



Short communication

Hydrodeoxygenation of guaiacol over Pt loaded zeolitic materials



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ABSTRACT

Hydrodeoxygenation (HDO) of guaiacol in a batch-type reactor at 40 bar and 250 °C was investigated using six different catalysts, Pt/HZSM-5, Pt/Mesoporous Beta, Pt/HBeta, Pt/MMZ_{Beta}, Pt/Al-MCM-48, and Pt/Si-MCM-48. Among various catalysts, Pt/Mesoporous Beta and Pt/HBeta, which have both large pores and strong acid sites, showed guaiacol conversions larger than 90%. The main product species of HDO of guaiacol was cyclohexane. Meanwhile, Pt/Al-MCM-48 and Pt/MMZ_{Beta}, which are mesoporous catalysts with weak acid sites, led to lower guaiacol conversions than Pt/Mesoporous Beta and Pt/HBeta and the main product components were cyclohexane and 1,1-bicyclohexyl resulting from C–C coupling reactions.

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1. Introduction

Since the industrial revolution, excessive use of fossil fuels has caused the reduction in the fuel reserves and global warming, requesting the development of new energy resources [1–3]. Lignocellulosic biomass has gigantic reserves distributed evenly over the world. It is also carbon-neutral because its production is based on photosynthesis using atmospheric carbon dioxide. Therefore, the production of biofuels or biochar from lignocellulosic biomass is currently an important research topic [4–17].

Bio-oil is a liquid fuel produced from the pyrolysis of lignocellulosic biomass [18–23]. Although bio-oil has a higher energy density than the feedstock biomass and is easier to transport, it has several drawbacks compared to petroleum-derived transport fuels: large oxygen content and the presence of corrosive acids and reactive aldehydes that require additional conversion processes. Catalytic hydrodeoxygenation (HDO) of bio-oil is one of the most adequate processes to convert bio-oil into a

transport fuel because it can reduce the O/C ratio and increase the H/C ratio significantly [18,24,25].

In the research on the HDO of bio-oil, model compounds that have similar properties to bio-oil, such as phenol, guaiacol, and anisole, are used instead of real bio-oil. In particular, guaiacol is regarded as a good model compound representing phenolics in bio-oil because it contains both –OH groups that phenol has and –OCH₃ groups that anisole has [26].

Sulfided NiMo/alumina and CoMo/alumina have widely been used for the HDO of guaiacol. However, these catalysts are known to cause several problems during the HDO reaction, one of which is the contamination of the product by sulfur detached from the active sites [27]. Transition metals, such as noble metals (Pd, Ru, Pt, Rh, etc.) and Ni, have been used for alternative catalysts replacing sulfided catalysts. As the support, various materials including carbon, Al₂O₃, SiO₂, ZrO₂, zeolite, and TiO₂ have been used.

HDO requires active sites at which hydrogenation can occur (e.g., metal) as well as acid sites [28]. Therefore, bifunctional catalysts that have both kinds of sites are usually used for the HDO research. In particular, the application of metal-impregnated zeolite in HDO has been investigated extensively because of its strong acidity, crystalline structure, and uniform pore size, showing high activity for HDO reactions. Hong et al. [29] reported high catalytic activities of Pt/HY, Pt/Hβ, and Pt/HZSM-5 for the

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HDO of phenol. Zhu et al. [30] studied the HDO of methoxybenzene (anisole) for a bifunctional catalyst Pt/H β and reported a higher catalytic activity than those for monofunctional catalysts Pt/SiO₂ and H β . Horáček et al. [31] used Pt/beta zeolite for the hydrogenation and HDO of model compounds of bio-oil. Beta zeolite has exhibited a particularly high catalytic activity for HDO of large bio-oil molecules because of its large pores consisting of 12 rings. Nimmanwudipong et al. [26] suggested a mechanism for the HDO of 2-methoxy phenol over Pt/Al₂O₃. Zhao and Lercher [32] produced cyclohexane from 2-methoxy phenol using bifunctional Pd/C and HZSM-5 catalysts. Lee et al. [33] also reported that the acidity of the support affected the catalytic activity of a bifunctional Rh catalyst for the hydroconversion of guaiacol. In this study, a decrease in the Si/Al ratio in Pt/HY increased the conversion of guaiacol.

In the meantime, the application of mesoporous beta zeolite to HDO has barely been studied. One of a handful of previous studies that used mesoporous beta in HDO is the study of Horáček et al. in which mesoporous beta was used in the HDO of phenol and led to a better result [31]. The HDO of guaiacol over Pt/HBeta or Pt/mesoporous beta has never been reported. The application of MCM-48, a representative mesoporous material, has not been applied to HDO, either.

In this study, two microporous zeolite catalysts, HZSM-5 and HBeta, and two mesoporous zeolite catalysts, mesoporous beta and MMZ_{Beta}, were applied to the HDO of guaiacol. Two other mesoporous catalysts, Al-MCM-48 and Si-MCM-48, were also used to investigate the effect of the mesoporous structure.

