Hydrodeoxygenation of Guaiacol Over Pt/Al-SBA-15 Catalysts

Mi Jin Yu[1], Sung Hoon Park[2], Jong-Ki Jeon[3], Changkook Ryu[4],
Jung Min Sohn[5], Sang Chai Kim[6], and Young-Kwon Park[1, 7, *]

[1] *Graduate School of Energy and Environmental System Engineering,*
University of Seoul, Seoul 130-743, Korea
[2] *Department of Environmental Engineering, Sunchon National University,*
Suncheon 540-950, Korea
[3] *Department of Chemical Engineering, Kongju National University, Cheonan 330-717, Korea*
[4] *School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, Korea*
[5] *Department of Mineral Resources and Energy Engineering, Chonbuk National University,*
Jeonju 561-756, Korea
[6] *Department of Environmental Education, Mokpo National University,*
Muan 534-729, Korea
[7] *School of Environmental Engineering, University of Seoul, Seoul 130-743, Korea*

Upgrading of bio-oil through catalytic hydrodeoxygenation (HDO) reaction was investigated for guaiacol as a model compound. A batch reactor was used for the reaction condition of 40 bar and 250 °C. The target product was cyclohexane. Pt/Al-SBA-15 with the Si/Al ratios of 20, 40, and 80 and Pt/HZSM-5 were used as the catalyst. The SBA-15 catalysts were characterized by N_2 adsorption–desorption, X-ray diffraction analysis, and temperature programmed desorption of ammonia. The order of cyclohexane yield was Pt/Al-SBA-15 (Si/Al = 20) > Pt/Al-SBA-15(40) > Pt/Al-SBA-15 (80), indicating that the quantity of acid sites plays an important role in the HDO reaction. On the other hand, Pt/HZSM-5 led to a very low cyclohexane yield, in spite of its abundant strong acid sites, due to its small pore size.

Keywords: Guaiacol, Hydrodeoxygenation, SBA-15, HZSM-5, Pt, Cyclohexane.

1. INTRODUCTION

Renewable energy has attracted much attention as the ultimate solution to fossil fuel exhaustion and global warming. Among the renewable energy sources, bio-energy has a unique advantage that it can be directly converted into transportation fuels and chemical feedstock. Biomass, raw material for bio-energy, includes a variety of materials that stem from plants, such as microorganisms, dead animals and plants, organic wastes, wood, and seaweeds.

Woody biomass has a multitude of advantages; it is carbon-neutral, renewable, and abundant. Woody biomass consists of hemicellulose (40~50%), cellulose (15~20%), and lignin (15~30%). Lignocellulosic biomass has a particularly high potential as a renewable resource for production of fuels and chemicals thanks to its abundance and low price.[1] Bio-oil is the main product from lignocellulosic biomass converted by pyrolysis. Representative compounds in bio-oil include guaiacol, phenol, anisole, and catechol.[2] Among the lignin-originated species contained in bio-oil, guaiacol is one of the most abundant. For instance, it accounts for 0.18~0.51 wt% in the pyrolysis oil derived from alfalfa stem and swichgrass forage.[3]

Although the bio-oil obtained from pyrolysis can be used as fuel or chemical feedstock, its high oxygen content, viscosity, and polarity cause instability and chemical complexity, requiring additional upgrading processes.[4] Upgrading of bio-oil is usually conducted using catalytic hydrotreating, catalytic vapor cracking, or physical methods such as hot-gas filtration, emulsification, and solvent addition.

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*Author to whom correspondence should be addressed.

Recently, upgrading of bio-oil through hydrodeoxygenation (HDO) has drawn significant attention. In a HDO process, oxygen is removed from oxygenate compounds by high-temperature catalytic reactions under hydrogen atmosphere. This requires a noble metal catalyst for hydrogenation and an acid catalyst for dehydration. Mo, CoMo, and NiMo catalysts have usually been used as the support material, while employment of other materials, such as SiO$_2$, activated carbon, TiO$_2$, ZrO$_2$, zeolite, and oxide mixtures, has recently been investigated.[5–8] Pt, Rh, Pd, Cu, and Ni have been used as the noble metal catalyst for HDO.[1, 9–11] Noble metals are effective for activation of hydrogen under mild conditions because hydrogen can be easily separated and activated on their surface to react with other reactants.[12]

