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Production of Phenolic Compounds by Fast Pyrolysis of Eucalyptus Woody Biomass Using Modified Zeolite Catalysts

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In fast catalytic pyrolysis of eucalyptus woody biomass, zeolites mainly enhanced the formation of both oxygenated and non-oxygenated aromatic hydrocarbons. Notably, H-ZSM-5 with a low Si/Al₂ ratio and H-Beta zeolites were highly efficient at catalyzing the formation of non-oxygenated aromatic compounds, while H-ZSM-5 with a high Si/Al₂ ratio, H-mordenite, and USY (ultra-stable Y) were moderately efficient at catalyzing the formation of phenolic compounds as well as non-oxygenated aromatics. There seems to be an inverse correlation between yields of non-oxygenated aromatic compounds and those of phenolic compounds. Strong solid acidity favored deoxygenation. Moderate solid acidity favored the formation of phenolic compounds. Micropore structure also affected type and distribution of products. The addition of Cr, Mn, Fe, Cu, Zn, Mo, Ag, Re, or Pt to USY improved the yield of phenol. Ag- or Pt-modification improved the yield of total phenolic compounds (phenol + methylphenols + dimethylphenols).

木質系バイオマスとしてユーカリを用いた急速熱分解反応において、ゼオライト触媒は主として酸素原子を含有する芳香族類と含有しない芳香族類の両方の生成を促進した。特に低 Si/Al₂ 比の H-ZSM-5 と H-Beta は無酸素芳香族類の生成に有効であり、一方、高 Si/Al₂ 比の H-ZSM-5 と H-mordenite と USY (ultra-stable Y) はフェノール類と無酸素芳香族類の両方の生成に対し適度の触媒活性を有していた。これらの反応において、無酸素芳香族類の収率とフェノール類の収率との間には負の相関が見られた。強い固体酸は脱酸素反応を促進し、適度な固体酸はフェノール類の生成を促進した。触媒の細孔構造も生成物の種類と分布に影響を与えた。Cr, Mn, Fe, Cu, Zn, Mo, Ag, Re, Pt の USY への添加はフェノールの収率を向上させ、Ag や Pt の添加はフェノール類 (フェノール + メチルフェノール + ジメチルフェノール) の生成を促進した。

Key Words

Phenolic compounds, Fast pyrolysis, Woody biomass, Modified zeolite, Catalyst, Eucalyptus

1. Introduction

Much attention has been paid to biomass as an alternative resource for petroleum production, since it is a renewable, readily available carbon-neutral resource. Two main methods are used to synthesize hydrocarbons for both fuels and chemicals from biomass: catalytic conversion of bioalcohol (obtained by fermentation) to hydrocarbons^{1)~4)}; and gasification of biomass, followed by Fischer-Tropsch reaction to hydrocarbons⁵⁾. A third method, the fast pyrolysis of biomass by zeolite catalysts, has been reported recently, using xylitol, glucose, cellobiose, and cellulose as

biomass^{6)~7)}; lignocellulosic feedstocks⁸⁾; pyrolytic lignins from bio-oil⁹⁾; and jatropha seed cake and wastes (husks, shells, and branches)^{10)~11)}. The main products were aromatic compounds.

Phenolic compounds are important materials. Phenol is produced from petroleum-derived benzene via cumene by the cumene oxidation method¹²⁾. More than 90% of phenol is produced by this process. It can be also obtained by separation of coal tar. Recently, Tada et al. reported the direct synthesis of phenol from benzene and O₂ using an H-ZSM-5 (zeolite)-supported active Re-cluster catalyst¹³⁾.

