

Article

Dehydrogenation of Ethanol to Acetaldehyde over Different Metals Supported on Carbon Catalysts

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Abstract: Recently, the interest in ethanol production from renewable natural sources in Thailand has been receiving much attention as an alternative form of energy. The low-cost accessibility of ethanol has been seen as an interesting topic, leading to the extensive study of the formation of distinct chemicals, such as ethylene, diethyl ether, acetaldehyde, and ethyl acetate, starting from ethanol as a raw material. In this paper, ethanol dehydrogenation to acetaldehyde in a one-step reaction was investigated by using commercial activated carbon with four different metal-doped catalysts. The reaction was conducted in a packed-bed micro-tubular reactor under a temperature range of 250–400 °C. The best results were found by using the copper doped on an activated carbon catalyst. Under this specified condition, ethanol conversion of 65.3% with acetaldehyde selectivity of 96.3% at 350 °C was achieved. This was probably due to the optimal acidity of copper doped on the activated carbon catalyst, as proven by the temperature-programmed desorption of ammonia (NH₃-TPD). In addition, the other three catalyst samples (activated carbon, ceria, and cobalt doped on activated carbon) also favored high selectivity to acetaldehyde (>90%). In contrast, the nickel-doped catalyst was found to be suitable for ethylene production at an operating temperature of 350 °C.

Keywords: ethanol dehydrogenation; activated carbon; copper catalyst; acetaldehyde

1. Introduction

Acetaldehyde is a valuable chemical that is widely used for the production of other chemicals, such as acetic acid, acetic anhydride, ethyl acetate, n-butanol, pyridine, and vinyl acetate. Acetaldehyde can be produced by many processes, such as partial oxidation of ethane, hydration of acetylene, oxidation of ethylene, oxidative dehydrogenation of ethanol, and dehydrogenation of ethanol. The partial oxidation of ethane uses an expensive catalyst, which also requires high operating temperature. The hydration of acetylene uses a mercuric complex as catalyst, which is toxic. The oxidation of ethylene, which is also called the Wacker-Hoechst process, refers to the formation of polymerization and condensation products of acetaldehyde. Therefore, it is costly and causes environmental problems [1]. The oxidative dehydrogenation of ethanol is an alternative route, which is quickly gaining widespread interest, but the use of air for the reaction affects the production cost of this process [2]. As compared with the above-mentioned synthesis processes, the production of acetaldehyde via the ethanol dehydrogenation route appears highly attractive due to its cleaner technology.

Direct dehydrogenation of ethanol to acetaldehyde has gained great attention because it is an economical and environmentally friendly alternative to conventional commercial processes [3–5]. In previous studies, the catalytic activities of catalysts, such as ZrO₂ [3,4], SiO₂ [3], Al₂O₃ [5,6], ZSM-5 [6], SBA-15 [7], and MCM-41 [8], with high acidities for ethanol reaction have been studied.

Although these catalysts showed high activities for ethanol dehydrogenation, low selectivity to acetaldehyde was observed. These results indicated that catalysts with acidities that were too high were not suitable for the dehydrogenation of ethanol to acetaldehyde. It appeared that different metals doped on support may be suitable for good surface basicities for ethanol dehydrogenation. Many pieces of research on the reaction of alcohols using heterogeneous catalysts have focused principally on highly active noble metals, such as platinum [9] and gold [10–12]. Therefore, more lasting solutions based on cheap, harmless, and stable metals to replace noble metals would be appealing. In this regard, the application of catalysts based on relatively inexpensive metals, including manganese [10], nickel [10,13,14], cobalt [13], copper [3,4,14–16], vanadium [17,18], silver [19–21], and iron [22], are being increasingly explored for dehydrogenation under ambient conditions. Moreover, a few studies have used activated carbon for ethanol dehydrogenation [22–25]. In contrast, these catalysts have very high selectivity to acetaldehyde.

In this work, the catalytic activities of Ce, Co, Ni, and Cu metals doped on activated carbon catalysts for ethanol dehydrogenation to acetaldehyde were investigated in a fixed-bed micro-reactor. The physiochemical properties of these catalysts were characterized by nitrogen-physisorption, X-ray diffraction (XRD), carbon dioxide temperature-programmed desorption (CO₂-TPD), ammonia temperature-programmed desorption (NH₃-TPD), transmission electron microscopy (TEM), and inductively coupled plasma (ICP).

2. Results and Discussion

2.1. Catalysts Characterization

Table 1 shows the structural parameters obtained from the N₂ adsorption/desorption, such as the Brunauer, Emmett and Teller (BET) surface area (S_{BET}), micropore surface area ($S_{\text{micropore}}$), external surface area (S_{external}), total pore volume, micropore volume, and average pore width. The original activated carbon exhibited the highest BET surface area and total pore volume. At ca. 10 wt% loading with different metals, the BET surface area and total pore volume of the catalysts decreased, which was attributed to the pore blockage by metal clusters [26].

Table 1. Surface areas and pore characteristics for activated carbon catalysts.

Catalysts	ACC	Ce/ACC	Co/ACC	Cu/ACC	Ni/ACC
S_{BET} (m ² /g)	852	837	744	823	699
$S_{\text{micropore}}$ (m ² /g)	310.4	805.5	723.0	779.1	626.8
S_{external} (m ² /g)	541.7	31.8	20.9	43.6	71.7
V_{total} (cm ³ /g)	0.86	0.45	0.38	0.44	0.40
V_{mic} (cm ³ /g)	0.16	0.38	0.34	0.37	0.31
D_p (nm)	1.4	3.7	3.8	3.9	3.7

S_{BET} , BET surface area; $S_{\text{micropore}}$, t-method micropore surface area; S_{external} , t-method external surface area; V_{total} , single-point adsorption total pore volume; V_{mic} , t-method micropore volume; D_p , average pore diameter adsorption calculated by the Barrett, Joyner, and Halenda (BJH) method.

