1. Introduction

The future prospect of depletion of fossil fuels and the need for emission control of carbon dioxide have focussed attention on the production of useful chemicals from plant-derived biomass, which is the most abundant biomass in nature and has high productivity.

Catalytic conversion of biomass wastes is possible based on iron oxide composite catalysts (ZrO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-FeO\textsubscript{x})\textsuperscript{1-6} and selective production of phenol and ketones from palm shell-derived oil\textsuperscript{2,4} and toluene and styrene from paper sludge-derived tar\textsuperscript{5}. Guaiacol and acetophenone were selectively converted into 54 C-mol\% of phenol and 29 C-mol\% of benzene, respectively. The methoxy and carbonyl groups were decomposed into gaseous products mainly consisting of CO\textsubscript{2}, whereas dehydration of the aliphatic hydroxyl group in 1-phenyl-1-propanol mainly occurred to produce 1-phenyl-1-propene. ZrO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-FeO\textsubscript{x} catalyst is effective for degrading alkyl ether bonds between aromatic rings, and the ring substituent methoxy and carbonyl groups.

Keywords
Iron oxide catalyst, Biomass, Lignin-constituent aromatic, Phenol, Oxidative cracking

Aromatic compounds in plant-derived biomass originate from lignin, which is a high molecular polymer composed of alkylyphenol units (Fig. 1). Accordingly, unidentified aromatic chemicals mainly produced from the decomposition of lignin were included in the palm shell-derived oil\textsuperscript{2,4}, and the production of phenol using FeO\textsubscript{x} composite catalysts was followed by a decrease in the unidentified chemicals in the tar. However, the details of the reactions for converting the oil into phenol remain unclear. The reaction mechanism of the production of phenols from plant-derived oil over the FeO\textsubscript{x} composite catalysts is important to understand.

In this study, the production of useful aromatics such

![Chemical Structures of (1) p-Coumaryl Alcohol, (2) Coniferyl Alcohol and (3) Sinapyl Alcohol](image)
as phenol from the plant-derived oil or tar was investigated by the catalytic cracking of mono- and di-aromatics selected based on lignin constituents using ZrO$_2$-Al$_2$O$_3$-FeO$_x$. The application of ZrO$_2$-Al$_2$O$_3$-FeO$_x$ to simplify the degraded aromatics from lignin was also investigated (Fig. 2).

2. Experimental

2.1. Catalyst Preparation and Characterization
ZrO$_2$-Al$_2$O$_3$-FeO$_x$ was prepared by a coprecipitation method using zirconium(IV) dinitrate hydrate, aluminium nitrate enneahydrate, and iron(III) nitrate enneahydrate. All reagents were purchased from Wako Pure Chemical Industries, Ltd. (Japan). The composition of the catalyst was found to be 8.9 wt% ZrO$_2$ and 10 wt% Al$_2$O$_3$. The structure of the catalyst was analyzed with an X-ray diffractometer (JDX-8020, JEOL).

2.2. Selection of Aromatic Compounds Related to Lignin Constituents
Feedstocks for the catalytic reactions were selected based on the lignin constituents. Figures 3 and 4 show the basic structural units of lignin and the main functional groups in the alkylphenol units of lignin, respectively. Linkages between the units of lignin consist of the ether bond-type and the condensed bond-type, and the primary inter-unit linkage is the alkyl ether bond (Fig. 3). According to these structures, 2-benzyloxyphenol, diphenyl ether, and diphenyl methane were used as the feedstock of the catalytic reaction for lignin constituent-related di-aromatics, as shown in Fig. 5(a). Figure 4 shows that the units contain many methoxy- and aliphatic hydroxyl-groups, and few carbonyl groups. Accordingly, guaiacol, 1-phenyl-1-propanol, and acetophenone were used as lignin constituent-related mono-aromatics, as shown in Fig. 5(b).

2.3. Catalytic Cracking of the Aromatic Compounds
Catalytic cracking of the above-mentioned aromatic compounds was carried out in a fixed-bed flow reactor at 773 K for 1 h under atmospheric pressure. Figure 6 shows the schematic of the reaction apparatus. The aromatic compound shown in Fig. 5 and water were separately introduced into the reactor using syringe pumps. The flow rates of the lignin-related model

![Fig. 2 Outline of the Process for Simplifying Degraded Aromatics from Lignin Using ZrO$_2$-Al$_2$O$_3$-FeO$_x$](image)

![Fig. 3 Types and Frequencies of Linkages between Alkylphenol Units in Softwood Lignin](image)

![Fig. 4 Types and Frequencies of Functional Groups in One Alkylphenol Unit of Lignin](image)
compound and water were 1.0 and 2.0 g·h⁻¹, respectively. The time factor \(W/F\) varied in the range of 0-2 h, where \(W\) is the amount of catalyst and \(F\) is the flow rate of the feedstock, and \(W\) was varied to change the ratio \(W/F\). The liquid and gas products were collected in an ice trap and a sampling back, respectively. To examine the catalyst stability, reaction for 6 h was also conducted, and the liquid and gas products were collected every 2 h.