The conversion of biomass to phenolic compounds has also been reported^{14)~17)}. The production of phenols from biomass by fermentation or by gasification and

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Fischer-Tropsch synthesis is difficult, but direct pyrolysis is effective. Nilsen et al. investigated the pyrolysis of grass (*Miscanthus*) using Fe-, Cu-, or Zn-modified Al-MCM-41 catalysts and found that Cu or Fe improved the yields of phenolic compounds over Al-MCM-41 alone, and that Zn reduced yields but inhibited carbon deposition¹⁴. Catalytic microwave pyrolysis of biomass (Douglas fir) using activated carbon catalysts yielded bio-oil containing phenol and phenolics at higher concentrations than pyrolysis without the addition of activated carbon^{15) 16)}. The yields were closely related to the decomposition of lignin¹⁵⁾. Microwave pyrolysis of Douglas fir sawdust pellets using wood-based and lignite-based activated carbon catalysts yielded high amounts of phenols, and the catalysts could be reused 3 or 4 times while still giving high concentrations of phenolic compounds¹⁶⁾. Karagoz et al. found that the use of Rb and Cs carbonate solutions for hydroliquefaction of pine sawdust by autoclaving increased oil products without changing water-soluble compounds, and hindered the formation of char. Phenolic compounds and benzenediol derivatives were major products¹⁷⁾.

In our laboratory, we tested the fast pyrolysis of eucalyptus woody biomass using zeolites as catalysts and investigated correlations between the types and proportions of products (especially aromatics and phenols) and the characteristics of the catalysts^{18) 19)}. Eucalyptus plant contains large amount of oil, especially in its leaves. Moreover, eucalyptus can resist the atmospheric dryness, and can be used for greening trees in dried regions such as deserts. Zeolites contain both SiO₂ and Al₂O₃, in a molar ratio indicated here as Si/Al₂. A higher ratio means fewer acidic sites in the zeolite.

In most cases of the fast pyrolysis of eucalyptus using unmodified zeolite catalysts (0.5 g eucalyptus, 1 g catalyst, 550 °C), about half of the C atoms end up as solid carbon. Al₂O₃ as a catalyst yields a large amount of solid carbon. The liquid products consist mainly of oxygenated monocyclic aromatics and non-oxygenated polycyclic aromatics. In contrast, H-ZSM-5 and H-Beta give high yields of non-oxygenated aromatics, although a higher Si/Al₂ ratio in H-ZSM-5 depresses the formation of non-oxygenated aromatics and enhances the formation of oxygenated compounds, and a higher Si/Al₂ ratio in H-Beta enhances the formation of both products and of non-oxygenated aromatics. A higher Si/Al₂ ratio in H-mordenite and USY (ultra-stable Y) favors liquid products, mainly oxygenated compounds. Owing to the large amount of solid carbon yielded, Al₂O₃ yields little liquid products, but its selectivity for non-oxygenated aromatics is high¹⁸⁾.

In this study, we prepared several element-modified

USY zeolite catalysts and investigated the effect of element addition on the yields and distribution of phenolic products.

2. Experimental

2.1 Preparation of catalysts

We used the zeolite catalysts H-Beta (Si/Al₂ = 27, 350), H-ZSM-5 (30, 190), H-mordenite (18.3), and USY (80). H-Beta (27), H-ZSM-5 (190), and H-mordenite (18.3) were purchased from Tosoh Corporation. H-Beta (350), H-ZSM-5 (30), and USY (80) were purchased from Zeolyst International. For reference, Al₂O₃ (purchased from Nippon Ketjen Co. Ltd.) was also used as a catalyst. Before use, these catalysts were calcined at 500 °C for 6 h and then at 600 °C for 3 h in a muffle furnace.

We loaded several elements on USY (Si/Al₂ = 80) supports calcined at 500 °C: P, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Y, Zr, Mo, Ru, Rh, Pd, Ag, La, Ce, Re, Ir, Pt, and Au (as pure elements); Cr, Co, Ni, Cu, Zn, Ga, Y, Rh, La, and Ce (as metal nitrate hydrates); Sr and Ag (as metal nitrates); Mn and Fe (as metal chloride hydrates); P as (NH₄)₃PO₄ · 3H₂O, Zr as ZrO(NO₃)₂ · 2H₂O, Mo as (NH₄)₆Mo₇O₂₄ · 4H₂O, Ru as Ru(NO₃)₂(NO), Re as NH₄ReO₄, Pt as Pt(NH₃)₄Cl₂ · H₂O, Au as HAuCl₄ · 4H₂O (all as aqueous solutions); and Pd as Pd(NO₂)₂(NH₃)₂ and Ir as (NH₄)₂IrCl₆ (as aqueous solutions containing dissolved ammonia). All elements were loaded as 1 wt.% in a volume equal to that of water which can be fully absorbed in the zeolite support. After impregnation, the catalysts were dried at 110 °C for several hours in an oven, then calcined at 600 °C in air for 3 h.