The characteristics of adsorption-desorption isotherms were efficiently used to specify the type of pore characteristics of the catalyst samples. The N₂ adsorption-desorption isotherms of all catalysts are displayed in Figure 1. The isotherms of the activated carbon and metal-doped catalysts presented a combination of types I (major) and IV (minor), according to the International Union of Pure and Applied Chemistry (IUPAC) [27]. A combination of type I and IV isotherms usually denotes the presence of both microporous and mesoporous structures. The isotherms show a sharp increase in N₂ adsorption in the initial relative pressure range, suggesting the formation of micropores. Furthermore, the isotherms also appear to contain a hysteresis loop at high relative pressure, suggesting that the pore structure is partly mesoporous. Thus, the activated carbons with different metal loadings presented with the dominant microporous structures. The activated carbon catalyst (ACC) exhibited a distinct

type IV isotherm, indicating that a mesoporous structure exists. Therefore, the addition of metals leads to a decrease in the pore size of the catalysts. The adsorption capacity was at the maximum of the ACC, showing that the pore volume was at the maximum for this sample.

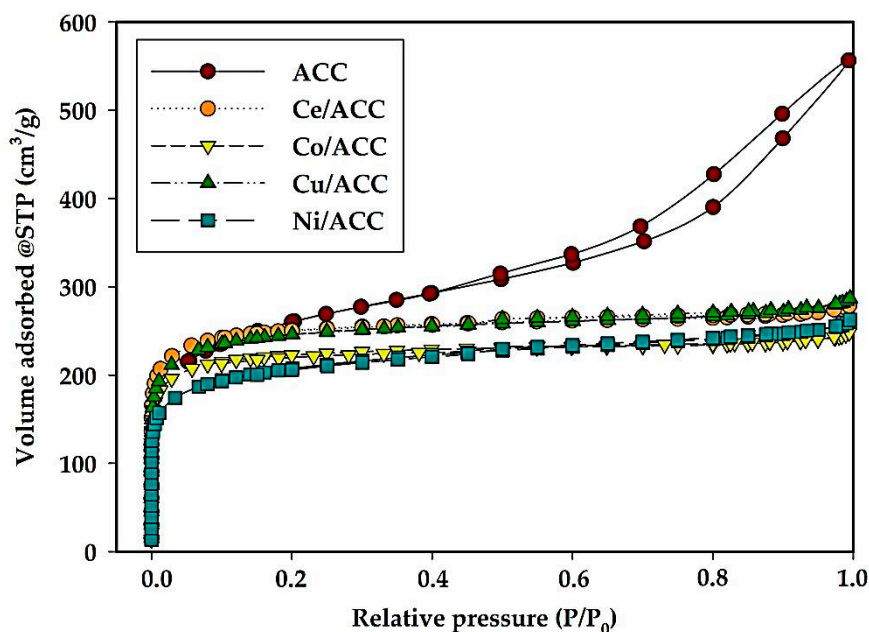


Figure 1. Adsorption-desorption isotherms of catalysts at -196°C .

The results of metal content of the catalyst samples using ICP technique are demonstrated in Table 2. The results show that the metal content in the bulk of catalysts was around 8 to 11 wt%. As seen from the TEM/EDX (Table S1) result, the Cu/ACC sample has the highest amount of metal among the catalysts, because the grids used in the measurement are copper. TEM micrographs of activated carbon doped with different metal catalysts are shown in Figure 2. The dark patches represent the metal species dispersing on all catalysts. As illustrated, all synthesized catalysts showed good dispersion of metal.

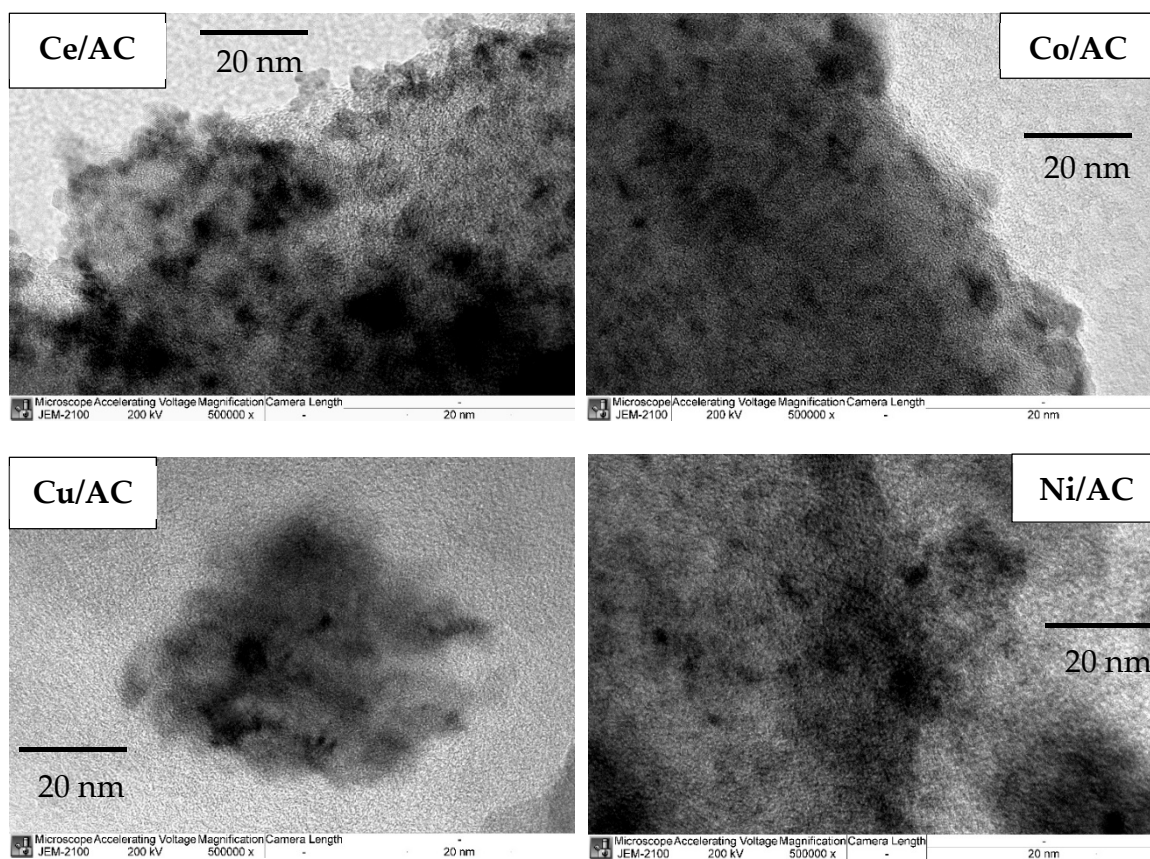
Table 2. Metal content (wt%) of different metals doped on commercial activated carbon catalysts.

