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Oxidative Cracking of Aromatic Compounds Related to Lignin Constituents with Steam Using $\text{ZrO}_2\text{--Al}_2\text{O}_3\text{--FeO}_x$ CatalystTakuya YOSHIKAWA^{†1)}, Duangkamol NA-RANONG^{†2)}, Teruoki TAGO^{†1)*} and Takao MASUDA^{†1)}^{†1)} Div. of Chemical System Engineering, Graduate School of Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo 060-8628, JAPAN^{†2)} Dept. of Chemical Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Ladkrabang, Bangkok 10520, THAILAND

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The catalytic activity of iron oxide composite catalyst ($\text{ZrO}_2\text{--Al}_2\text{O}_3\text{--FeO}_x$) was investigated for converting aromatic compounds derived from plant biomass into useful aromatics. Catalytic cracking of lignin constituent-related di-aromatics such as diphenyl ether, diphenyl methane, and 2-benzyloxyphenol, and mono-aromatics such as guaiacol, acetophenone, and 1-phenyl-1-propanol was carried out over $\text{ZrO}_2\text{--Al}_2\text{O}_3\text{--FeO}_x$. The catalytic reactions were conducted in a fixed-bed reactor at 773 K under atmospheric pressure. Diphenyl ether and diphenyl methane were stable, whereas 2-benzyloxyphenol was thermally decomposed, followed by the production of toluene and phenol over $\text{ZrO}_2\text{--Al}_2\text{O}_3\text{--FeO}_x$. 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_2 , whereas dehydration of the aliphatic hydroxyl group in 1-phenyl-1-propanol mainly occurred to produce 1-phenyl-1-propene. $\text{ZrO}_2\text{--Al}_2\text{O}_3\text{--FeO}_x$ 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

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 ($\text{ZrO}_2\text{--FeO}_x$ and $\text{ZrO}_2\text{--Al}_2\text{O}_3\text{--FeO}_x$)^{1)~6)}, and selective production of phenol and ketones from palm shell-derived oil^{2),4)}, and toluene and styrene from paper sludge-derived tar⁵⁾ have been achieved. The reaction appears to proceed through the following catalytic cycle^{2),7)}:

(1) The lattice oxygen in FeO_x decomposes the organic molecule adsorbed on the catalyst.

(2) ZrO_2 generates active oxygen species from H_2O , which spill into the defects of oxygen in FeO_x .

Moreover, addition of Al_2O_3 is effective for achieving high dispersion of ZrO_2 in FeO_x and resistance to sintering^{8),9)}.

Aromatic compounds in plant-derived biomass originate from lignin, which is a high molecular polymer composed of alkylphenol units (**Fig. 1**). Accordingly, unidentified aromatic chemicals mainly produced from the decomposition of lignin were included in the palm shell-derived oil^{2),4)}, and the production of phenol using FeO_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_x composite catalysts is important to understand.

In this study, the production of useful aromatics such

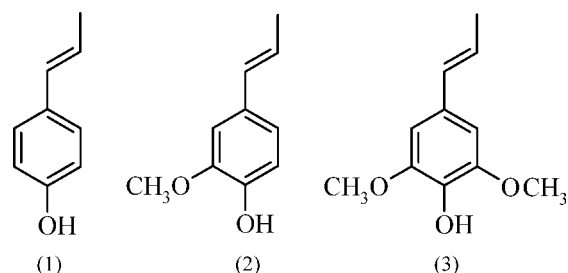


Fig. 1 Chemical Structures of (1) *p*-Coumaryl Alcohol, (2) Coniferyl Alcohol and (3) Sinapyl Alcohol

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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 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$. The application of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ to simplify the degraded aromatics from lignin was also investigated (Fig. 2).

