catalyst, the hierarchical sample presented a better catalytic performance and stability (ethanol conversion of 89.8% vs. 88% and BD selectivity 61.4% vs. 39% at 6 h).

It is predictable that the combination of suitable acid-base properties and larger pore volume could further improve catalytic performance. In this study, trimetallic CuZnY/SiBEA zeolite catalysts were prepared by partially substituting copper for zinc. The suitable substitution of copper for zinc could effectively increase medium acid sites and total pore volume, decrease weak and strong basic sites, and improve the metal dispersion of the catalysts, which synergistically generate the high ethanol conversion, butadiene selectivity, and long lifetime of catalysts in ETB reaction.

2. Results and Discussion

2.1. Characterization of Catalysts by XRD, XPS, and DR UV-Vis

X-ray diffraction patterns of fresh and spent samples are presented in Figure 1. The XRD spectra of fresh catalysts are shown in Figure 1a and Figure S1. Typical diffraction peaks of the BEA topological structure can be observed for all samples, indicating that the zeolite structure is well preserved after doping with metal oxide. Several small diffraction peaks at 31.7, 36.2, and 56.6$^\circ$ are assigned to (100), (101), and (110) of zinc oxide in the Cu$_{10}$Zn$_{10}$Y$_5$/SiBEA catalyst (with Cu/(Zn + Cu) mass ratio of 0), revealing the existence of a small number of zinc oxide clusters [16]. With the partial substitution of copper for zinc, the crystal phase of ZnO in Cu$_1$Zn$_2$Y$_5$/SiBEA and Cu$_2$Zn$_1$Y$_5$/SiBEA catalysts disappears,
indicating that the ZnO is highly dispersed in the zeolite matrix [17,18]. However, with the Cu/(Zn + Cu) mass ratio increase to 1, new diffraction peaks at 35.5, 38.7, and 48.7° assigned to (−111), (111), and (−202) of the CuO phase in Cu3Zn0Y5/SiBEA are observed [19]. The dispersion of Cu and Zn is related to the loading; the metal oxide loading reaching 3 wt.% could produce oxide clusters leading to the poor dispersion. No characteristic diffraction peaks of Y2O3 are observed in all CuZnY/SiBEA catalysts, implying its high dispersion on the SiBEA carrier [18].

Figure 1. XRD patterns of (a) the fresh CuZnY/SiBEA catalysts and (b) the spent CuZnY/SiBEA catalysts.

The XRD results of spent catalysts are shown in Figure 1b. The BEA topological structures are well preserved for all samples after the ETB reaction, indicating that the SiBEA carriers have excellent hydrothermal stability without framework collapse in the ETB reaction. The characteristic peak of ZnO in the spent Cu0Zn3Y5/SiBEA is more evident than in the fresh catalyst. In addition, no characteristic peaks of ZnO are found in the fresh Cu1Zn2Y5/SiBEA, but they appear in the corresponding spent catalyst. These results imply that some zinc ions are gradually separated from the zeolite matrix to form zinc oxide clusters during the ETB reaction. This observation is consistent with Yuan group’s literature [20], in which Zn species accommodated in the vacant T-atom sites of zeolite, after heat treatment for a time, produced small ZnO nanoclusters. For all copper-containing catalysts, the crystal phase of copper oxide disappears after the reaction, and the characteristic peaks of metallic copper appear at 43.3, 50.4, and 74.1° instead. This suggests that copper oxide clusters outside the zeolite framework could be reduced to metallic copper particles [16,21]. Significantly, no characteristic peaks of yttrium oxide or metallic yttrium have been found in the XRD patterns, either fresh or spent catalysts, indicating that Y(III) species are very stable during the ETB conversion.

The nature of the surface Cu, Zn, and Y species in the fresh and spent Cu0Zn3Y5/SiBEA and Cu3Zn0Y5/SiBEA catalyst is further studied by X-ray photoelectron spectroscopy (XPS) as shown in Figure 2. The XPS spectrum in the Zn 2p region (Figure 2a) of the fresh Cu0Zn3Y5/SiBEA catalyst exhibits a main Zn2p3/2 band at a binding energy of about 1022.9 eV and a less intense Zn 2p1/2 signal at 1046.1 eV. The Zn 2p binding energy of the Cu0Zn3Y5/SiBEA sample is higher than bulk zinc oxide, attributed to highly dispersed Zn(II) species strongly interacting with the SiBEA zeolite matrix to construct Zn-O-Si bonds [18,20,22]. After the ETB reaction, no additional signals are found, indicating that the chemical state of zinc does not change. However, an apparent decline in the Zn signals occurs for the spent Cu0Zn3Y5/SiBEA catalyst, hinting at the partial coverage of the Zn species by coke compounds [18].
The XPS spectrum of the Cu 2p region of the fresh Cu\textsubscript{3}Zn\textsubscript{0}Y\textsubscript{5}/SiBEA catalyst is shown in Figure 2b. The Cu 2p spectrum (Figure 2b, top) evidences the presence of two chemical environments for copper atoms, in which the Cu 2p signals are deconvoluted into two doublets. The first doublet peaks at 933.7 eV in the 2p 3/2 range and 953.1 eV in the 2p 1/2 range are characteristic of the Cu(II) species in CuO, which is also observed in the XRD patterns. The second doublet peaks, with higher intensity, are located at a higher binding of 935.7 eV in the Cu 2p3/2 range and 955.4 eV in the Cu 2p 1/2 range attributed to Cu(II) species incorporated in the BEA zeolite matrix (Cu–O–Si bonds) [23,24]. The Si–O bond attracts the electrons in the outer layer of Cu(II), leading to the increase in binding energy of the Cu atom in Cu–O–Si compared to CuO, indicating a strong interaction between Cu and the zeolite structure [24]. The broad peaks from 940 to 947.5 eV are characteristic satellite peaks of Cu(II), which might be due to the vibrational transition of electrons in copper ions [23].