Mesoporous silica materials have attracted considerable attention as a catalyst support due to their large specific surface area, controllable pore diameter, narrow pore size distribution, and large pore volume.[13–16] Among others, in particular, SBA-15 possesses high structural regularity. It is also more stable against moisture and has larger pores than MCM-41.[17]

In this study, Pt/Al-SBA-15 catalysts synthesized using Al-SBA-15 supports with three different Si/Al ratios were applied, for the first time, to HDO of guaiacol to upgrade the fuel quality by producing cyclohexane. Microporous Pt/HZSM-5 was also used for the HDO reaction to investigate the effect of the pore size on the catalytic activity for HDO reaction.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

HZSM-5(11.5) was purchased from Zeolyst International. Al-SBA-15 was synthesized using the procedure reported by Lee et al.[18] controlling the Si/Al ratio at 20, 40, and 80. 0.5 wt% Pt was impregnated on the Al-SBA-15 support using Pt(NH$_3$)$_4$(NO$_3$)$_2$ solution, based on the incipient wetness impregnation method. The impregnated catalyst was calcined for 3 h at 500 °C under nitrogen atmosphere and then reduced for 3 h at 500 °C under hydrogen atmosphere.

2.2. Catalyst Characterization

Nitrogen adsorption/desorption isotherms were obtained using a surface area analyzer (TriStar, Micromeritics). Specific surface area was calculated using the Brunaure–Emmett–Teller (BET) method over the relative pressure range of $P/P_0 = 0.05 \sim 0.20$. Pore size distribution was calculated by the Barrett–Joyner–Halenda method.

X-ray diffraction (XRD) patterns were obtained in the reflection mode using an XRD system (Rigaku D/MAX-2200 Ultima) equipped with Cu light source (Kα radiation = 1.541 Å) at 30 kV and 40 mA.

Temperature programmed desorption of ammonia (NH$_3$-TPD) was performed using a chemisorption analyzer

(BELCAT, BEL Japan Inc.) equipped with a thermal conductivity detector to compare the acid properties of the catalyst surface.

2.3. HDO of Guaiacol

HDO of guaiacol was performed using a batch reactor. 0.4 g of reduced catalyst and 40 ml of 7.5-wt% guaiacol in decane solution were introduced into the reactor. The reactor was purged three times with hydrogen gas and then filled with 40-bar hydrogen gas. The reactor temperature was increased to 250 °C at a rate of 5 °C/min. At this temperature, stirring began at 400 rpm, which was considered to be the beginning of the reaction. After 2 h of reaction time, the reactor temperature was decreased to room temperature to sample the products. Liquid-phase products were analyzed by gas chromatography/mass spectroscopy (GC/MS, Agilent Technologies). As the metal capillary column for GC/MS, Ultra ALLOY-5 (MS/HT) (5% diphenyl and 95% dimethylpolysiloxane, length 30 m, i.d. 0.25 mm, film thickness 0.5 μm, Frontier Laboratories Ltd. Japan) was used.

3. RESULTS AND DISCUSSION

3.1. Characterization of Catalysts

Table I summarizes the physical properties of the catalysts used in this study. The specific surface areas of Pt/Al-SBA-15(20), Pt/Al-SBA-15(40), and Pt/Al-SBA-15(80) were 517, 547, and 559 m^2/g, respectively, while their pore volumes were 0.74, 0.88, and 0.81 cm^3/g, respectively. On the whole, both properties increased with increasing Si/Al ratio. The specific surface area of Pt/HZSM-5(11.5) was 386 m^2/g, being smaller than that of Pt/Al-SBA-15. Pt/Al-SBA-15 was shown to have mesopores with their size of 6 nm or larger.

Therefore, Pt/Al-SBA-15 with larger pore size was expected to be more effective, than HZSM-5 with smaller pore size (*ca.* 0.56 nm), for diffusion of reactant molecules into the pores and hence for their cracking.