2. Experimental

2.1. Catalyst Preparation and Characterization

$\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ was prepared by a coprecipitation method using zirconium(IV) dinitrate oxide 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_2O_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 lignin¹⁰⁾ and the main functional groups in the alkylphenol units of lignin^{11),12)}, 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

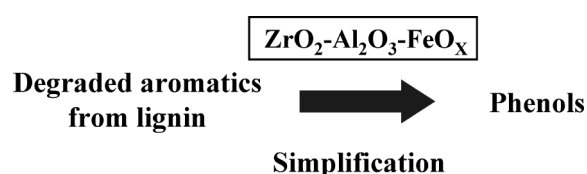
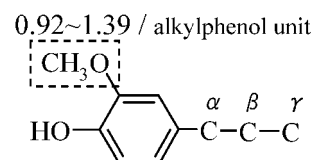


Fig. 2 Outline of the Process for Simplifying Degraded Aromatics from Lignin Using $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$



α	(%)	β	(%)	γ	(%)
C-OH	20	C=O	9	C-OH	84
C=O	20	C α =C β		C=O	3
C α =C β	9	others ^a		others ^a	13
others ^a	51				

a) others: linkages with another alkylphenol unit.

Fig. 4 Types and Frequencies of Functional Groups in One Alkylphenol Unit of Lignin^{7),8)}

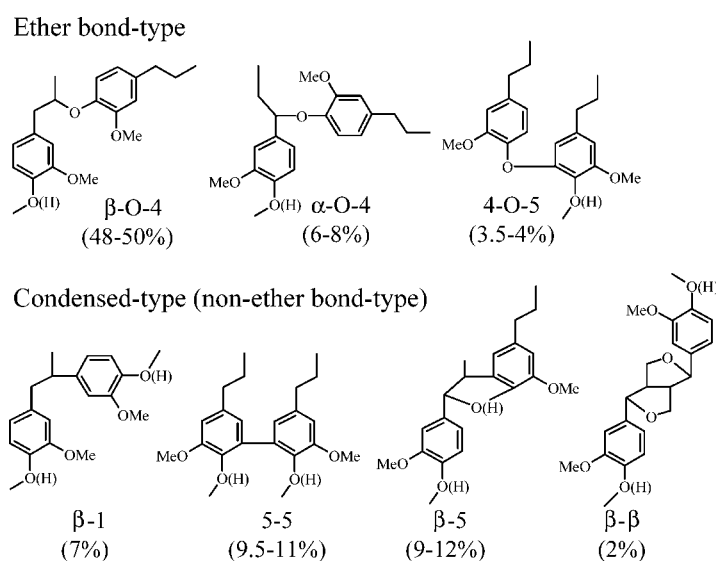
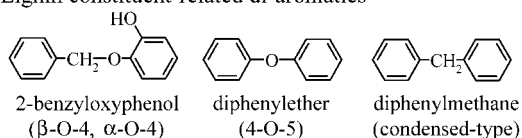


Fig. 3 Types and Frequencies of Linkages between Alkylphenol Units in Softwood Lignin⁶⁾

(a) Lignin constituent-related di-aromatics



(b) Lignin constituent-related mono-aromatics

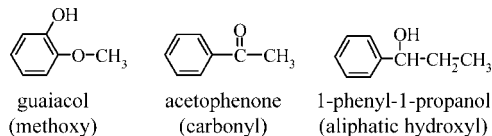


Fig. 5 Lignin Constituent-related Aromatic Compounds Used for Catalytic Cracking over $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$, (a) Lignin Constituent-related Di-aromatics, (b) Lignin Constituent-related Mono-aromatics