As shown in Figure 2b, bottom, after the ETB reaction, the doublet peaks of CuO shift to lower binding energy (932.6 eV and 952.4 eV, attributed to Cu(0)); this demonstrates that copper oxide is reduced to metallic Cu(0) species [24]. The doublet peaks attributed to the Cu–O–Si structure are still observed after the reaction, this suggests that the Cu–O–Si structure could be more stable than CuO. The intensity and range of satellite peaks also decrease significantly, implying the reduction in a significant part of copper ions. The above results indicate that the reduction of Cu(II) to Cu(0) mainly occurs in the CuO species, and the Cu–O–Si structure is relatively stable.
The Y species XPS spectrum of the Cu$_0$Zn$_3$Y$_5$/SiBEA and Cu$_3$Zn$_0$Y$_5$/SiBEA catalysts are shown in Figure 2c,d. Two almost identical peaks at 160.6 and 158.6 eV corresponding to Y 3d 3/2 and 3d 5/2 in the Y–O–Si structure are observed before and after the ETB reaction, their binding energy is higher than that of bulk Y$_2$O$_3$ [18,25]. The coke compounds and free hydrogen have not affected the chemical environment of the yttrium species during the ETB conversion.

DR UV–Vis spectra of SiBEA and CuZnY/SiBEA catalysts are shown in Figure 3. In the spectra of Cu$_1$Zn$_2$Y$_5$/SiBEA, Cu$_2$Zn$_1$Y$_5$/SiBEA, and Cu$_3$Zn$_0$Y$_5$/SiBEA, the bands are composed of a broad band around the near-infrared region (red background) and another intense band in the ultraviolet region (purple background). These two bands could be attributed to d–d transitions of Cu$^{2+}$(3d$^9$) and the charge-transfer (CT) O$^2−$→Cu$^{2+}$ transitions, respectively, derived from tetra-coordinate Cu(II) with (≡Si-O)$_2$-Cu⋯(OH-Si≡)$_2$ structure [23]. In the spectrum of Cu$_3$Zn$_0$Y$_5$/SiBEA, the bands in the range 350–550 nm assigned to the O$^2−$→Cu$^{2+}$ CT and/or d–d transitions of octa-coordinate Cu(II) indicate the existence of some bulk copper oxides on the surface of catalyst with high copper content [17]. This result is consistent with XRD and XPS spectra of Cu$_3$Zn$_0$Y$_5$/SiBEA sample.

2.2. N$_2$ Adsorption–Desorption Measurement of All Samples

N$_2$ adsorption–desorption measurement is investigated to characterize the textural properties of all samples; the results are shown in Table 1 and Figure 4. Metal doping could actually modify the pore volume and specific surface area of the zeolite carrier [26]. In this contribution, the suitable substitution of zinc by copper could effectively increase the pore volume and specific surface area, hence the Cu$_1$Zn$_2$Y$_5$/SiBEA sample has the highest total pore volume of 0.25 cm$^3$/g and specific surface area of 421 m$^2$/g compared to other CuZnY/SiBEA catalysts (Table 1). The highest total pore volume and specific surface area mean high metal dispersion, which could expose more active sites to ensure catalytic activity [27]. After the metal doping, the total pore volumes and specific surface areas of all catalysts decrease somewhat compared to BEA zeolite. All samples, including SiBEA carrier and catalysts, present a combination of type I and type H$_4$ isotherms (Figure 4), and
the hysteresis loops are observed in high pressure area (P/P_0 = 0.55–0.95). This indicates that all samples still have abundant microporous and mesoporous structure.

