Research Article
Carbon-Based Catalyst from Pyrolysis of Waste Tire for Catalytic Ethanol Dehydration to Ethylene and Diethyl Ether

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This work investigated the use of waste tire as a source of carbon in preparation of carbon-based catalysts for applying in ethanol dehydration. The pyrolysis of waste tire was performed to obtain the solid carbon, and then it was treated with two different acids including HCl and HNO₃ prior to the activation process with different temperatures to gain suitable carbon catalysts. All carbon catalysts were characterized using nitrogen physisorption, XRD, FTIR, and acid-base titration. The catalysts were tested for catalytic ethanol dehydration in a micropacked-bed reactor under the temperature range from 200°C to 400°C. It revealed that the ethanol conversion increased with increasing the reaction temperature for all catalysts. The carbon catalyst treated with HCl and calcined at 420°C (AC_H420) exhibited the highest ethanol conversion of 36.2% at 400°C having ethylene and diethyl ether selectivity of 65.9 and 33.5%, respectively. The high activity of this catalyst can be attributed to the high acid density at the surface (18.5 μmol/m²), which was significantly higher than those of most other catalysts (less than 8.0 μmol/m²).

1. Introduction

It has been reported that global tire manufacturing output is estimated to be over 17 million tons in 2016 and is growing nearly by 4% per year through 2022 [1]. This leads to large amounts of waste tires produced annually. A common way for disposal of these waste tires is land filling. However, due to their large volume and high void space (about 75%), they consume a considerable amount of space if directly dumped into landfill [2]. Burning waste tires also release various harmful gases such as CO₂ and CO, and volatile organic compounds such as benzene, styrene, butadiene, and phenol-like substances [3].

One of the most interesting and dynamically developing methods for reducing waste tires is a pyrolysis process [4]. The pyrolysis process is not only the waste disposal, but also produces alternative fuel for internal combustion engines. In addition, the pyrolysis is nontoxic without emission of harmful gas, unlike incineration [5]. The proportions of pyrolysis products including gas, oil, and solid carbon depend on the rate of temperature rise, time of decomposition, temperature, and pressure [6].

In general, flash pyrolysis process (heating rate around 100°C/s to 10,000°C/s) produces 45–75 wt% of liquid, 15–25 wt% of solid, and 10–20 wt% of noncondensable gases [7]. The obtained pyrolysis gas and liquid can be efficiently used as fuel. In general, the pyrolysis liquid has an average heating value of 12 MJ/kg and the pyrolysis gas has an average heating value of 23–26.3 MJ/kg. For the obtained pyrolysis solid (solid carbon), it can be used to produce low-grade carbon black, and also adsorbent materials after applying an activation step (known as activated carbon, AC) [8]. Thus, the use of solid carbon from waste tire as a catalyst or a catalyst support is also an alternative way for valorization of waste tires. Sanchez-Olmos et al. [9] prepared a new acid catalyst based from a solid carbon from waste tire pyrolysis.
The solid carbon was functionalized using sulfuric acid as source of \(-\text{SO}_3\text{H}\) acid groups prior using in biodiesel production. It was found that this catalyst exhibited a high catalytic performance, which required shorter times, low temperature, and significantly a low amount of methanol compared to other studies for the biodiesel production. Hood et al. [10] compared waste tire-derived carbons prepared using two different methods including the treatment with concentrated sulfuric and a newly developed method involving the sequential treatment with L-cysteine, dithiothreitol, and \(\text{H}_2\text{O}_2\) under mild conditions. The catalysts were applied for the waste to biofuel conversion. It was found that both catalysts could also effectively convert oleic acid or a mixture of fatty acids and soybean oil to usable biofuels.

In addition, one of the interesting reactions in which carbon-based catalyst from pyrolysis could be employed is catalytic ethanol dehydration that converts ethanol into ethylene and diethyl ether (DEE) [11–14]. This reaction undergoes via suitable solid acid catalysts. Ethylene is one of the most usable upstream chemicals, while DEE is mostly used as a solvent in chemical processes including fragrance and pharmaceutical processes. However, only a few research works studied in the catalytic ethanol dehydration with using the carbon-based catalyst. Bedia et al. [15] used acid carbon catalyst derived from olive stone activated with phosphoric acid (\(\text{H}_3\text{PO}_4\)) for catalytic decomposition of ethanol, which yields mainly dehydration products, mostly ethylene with lower amounts of diethyl ether. It was also found that characteristic of the carbon catalyst such as surface functional groups significantly affected the catalytic activity during the reactions. The mentioned characteristics varied with the activation temperature and the chemical concentration in impregnation step. Therefore, adjusting conditions in preparation processes of carbon catalyst can tailor the reaction and obtain the desired products.