Activated Carbons	wt% of Metal
Ce/ACC	8.8
Co/ACC	8.0
Cu/ACC	7.7
Ni/ACC	11.4

The total surface acidity and basicity of the samples were measured by NH_3 -TPD and CO_2 -TPD, respectively. The number of acid sites and basic sites on the catalysts was calculated throughout the temperature range of 40°C to 400°C by integration of desorption peaks of ammonia and carbon dioxide, which are related to the acid sites and basic sites on the catalysts, according to the Fityk curve fitting method. The typical NH_3 -TPD profiles for all activated carbon catalysts are illustrated in Figure 3 for the temperature range of 40°C to 400°C . The total acidity results are listed in Table 3, and can be ordered from greatest to least as follows: Cu/ACC > Co/ACC > Ni/ACC > Ce/ACC > ACC. Thus, addition of transition metal cations (Lewis acids) apparently results in more active centers [25]. It is notable that the Cu/ACC catalyst exhibits the highest total acid sites, at $549\ \mu\text{mol/g}$. Moreover, the total basicity results of catalysts, as presented in Table 3 and Figure 4, reveal that the Co/ACC catalyst has the greatest basicity, followed by Ce/ACC, which is similar to Ni/ACC. The order of the total basicity is as follows: Co/ACC > Ce/ACC > Ni/ACC > Cu/ACC > ACC.

Table 3. Total acidity and total basicity of catalysts.

Activated Carbons	Total Acidity ^a ($\mu\text{mol/g}$)	Total Basicity ^b ($\mu\text{mol/g}$)
ACC	133	56
Ce/ACC	164	174
Co/ACC	358	319
Cu/ACC	549	90
Ni/ACC	199	158

^a NH_3 -TPD; ^b CO_2 -TPD.**Figure 2.** TEM images of activated carbon doped with different metal catalysts.

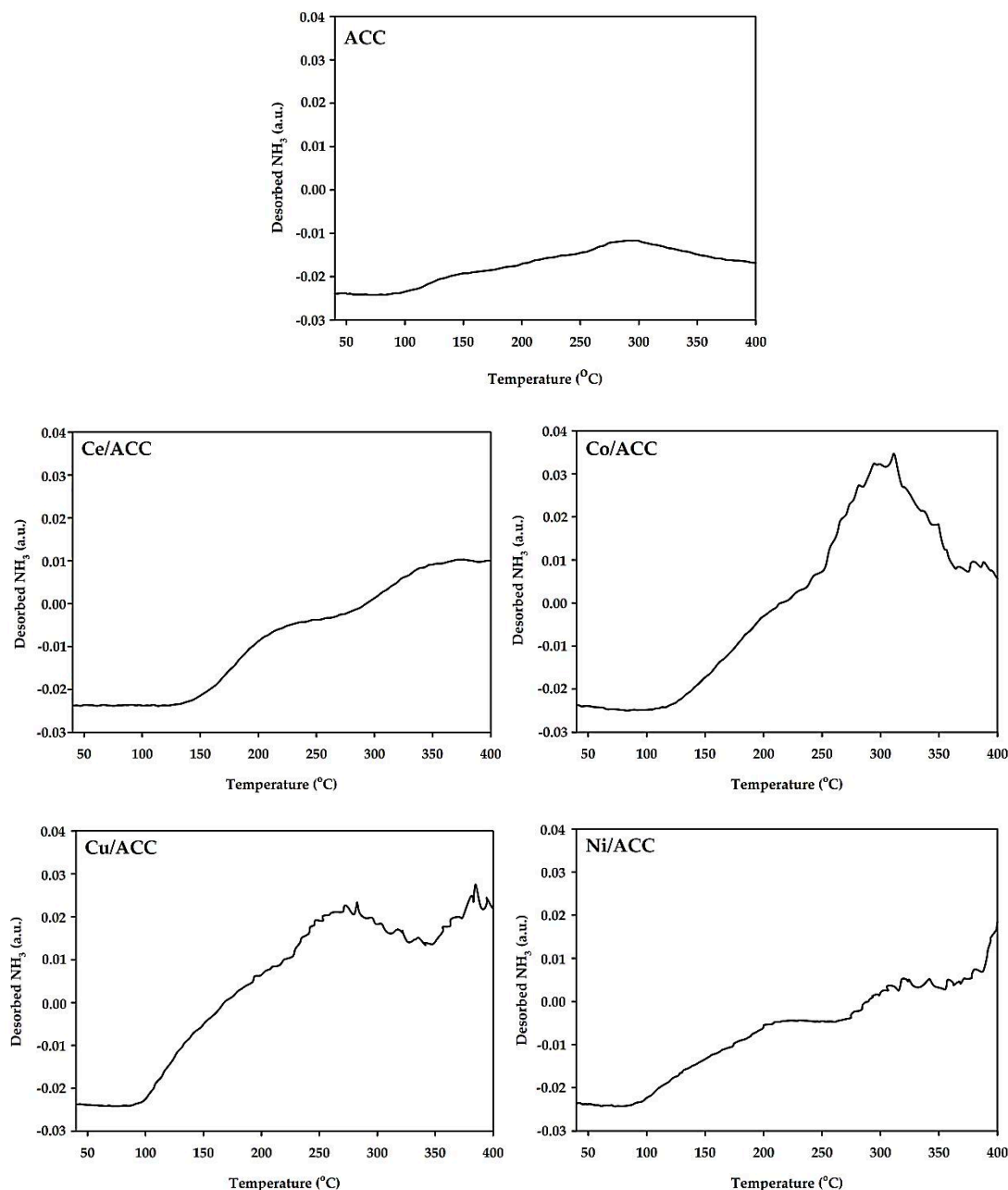


Figure 3. NH_3 -TPD profiles of catalysts.