**Table 1.** Specific surface area, pore volume, and pore size of SiBEA carrier and CuZnY/SiBEA catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET}^a (m^2/g)</th>
<th>V_{total}^b (cm^3/g)</th>
<th>V_{mic}^c (cm^3/g)</th>
<th>V_{meso}^d (cm^3/g)</th>
<th>Pore Size (e) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiBEA</td>
<td>459</td>
<td>0.2827</td>
<td>0.1397</td>
<td>0.1429</td>
<td>4.4</td>
</tr>
<tr>
<td>Cu_{0.5}Zn_{0.5}Y/SiBEA</td>
<td>386</td>
<td>0.2356</td>
<td>0.1199</td>
<td>0.1157</td>
<td>4.6</td>
</tr>
<tr>
<td>Cu_{1}Zn_{1}Y/SiBEA</td>
<td>421</td>
<td>0.2508</td>
<td>0.1320</td>
<td>0.1188</td>
<td>4.4</td>
</tr>
<tr>
<td>Cu_{2}Zn_{0.5}Y/SiBEA</td>
<td>395</td>
<td>0.2323</td>
<td>0.1261</td>
<td>0.1063</td>
<td>4.8</td>
</tr>
<tr>
<td>Cu_{3}Zn_{0.5}Y/SiBEA</td>
<td>384</td>
<td>0.2294</td>
<td>0.1226</td>
<td>0.1067</td>
<td>4.8</td>
</tr>
</tbody>
</table>

^a S_{BET} (total surface area) is derived by applying the multi-point BET model. ^b V_{total} (total volume) is the single point adsorption total pore volume. ^c V_{mic} (micropore volume) is calculated using the t-plot method. ^d V_{meso} (mesopore volume) = V_{total} - V_{mic}. ^e Pore size is derived via the BJH method.

**Figure 4.** N\(_2\) adsorption–desorption isotherms of SiBEA, CuZnY/SiBEA catalysts.

**2.3. The Acidity and Basicity of Fresh Catalysts by NH\(_3\)-TPD and CO\(_2\)-TPD**

NH\(_3\)-TPD (CO\(_2\)-TPD) is used to evaluate the acidity (basicity) of all samples, as shown in Figure 5 and Tables 2 and 3. All CuZnY/SiBEA catalysts present three NH\(_3\) desorption peaks corresponding to the weak, medium, and strong acid sites.

**Figure 5.** (a) NH\(_3\)-TPD curves and (b) CO\(_2\)-TPD curves of fresh CuZnY/SiBEA catalysts.
Table 2. The acidity of the fresh CuZnY/SiBEA catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Position a (°C)</th>
<th>Amount of Acid Sites b (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>Mild</td>
</tr>
<tr>
<td>Cu$_0$Zn$_3$Y$_5$/SiBEA</td>
<td>131</td>
<td>196</td>
</tr>
<tr>
<td>Cu$_1$Zn$_2$Y$_5$/SiBEA</td>
<td>135</td>
<td>216</td>
</tr>
<tr>
<td>Cu$_2$Zn$_1$Y$_5$/SiBEA</td>
<td>131</td>
<td>214</td>
</tr>
<tr>
<td>Cu$_3$Zn$_0$Y$_5$/SiBEA</td>
<td>133</td>
<td>208</td>
</tr>
</tbody>
</table>

a Peak position is obtained from Gaussian decomposition of the NH$_3$-TPD profiles. b Acid amount is obtained by integrating NH$_3$-TPD profiles.

Table 3. The basicity and acid/base ratio of the fresh CuZnY/SiBEA catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Position a (°C)</th>
<th>Amount of Basic Sites b (µmol/g)</th>
<th>M$<em>{\text{acid}}$/((W + S)$</em>{\text{base}}$) c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>Mild</td>
<td>High</td>
</tr>
<tr>
<td>Cu$_0$Zn$_3$Y$_5$/SiBEA</td>
<td>127</td>
<td>445</td>
<td>630</td>
</tr>
<tr>
<td>Cu$_1$Zn$_2$Y$_5$/SiBEA</td>
<td>127</td>
<td>452</td>
<td>648</td>
</tr>
<tr>
<td>Cu$_2$Zn$_1$Y$_5$/SiBEA</td>
<td>152</td>
<td>473</td>
<td>649</td>
</tr>
<tr>
<td>Cu$_3$Zn$_0$Y$_5$/SiBEA</td>
<td>247</td>
<td>560</td>
<td>665</td>
</tr>
</tbody>
</table>

a Peak position is obtained from Gaussian decomposition of the CO$_2$-TPD profiles. b Basic amount is obtained by integrating CO$_2$-TPD profiles. c M$_{\text{acid}}$/((W + S)$_{\text{base}}$) represents the ratio of the medium acid sites with weak and strong base sites.

As the Cu/(Cu + Zn) mass ratio increases from 0 to 1, the total acid amount of all catalysts shows a trend of first increase and then decrease, the corresponding total acid sites are 253, 417, 316, and 222 µmol/g (Table 2); in particular, the medium acid sites show the most obvious change with 134, 253, 167, and 103 µmol/g, respectively, and the Cu$_1$Zn$_2$Y$_5$/SiBEA catalyst has the highest medium acid sites.