Hence, in this study, waste tires were used to prepare carbon-based catalysts via pyrolysis with various conditions including activation temperatures and types of treatment acid (HCl and HNO\(_3\)). All prepared carbons were then activated with \(\text{H}_2\text{PO}_4\) prior to sulfonating with \(\text{H}_2\text{SO}_4\) to obtain the acidic carbon-based catalysts for ethanol dehydration to ethylene and diethyl ether. The carbon catalysts were characterized with different techniques such as \(\text{N}_2\) physisorption, acid-based titration, Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The catalysts were then tested in the gas-phase ethanol dehydration under a reaction temperature of 200°C to 400°C. The catalytic performance for all catalysts in terms of catalytic activity and product selectivity was determined and further discussed.

2. Materials and Methods

2.1. Materials. Waste tires were obtained from the local supplier in Bangkok, Thailand. Hydrochloric acid (HCl), nitric acid (HNO\(_3\)), and phosphoric acid (\(\text{H}_3\text{PO}_4\)) were purchased from QRÉC, New Zealand. The proximate analysis of waste tire is shown in Table 1.

<table>
<thead>
<tr>
<th>Item</th>
<th>Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>2.81</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>1.86</td>
</tr>
<tr>
<td>Ash</td>
<td>15.42</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>79.91</td>
</tr>
</tbody>
</table>

2.2. Pyrolysis of Waste Tire. Waste tires were washed, dried, and cut into pieces. They were then pyrolyzed at 400°C in nitrogen with a heating rate of 10°C/min and held at that temperature for 1 h. Products from pyrolysis included three phases: liquid (bio-oil), solid (carbon), and gas. In this study, only solid carbon was further investigated.

2.3. Preparation of Carbon Catalyst. At first, waste tires were pyrolyzed at 420°C in 0.5 batch reactor with \(\text{N}_2\) flowing at 50 mL/min. The pyrolysis process was conducted as illustrated in Scheme 1.

All solid material from the pyrolysis of waste tires known as solid carbon was brought into a magnetic separator to remove the tire wire. After that, the carbon was treated with 5 M hydrochloric (HCl) or nitric acid (HNO\(_3\)) at 125°C for 1 h, neutralized with water, and dried. The activation process was carried out with 1 M phosphoric acid (1 : 2 w/v) at three different temperatures including 420, 520, and 620°C for 3 h in a vacuum oven.

Six carbon catalysts are donated as follows: $\text{AC}_{XY}$, where X refers to hydrochloric (H) or nitric acid (N) treatment and Y is the activation temperatures. For instance, $\text{AC}_{\text{H}420}$ refers to the catalyst obtained using hydrochloric acid, activated at 420°C.

2.4. Sulfonating of Catalyst. The prepared carbon catalyst was mixed with sulfuric acid (98 %) in the ratio of 1 g carbon per 1 mL acid. The mixture was stirred at 125°C for 20 h. The obtained catalyst was washed with water until it become neutral, and then dried at 125°C for 6 h.

2.5. Characterization of Carbon Catalyst

2.5.1. Nitrogen Physisorption. The surface area and pore characteristics of all catalysts were determined by the nitrogen physisorption technique using Micromeritics ASAP 2020 surface area and porosity analyzer. The catalyst sample was thermally heated at 150°C for 1 h before nitrogen adsorption at the temperature of –196°C.

2.5.2. Iodine Adsorption Test. The adsorption of iodine was determined using 0.5 N standardized iodine solution and conducted according to ASTM D1510 [16].

2.5.3. X-Ray Diffraction (XRD). XRD was used to determine the bulk crystalline phases of all catalysts using a SIEMENS
D5000 X-ray diffractometer with CuKα radiation through an Ni filter in the 2θ range of 20° to 80° [17].

2.5.4. Acidity Determination. 0.1 g of catalyst was soaked in 60 ml of 0.08 M sodium hydroxide (NaOH) for 24 h at room temperature. A few drops of phenolphthalein were added into the mixture, and then titrated with 0.02 M HCl until the equivalent point was reached.