The XRD patterns of different metals doped on activated carbon catalysts are shown in Figure 5. The XRD patterns of the ACC samples used as catalyst and support show a diffraction peak at $2\theta = 26.8^\circ$, which can be assigned to a graphite structure on activated carbon [28], and the peak at $2\theta = 45^\circ$ reveals the graphene structure [9]. For the Ce/ACC, CeO_2 peaks evidently appeared at $2\theta = 28, 33, 47.5, 56, 69.5$ and 77° [29]. Considering the Ni/ACC, NiO peaks evidently appeared at $2\theta = 37.3, 43.3, 62.8$ and 75.5° [30]. For the Co/ACC, slight XRD peaks of Co_3O_4 and CoO were observed at 36.8 and 42.5 , respectively [31]. In addition, for the Cu/ACC, the characteristic peaks of CuO were observed at $35.5, 38.7, 61.6, 72.3$ and 74.7° [4,32]. Typically, Cu_2O cubic phase could be observed at 36.4 and 42.3° [3], and these were assigned to the Cu+ species.

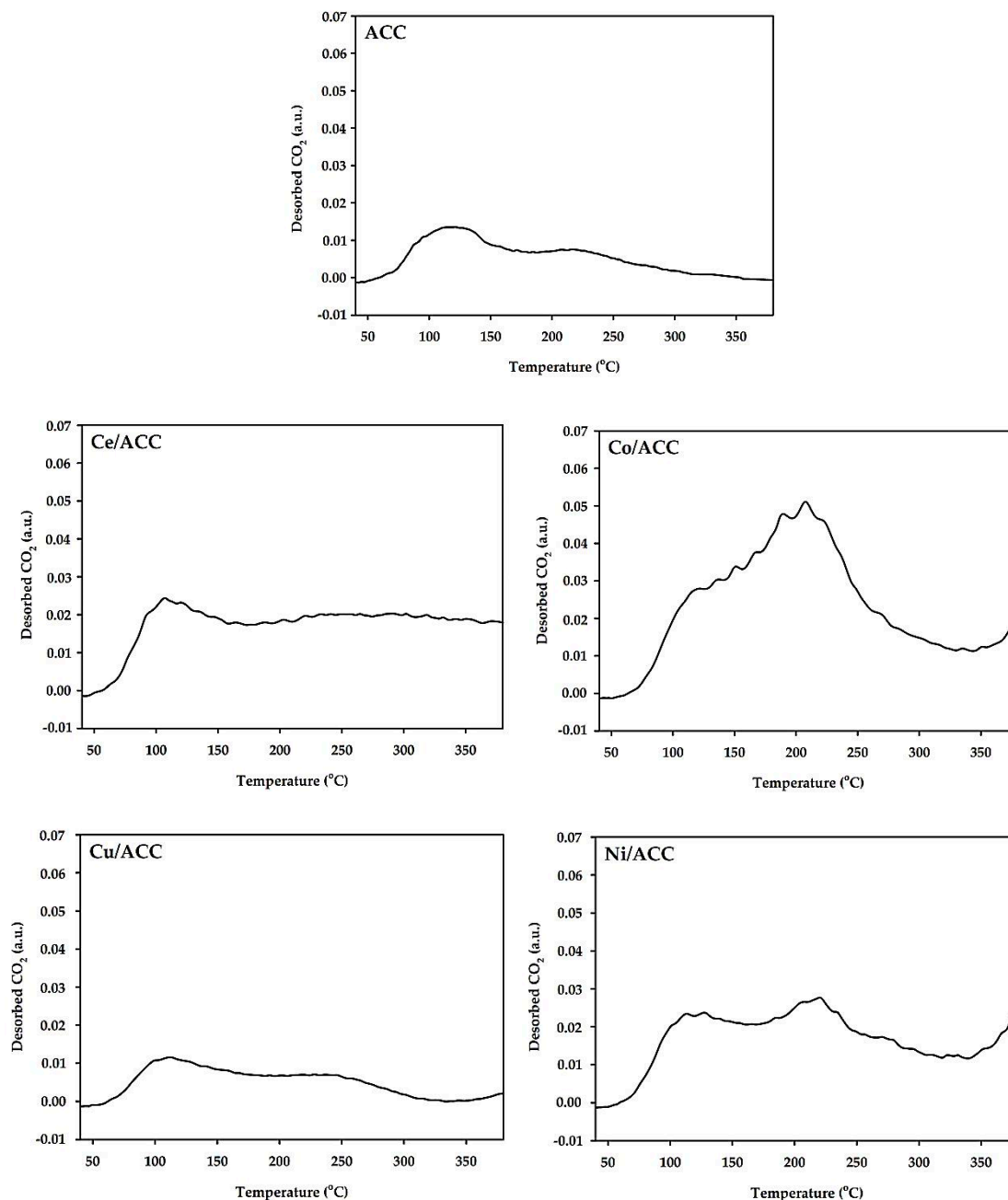


Figure 4. CO₂-TPD profiles of catalysts.

2.2. Catalyst Testing

Figure 6 shows the catalytic activities in terms of ethanol conversion of different metals doped on activated carbon catalysts for ethanol dehydrogenation from 250 to 400 °C. As expected, ethanol conversion increases with increased reaction temperature because of its endothermic reaction, with the exception of the Cu/ACC catalyst, which shows maximum conversion at a temperature of 350 °C. For temperatures of 250 to 400 °C, both Cu and Ni doping evidently improved catalytic activities of these Cu/ACC and Ni/ACC catalysts. In particular, the Cu/ACC catalyst remarkably exhibited the highest ethanol conversion among other catalysts for all reaction temperatures. Meanwhile, this catalyst showed the highest total acidity, as shown in Figure 3. This result correlates with previous studies, which claimed that the dehydrogenation of ethanol is favored in Lewis acid sites [23,24]. The highest ethanol conversion of 65% at 350 °C was obtained from the Cu/ACC catalyst. Then, the rapid decrease of conversion to less than 12% at 400 °C was observed due to the agglomeration and pore blockage by

coke. This agreement was confirmed by other studies [32–34]. Additionally, the proposed mechanism of catalytic dehydrogenation of this catalyst is shown in Scheme 1 [35,36]. Volanti et al. [35] claimed that Cu^+ species are usually located over Cu^0 on the metal surface of the Cu/SiO_2 catalyst, and the ionic species is more selective to acetaldehyde production. Sato et al. [36] reported in 2013 that ethanol is activated to $\text{CH}_3\text{CH}_2\text{O}^*$ by Cu^+ sites or on the zirconia surface. Figure S5 shows TPR results indicating that bulk CuO (Cu^{2+}) on the surface of Cu/ACC catalyst could be reduced to Cu^+ at 160°C , while Cu_2O (Cu^+) was habitually reduced at high temperatures of around $580\text{--}590^\circ\text{C}$ [32]. Therefore, the presence of Cu^+ sites on Cu/ACC can be proven by the formation of acetaldehyde via ethanol dehydrogenation on these sites. From TPR, it should be noted that after reduction at 400°C , some portion of non-reducible CuO still remains based on H_2 consumption.