As shown in Figure 5b, CuZnY/SiBEA catalysts present three CO$_2$ desorption peaks corresponding to the weak, medium, and strong basic sites. As the Cu/(Cu + Zn) mass ratio increases from 0 to 1 in all catalysts, the total basic amount first decreases and then increases, which is 206, 93, 229, and 264 µmol/g, respectively (Table 3); the variation trend of total basic amount is contrary to the acid amount. In particular, the weak and strong basic sites show obvious changes (weak: 22, 8, 86, and 107; strong: 135, 33, 132, and 141) with the different copper loadings; the Cu$_1$Zn$_2$Y$_5$/SiBEA catalyst has the lowest weak plus strong basic sites.

The metal doping could effectively modify the acidity and basicity of catalysts. Cu@ZnO catalysts are prepared with a deposition–precipitation method by Liu group [28]. With the increase of Zn/Cu molar ratio from 0.1 to 1.0, the amount of basic sites increases from 17.9 to 98.1; the weakly basic sites is assigned to OH$^-$ group of catalysts, the medium basic sites is ascribed to Zn–O pairs, and the strong basic sites is related to low-coordinated oxygen atoms due to the absence of metal. Besides, the incorporation of copper into zeolite framework could create new Lewis acidic sites [29]. The Lewis acid centers of Cu$_2$O-SiBEA loaded with copper is 52 compared to about 2 µmol/g of SiBEA zeolite. The new Lewis acid centers are due to the reaction between SiO–H and Cu(II) ions. In this contribution, with the partial substitution of zinc by copper, ZnO clusters disappear and abundant Cu-O-Si structures are formed at the expense of SiO–H species which are verified by the above XRD and XPS measurements; hence the strong and weak basic sites decrease, and the medium acid sites increase obviously. It is noted that Cu$_1$Zn$_2$Y$_5$/SiBEA catalyst in all samples has the highest ratio (6.17) of medium acid sites with weak plus strong base sites.

2.4. Catalytic Properties of CuZnY/SiBEA Catalysts

The main products of ethanol conversion on CuZnY/SiBEA are BD, acetaldehyde (AA), ethylene, diethyl ether (DEE), propene, butene, and other products (C$_{5+}$). The catalytic performances of all samples are shown in Figure 6 and Table 4.
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**Figure 6.** (a) EtOH conversion, BD yield, and (b) product selectivity over Cu_{0}Zn_{3}Y_{5}/SiBEA catalyst; (c) EtOH conversion, BD yield, and (d) product selectivity over Cu_{1}Zn_{2}Y_{5}/SiBEA catalyst; (e) EtOH conversion, BD yield, and (f) product selectivity over Cu_{2}Zn_{1}Y_{5}/SiBEA catalyst; (g) EtOH conversion, BD yield, and (h) product selectivity over Cu_{3}Zn_{0}Y_{5}/SiBEA catalyst. ETB reaction conditions: T = 375 °C, WHSV = 1 h^{-1}.
Table 4. The catalytic performances of catalysts with different Cu/(Cu + Zn) mass ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TOS (min)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
<th>BD Output of 10 h b</th>
<th>grid cat⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>BD</td>
<td>Ethylene</td>
<td>DEE</td>
<td>AA</td>
</tr>
<tr>
<td>Cu₂Zn₅Y₅</td>
<td>40</td>
<td>99.70</td>
<td>69.95</td>
<td>7.94</td>
<td>0.46</td>
<td>0.85</td>
</tr>
<tr>
<td>/SiBEA</td>
<td>600</td>
<td>98.91</td>
<td>57.71</td>
<td>3.03</td>
<td>0.52</td>
<td>4.66</td>
</tr>
<tr>
<td>Cu₂Zn₂Y₅</td>
<td>40</td>
<td>98.76</td>
<td>70.40</td>
<td>11.41</td>
<td>0.83</td>
<td>2.15</td>
</tr>
<tr>
<td>/SiBEA</td>
<td>600</td>
<td>98.23</td>
<td>66.01</td>
<td>5.11</td>
<td>0.87</td>
<td>2.92</td>
</tr>
<tr>
<td>Cu₂Zn₃Y₅</td>
<td>40</td>
<td>98.63</td>
<td>64.41</td>
<td>15.49</td>
<td>0.86</td>
<td>2.09</td>
</tr>
<tr>
<td>/SiBEA</td>
<td>600</td>
<td>85.14</td>
<td>61.94</td>
<td>5.52</td>
<td>1.10</td>
<td>6.92</td>
</tr>
<tr>
<td>Cu₂Zn₅Y₅</td>
<td>40</td>
<td>95.43</td>
<td>46.69</td>
<td>39.56</td>
<td>3.45</td>
<td>0.83</td>
</tr>
<tr>
<td>/SiBEA</td>
<td>600</td>
<td>84.14</td>
<td>47.94</td>
<td>33.38</td>
<td>7.50</td>
<td>1.05</td>
</tr>
</tbody>
</table>

а Other products represent butyral, butanol, ethyl acetate and C₅+. b BD output of 10 h represents the BD output per gram catalyst from 0 to 10 h. ETB reaction conditions: T = 375 °C, WHSV = 1 h⁻¹.