2.5.5. Scanning Electron Microscopy (SEM). The morphology of the catalysts was investigated with using JEOL JSM-35F scanning electron microscope (SEM). The sample was conductive to prevent charging by coating with gold particle by ion 45 sputtering device.

2.5.6. Fourier Transform Infrared Spectroscopy (FTIR). The functional groups of the catalysts were determined by a Nicolet 6700 FTIR spectrometer. The infrared spectra were recorded under the wavenumber scanning from 400 to 4,000 cm⁻¹ with a scanning frequency of 64 times.

2.6. Reaction Study. The ethanol dehydration process was conducted in a fixed-bed continuous flow reactor with 0.7 cm inside diameter. First, 0.01 g of quartz wool and 0.05 g of catalyst were packed into the middle of reactor. The process began with pretreating the catalyst with argon (50 ml/min) at 200°C for 1 h under atmospheric pressure (WHSV = 8.4 h⁻¹). The reaction was carried out in the temperature range from 200°C to 400°C. The obtained products were analyzed by a Shimadzu GC14B gas chromatographer with capillary column (DB-5 for separation of ethylene, diethyl ether, and acetaldehyde) and FID detector. The catalytic ethanol dehydration system (Scheme 2) was conducted as reported in our previous work [12].

3. Results and Discussion

3.1. Characterization. Characterization results of the carbon catalysts prepared from pyrolysis of waste tires treated with two different acids (HCl and HNO₃), and activated with phosphoric acid at various temperatures are shown in Table 2. From a nitrogen adsorption-desorption technique, which gave details of surface and pore characteristics, it was found that surface areas and pore volume of all activated carbons increased with increasing the activation temperature indicating no sintering occurred. The higher temperatures enhance a removal of organic volatile compounds and also noncarbon atom remained in the activated carbons resulting in the additional pores inside the structure, thus leading to the higher pore volume and the larger surface [18]. However, the small new pores dragged the average pore values of the activated carbons down as seen from the result. Similar trends were found for both types of activated carbons, treated with HCl or HNO₃.

It was observed that iodine adsorption capacities of the catalysts did not linearly increase with increasing of surface area. Change in pore size could affect the adsorption capacity of the catalyst. Decrease in pore size in the catalysts activated at higher temperature obstructs the adsorption of iodine molecules onto the catalyst surface. Even though the iodine molecules are relatively smaller (0.6 nm, [19]) than the average pore sizes of the catalyst, the new pores generated at the high activation temperature may be smaller than or nearly the same size as the iodine molecules, thus hindering the adsorption process. Shimada et al. [20] also found a remarkable decrease in the iodine adsorption number which is attributed to the collapse of pores by the excessive activation and an increase in the ash content in the activated carbon. Change in adsorption characteristic could influence the performance of catalysts, especially when catalysts have to be immobilized prior to use.

Adsorption isotherms of the catalysts were also obtained from a nitrogen adsorption-desorption technique. It can be observed that all samples exhibited type IV isotherm with a hysteresis loop indicating to a mesoporous structure of the materials according to the IUPAC classification (Figure 1).

Crystal structures of the catalyst samples were detected with an X-ray diffractometer (XRD). It can be seen from the

![Scheme 1: Pyrolysis process.](image_url)
XRD patterns in Figure 2 that all samples exhibited the similar crystal structures revealing the characteristic peaks of graphite at around $2\theta \approx 26^\circ$ [21]. The sharper peaks appeared with the higher activation temperature. This suggests that the higher activation temperature causes more crystallinity to the samples.

Morphologies of the catalysts were investigated with a scanning electron microscope (SEM) as shown in the SEM micrographs in Figure 3. It can be observed that all catalysts exhibited spherical-like particles with smooth surface. No differences in morphologies caused by different activation temperatures or acids were observed.

For efficient use in the ethanol dehydration, the acidity of the catalysts was improved by sulfonating with H$_2$SO$_4$ onto the carbon. The finished catalysts were then investigated with the FTIR to detect functional groups on the catalyst surface. The FTIR spectra of all catalysts are shown in Figure 4. It can be seen that all catalysts clearly exhibited peaks around 1184 cm$^{-1}$, which are attributed to sulfate groups ($S=O$) from the substitution of hydrogen in surface hydroxyl groups ($O\cdots H$). This is evident for the presence of acid groups derived from sulfonation with H$_2$SO$_4$ on the catalyst surfaces. The peaks attributed to alcohols (R–OH) around 3400–3600 cm$^{-1}$ and carboxylic (C=O) around 1711 cm$^{-1}$ were also observed in all catalysts.