The liquid products were analyzed with two gas chromatograph mass spectrometers (GC17A-QP5000 and GC17A-QP5050A; Shimadzu Corp.) equipped with a CP-PoraPLOT Q or DB-WAX capillary column, and gas chromatographs (GC17A and GC2014; Shimadzu Corp.) with the same column. The gas products were analyzed using gas chromatographs (GS20B, Shimadzu Corp.) with a thermal conductivity detector equipped with active carbon, and a flame ionization detector equipped with Porapak Q columns.

### 3. Results and Discussion

#### 3.1. Catalytic Cracking of Lignin Constituent-related Di-aromatics

Figures 7(a) and 7(b) show the product yields after the reaction of diphenyl ether and diphenyl methane, respectively. Benzene and phenol were formed from diphenyl ether, and the carbon yield of benzene was almost the same as that of phenol. However, the total yields remained 9.8 C·mol% and the conversion of diphenyl ether was also low. The 4-O-5 (diphenyl
ether)-type bond (shown in Fig. 3) was considered to be stable over ZrO₂-Al₂O₃-FeO₃ due to the aromaticity or steric hindrance around the two aromatic rings. The yields using diphenyl methane as the feedstock were similar to those of diphenyl ether, as shown in Fig. 7(b). Therefore, condensed-type linkages were also considered to be stable over ZrO₂-Al₂O₃-FeO₃.

Figure 7(c) shows the effect of W/F on the product yield after the reaction of 2-benzyloxyphenol. Only this aromatic compound was diluted three times with benzene to reduce its viscosity, because benzene is not affected by the FeO₃ composite catalyst(7,13). All other aromatic compounds were introduced into the reactor without diluent. After the reaction, unreacted 2-benzyloxyphenol could not be detected by gas chromatography due to its high boiling point. Accordingly, the products detected by gas chromatography are shown without the diluent benzene in Fig. 7(c). At W/F = 0 h, only thermal cracking occurred, and catechol and dimers such as bibenzyl and 2-benzylphenol were mainly produced. 2-Benzylphenol was presumably thermally decomposed into benzyl radical and phenoxyl radical, and these active radicals reacted further to produce catechol and various dimers. Catalysis of the reaction by ZrO₂-Al₂O₃-FeO₃ resulted in decreased yields of the dimers and catechol, and formation of toluene and phenol. Presumably some of the benzyl radicals reacted with active hydrogen species over ZrO₂-Al₂O₃-FeO₃ to produce toluene, and catechol was converted into phenol over the catalyst. We previously reported that ZrO₂ in FeO₃ generates active oxygen and hydrogen species from H₂O in(7), and that these active species help to stabilize the radicals. However, the yields of toluene and phenol were almost unaffected by the value of W/F. These results indicate that thermal cracking of 2-benzyloxyphenol occurred, followed by the formation of toluene and phenol over ZrO₂-Al₂O₃-FeO₃.

The primary linkage between alkylphenol units of lignin is the alkyl ether bond type (Fig. 3), which can be decomposed over ZrO₂-Al₂O₃-FeO₃ to produce mono-aromatics. Accordingly, ZrO₂-Al₂O₃-FeO₃ is effective for degrading lignin constituent-related diaromatics.

To further examine the catalytic stability of ZrO₂-Al₂O₃-FeO₃, catalytic reaction for 6 h was carried out using 2-benzyloxyphenol as a feedstock. Figures 8 and 9(a) show the time course for the product yields and XRD patterns prior to and after the reactions over ZrO₂-Al₂O₃-FeO₃, respectively. The composition of the products was almost constant for 0-2 h, but the yield of phenol decreased and that of catechol increased with longer reaction time. On the other hand, the yield of toluene was constant during 0-6 h reaction time, and the yields of dimers and others were also constant for 2-6 h. Therefore, the catalytic conversion from catechol to phenol over ZrO₂-Al₂O₃-FeO₃ was suppressed with reaction time, but the activity to generate active oxygen and hydrogen species from H₂O remained stable and the radicals produced by the thermal cracking were stabilized, as discussed above. Moreover, ZrO₂-Al₂O₃-FeO₃ has stable activity for producing mono-aromatics from di-aromatics with the most common type of linkages between lignin constituents because hematite was maintained after the reaction, as shown in Fig. 9(a).

3.2 Catalytic Cracking of Lignin Constituent-related Mono-aromatics

Figure 10(a) shows the product yield after the reaction of guaiacol. Without catalyst (W/F = 0 h), 2-hydroxybenzaldehyde and o-cresol were mainly produced in the thermal cracking of guaiacol, and the yield of phenol was low. However, phenol was selectively produced from guaiacol over ZrO₂-Al₂O₃-FeO₃. Furthermore, the phenol yield increased as W/F increased.
The major gaseous product was CO₂, so the methoxy group in guaiacol was oxidatively decomposed. The reaction conditions: \( T = 773 \text{ K}, P = 0.1 \text{ MPa}, H_2O/F = 2 \), reaction time = 1 h.