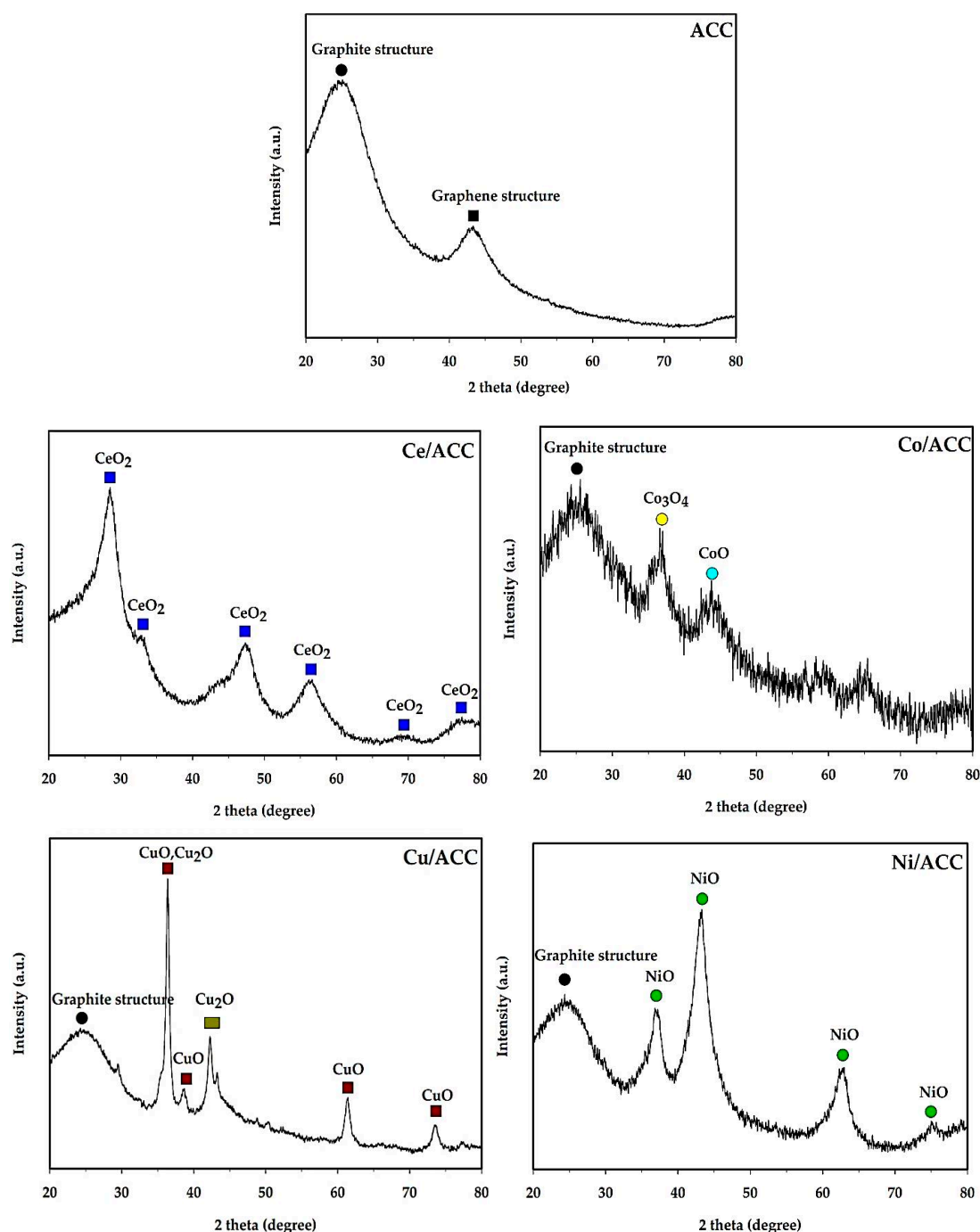
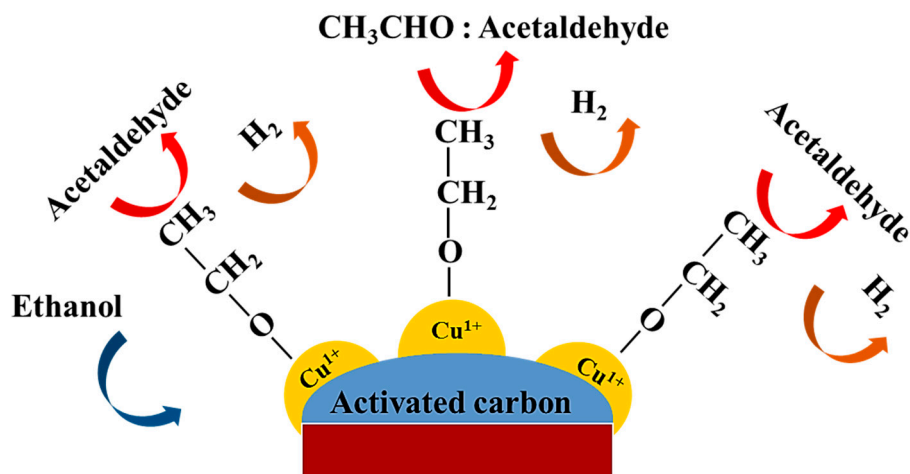


Figure 5. X-ray diffraction patterns of catalysts.