2. Experimental

2.1. Preparation of catalysts

HZSM-5 with the SiO₂/Al₂O₃ ratio of 23 and HBeta with the SiO₂/Al₂O₃ ratio of 25 were purchased from Zeolyst International. Mesoporous beta (Meso Beta) with the SiO₂/Al₂O₃ ratio of 40 was synthesized using a method suggested previously by Choi et al. [34]. MMZ_{Beta} with the SiO₂/Al₂O₃ ratio of 300, Al-MCM-48 with the SiO₂/Al₂O₃ ratio of 40, and Si-MCM-48 were synthesized using the methods suggested previously [35,36]. The zeolite materials were impregnated with 0.5 wt% Pt using the incipient wetness method. Pt(NH₃)₄(NO₃)₂ in aqueous solution was used as the precursor. Impregnation was followed by calcination for 3 h in 500 °C nitrogen gas and reduction for 3 h in 500 °C hydrogen gas.

2.2. Characterization of the catalysts

N₂ adsorption–desorption isotherms were measured at 77 K using an automated gas sorption system (TriStar, Micromeritics). The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method in a N₂ partial pressure range of 0.05–0.2. To characterize the surface acid sites, temperature-programmed desorption of ammonia (NH₃-TPD) was conducted using a BELCAT (BEL Japan Inc.) equipped with a thermal conductivity detector.

2.3. Reaction conditions for HDO

Reduction of catalysts was conducted for 3 h using hydrogen gas at 500 °C. 0.4 g of reduced catalyst was mixed with 40 ml of 7.5 wt% guaiacol solution in decane in a batch-type reactor. After purging the reactor three times with high-purity hydrogen gas, the hydrogen pressure in the reactor was increased to 40 bar and the reactor temperature was increased to 250 °C at a rate of 5 °C/min. Temperature was then maintained at 250 °C for 2 h continuing to stir the reactor at 400 rpm for HDO reaction to occur. The reaction

product in liquid phase was obtained after cooling the reactor to room temperature and analyzed using gas chromatography/mass spectroscopy (GC/MS, Agilent Technologies) equipped with Ultra ALLOY-5 (MS/HT) (5% diphenyl and 95% dimethylpolysiloxane, length 30 m, i.d. 0.25 mm, film thickness 0.5 μ m, Frontier Laboratories Ltd. Japan) metal capillary column.

3. Results and discussion

3.1. Characterization of catalysts

The physical properties of the microporous and mesoporous catalysts used in this study are summarized in Table 1.

Fig. 1 compares the NH₃-TPD results of three catalysts with BEA structure. HBeta had the largest quantity of acid sites, whereas MMZ_{Beta} had the smallest quantity of acid sites. All three catalysts exhibited a peak below 200 °C representing weak acid sites. HBeta and Meso Beta showed a peak representing strong acid sites at 310 and 350 °C, respectively. HZSM-5 is known to have more acid sites than HBeta and the acid strength is also higher (data not shown) [37]. Al-MCM-48 has only weak acid sites and Si-MCM-48 has no acid sites (data not shown) [38].

3.2. Catalytic activities

Fig. 2 compares the guaiacol conversions obtained with six different catalysts. Pt/HZSM-5 showed the lowest guaiacol conversion (15%) although it had the strongest Brönsted acid sites. This result is attributed to the small pore size of HZSM-5, which is smaller than the kinetic diameter of guaiacol molecules (0.668 nm) and thus hinders the diffusion of guaiacol molecules into the pores. Therefore, the guaiacol conversion reaction is thought to have occurred outside the pores of HZSM-5. In the cases of other catalysts, the guaiacol conversion reaction can take place on the acid sites inside the pores because the pore size is larger than the kinetic diameter of guaiacol molecules. Pt/Meso Beta and

Table 1
Physical properties of catalysts.

Catalyst	Surface area (m ² /g)	Pore size (nm)	Si/Al
HBeta	617	ca. 0.7	12.5
Meso Beta	733	9.7	20
MMZ _{Beta}	758	2.4	300
HZSM-5	425	ca. 0.56	11.5
Al-MCM-48	848	2.9	40
Si-MCM-48	1025	2.9	–

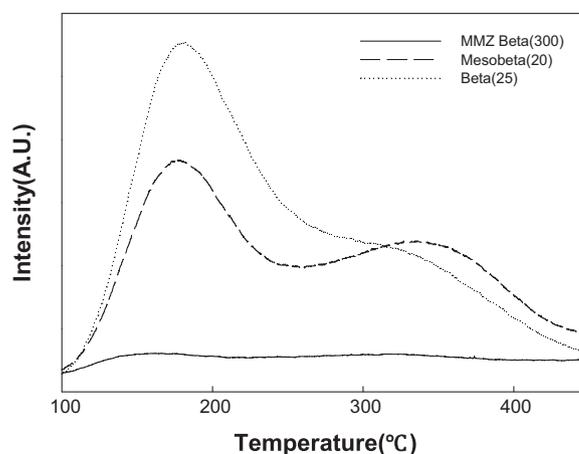


Fig. 1. NH₃-TPD of catalysts.

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