Before reaction, the catalysts were crushed into particles between 500 μm and 2 mm across.

2.2 Fast pyrolysis reaction

Eucalyptus branches were shredded into particles smaller than 5 mm. Elemental analysis of oven-dried samples gave a weight ratio of C 46.80 : H 5.91 : O(dif) 44.72 : N 0.12 : S 0.00 : other (ash) 2.45 and a molar ratio of C 1.00 : H 1.51 : O 0.72 : N 0.002 : S 0.000. Each 0.5 g sample of biomass contained a calculated 19 500 μmol of C atoms. In general, broadleaf trees such as eucalyptus contain 40%-50% cellulose, 25%-40% hemicellulose, and 20%-25% lignin.

Reactions were carried out in a quartz tube reactor (Fig. 1) at 550 °C in N₂ gas at a flow rate of 50 mL min⁻¹. First, 1 g of catalyst was placed in the reactor. Then, 0.5 g of shredded biomass was dropped in at the top in seven equal parts. Liquid products were collected in two glass tubes, one cooled by ice water, the other cooled by toluene and liquid N₂. Gases were collected in a bag for gas chromatography (GC) analysis (Shimadzu, GC-8A) using Molecular Sieve 5A and Porapak Q columns with a thermal conductivity

Fig. 1 Image of fast pyrolysis reaction system

detector to detect hydrogen, carbon monoxide, and carbon dioxide and a flame ionization detector to detect hydrocarbons.

After cooling to room temperature, the inner walls of the reactor and the glass tubes were washed with acetone, and the eluate was analyzed on an Agilent Technologies 7890A GC interfaced with a 5975C mass spectrometer (MS). The products were separated by a capillary column. Product selectivity was evaluated by area % of each peak detectable in GC/MS.

Thermogravimetry analyses (Mac Science, TG-DTA2000) of catalysts after the reaction were carried out to evaluate the amount of solid carbon yielded (C deposited on catalyst + C remaining above catalyst layer). We assumed that the amount of C remaining above the catalyst layer was not affected by the catalyst, since it formed without contacting the catalyst. The analysis was carried out in a flow of air at temperatures rising from room temperature to 800 °C at 10 °C min⁻¹. From the results, the mole number of C atoms was calculated.

Carbon selectivity was calculated from the mole number of C atoms. The mole number of C atoms in liquid products was calculated as (total C atoms in biomass [19 500 μmol]) - (C atoms in gaseous products) - (C atoms in solid C). The yield of each liquid product was calculated as (C atoms in total liquid product) × (selectivity of each liquid product).

2.3 Characterization

NH₃-temperature-programmed-desorption (TPD) experiments of catalysts were carried out on NH₃-TPD apparatus (Nihon BEL, BEL-CAT) interfaced to a personal computer to measure the solid acidity. After pretreatment in a flow of He at 500 °C for 60 min, adsorption of NH₃ at 100 °C for 90 min, and desorption of the adsorbed NH₃ in a flow of He at 100 °C for 30 min, TPD profiles were obtained in a flow of He at temperatures rising from 100 to 800 °C at 10 °C min⁻¹. The amount of solid acidity was defined as the

NH₃-desorption peak area ratio of (300-600 °C) / (100-600 °C).

3. Results and Discussion

3.1 Results of pyrolysis using unmodified catalysts

In the absence of catalyst, only non-phenolic monocyclic oxygenated aromatics were obtained (Fig. 2). Conversely, Al₂O₃ and H-ZSM-5 (Si/Al₂ = 30) yielded little or no monocyclic oxygenated aromatics, because Al₂O₃ yielded a lot of solid C, while H-ZSM-5 (30) highly selectively yielded non-oxygenated aromatics. H-Beta gave low yields of oxygenated aromatics independent of Si/Al₂ ratio, and high yields of non-oxygenated aromatics. On the other hand, H-ZSM-5 (190), H-mordenite, and USY gave high yields of oxygenated aromatics, and USY gave high yields of phenol and methylphenols. These results show that moderately strong solid acidity is essential for the formation of phenolic compounds, since strong solid acidity enhances the formation of non-oxygenated aromatics¹⁹. As previously reported, H-ZSM-5 and H-mordenite possess stronger solid acidity than USY¹⁸.