Scheme 1. A proposed mechanism for the dehydrogenation reaction of ethanol on Cu/ACC catalyst.

It was found that the cobalt doping only slightly enhanced the activity of the catalyst, whereas the cerium doping apparently produced acetaldehyde without a significant improvement of activity. With respect to the selectivity of acetaldehyde and ethylene for all catalysts, the results are shown in Figures 7 and 8, respectively. The results of the catalytic reaction test in this study confirmed that most activated carbons acted as catalysts of ethanol dehydrogenation to acetaldehyde with a very high selectivity of more than 90%, which is similar to that reported in other studies [24]. Only Ni/ACC showed a decreased selectivity of acetaldehyde after 300 °C, but this is compensated by the increased selectivity of ethylene (ca. 100% at 400 °C) with increasing reaction temperature [37,38]. An increase in reaction temperature also improves the dehydration selectivity. For the ACC sample, the dehydrogenation selectivity also increases with increased temperature until 300 °C, and then decreases [25]. Moreover, all catalysts exhibited extremely low selectivity (less than 1%) of diethyl ether and acetic acid (not shown).

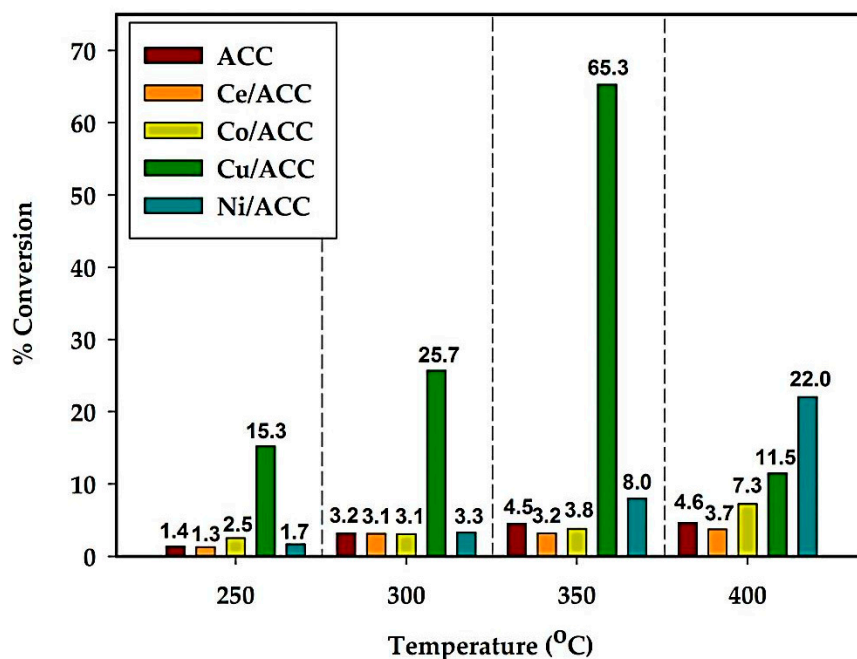


Figure 6. Ethanol conversion of catalysts.

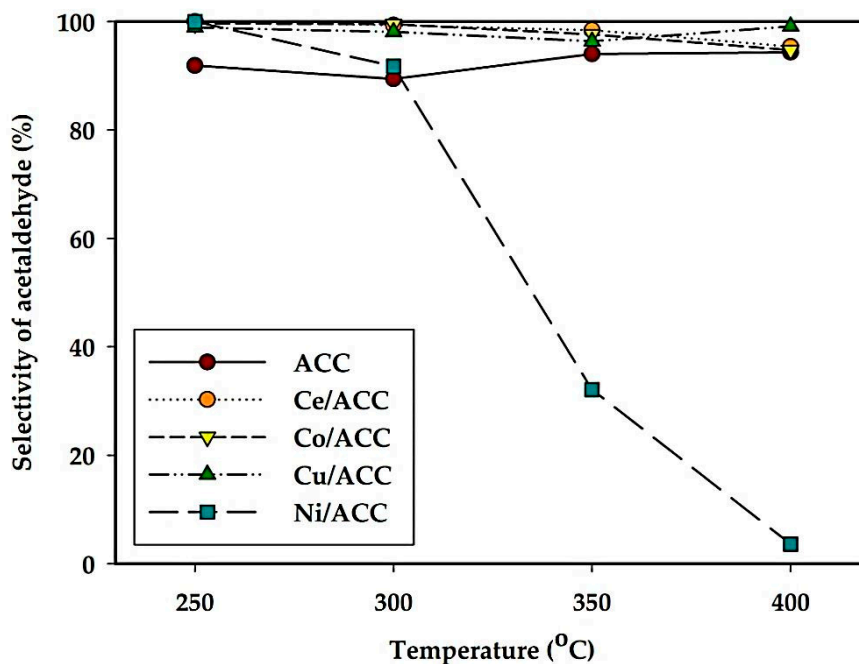


Figure 7. Selectivity of acetaldehyde of catalysts.

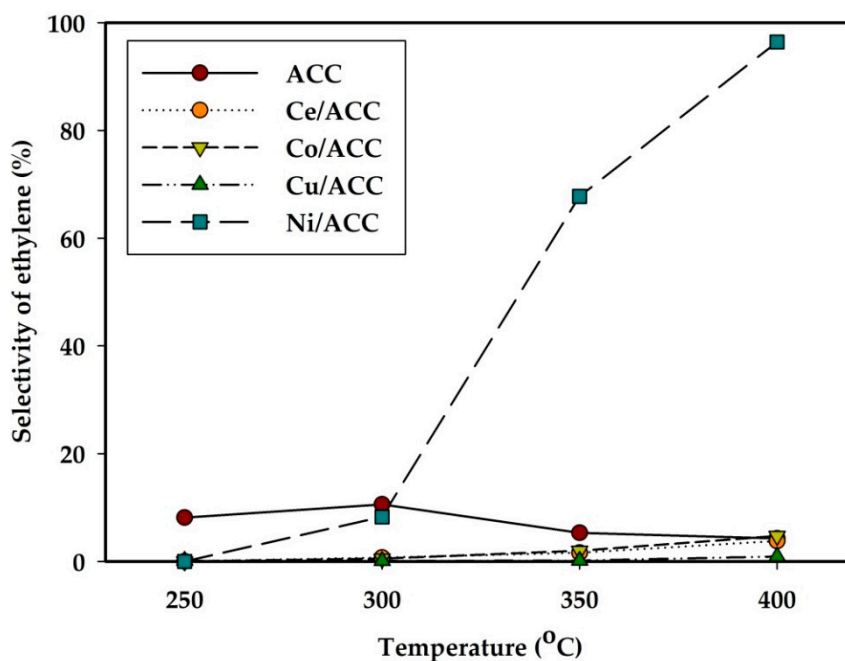


Figure 8. Selectivity of ethylene of catalysts.