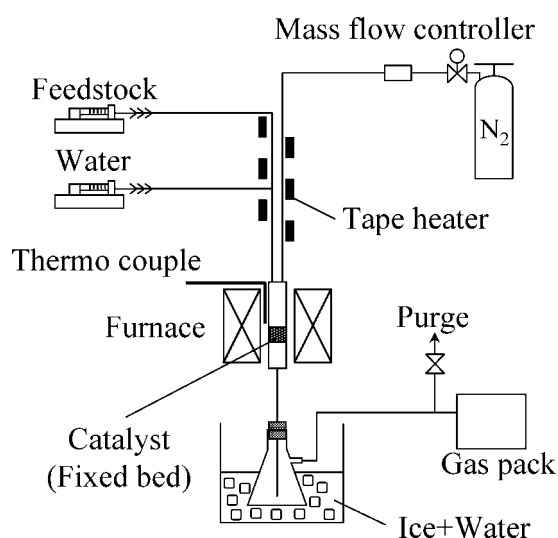
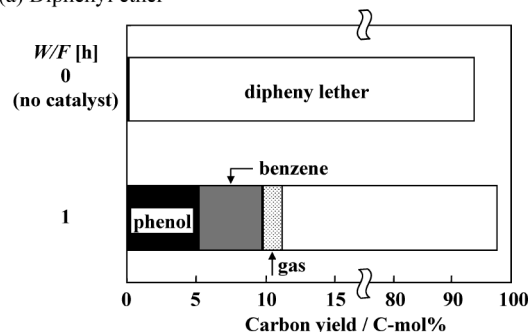


Fig. 6 Experimental Apparatus of the Fixed Bed Flow Reactor

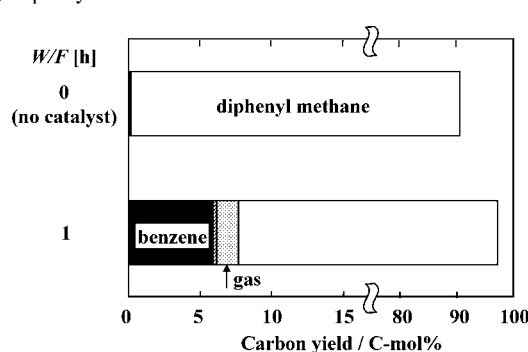
compound and water were 1.0 and $2.0 \text{ g} \cdot \text{h}^{-1}$, respectively. The time factor W/F varied in the range of $0\text{-}2 \text{ h}$, where W is the amount of catalyst and F is the flow rate of the feedstock, and W was varied to change the ratio W/F . The liquid and gas products were 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.

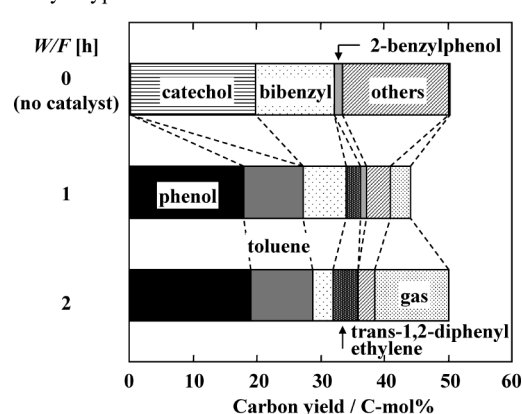
(a) Diphenyl ether



(b) Diphenyl methane



(c) 2-Benzyloxyphenol



Reaction conditions: $T = 773 \text{ K}$, $P = 0.1 \text{ MPa}$, $\text{H}_2\text{O}/F = 2$, reaction time = 1 h .

Fig. 7 Product Yield after the Reaction of Lignin Constituent-related Di-aromatics, (a) Diphenyl Ether, (b) Diphenyl Methane and (c) 2-Benzyloxyphenol

3. Results and Discussion

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

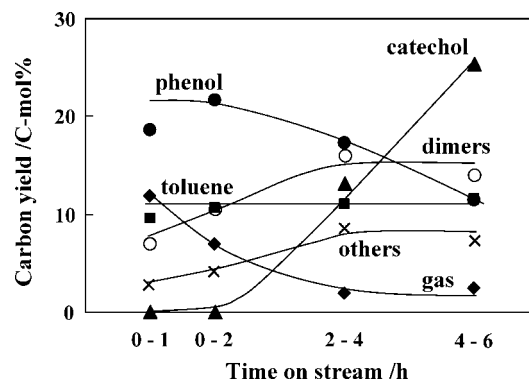
Figures 7(a) and 7(b) show the product yields after the reaction of diphenyl ether and diphenyl methane, respectively. Benzene and phenol were formed from diphenyl ether, and the carbon yield of benzene was almost the same as that of phenol. However, the total yields remained $9.8 \text{ C-mol}\%$ and 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 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ 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 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$.