The acidity of the catalysts was determined by back titration with NaOH. The result of acidity determination with regard to surface acidity (moles of acidic sites) and acid density is shown in Table 3. It was observed that the surface acidities of all catalysts are nearly similar probably due to same amount of sulfonic acid sites present on all catalysts. This indicates that all catalysts have similar adsorption capacities for sulfonic acid, in consistent with the adsorption capacities of iodine as observed previously. The differences in surface areas of the catalysts insignificantly affected the acidity of the catalyst. However, as a result of the differences in surface areas of the catalysts, it leads to the variation of acid density among all catalysts. The highest acid density belonged to the catalysts activated at the low temperature (400°C) for both series of catalysts (previously treated with HCl or HNO$_3$) due to their low surface areas. These acid properties may influence catalytic performances of the catalyst during ethanol dehydration, which will be further discussed in the next part.

### 3.2. Reaction Study

The catalytic ethanol dehydration was conducted under temperature programming from 200°C to 400°C for all catalysts to evaluate their catalytic performance.

### Table 2: Surface areas, pore characteristics, and iodine adsorption of carbon catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore size (nm)</th>
<th>Iodine adsorption (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC_H420</td>
<td>119.2</td>
<td>0.85</td>
<td>28.3</td>
<td>125</td>
</tr>
<tr>
<td>AC_H520</td>
<td>273.6</td>
<td>1.49</td>
<td>23.4</td>
<td>129</td>
</tr>
<tr>
<td>AC_H620</td>
<td>293.3</td>
<td>1.81</td>
<td>20.4</td>
<td>139</td>
</tr>
<tr>
<td>AC_N420</td>
<td>105.8</td>
<td>0.85</td>
<td>32</td>
<td>124</td>
</tr>
<tr>
<td>AC_N520</td>
<td>263.6</td>
<td>1.34</td>
<td>23.9</td>
<td>126</td>
</tr>
<tr>
<td>AC_N620</td>
<td>290.0</td>
<td>1.62</td>
<td>21.3</td>
<td>129</td>
</tr>
</tbody>
</table>

Scheme 2: Ethanol dehydration system.
in terms of catalytic activity (% ethanol conversion) and product selectivity. The ethanol conversions of all catalysts at various temperatures are shown in Figure 5. The ethanol conversions at 400°C (the best condition) are also listed in Table 3 along with the product selectivities at this temperature.

From Figure 5, it can be observed that for all catalysts except AC_N620, the ethanol conversion increased with reaction temperatures. This could be an effect of an endothermic reaction which favors high temperature. The synthesis pathway of ethanol into ethylene is considered an endothermic reaction as proposed in reaction (2) [22]. Therefore, the results confirm the existence of this reaction.

$$\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad (\Delta H = +44.9 \text{ kJ/mol})$$ (2)
Considering the ethanol conversions at 400 °C in Table 3, it was found that for both series of catalysts, the ethanol conversions increased with surface acidity and acid density of the catalysts. Nevertheless, the acid density apparently influenced the ethanol conversion more than the total acidity. It has been known that the dehydration process increases with increased total acidity of the carbon surfaces and takes place mainly at the active centers of the Brønsted acid. Accordingly, sulfonic groups on the catalysts, which easily give up a proton can be classified as the Brønsted acid, essentially enhance catalytic activities of the catalysts. Thus, high acidity (Brønsted acid sites) of the catalysts increased the ethanol conversion as expected. The reaction pathway of ethanol dehydration with the sulfonic acid carbon-based catalyst can be proposed as Figure 6. In the first step, protonation takes place at alcoholic oxygen in the ethanol
molecule. Then, the C-O bond is broken causing the loss of a water molecule and resulting in a carbocation intermediate. Finally, a hydrogen ion is removed from the carbocation, forming a double bond of ethylene.