Eventually, the stability test of Cu/ACC catalyst under time on stream of 10 h was carried out at a reaction temperature of 350 °C. The stability result is displayed in Figure 9. The ethanol conversion is fairly constant within 5 h of reaction. After 5 h, the ethanol conversion continuously decreases because of possible coke formation or pore blockage from the thermal destruction due to the long-time reaction [33,34].

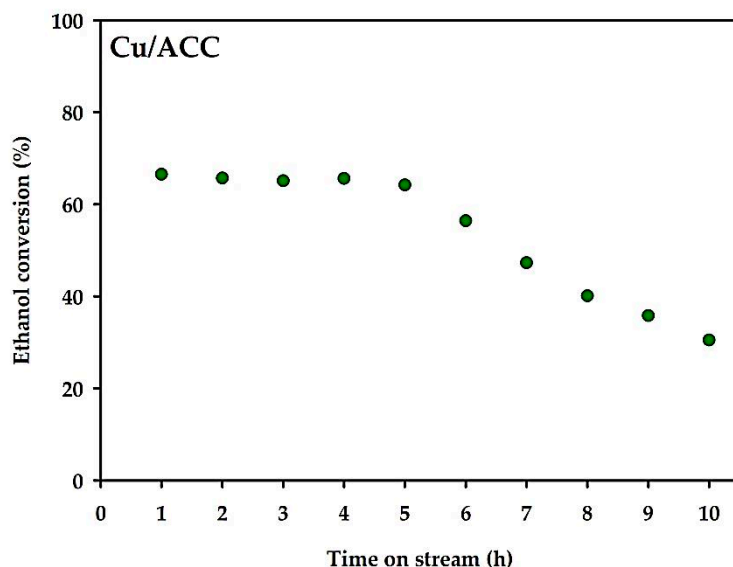


Figure 9. Stability test of Cu/ACC catalyst at 350 °C.

The comparisons of catalytic performance of activated carbon catalysts in this work and other works are summarized in Table 4. It appears that, apart from when higher liquid hourly space velocity (LHSV) was carried out, Cu/ACC catalyst was quite promising compared to other previous catalysts.

Table 4. Comparison of metal on commercial activated carbon for ethanol dehydrogenation and their catalytic ability.

Catalysts	Reaction Temperature (°C)	Ethanol Conversion (%)	Acetaldehyde Yield (%)	LHSV [mL/(h·g _{cat})]	Refs
Cu-CeO ₂ /ACC	250	46	3.3	4	[39]
Co-CeO ₂ /ACC	250	34	2.5	4	[39]
Ni-CeO ₂ /ACC	250	32	1.5	4	[39]
CeO ₂ /ACC	250	3	0.4	4	[39]
4Cu1Ce/ACC	250	46	3.6	4	[39]
5%Ni/ACC	250	17	16.1	290	[37]
Cu/ACC	250	15	15.1	290	[this work]

3. Materials and Methods

3.1. Raw Materials and Chemicals

The chemicals used were as follows: commercial activated carbon (C = 90.81 wt%, O = 9.02 wt% and P = 0.18 wt%), cerium (III) nitrate hexahydrate [Ce(NO₃)₂·6H₂O], cobalt (II) nitrate hexahydrate [Co(NO₃)₂·6H₂O], copper (II) nitrate hemi(pentahydrate) [Cu(NO₃)₂·2.5H₂O] and nickel (II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O] were purchased from Sigma-Aldrich (Germany), distilled water, ultra-high purity nitrogen gas and ultra-high purity hydrogen gas were purchased from Linde, Thailand.

3.2. Preparation of Activated Carbons

The desired amounts of 10 wt% of different metals were used. Deionized water was used as a solvent having a volume equal to the pore volume of the catalyst. Then, the aqueous solution of different metals was slowly impregnated onto activated carbons. The samples were dried in an oven at 110 °C for 24 h. Finally, the catalysts were calcined in N₂ at 400 °C for 6 h.

3.3. Characterization of Activated Carbons

The surface area, pore volume, and pore diameter of the activated carbon were measured by N_2 adsorption-desorption at liquid nitrogen temperature ($-196\text{ }^\circ\text{C}$) using a Micromeritics ASAP 2020 analyzer. The surface area and pore distribution were calculated according to the BET and BJH methods, respectively.

X-ray diffraction (XRD) was performed to determine crystalline structures of activated carbon and raw material using a Siemens D 5000 X-ray diffractometer having $\text{CuK}\alpha$ radiation with Ni filter in the 2θ range of $10\text{--}80$ with a resolution of 0.04 .

Transmission electron microscopy (TEM; JEOL JEM-2010; JEOL Solutions for Innovation, Peabody, MA, USA) was used to determine the morphology and size of metal on the catalyst with thermionic electron type LaB_6 as a source, operating at 200 kV .

Temperature-programmed desorption of carbon dioxide (CO_2 -TPD) was performed using Micromeritics Chemisorp 2750 automated system (Micromeritics Instrument Corporation, Frankfurt, Germany) to study the basic properties. In the study, 0.05 g of catalyst was packed in a U-tube quartz cell with 0.03 g of quartz wool and pretreated at $500\text{ }^\circ\text{C}$ under a helium flow rate of $25\text{ cm}^3/\text{min}$ for 1 h . The catalyst sample was saturated with CO_2 at ambient temperature for 30 min . Then, the physisorbed CO_2 on the catalyst surface was removed by the He flow rate of $25\text{ cm}^3/\text{min}$ for 15 min . After that, the temperature-programmed desorption was carried out from $40\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The amount of CO_2 in effluent gas was analyzed via thermal conductivity detector (TCD) as a function of temperature. The total basicity was calculated from the relation of TCD and temperature from $40\text{ }^\circ\text{C}$ to $550\text{ }^\circ\text{C}$. After $550\text{ }^\circ\text{C}$, the TPD peak was only the decomposition of the catalyst, as proven by the TGA result.