As displayed in Table 4, with partial substitution of zinc by copper, the ethanol conversion, BD selectivity, and yield at 40 min of Cu₁Zn₂Y₅/SiBEA catalyst are 98.7, 70.4, and 69.5%, which are near with Cu₂Zn₅Y₅/SiBEA catalyst; yet the ethylene selectivity is 11.4% (Cu₁Zn₂Y₅/SiBEA) higher than 7.9% (Cu₂Zn₅Y₅/SiBEA), the other products’ selectivity is 3.91% (Cu₁Zn₂Y₅/SiBEA) lower than 6.63% (Cu₂Zn₅Y₅/SiBEA). The other products consist of butyraldehyde, butanol, ethyl acetate, and C₅+ species. When the reaction time reaches 10 h, the ethanol conversion of both Cu₁Zn₂Y₅/SiBEA and Cu₂Zn₅Y₅/SiBEA catalysts have few changes. The BD yield of Cu₁Zn₂Y₅/SiBEA is 64.8%, about 8% higher than Cu₂Zn₅Y₅/SiBEA; meanwhile, the ethylene selectivity of Cu₁Zn₂Y₅/SiBEA is 5.1% higher than 3.0% of Cu₂Zn₅Y₅/SiBEA, the other products’ selectivity is 14.0% (Cu₁Zn₂Y₅/SiBEA), around 10% lower than Cu₂Zn₅Y₅/SiBEA catalyst.

In brief, with the partial substitution of zinc by copper, after reacting for 10 h, Cu₁Zn₂Y₅/SiBEA present 8% higher BD yield, 2% higher ethylene selectivity, and 10% lower other products’ selectivity. Ethylene is produced from ethanol dehydration, which hints that the introduction of copper may be in favor of the dehydration of ethanol. The Liu group found that the introduction of the Cu species could increase the medium acid sites of catalysts, which are active for the dehydration of ethanol to ethylene [30]. Increase in medium acid sites due to the introduction of copper is also observed in this contribution, the medium acid sites of Cu₁Zn₂Y₅/SiBEA are 253 μmol/g, higher than 134 μmol/g of Cu₂Zn₅Y₅/SiBEA. The more water vapor produced by the ethanol dehydration of Cu₁Zn₂Y₅/SiBEA could absorb the strong acid sites, which are active in the formation of other heavy products; the decrease in other heavy products would reduce the consumption of acetaldehyde intermediates, hence increase the BD selectivity slightly [18]. Meanwhile, the suitable acid properties generated by the moderate substitution of zinc by copper not only promotes the aldol condensation of acetaldehyde, but also effectively inhibits the occurrence of side reactions and improves the formation of desired BD; this is consistent with the report of the Tsubaki group [31].

With further substitution of zinc by copper, Cu₂Zn₅Y₅/SiBEA presents an obvious decrease in ethanol conversion (85.1%) and BD yield (52.7%) at a reaction time of 10 h, the corresponding ethylene and other products’ selectivity are 5.5% and 13.8%. For Cu₂Zn₅Y₅/SiBEA catalyst, having no introduction of zinc, the ethanol conversion and BD yield at 10 h decrease further with values of 84.1% and 40.3%, the corresponding ethylene and other products’ selectivity are 33.4% and 2.1%, respectively. The ethylene selectivity increases significantly, yet that of the other products decreases substantially.

Catalytic performance is related to many factors including acid and base properties, pore volume, and chemical composition [3]. In 2022, the Tsubaki group rationally designed Y-ZnZr/Si-beta catalyst, the synergy of active sites and a suitable balance of acid properties promoted the conversion of ethanol and the production of butadiene; thus, this catalyst exhibited an excellent ethanol conversion of 80.2% and butadiene yield of 48.4% [31]. Here,
with the increase in substitution of zinc by copper, the BD outputs of four CuZnY/SiBEA catalysts from 0 to 10 h increase first then decrease, the corresponding values are 3.78, 3.99, 3.66 and 2.65 g_{BD}/g_{cat}, respectively (Table 4). The correlations between BD yield and acid/base ratio, total pore volume are displayed in Figure 7. The Cu_{1}Zn_{2}Y_{5}/SiBEA catalyst, with a 0.33 Cu/(Cu + Zn) mass ratio, has the highest medium acid sites/weak plus strong basic sites’ value of 6.17 and the largest total pore volume of 0.251 cm^{3}/g, which contribute to the highest BD yield of 64.9% out of all the catalysts. The introduction of copper and suitable Cu/(Cu + Zn) ratio are crucial, they have important influences on the acid/base properties and the pore volume of catalysts.

