1. Introduction

Sulfur dioxide formed by the oxidation of sulfur compounds in petroleum or coal burned as fuels causes acid rain. Several methods for the removal of sulfur compounds from the fuels or exhaust gases are utilized. Oxidation and neutralization of sulfur dioxide in the presence of oxygen, water vapor and calcium oxide powder into calcium sulfate (gypsum) has been utilized for a boiler using heavy oil1). However, the use of gypsum has been limited in recent years. Therefore, in civilized countries, gypsum formed by this process is treated as an industrial waste. Sulfur dioxide is oxidized into sulfuric acid over an activated carbon catalyst in the presence of water2). Therefore, the latter catalytic reaction has recently drawn attention, because the formed sulfuric acid can be utilized for industrial processes, so the harmful waste, sulfur dioxide, can be recycled as a useful resource, sulfuric acid3). The study on the catalytic oxidation of sulfur dioxide has a long history. The relationship between the surface composition and catalytic activity was investigated to propose a model of active site in early studies4). Subsequently improvement of the trickle bed reactor was attempted5)–8). Recent studies of several catalysts such as activated carbon fiber9) and fluorocarbon-treated carbon10) have found quite high performance. Production of activated carbon from wood has recently become important for the utilization of waste wood10),11). Conventionally, the production of activated carbon from wood has been carried out using a reagent such as zinc chloride or water vapor at quite high temperatures such as 1473 K12). The present authors previously developed a method to produce activated carbon with high surface area by the water vapor treatment of wood at a moderate temperature such as 1073 K13). Here we report the catalytic activity of the activated carbon for the oxidation of sulfur dioxide.

2. Experimental

Table 1 shows a list of activated carbons used in this study. The sample YS-1 was prepared according to our previous patent13). Chips of sugi wood (Japanese cedar, ca. 5 cm in length) were continuously fed into a stainless steel reactor with 543 cm$^2$ cross sectional area at 5 kg·h$^{-1}$. A gaseous mixture of water vapor and nitrogen (7.50 mol·h$^{-1}$ and 3.68 mol·h$^{-1}$, respectively) was also continuously supplied. The wood was passed over a heated zone in which the temperature was kept at 1073 K for ca. 20 min. In other words, the water vapor treatment of sugi wood was carried out at 1073 K for ca. 20 min in a nitrogen flow containing 67 mol% of water vapor.

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[Research Note]

Oxidation of Sulfur Dioxide to Sulfuric Acid over Activated Carbon Catalyst Produced from Wood

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Sulfur dioxide can be removed from exhaust gases by oxidation to sulfuric acid over an activated carbon catalyst in the presence of water. A manufacturing method for activated carbon was developed based on the steam-gasification of wood at relatively low temperature. The catalytic activity of the activated carbon produced from wood for the oxidation of sulfur dioxide was compared with those of commercially available activated carbons. The carbon produced from wood showed high activity, but it was lower than that of a highly developed catalyst such as activated carbon fiber. However, the potential utilization of waste wood as an environmental catalyst was clearly demonstrated.

Keywords
Sulfur dioxide, Catalytic oxidation, Activated carbon catalyst, Waste wood, Sulfuric acid

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2 and 3 were prepared from waste wood at 1123 K for ca. 20 min in a nitrogen flow containing water vapor (67 mol% and 82 mol% for YS-2 and 3, respectively). Other samples were supplied commercially. Surface area was determined from the adsorption capacity of nitrogen at 77 K according to the BET (Brunauer–Emmett–Teller) equation after evacuation at 373 K.

The activated carbon (3.8 g) was placed in a Pyrex tube (30 mm i.d.) and evacuated at 318 K for 1 h. After evacuation, the reactant mixture was directly supplied to the catalyst bed, and the adsorption of sulfur dioxide on the carbon surface took several hours to reach saturation. The catalytic activity could then be measured from the consumption of sulfur dioxide

In order to avoid this long equilibration period, the catalyst bed was filled with a 0.5 mol dm\(^{-3}\) aqueous solution of sulfuric acid to fully adsorb sulfuric acid. The solution was soon exhausted. This pretreatment method was adopted for quick evaluation of catalysts in the previous studies

Figure 2 shows the catalytic activities of various activated carbons as their supplied forms. The commercially available samples showed initial conversions of 40 to 80%, and slow degradation of the activity was generally observed. The activity was apparently independent of the surface area. The activated carbons prepared from wood (YS-1, 2 and 3) showed higher activities. Especially, the samples prepared from waste wood (YS-2 and 3) showed initial conversions close to 100% under these conditions.