Figure 1 shows the XRD analysis results of Pt/Al-SBA-15(20), Pt/Al-SBA-15(40), and Pt/Al-SBA-15(80). All the samples exhibited three typical peaks, indexed as (100), (110), and (200),[16] representing the 2D-hexagonal structure of SBA-15. This indicates that the structure of SBA-15 was not altered by impregnation of Pt.

Table I. Physical properties of the catalysts.

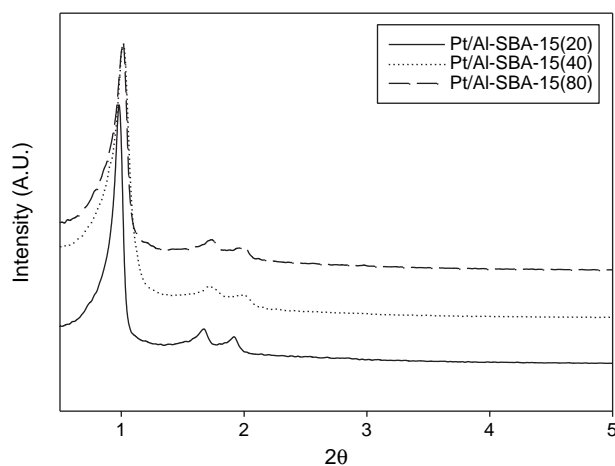| Catalysts	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Si/Al
Pt/Al-SBA-15(20)	517	0.74	6.6	20
Pt/Al-SBA-15(40)	547	0.88	6.6	40
Pt/Al-SBA-15(80)	559	0.81	7.3	80
Pt/HZSM-5(11.5)	317	–	0.51 × 0.55, 0.53 × 0.56	11.5

Figure 1. Low-angle XRD pattern of Pt/Al-SBA-15(20), Pt/Al-SBA-15(40), and Pt/Al-SBA-15(80).
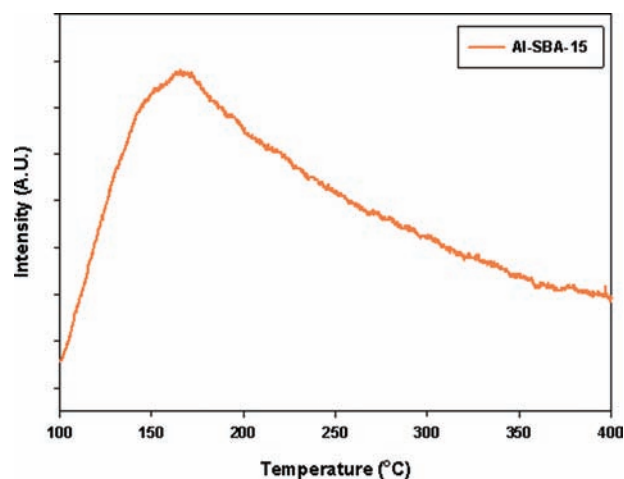

Figure 3. NH_3-TPD of Al-SBA-15.

The type of surface acidity of the Al-SBA-15 catalyst was examined using pyridine adsorption tests. As shown in Figure 2 for the spectroscopic results, Al-SBA-15 had the characteristic bands for pyridine adsorbed on Lewis acid sites at 1445 cm^{-1} and 1587 cm^{-1}. The less intense band at 1540 cm^{-1} indicated the formation of Brønsted acid sites. Figure 3 shows the NH_3-TPD analysis results of Al-SBA-15. Al-SBA-15 is shown to have weak acid sites, whereas HZSM-5 has strong Brønsted acid sites (data not shown). HZSM-5 is also shown to have a larger quantity of acid sites than Al-SBA-15 (data not shown). The quantity of acid sites of Al-SBA-15 increased with decreasing Si/Al ratio; the order of the quantity of acid sites was Pt/Al-SBA-15(20) > Pt/Al-SBA-15(40) > Pt/Al-SBA-15(80) (data not shown), which is in accordance with previous reports.[19, 20]