![Figure 7. Correlations of pore volume and acid/base ratio with BD yield in all catalysts (acid/base is medium acid sites/weak plus strong base sites ratio).](image)

2.5. The Catalyst Stability over a Long Period

Good stability is very important for catalysts used in the industrialization process. Here, stabilities of Cu_{0}Zn_{3}Y_{5}/SiBEA and Cu_{1}Zn_{2}Y_{5}/SiBEA over 60 h are particularly studied. As displayed in Figure 8, the initial ethanol conversions and BD selectivity of both catalysts are near 100% and 70%; yet when the reaction time is 2.5 h, the BD selectivity of Cu_{1}Zn_{2}Y_{5}/SiBEA (73%) is obviously higher than the Cu_{0}Zn_{3}Y_{5}/SiBEA (69%) catalyst. After reacting for 50 h, the ethanol conversions for both catalysts are still near 98%, and the BD selectivity of Cu_{1}Zn_{2}Y_{5}/SiBEA is 50% compared to 40% of the Cu_{0}Zn_{3}Y_{5}/SiBEA catalyst. When the reaction time is 60 h, the ethanol conversion and BD selectivity of Cu_{1}Zn_{2}Y_{5}/SiBEA are 80.7% and 46.0%, higher than 76.6% and 32.0% of the Cu_{0}Zn_{3}Y_{5}/SiBEA catalyst. With a suitable substitution of zinc by copper, the Cu_{1}Zn_{2}Y_{5}/SiBEA catalyst displays better catalytic stability.

The contents of the deposited substance are determined by TGA (in Supplementary Materials Figure S6), summarized in Table 5. The total coke of the spent Cu_{1}Zn_{2}Y_{5}/SiBEA catalyst is about 8.4%, which is a little lower than 8.8% of spent Cu_{0}Zn_{3}Y_{5}/SiBEA catalyst. Meanwhile, the volatile compound proportion of Cu_{1}Zn_{2}Y_{5}/SiBEA is 12.0%, compared to 6.1% of Cu_{0}Zn_{3}Y_{5}/SiBEA catalyst. This is consistent with the above analysis that the introduction of copper would produce more volatile compounds, such as ethylene and diethyl ether. Overall, the deactivation of catalysts is due to the carbonaceous substance deposition on active sites; with the increase in reaction time, the coke content rises gradually.
2.6. Effects of Reaction Temperature and WHSV on ETB Performance

Figure 9 shows the effects of the reaction temperature on catalytic performances over Cu1Zn2Y5/SiBEA. It is clearly that the ethanol conversion increases from 28.63% to 98.63% with the enhancement of reaction temperature from 300 °C to 400 °C. The BD selectivity increases first and then decreases with the temperature increase, and the highest value is 71.19% at 350 °C. When the temperature exceeds 350 °C, the formation of heavy products via unfavorable aldol condensation reactions is notably accelerated, hence the selectivity of other products increases significantly. The BD yield also increases first and then decreases with the increase in temperature, yet the highest BD yield of 65.87% is at 375 °C.

Table 6 shows the effects of WHSV on catalytic performances over Cu1Zn2Y5/SiBEA. With the increase of WHSV from 0.5 to 6 h\(^{-1}\), BD selectivity decreases slightly from 65.6% to 62.2%, and ethanol conversions decrease significantly from 98.8% to 76.8%. The increasing unreacted ethanol molecules could be due to the lesser contact time with the increase of WHSV. Yet the selectivity of ethylene, DEE, and propene demonstrate little change. It is notable that the BD productivities present a linear increase from 0.19 to 1.68 g\(_{BD}\cdot cat^{-1}\cdot h^{-1}\) with the increasing WHSV.
Figure 9. Effect of temperature on catalytic activities over the Cu$_1$Zn$_2$Y$_5$/SiBEA catalyst. ETB reaction conditions: WHSV = 1 h$^{-1}$; TOS of 8 h.

Table 6. Effect of WHSV on catalytic activities over the Cu$_1$Zn$_2$Y$_5$/SiBEA catalyst.

<table>
<thead>
<tr>
<th>WHSV (h$^{-1}$)</th>
<th>Conversion (%)</th>
<th>BD</th>
<th>Ethylene</th>
<th>DEE</th>
<th>AA</th>
<th>Propene</th>
<th>Butene</th>
<th>Other Products</th>
<th>Yield (%)</th>
<th>BD Productivity gBD·gcat$^{-1}$·h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>98.75</td>
<td>65.67</td>
<td>5.66</td>
<td>1.86</td>
<td>7.19</td>
<td>6.36</td>
<td>4.37</td>
<td>8.89</td>
<td>64.85</td>
<td>0.19</td>
</tr>
<tr>
<td>1</td>
<td>98.30</td>
<td>67.01</td>
<td>5.53</td>
<td>0.99</td>
<td>2.80</td>
<td>6.00</td>
<td>4.91</td>
<td>12.76</td>
<td>65.87</td>
<td>0.39</td>
</tr>
<tr>
<td>2.5</td>
<td>87.34</td>
<td>62.36</td>
<td>5.36</td>
<td>0.71</td>
<td>7.75</td>
<td>6.02</td>
<td>3.44</td>
<td>14.36</td>
<td>54.46</td>
<td>0.80</td>
</tr>
<tr>
<td>4.5</td>
<td>80.67</td>
<td>62.21</td>
<td>5.24</td>
<td>1.15</td>
<td>9.00</td>
<td>4.99</td>
<td>3.34</td>
<td>14.06</td>
<td>50.18</td>
<td>1.33</td>
</tr>
<tr>
<td>6</td>
<td>76.80</td>
<td>62.18</td>
<td>5.16</td>
<td>1.09</td>
<td>8.79</td>
<td>5.11</td>
<td>3.52</td>
<td>14.16</td>
<td>47.75</td>
<td>1.68</td>
</tr>
</tbody>
</table>

ETB reaction conditions: T = 375 °C, TOS = 8 h.