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 FeO_x 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-Benzyloxyphenol was presumably thermally decomposed into benzyl radical and phenoxy radical, and these active radicals reacted further to produce catechol and various dimers. Catalysis of the reaction by $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ 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 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ to produce toluene, and catechol was converted into phenol over the catalyst. We previously reported that ZrO_2 in FeO_x generates active oxygen and hydrogen species from H_2O ^{2),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 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$.

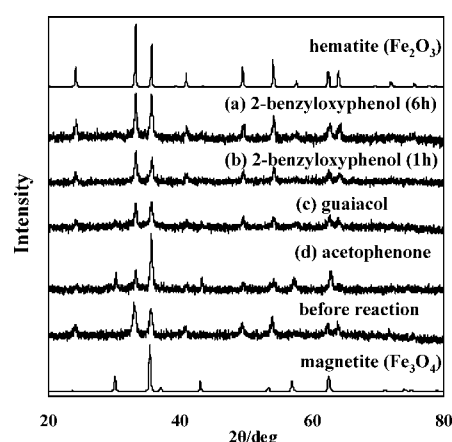
The primary linkage between alkylphenol units of lignin is the alkyl ether bond type (**Fig. 3**), which can be decomposed over $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ to produce mono-aromatics. Accordingly, $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ is effective for degrading lignin constituent-related di-aromatics.

To further examine the catalytic stability of $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$, 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 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$, 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



Reaction conditions: $T = 773$ K, $P = 0.1$ MPa, $W/F = 2$ h, $\text{H}_2\text{O}/F = 2$.

Fig. 8 Effect of the Time on Stream on Product Yields after the Reaction of 2-Benzyloxyphenol



Reaction conditions: $T = 773$ K, $P = 0.1$ MPa, $W/F = 2$ h (a), 1 h (b, c, d), $\text{H}_2\text{O}/F = 2$, reaction time = 6 h (a), 1 h (b, c, d).

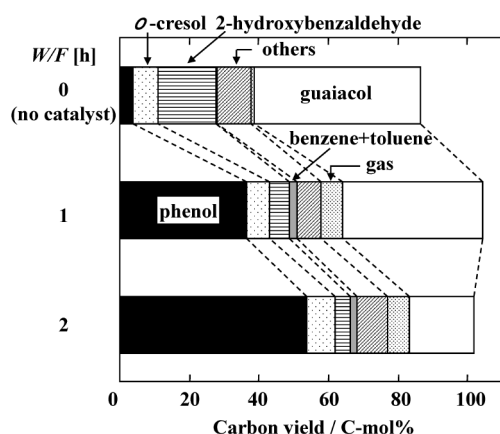
Fig. 9 XRD Patterns of the Catalysts before and after the Reaction of (a, b) 2-Benzyloxyphenol, (c) Guaiacol and (d) Acetophenone

phenol over $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ was suppressed with reaction time, but the activity to generate active oxygen and hydrogen species from H_2O remained stable and the radicals produced by the thermal cracking were stabilized, as discussed above. Moreover, $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ 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)**.