Temperature-programmed desorption of ammonia (NH_3 -TPD) was performed using Micromeritics Chemisorp 2750 automated system (Micromeritics Instrument Corporation, Frankfurt, Germany) to study the acid properties. In the study, 0.05 g of catalyst was packed in a U-tube quartz cell with 0.03 g of quartz wool and pretreated at $500\text{ }^\circ\text{C}$ under helium flow rate $25\text{ cm}^3/\text{min}$ for 1 h . The catalyst sample was saturated with NH_3 at ambient temperature for 30 min . Then, the physisorbed NH_3 on the catalyst surface was removed at a He flow rate of $25\text{ cm}^3/\text{min}$ for 15 min . After that, the temperature-programmed desorption was carried out from $40\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ at a heating rate $10\text{ }^\circ\text{C}/\text{min}$. The amount of NH_3 in the effluent gas was analyzed via thermal conductivity detector (TCD) as a function of temperature. The total acidity was calculated from the relation between the TCD results and the temperature, from $40\text{ }^\circ\text{C}$ to $550\text{ }^\circ\text{C}$. After $550\text{ }^\circ\text{C}$, the TPD peak was only the decomposition of the catalyst, as proven by the TGA result. Inductively coupled plasma mass spectrometer (ICP) was used to determine the actual amount of the metals loading.

3.4. Catalytic Activity with Ethanol Dehydrogenation

3.4.1. Temperature-Programmed Reaction

The similar ethanol reaction (temperature-programmed reaction) system, as reported by Autthanit and Jongsomjit [7], was used. The catalytic dehydrogenation of ethanol was performed in a fixed-bed continuous flow microreactor. First, 0.05 g of catalyst and 0.01 g of quartz wool bed were packed in the middle of the glass tube reactor, which is located in the electric furnace. Before the reaction was carried out, the catalyst was preheated at $200\text{ }^\circ\text{C}$ for 30 min in nitrogen to remove the moisture. Then, the catalyst was activated at $400\text{ }^\circ\text{C}$ for 3 h by hydrogen gas flow. The absolute ethanol was vaporized at $120\text{ }^\circ\text{C}$ with nitrogen gas ($60\text{ mL}/\text{min}$) by controlled injection with a single syringe pump at a constant flow rate of ethanol at $1.45\text{ mL}/\text{h}$. The gas stream was introduced to the reactor with a weight hourly space velocity (WHSV) of $22.9\text{ g}_{\text{ethanol}}/\text{g}_{\text{cat}}\text{ h}^{-1}$, and the reaction was carried out in a temperature range from $250\text{ }^\circ\text{C}$ to $400\text{ }^\circ\text{C}$ under atmospheric pressure. The gaseous products were analyzed by a Shimadzu (GC-14B) gas chromatograph with flame ionization detector (FID) using a capillary column (DB-5) at $150\text{ }^\circ\text{C}$. Upon the reaction test, measurements were recorded at least

three times for each sample. The average values for ethanol conversion and product distribution as a function of temperature were reported. All parameters, along with the conversion of ethanol (X_{EtOH}), concerned-product selectivity (S_i) and concerned-product yield ($Yield_i$), indicated catalytic activity. These were calculated following Equations (1)–(3):

$$X_{EtOH} = \frac{mol_{EtOH}(in) - mol_{EtOH}(out)}{mol_{EtOH}(in)} \times 100 \quad (1)$$

$$S_i(\%) = \frac{mol_i}{\sum mol_i} \times 100 \quad (2)$$

$$Yield_i(\%) = \frac{X_{EtOH} \times S_i}{100} \quad (3)$$

where mol_i is the mole of concerned product and $\sum mol_i$ is the total moles of obtainable products.

3.4.2. Stability Test

The experimental equipment and preparation were similar to those described in Section 3.4.1, above. The ethanol dehydrogenation temperature was maintained at 350 °C. After pretreatment and reduction of the catalyst, ethanol was fed into the reactor for 1 h with a WHSV of 22.9 g_{ethanol}/g_{cat} h^{−1} before sampling of the first product. Then, the products were garnered every 1 h for 10 h. They were analyzed using the same procedure described previously.

4. Conclusions

The catalytic performances of different metals, including Ce, Co, Cu, and Ni, doped on activated carbon catalyst (ACC) for ethanol dehydrogenation within a temperature range of 250 to 400 °C were examined. It was found that the type of metal has a significant impact on catalytic performance, because it affects the surface acidity. It appears that Cu/ACC catalyst exhibits the highest catalytic activity, at 65.3% ethanol conversion, with an acetaldehyde selectivity of 96.3%, resulting in an acetaldehyde yield of ca. 62.9% at 350 °C. This can be attributed to its optimal total acid amount and Cu⁺ species. It should be mentioned that the Ni/ACC catalyst was potentially suitable to produce ethylene via ethanol dehydration at 400 °C, giving an ethylene yield of around 21.3%.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/1/66/s1>, Figure S1: SEM images of activated carbon-supported metal catalysts, Figure S2: EDX of metal on commercial activated carbons, Figure S3: FTIR spectra of activated carbon-supported metal catalysts, Figure S4: Thermal analysis of activated carbon-supported metal catalysts, Figure S5: TPR profiles of activated carbon-supported metal catalysts. Table S1: %metal content of the different commercial activated carbon catalysts, Table S2: Functional group of activated carbons.

Author Contributions: Conceptualization, J.O.-e. and B.J.; Methodology, J.O.-e.; Validation, J.O.-e.; Formal Analysis, J.O.-e.; Investigation, J.O.-e.; Resources, B.J. and P.P.; Data Curation, J.O.-e.; Writing—Original Draft Preparation, J.O.-e.; Writing—Review & Editing, J.O.-e. and B.J.; Visualization, B.J.; Supervision, B.J.; Project Administration, J.O.-e.; Funding Acquisition, P.P. and B.J.

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

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