The apparent rate of this reaction was affected by the morphology of activated carbon generally in a trickle bed reactor, because the reaction occurs at the triple phase interface between the liquid (water and produced sulfuric acid), gas (oxygen and sulfur dioxide) and solid (carbon) phases; so the macro porosity of the catalyst affected the accessibility of liquid drops and gas bubbles to the triple phase interface

Figure 1 shows the catalytic activities of various activated carbons as their supplied forms. The

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Manufacturer</th>
<th>Raw material</th>
<th>BET surface area [m(^2) g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>YS-1</td>
<td>Y.S. Engineering Ltd.</td>
<td>Sugi wood (Japanese cedar)(^{a})</td>
<td>659</td>
</tr>
<tr>
<td>YS-2</td>
<td>Y.S. Engineering Ltd.</td>
<td>Waste wood from scrapped house(^{b})</td>
<td>677</td>
</tr>
<tr>
<td>YS-3</td>
<td>Y.S. Engineering Ltd.</td>
<td>Waste wood from scrapped house(^{c})</td>
<td>680</td>
</tr>
<tr>
<td>4SA</td>
<td>Kuraray Chemical Co., Ltd.</td>
<td>Coconut shell</td>
<td>958</td>
</tr>
<tr>
<td>4GG</td>
<td>Kuraray Chemical Co., Ltd.</td>
<td>Coconut shell</td>
<td>1047</td>
</tr>
<tr>
<td>PG-3</td>
<td>Cataler Corp.</td>
<td>Coal</td>
<td>1240</td>
</tr>
<tr>
<td>G-BAC G-70R</td>
<td>Kureha Chemical Industry Co., Ltd.</td>
<td>Pitch from petroleum</td>
<td>1236</td>
</tr>
<tr>
<td>JXN</td>
<td>Nippon Carbon Co., Ltd.</td>
<td>Coconut shell</td>
<td>1144</td>
</tr>
<tr>
<td>HG</td>
<td>Ajinomoto Fine-Techno Co., Inc.</td>
<td>Coconut shell and coal</td>
<td>1143</td>
</tr>
<tr>
<td>GX</td>
<td>Takeda Chemical Industries, Ltd.</td>
<td>Coconut shell</td>
<td>1229</td>
</tr>
</tbody>
</table>

\(a\) 1073 K, H\(_2\)O : N\(_2\) = 0.67 : 0.33 (molar ratio). \(b\) 1123 K, H\(_2\)O : N\(_2\) = 0.67 : 0.33. \(c\) 1123 K, H\(_2\)O : N\(_2\) = 0.82 : 0.18.

3. Results and Discussion

Figure 1 shows the catalytic activities of various activated carbons as their supplied forms. The

![Fig. 1 Conversion of SO\(_2\) over Various Activated Carbons in Supplied Form](image-url)
The activity of carbon for this reaction is affected by the macroporosity, surface composition and hydrophobic/hydrophilic property. Elemental analysis of the surface by XPS showed a positive relationship between the oxygen concentration and activity after milling, as shown in Fig. 3. This is in agreement with previous findings, and therefore the high activity of the activated carbon produced from wood can be explained by the high oxygen concentration. However, the origin of the high oxygen concentration on the carbon produced from wood remains unclear. In addition, the observed oxygen may be contained in impurity metal oxides and functional groups such as phenol, ketone, carboxylic acid and alcohol groups, and the effects of these species were not clear. Further study is needed.

The activity of the activated carbons in the supplied form was not related to the oxygen concentration. This is presumably because the morphology of the carbon strongly affects the apparent reaction rate.

To evaluate the catalytic performance, the space velocity was increased to ca. 2400 h⁻¹ with constant molar ratios of the reactants; the flow rate of sulfur dioxide was increased to 2.2 × 10⁻⁷ mol·s⁻¹ with the catalyst amount of 3.8 g. The conversion over YS-3 was 69%, and the activity was stable within 5 h on the stream (data not shown). Therefore, the reaction rate was 4 × 10⁻⁸ mol·s⁻¹·g·C⁻¹. Also under these conditions, the activity was higher than those of the commercially available activated carbons, e.g., the conversion of 4GG was 36%. The conversion of sulfur dioxide on the best activated carbon fiber was ca. 93% at 303 K in a gaseous mixture of 1000 ppm of sulfur dioxide (double that of the present study), 5 mol% and 10 mol% of oxygen and water, respectively (same as in the present study) with 5 × 10⁻⁴ g·min·cm⁻³ for the W (weight of carbon)/F (total flow rate) ratio. The reaction rate is calculated to be ca. 10⁻⁶ mol·SO₂·s⁻¹·g·C⁻¹. This is the highest activity reported for this reaction. Although the reaction temperature was a little different, the activity presently observed over the activated carbon produced from wood was approximately 1/20 of that over the activated carbon fiber. Therefore, the activity per unit weight was lower than that reported on a carefully designed catalyst such as carbon fiber. However, from the view point of the utilization of waste material, the present activated carbon was easily produced from the waste wood, so the difference in the activity was not so large. The potential utilization of waste wood as an environmental catalyst was thus demonstrated.

4. Conclusion

High activity for the oxidation of sulfur dioxide was observed over activated carbon prepared by the water vapor treatment of wood. The potential utilization of the waste wood as an efficient environmental catalyst was thus demonstrated for the utilization of sulfur dioxide as a source of sulfuric acid.

Acknowledgment

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References


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要 旨

木材から製造した活性炭触媒による二酸化硫黄の硫酸への酸化

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二酸化硫黄は水の共存下, 活性炭触媒上で硫酸へ酸化することで排気中から除去できる。一方, 著者らは比較的低温で木材を水蒸気処理することによる活性炭の製造方法を開発した。本研究では, 木材から製造した活性炭の二酸化硫黄酸化活性を市販の活性炭の活性と比較した。木材から製造した活性炭は高い活性を示した。活性は活性炭素繊維のような非常に優れた触媒のもののよりは低かったが, 鳥取県の環境触媒としての利用可能性が示された。