3.2. Catalytic Activities

The guaiacol conversions obtained over Pt/Al-SBA-15 with various Si/Al ratios are compared in Figure 4.
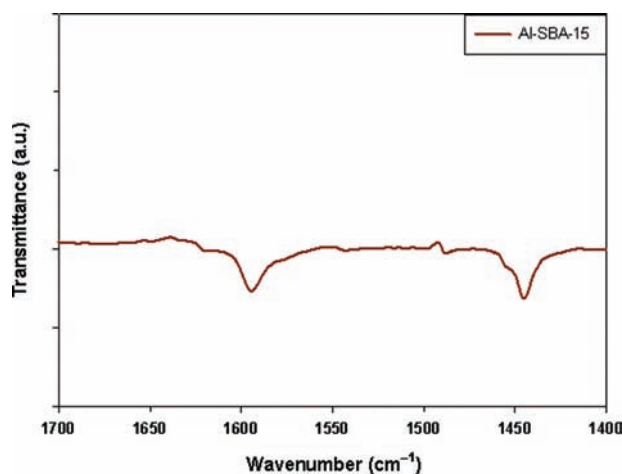
The catalytic activity was the highest when the Si/Al ratio was the smallest (20), while it was the lowest when the Si/Al ratio was the largest (80). Because the quantity of acid sites of Al-SBA-15 increases with decreasing Si/Al ratio, the guaiacol conversion appears to be in positive correlation with the quantity of acid sites. This may be due to the fact that the propensity of deoxygenation increases with the number of active sites. Lee et al.[21] also reported that the yield of cyclohexane increased with increasing acidity of the catalyst support material. At a low stirring rate (200 rpm), the guaiacol conversion was lower than that obtained with a stirring rate of 400 rpm, which is attributed to a lower accessibility of reactant to active sites of the catalyst due to weak stirring.

Table II lists the main products of catalytic HDO of guaiacol over Pt/Al-SBA-15(20). Besides the main target cyclohexane, a variety of species were produced.
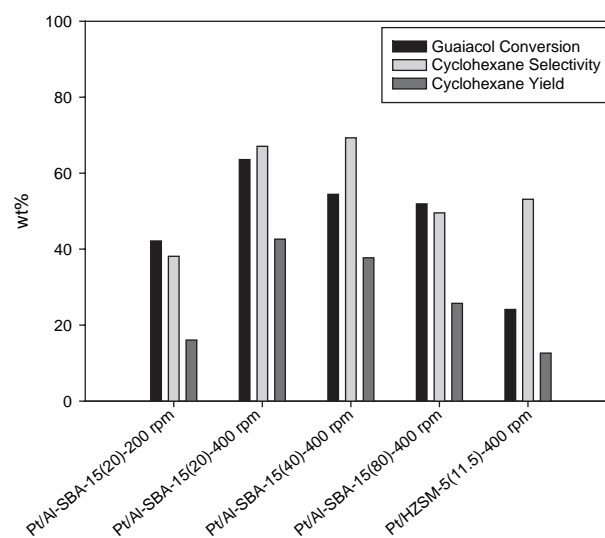

Figure 4. Effect of the Si/Al ratio of Al-SBA-15 and the pore size on the catalytic activity.

Figure 2. Pyridine FT-IR spectra of Al-SBA-15.

Table II. Products of HDO of guaiacol over Al-SBA-15(20) catalyst at two stirring rates.

	200 rpm	400 rpm
Cyclohexane	16.07	42.63
Cyclopentane	0.36	0.27
Methyl cyclopentane	0.42	1.13
Benzene		3.93
Methyl cyclohexane	0.45	0.27
Methoxy benzene (anisole)	3.83	–
Pentyl cyclopentane	1.35	–
2-methoxy-4-methyl-phenol	9.77	–
1,2-dimethoxy benzene	2.43	–
Cyclohexane (cyclopentylmethyl)	6.65	4.11
1,1′-bicyclohexyl	0.83	11.21
Cyclohexyl benzene	16.07	–

Cyclopentane and methyl cyclopentane are produced by isomerization, while cyclohexyl benzene and 1,1′-bicyclohexyl are formed by aromatic ring condensation. Under a low stirring rate (200 rpm), more reaction intermediates were observed because of insufficient progress of the reaction. Gates et al.[1] suggested a mechanism for deoxygenation of guaiacol over Pt/Al_2O_3 in which several possible reactions were incorporated. According to their suggestion, cyclohexane can be produced via phenol or anisole. Phenols were not detected in this study, while anisole and 1,2-dimethoxy benzene were observed, implying that cyclohexane could be produced via anisole. However, Gates et al.[1] argued that the reaction kinetic of phenol formation is 40 times faster than that of anisole formation. Therefore, we cannot rule out the possibility of formation of phenol and subsequent conversion to other species. Further investigation is needed to better constrain the mechanism of cyclohexane formation.