3. Experimental

3.1. Catalyst Preparation

CuZnY/SiBEA catalysts were synthesized via solid-state grinding of Cu, Zn, and Y precursors into the commercial SiBEA zeolite (pure-silica BEA zeolite; Zhuoran Co., Dalian, China). Copper nitrate trihydrate (Tianjin Damao Chemical Reagent Factory, Tianjin, China, 99.5 wt.%), zinc acetate dihydrate (Tianjin Damao Chemical Reagent Factory, Tianjin, China, 99.5 wt.%), and yttrium nitrate hexahydrate (Aladdin, 99.5 wt.%) were weighed and mixed with SiBEA in the mortar. The collected solids were ground together for 20 min until the mixed powder was homogeneous green without visible blue particles. The resulting solids were heated in air at 550 °C for 4 h (heating rate of 2.2 °C/min). Monometallic and bimetallic catalysts (Y/SiBEA, CuY/SiBEA, and ZnY/SiBEA) were synthesized using a similar procedure. The nominal loadings of Cu and Zn varied between 0 and 3.0 wt.%; Y loadings were kept constant as 5.0 wt.%; the catalysts were labeled Cu$_x$Zn$_y$Y$_z$/SiBEA, where the subscript x, y, and z indicated the nominal metal oxides loading. For the Cu$_1$Zn$_2$Y$_5$/SiBEA catalyst, the masses of copper precursor, zinc precursor, yttrium precursor, and SiBEA zeolite are 0.0321 g, 0.0567 g, 0.1703 g, and 1 g, respectively.
3.2. Catalyst Evaluation

The ethanol to butadiene (ETB) reaction was tested with a tubular fixed-bed reactor at 300–450 °C under atmospheric pressure. A total of 0.3 g of calcined catalyst (40–80 mesh) was pretreated in flowing N\textsubscript{2} (40 mL/min) at 450 °C for 1 h. After the sample was cooled down to the required reaction temperature, ethanol (Macklin, 99.5 wt.%) was first vaporized at 200 °C through a preheater, then mixed with N\textsubscript{2} carrier gas (20 mL/min) and pumped into the reactor with a weight hourly space velocity (WHSV) of 0.5–6 h\textsuperscript{-1}.

The gaseous products were analyzed using an online gas chromatograph (Shimadzu GC-2014C/PAF/AC) equipped with a flame ionization detector (FID) and a HP-PLOT/Q + PT capillary column (30 m × 0.320 mm × 20 µm). Two trials with the same experimental condition were completed, the margin of error was 5%. The ethanol conversion and butadiene selectivity are defined as follows:

\[ \text{ethanol conversion (mol\%)} = \frac{[\text{ethanol}]_{\text{inlet}} - [\text{ethanol}]_{\text{outlet}}}{[\text{ethanol}]_{\text{inlet}}} \times 100\% \quad (1) \]

\[ \text{butadiene selectivity (mol\%)} = \frac{2 \times [\text{butadiene}]_{\text{outlet}}}{[\text{ethanol}]_{\text{inlet}} - [\text{ethanol}]_{\text{outlet}}} \times 100\% \quad (2) \]

\[ \text{butadiene yield (\%)} = \frac{\text{ethanol conversion (\%)} \times \text{butadiene selectivity (\%)}}{100} \quad (3) \]

3.3. Catalyst Characterization

Catalysts were analyzed with power X-ray diffraction (XRD) by a Rigaku Ultima IV diffractometer (Rigaku Corp., Tokyo, Japan) using Cu K\textalpha\ radiation (\(\lambda = 0.1542 \text{ nm}\)) with a scanning rate of 5°/min in the range of 2\(\theta\) = 5–80°. The composition and nature of the Cu, Zn, and Y species present on the catalyst surface were studied by X-ray photoelectron spectroscopy (XPS). XP spectra were recorded on an ESCALAB Xi+ spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) using Al K\textalpha\ radiation (1486.6 eV, pass energy 20 eV). The charge correction of the XP spectra was made based on the Si 2p peak located at 103.5 eV.

The acidity of samples was measured by ammonium temperature-programmed desorption (NH\textsubscript{3}-TPD) on a TP-5080 apparatus. Samples (100 mg) were activated at 500 °C under He flow (30 mL/min) for 1 h, then cooled to 50 °C, saturated with an NH\textsubscript{3}/He mixture (5 vol\% NH\textsubscript{3}) for 30 min, and then purged with He for 45 min at 50 °C to remove the physically adsorbed NH\textsubscript{3}. The desorption of NH\textsubscript{3} was measured from 50 to 800 °C at a heating rate of 10 °C/min under He.