3.2 Results of NH₃-TPD measurements of modified USY zeolite

Unmodified USY showed an NH₃-desorption peak at about 420 °C (Fig. 3). The addition of Cr, Fe, Ni, Ga, Y, Zr, Mo, Rh, La, Ce, Re, Pt, or Au did not affect the position of the NH₃-desorption peak. The addition of P, Sr, Pd, or Ir decreased the strength of the peak. P-modification decreases the solid acidity²⁰, and the addition of alkali earth metals such as Sr can also do so²¹. The addition of Mn, Co, Zn, or Ru shifted the desorption peak to about 400 °C, weakening the solid acidity. The addition of Cu shifted the peak to 310 °C, weakening it further. On the other hand, the addition of Ag shifted the peak to about 440 °C, increasing the solid acidity.

Fig. 2 Yields of oxygenated and non-oxygenated aromatic products over non-modified zeolites and Al₂O₃. Numbers in parentheses stand for Si/Al₂ ratio

Fig. 3 NH₃-TPD profiles of USY and modified USY catalysts. Numbers in parentheses stand for NH₃-desorption peak area ratio of (300-600 °C)/(100-600 °C)

Fig. 4 Carbon selectivity of each kind of product

Cr species introduced into zeolites by ion-exchange can increase the number and strength of acid sites²²⁾. Similarly, multivalent metal cations (M^{n+}) may enhance both acid strength and acid number for metal-exchanged zeolite catalysts.

3.3 Results of pyrolysis using modified USY catalysts

Rh-modification gave high yields of gaseous products, but the other catalysts gave consistently low yields (Fig. 4). As Tomishige et al. reported, Rh catalysts are effective for gasification of woody biomass^{23)~25)}. In most cases, CO,

Fig. 5 Yields of liquid products

H₂, and CH₄ were mainly obtained, while organic products with longer carbon chains were obtained at lower yields. Rh-modification gave high yields of CO₂, but the other catalysts gave low yields. Element-modification of USY generally enhanced the formation of solid carbon, although the addition of P, Ir, or Au did not alter it, and Sr inhibited it. The presence of P²⁰⁾ and Sr²¹⁾ can block acidic sites of zeolite, and Ir and Au can inhibit carbon deposition in the conversion of ethanol to hydrocarbons¹⁾. In particular, the addition of Ni, Ce, or Pt substantially increased the formation of solid carbon. Ni enhances the deposition of C in methane decomposition^{26) 27)}, and Pt enhances the deposition of C in the conversion of ethanol to hydrocarbon using Pt-modified H-ZSM-5 catalyst¹⁾.

The addition of P or Sr enhanced the formation of total liquid products (Fig. 5). The addition of Ir or Au slightly reduced it. On the other hand, the addition of other metals inhibited it, especially Ni and Rh. Ni enhances carbon deposition^{26) 27)}, and Rh enhances gasification of woody biomass^{23)~25)}. These behaviors may be responsible for the decrease. The addition of Co favored the formation of non-aromatic oxygenated compounds. The addition of P, Sr, or Ir improved the formation of non-oxygenated aromatic compounds, but the addition of Co, Ni, Cu, Zn, Ga, Rh, Ag, Re, or Pt greatly reduced it. The addition of Ag improved the formation of monocyclic oxygenated aromatic compounds, Fe and Pt did not alter it, but the others decreased it, notably Ni and Rh.

Most monocyclic oxygenated aromatic products are phenol and methylphenols. Total yields of these were improved by the addition of Ag or Pt relative to unmodified

Fig. 6 Yields of monocyclic oxygenated aromatic products

Fig. 7 Plots of phenol yield vs. non-oxygenated aromatics yields

USY (Fig. 6). The addition of Cr, Mo, Ag, Re, or Pt significantly improved the yield of phenol.

Except for Rh, Ni, and Co, which gave especially low yields of both non-oxygenated aromatics and phenol, there seems to be an inverse correlation between yields of the two, suggesting that catalysts that produce large amounts of non-oxygenated aromatics are not effective for the formation of phenols (Fig. 7).