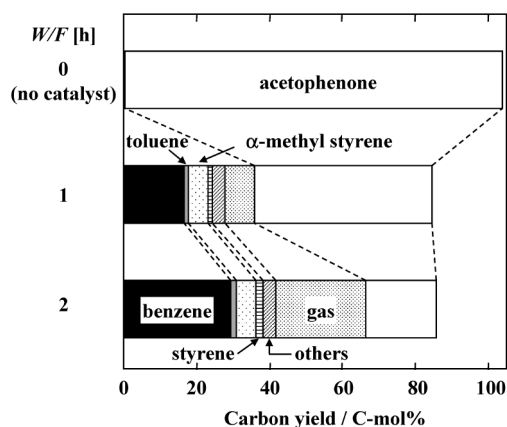
3. 2. Catalytic Cracking of Lignin Constituent-related Mono-aromatics

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 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$. Furthermore, the phenol yield increased as W/F

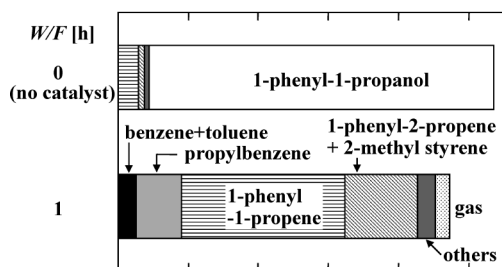
(a) Guaiacol



(b) Acetophenone



(c) 1-Phenyl-1-propanol



Reaction conditions: $T = 773 \text{ K}$, $P = 0.1 \text{ MPa}$, $H_2O/F = 2$, reaction time = 1 h.

Fig. 10 Product Yield after the Reaction of Lignin Constituent-related Mono-aromatics, (a) Guaiacol, (b) Acetophenone and (c) 1-Phenyl-1-propanol

increased. The major gaseous product was CO_2 , so the methoxy group in guaiacol was oxidatively decomposed.

Figure 10(b) shows the product yield after the reaction of acetophenone. Acetophenone showed little reaction without catalyst, but was selectively converted into benzene over $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$. The gaseous product mainly consisted of CO_2 , so that the carbonyl

group in acetophenone was also effectively decomposed over $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ 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 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$. However, the dehydration reaction mainly occurred to produce 1-phenyl-1-propene and its constitutional isomers such as 1-phenyl-2-propene and *o*-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 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$. The organics adsorbed on the FeO_x composite catalyst were oxidatively decomposed using the lattice oxygen in FeO_x , which can be regenerated by active oxygen species produced from H_2O over $\text{ZrO}_2^{2,7)}$, and the degree of catalyst deactivation was observed by transforming the crystallinity of the FeO_x composite catalyst from hematite to magnetite. However, no peaks attributed to Al_2O_3 and ZrO_2 were observed, as shown in Fig. 9, indicating that Al_2O_3 and ZrO_2 were highly dispersed in the lattice of FeO_x . Therefore, the highly dispersed ZrO_2 in FeO_x was effective in regenerating the lattice oxygen, which was consumed by the oxidation reaction.

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 CO_2 from acetophenone was higher than that from the other model compounds, so the carbonyl group in acetophenone was probably completely oxidized to generate CO_2 , which led to excessive consumption of the lattice oxygen in FeO_x . On the other hand, $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ showed stable activity due to the regeneration mechanism for the decomposition of the alkyl ether bond and the methoxy group, which are common in lignin.

4. Conclusion

The reaction mechanisms of plant-derived aromatic compounds produced by various biomass treatments over $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ 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 thermally decomposed, followed by the production of mono-aromatics over $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$. The methoxy and carbonyl groups in mono-aromatics were effectively decomposed over $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$. Moreover, $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ showed stable activity for decomposition of the alkyl ether bond and methoxy group. Therefore, $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ catalyst is effective for simplifying degraded aromatics from lignin.

Acknowledgment

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要 旨

$\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ 触媒を用いた水蒸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 ($\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ 触媒) を用いて、植物バイオマス由来芳香族を有用芳香族へ転換するためにそ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として、2環芳香族化合物 (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 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ 触媒を用いて接触分解を行った。反応実験は常圧の固定床流通式反応器を用いて行い、反応温度 773 K とした。2環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や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、 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ 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た実験では、グアヤコールとアセトフェノンからフェノール (54 C-mol%) とベンゼン (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-プロペンが生成した。したがって、本触媒は、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。