For the effect of acid density, it can be seen that the ethanol conversion of the catalysts significantly increased with the acid density. This effect was also observed in our previous study [23], which revealed that high acid density of the alumina catalysts apparently results in high catalytic activity in the ethanol dehydration. This is because the shorter distances between two nearby neighboring acid sites (high acid density) probably lead to rapidly react to form diethyl ether. The diethyl ether can be formed through a bimolecular nucleophilic substitution mechanism which is preferred with two adjacent ethanol molecules adsorbed on the catalyst surface as shown in Figure 7. It can be see that

![Figure 5: Ethanol conversion of the catalysts for ethanol dehydration at various temperatures.](image1)

![Figure 6: The mechanism of ethanol dehydration to ethylene.](image2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acidity (µmol/g)</th>
<th>Acid density (µmol/m²)</th>
<th>Ethanol conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC_H420</td>
<td>2210</td>
<td>18.5</td>
<td>36.2</td>
<td>65.9</td>
</tr>
<tr>
<td>AC_H520</td>
<td>2200</td>
<td>8.0</td>
<td>19.9</td>
<td>66.2</td>
</tr>
<tr>
<td>AC_H620</td>
<td>2170</td>
<td>7.4</td>
<td>14.3</td>
<td>69.0</td>
</tr>
<tr>
<td>AC_N420</td>
<td>2270</td>
<td>21.5</td>
<td>29.1</td>
<td>69.4</td>
</tr>
<tr>
<td>AC_N520</td>
<td>2040</td>
<td>7.7</td>
<td>22.7</td>
<td>75.6</td>
</tr>
<tr>
<td>AC_N620</td>
<td>1980</td>
<td>6.8</td>
<td>22.1</td>
<td>73.9</td>
</tr>
</tbody>
</table>
the intermediate carbocation combines with the near ethanol molecule and then produces diethyl ether. Converting the ethanol into diethyl ether can increase the ethanol conversion. In addition, diethyl ether also acts as reaction intermediate and is subsequently decomposed to ethylene [24]. Nevertheless, this process still increased the catalytic activity anyway.

It should be noted that the catalytic activity also decreased with increasing of the activation temperature of the catalysts. The reason may be a gradual decomposition of carboxyl groups present on the carbon surface prior to sulfonation, which already becomes unstable at 180°C [25]. It has also been reported that heat treatment will create unsaturated surfaces as a result of thermal desorption of acidic functional groups [26]. Several researchers found that the decomposition of oxygen functional groups occurs at elevated temperatures and leads to an increase in basicity of the carbon surface [27–29]. Therefore, an increase of the activation temperature led to lower acidity on the catalyst and consequently reduced the ethanol conversion. This indicates that the other acidic functional groups such as carboxyl group could involve in the reaction mechanism of the ethanol dehydration besides sulfonic acid on the catalyst surface.

When comparing between two series of the catalysts, it was found that with the high activation temperatures (520°C and 620°C) the HNO₃-treated catalysts gave the higher catalytic activity than the HCl-treated catalysts. However, at 420°C, the HCl-treated catalyst (AC_H420) conversely gave the higher catalytic activity than the HNO₃-treated catalyst (AC_N420). This was because at the same activation temperatures (520°C and 620°C), the HNO₃-treated activated carbons have a slightly larger pore diameter than the HCl-treated activated carbons (Table 1). Therefore, after sulfonation the sulfonic acid sites located inside the pores of the HNO₃-treated catalysts could be more easily access than those of the HCl-treated catalysts. This is attributed to the higher catalytic activity of the HNO₃-treated catalysts. Nevertheless, at 420°C both types of activated carbons (AC_H420 and AC_N420) have the relatively larger pore diameter, thus an effect of pore diameter becoming lower. The higher catalytic activity of AC_H420 than AC_N420 was due to that HNO₃ having a higher oxidizing strength that destroyed the pore walls to a large extent, fixing a large amount of oxygen surface groups [30]. The higher degree of oxidation at the catalyst surface could convert surface hydroxyl groups into other oxygen contained groups, thus consequently affecting the addition of the sulfonic groups through hydroxyl groups during sulfonation. This leads to the higher active acidic centers on the surface of AC_H420 than AC_N420, and then provided the higher catalytic activity.