3.4 Effect of solid acidity of zeolite on catalytic performance

We investigated the effect of solid acidity on catalytic performance. As mentioned in section 2.3, index of amount

of solid acid of catalyst was defined as NH_3 -desorption peak area ratio of $(300\text{--}600\text{ }^\circ\text{C})/(100\text{--}600\text{ }^\circ\text{C})$.

The addition of P, Sr, Mo, Pd, or Ir decreased the amount of solid acidity (Fig. 8). In most cases, the addition of metals to USY enhanced both the amount of solid acidity and the deposition of C, and there seems to be a correlation between the NH_3 -desorption peak area ratio and the amount of solid C, suggesting that a large amount of solid acidity enhances C deposition.

There seems to be an inverse correlation between NH_3 -desorption peak area ratio and yield of non-oxygenated aromatic products (Fig. 9). In general, solid acidity enhances deoxygenation¹⁸⁾, but this result is paradoxical. It can be explained by the fact that the enhanced C deposition decreases the yield of non-oxygenated aromatics, since non-

Fig. 8 Plots of NH_3 -desorption peak area ratio of $(300\text{--}600\text{ }^\circ\text{C})/(100\text{--}600\text{ }^\circ\text{C})$ vs. amount of solid carbon after reaction Fig. 9 Plots of NH_3 -desorption peak area ratio of $(300\text{--}600\text{ }^\circ\text{C})/(100\text{--}600\text{ }^\circ\text{C})$ vs. yields of non-oxygenated aromatic products

Fig. 10 Plots of NH_3 -desorption peak area ratio of (300-600 °C) / (100-600 °C) vs. yield of phenol

oxygenated aromatics can be converted by solid acidity to deposited C.

There seems to be a weak correlation between NH_3 -desorption peak area ratio and yield of phenol (Fig. 10). This result is reasonable as catalysts that produce large amounts of non-oxygenated aromatics are not effective for the formation of phenols (section 3.3).

In general, strong solid acidity is essential for the formation of non-oxygenated aromatics. Moderately strong solid acidity is essential for phenol production, while weak solid acidity led to lower yields of both non-oxygenated aromatics and phenols and to higher yields of non-phenolic oxygenated aromatics¹⁹. These facts suggest that strong solid acidity enhances the following reaction: woody biomass $\rightarrow$ non-phenolic oxygenated aromatics $\rightarrow$ phenols $\rightarrow$ non-oxygenated aromatics $\rightarrow$ carbon deposition. The moderately strong solid acidity of USY cannot fully enhance the formation of non-oxygenated aromatics. As a result, phenolic compounds were obtained in high yield.

Among different kinds of zeolites, the strength of solid acidity affects yields of liquid products. However, among modified forms of the same zeolite (USY), there are smaller differences in the strength of solid acidity affecting catalytic performance (yields of gaseous products, liquid products, and solid C).

Moreover, not only the amount of solid acidity but also the special character of elements added to the USY might affect the phenol yield. For example, P²¹ and Sr²⁰ can reduce the amount of solid acidity, Ni enhances carbon deposition²⁶ ²⁷, and Rh enhances gasification of woody biomass²³ $\sim$ ²⁵.

4. Conclusions

In the fast pyrolysis of eucalyptus to form phenolic compounds, USY was an effective catalyst; H-ZSM-5 (Si/Al₂ = 30) and H-Beta were effective for the formation of non-oxygenated aromatic compounds; and H-ZSM-5 (190) and H-mordenite yielded oxygenated aromatics, including non-phenolic compounds. There seems to be an inverse correlation between yields of non-oxygenated aromatic compounds and those of phenolic compounds. Moderately strong solid acidity is essential for the formation of phenolic products, while strong solid acidity favors deoxygenation to form non-oxygenated aromatics. The addition of Cr, Mn, Fe, Cu, Zn, Mo, Ag, Re, or Pt to USY improved the yield of phenol. The addition of Ag or Pt improved the yield of total phenolic compounds (phenol + methylphenols + dimethylphenols), but other metals inhibited it. Some metals may increase the deposition of C, reducing the yields of liquid products. However, they can inhibit the formation of non-oxygenated aromatic compounds, and some may improve the yield of phenolic compounds.

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