Figure 10(b) shows the product yield after the reaction of guaiacol, acetophenone, and 1-phenyl-1-propanol. The structure of the catalyst included magnetite after the reaction of acetophenone, whereas hematite was maintained after the reaction of 2-benzyloxyphenol and guaiacol. The yield of CO₂ from acetophenone was higher than that from the other model compounds, so the carbonyl group in acetophenone was also effectively decomposed over ZrO₂-Al₂O₃-FeO, by the similar reaction of guaiacol.

1-Phenyl-1-propanol underwent slight dehydration of the aliphatic hydroxyl group to produce 1-phenyl-1-propene without catalyst (Fig. 10(c)). In contrast, benzene and toluene were produced from the oxidative cracking of the aliphatic hydroxyl group over ZrO₂-Al₂O₃-FeO. However, the dehydration reaction mainly occurred to produce 1-phenyl-1-propene and its constitutional isomers such as 1-phenyl-2-propene and \( \alpha \)-methylstyrene. Therefore, dehydration and dehydrogenation of the aliphatic hydroxyl group occurred to produce 1-phenyl-1-propene and 1-phenyl-1-ketones such as 1-phenyl-1-propanone, respectively, and the 1-phenyl-1-ketones were converted to benzene by the same reaction path as for acetophenone, shown in Fig. 10(b).

3.3 X-ray Diffraction Analysis of the Catalyst

Figure 9 shows the XRD patterns before and after the reactions of (b) 2-benzyloxyphenol, (c) guaiacol, and (d) acetophenone for 1 h over ZrO₂-Al₂O₃-FeO. The organics adsorbed on the FeO⁺ composite catalyst were oxidatively decomposed using the lattice oxygen in FeO⁺, which can be regenerated by active oxygen species produced from H₂O over ZrO₂⁻⁷, and the degree of catalyst deactivation was observed by transforming the crystallinity of the FeO⁺ composite catalyst from hematite to magnetite. However, no peaks attributed to Al₂O₃ and ZrO₂ were observed, as shown in Fig. 9, indicating that Al₂O₃ and ZrO₂ were highly dispersed in the lattice of FeO⁺. Therefore, the highly dispersed ZrO₂ in FeO⁺ was effective in regenerating the lattice oxygen, which was consumed by the oxidation reaction.

The reaction mechanisms of plant-derived aromatic compounds produced by various biomass treatments over ZrO₂-Al₂O₃-FeO were investigated by the catalytic cracking of selected aromatic compounds based on lignin constituents. The alkyl ether bond, which is the most common type of linkage between the units of lignin, was effectively decomposed.
lignin, was thermally decomposed, followed by the production of mono-aromatics over ZrO$_2$-Al$_2$O$_3$-FeO. The methoxy and carbonyl groups in mono-aromatics were effectively decomposed over ZrO$_2$-Al$_2$O$_3$-FeO. Moreover, ZrO$_2$-Al$_2$O$_3$-FeO showed stable activity for decomposition of the alkyl ether bond and methoxy group. Therefore, ZrO$_2$-Al$_2$O$_3$-FeO catalyst is effective for simplifying degraded aromatics from lignin.

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References


要 旨
ZrO$_2$-Al$_2$O$_3$-FeO 触媒を用いた水蒸気気雰囲気下におけるリグニン構成物質関連芳香族化合物の酸化分解

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酸化鉄複合触媒 (ZrO$_2$-Al$_2$O$_3$-FeO 触媒) を用いて、植物バイオマス由来芳香族触媒を有効芳香族へ再構するための触媒活性について検討した。リグニン構成物質関連芳香族化合物を触媒に用いたリグニンソルビッドを用いて、2 種類の芳香族化合物（ジフェニルエーテル、ジフェニルメタン、2-ベンジルオキシフェノール）および単環芳香族化合物（グアヤコール、アセトフェノン、1-フェニル-1-プロパノール）を原料に ZrO$_2$-Al$_2$O$_3$-FeO 触媒を用いて接触分解を行った。反応温度は 773 K とした。2 種類の芳香族化合物を原料とした実験では、ジフェニルエーテルおよびジフェニルメタンは分解されず、2-ベンジルオキシフェノールは熱分解の後、ZrO$_2$-Al$_2$O$_3$-FeO 触媒上での反応によりトルエンとフェノールが生成した。単環芳香族化合物を原料とし、アセトフェノンからフェノール (54 C-mol%) とベンゾール (29 C-mol%) がそれぞれ選択的に生成した。その際、メトキシ基とカルボニル基の酸化分解により主に CO$_2$ が生成したが、1-フェニル-1-プロパノールでは、主に脂肪族水酸基の脱水反応が起こり、1-フェニル-1-プロパノールを原料とし、触媒を用いて、触媒は、芳香環どうしのアルキルエーテル結合、および芳香環に結合するメトキシ基とカルボニル基の分解に有効であることが分かった。