With regard to the product selectivity of the catalyst, it was found that all HNO₃-treated catalysts had higher ethylene selectivities than those obtained from HCl-treated catalysts. The opposite was true for the diethyl ether selectivities. The acetaldehyde selectivities were insignificant for both series of catalysts. The different natures of catalysts, which were previously treated with different acids, may be the reasons for the different selectivities. It is generally accepted that the ethanol conversion to ethylene occurs on weak acid sites [24, 31]. Therefore, this suggests that the HNO₃-treated catalysts have the higher proportion of weak acid sites than the HCl-treated catalysts. From the results of the reaction study, it can be concluded that the types of acid used in treatment process, and also the activation temperatures, influence the catalytic performance of the solid carbon catalysts prepared from the pyrolysis of waste tire. Therefore, tuning the ethanol dehydration production with solid carbon catalysts by variation of the acid types would be plausible and worth further investigation.

In Table 4, summarized reports of catalytic performance for ethanol dehydration to ethylene over various catalysts are compared. It can be seen that the solid carbon catalysts in this study exhibited the lower catalytic activity than most catalysts in the previous studies. Nevertheless, when comparing among the carbon-based catalysts, the waste tire-derived carbon is still comparable. Thus, waste tires have the considerable potential to be developed as a catalyst for ethanol dehydration.

4. Conclusion

Waste tires were pyrolyzed to obtain carbon and then sulfonated to achieve the carbon-based catalysts. The catalysts were divided into two series according to the acid types in the treatment process. Both series of catalysts have the same trends that increasing the activation temperature decreased the catalytic activity due to the reduction of acid density. The HNO₃-treated catalysts had higher catalytic activities than the HCl-treated catalysts except at the activation temperature of 400°C. The ethylene selectivities of the HNO₃-treated catalysts were rather higher than those of.
HCl-treated catalysts. This was probably resulted from the higher proportion of weak acid sites.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References


Table 4: Comparison of catalysts for ethylene dehydration and their catalytic ability.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction temperature (°C)</th>
<th>Ethanol conversion (%)</th>
<th>Ethylene selectivity (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBZ</td>
<td>200–400</td>
<td>7–100</td>
<td>1–100</td>
<td>[17]</td>
</tr>
<tr>
<td>Al-HBZ</td>
<td>200–400</td>
<td>9–92</td>
<td>0–98</td>
<td>[17]</td>
</tr>
<tr>
<td>M-Al</td>
<td>200–400</td>
<td>12–92</td>
<td>0–96</td>
<td>[17]</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>400</td>
<td>99</td>
<td>10</td>
<td>[32]</td>
</tr>
<tr>
<td>20HP-ZSM-5</td>
<td>250–450</td>
<td>25–100</td>
<td>3–98</td>
<td>[32]</td>
</tr>
<tr>
<td>γ-Al2O3</td>
<td>400–550</td>
<td>70–100</td>
<td>40–95</td>
<td>[11]</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>500</td>
<td>100</td>
<td>100</td>
<td>[33]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbon based</th>
<th>Activator</th>
<th>Modifier</th>
<th>Reaction temperature (°C)</th>
<th>Ethanol conversion (%)</th>
<th>Ethylene selectivity (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacterial cellulose</td>
<td></td>
<td></td>
<td>200–400</td>
<td>41–65</td>
<td>0–65</td>
<td>[34]</td>
</tr>
<tr>
<td>Olive stone</td>
<td>Steam</td>
<td>(NH4)2S2O8</td>
<td>180</td>
<td>1–22</td>
<td>16–26</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HNO3</td>
<td>150–450</td>
<td>n.a.</td>
<td>0–50*</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH3COOOH</td>
<td>150–450</td>
<td>n.a.</td>
<td>0–15*</td>
<td>[25]</td>
</tr>
<tr>
<td>Polish brown coal</td>
<td>HCl, HF</td>
<td>H2SO4</td>
<td>150–450</td>
<td>n.a.</td>
<td>0–14*</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Air</td>
<td>150–450</td>
<td>n.a.</td>
<td>0–18*</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl2</td>
<td>150–450</td>
<td>n.a.</td>
<td>0–5*</td>
<td>[25]</td>
</tr>
<tr>
<td>Waste tire</td>
<td>HCl</td>
<td>H2SO4</td>
<td>200–400</td>
<td>14–36</td>
<td>65–69</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>HNO3</td>
<td>H2SO4</td>
<td>200–400</td>
<td>22–29</td>
<td>69–75</td>
<td>This work</td>
</tr>
</tbody>
</table>

*Based on the ethanol conversion to ethylene only and the values are approximate.