The basicity of samples was measured by carbon dioxide temperature-programmed desorption (CO\textsubscript{2}-TPD) on a TP-5080 apparatus. Samples (100 mg) were activated at 500 °C under He flow (30 mL/min) for 1 h, then cooled to 50 °C, saturated with an CO\textsubscript{2}/He mixture (10 vol\% CO\textsubscript{2}) for 30 min, and then purged with He for 45 min at 50 °C to remove the physically adsorbed CO\textsubscript{2}. The desorption of CO\textsubscript{2} was measured from 50 to 800 °C at a heating rate of 10 °C/min under He.

Nitrogen physisorption isotherms were performed on the Micromeritics ASAP2460 analyzer (Norcross, GA, USA) at 77 K after the sample was degassed at 350 °C for 8 h under vacuum. Thermogravimetric analysis (TGA) of the spent catalyst was performed in a NETZSCH TG209F1 Libra analyzer (NETZSCH GmbH, Selb, Germany) under flowing air (20 mL/min) by linearly increasing the temperature from 50 to 800 °C at a rate of 10 °C/min.

Diffuse reflectance (DR) UV–Vis spectra were recorded on an UV-2600 (Shimadzu, Kyoto, Japan) spectrometer with barium sulfate as reference.

4. Conclusions

With the partial substitution of zinc by copper, (≡Si–O)\textsubscript{2}Cu···(OH–Si≡)\textsubscript{2} structures are formed in CuZnY/SiBEA catalysts; the acidity, basicity, and pore volume of cata-
lysts could be regulated by the copper content. With the suitable copper percentage, the Cu\textsubscript{1}Zn\textsubscript{5}Y/SiBEA catalyst presents the highest ratio (6.17) of medium acid sites with weak plus strong base sites, the largest pore volume of 0.25 cm\textsuperscript{3}/g, and specific surface area 421 m\textsuperscript{2}/g; these characteristics contribute to its excellent ethanol to butadiene performance: 99.01% ethanol conversion and 73.36% butadiene selectivity. The butadiene output of Cu\textsubscript{1}Zn\textsubscript{2}Y/SiBEA catalyst from 0 to 10 h reach 3.99 g\textsubscript{BD}/g\textsubscript{cat}. the suitable temperature is 375 °C for the highest butadiene yield.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/catal12101147/s1, Figure S1: XRD patterns in the range of 2 theta from 5 to 80° (left) and enlarged XRD patterns (right) of SiBEA, Cu\textsubscript{5}Zn\textsubscript{3}Y/SiBEA, Cu\textsubscript{1}Zn\textsubscript{2}Y/SiBEA, Cu\textsubscript{2}Zn\textsubscript{1}Y/SiBEA and Cu\textsubscript{3}Zn\textsubscript{0}Y/SiBEA, Figure S2: (a) Zn 2p, (b) Cu 2p and (c) Y 3d XPS spectra of fresh catalysts, Figure S3: (a) Zn 2p, (b) Cu 2p and (c) Y 3d XPS spectra of spent catalysts, Figure S4: Pore size distribution curves of SiBEA, Cu\textsubscript{5}Zn\textsubscript{3}Y/SiBEA, Cu\textsubscript{1}Zn\textsubscript{2}Y/SiBEA, Cu\textsubscript{2}Zn\textsubscript{1}Y/SiBEA and Cu\textsubscript{3}Zn\textsubscript{0}Y/SiBEA, Figure S5: (a) EtOH conversion, BD yield (b) and product selectivity over Y/SiBEA catalysts. (ETB reaction conditions: T = 375 °C, WHSV = 1 h\textsuperscript{-1}), Figure S6: (a) TGA curves, (b) DTG curves, and (c) the variations of other products and coke percentage with the different Cu/(Cu+Zn) mass ratio in spent catalysts, Table S1: The carbon deposition distribution of spent catalysts according to their weight determined by TGA, Table S2: Specific surface area, pore volume and pore size of Cu\textsubscript{5}Zn\textsubscript{3}Y/SiBEA—spent (60 h) and Cu\textsubscript{1}Zn\textsubscript{2}Y/SiBEA—spent (60h). Reference [32] is cited in the supplementary materials.

**Author Contributions:** Conceptualization, M.Z.; methodology, M.Z. and H.D.; validation, M.Z. and G.O.; formal analysis, M.Z., H.D., T.Y. and K.W.; investigation, H.D.; resources, M.Z., G.O. and L.-M.W.; data curation, H.D., T.Y. and K.W.; writing—original draft preparation, H.D.; writing—review and editing, M.Z., G.O. and L.-M.W.; visualization, H.D.; supervision, M.Z.; project administration, M.Z.; funding acquisition, M.Z. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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