In order to examine the effect of the pore size of the catalyst, Pt/HZSM-5(11.5) was used additionally. Because HZSM-5 has a larger quantity of acid sites with stronger acidity than Al-SBA-15 (data not shown), a higher conversion of guaiacol may be expected. As shown in Figure 4, however, the employment of Pt/HZSM-5 resulted in a very low guaiacol conversion.

Al-SBA-15 has large pores with the average pore diameter of 6 nm so that the diffusion limitation against the approach of guaiacol molecules to active sites of the catalyst is low. To the contrary, the pore size of HZSM-5 is much smaller (*ca.* 0.56 nm), hindering the access of guaiacol molecules to the active sites existing in the catalyst pores. This is believed to have contributed to the low guaiacol conversion over HZSM-5. Prochazkova et al.[22] studied the HDO reaction of benzaldehyde over Pd-impregnated Beta and ZSM-5. ZSM-5 showed, due to its smaller pore size, lower selectivity to and yield of the target product. Based on this result, they suggested that catalytic supports with large pore size are adequate for HDO reaction. The result of the present study is in good agreement of that of Prochazkova et al.[22] in terms of the effect of the pore size.

Because cyclohexane has a high octane number, the bio-oil upgraded over Pt/Al-SBA-15 is believed to have a high potential as a transportation fuel. High potential of bio-oil containing cyclohexane as a transportation fuel was presented in a study by Ahmad et al.[23]

4. CONCLUSION

Pt/Al-SBA-15(20), Pt/Al-SBA-15(40), Pt/Al-SBA-15(80), and Pt/HZSM-5(11.5) were applied to the HDO of guaiacol. Pt/Al-SBA-15(20) exhibited the highest guaiacol conversion and cyclohexane yield, whereas Pt/HZSM-5(11.5) exerted the lowest catalytic activity. The poor catalytic activity of Pt/HZSM-5(11.5) was attributed to its small pore size that hinders diffusion of guaiacol molecules into the pores containing active sites. The catalytic activity of Pt/Al-SBA-15 increased with decreasing Si/Al ratio because the quantity of acid sites increases with decreasing Si/Al ratio. The results of this study indicate that the pore size and the quantity of acid sites play important roles in the conversion of guaiacol to cyclohexane.

References and Notes

1. T. Nimmanwudipong, R. C. Runnebaum, D. E. Block, and B. C. Gates, *Energy Fuels* 25, 3417 (**2011**).
2. J. C. Hicks, *J. Phys. Chem. Lett.* 2, 2280 (**2011**).
3. C. A. Mullen and A. A. Boateng, *Energy Fuels* 22, 2104 (**2008**).
4. C. H. Ko, S. H. Park, J. K. Jeon, D. J. Suh, K. E. Jeong, and Y. K. Park, *Korean J. Chem. Eng.* 29, 1657 (**2012**).
5. Y. Yang, A. Gilbert, and C. C. Xu, *Appl. Catal. A: Gen.* 360, 242 (**2009**).
6. M. Breysse, J. L. Portefaix, and M. Vrinat, *Catal. Today* 10, 489 (**1991**).
7. P. T. Vasudevan and J. L. G. Fierro, *Catal. Rev. Sci. Eng.* 38, 161 (**1996**).
8. L. R. Radovic and F. Rodríguez-Reinoso, *Chem. Phys. Carbon* 25, 243 (**1997**).
9. X. Zhu, L. L. Lobban, R. G. Mallinson, and D. E. Resasco, *J. Catal.* 281, 21 (**2011**).
10. A. Gutierrez, R. K. Kaila, M. L. Honkela, R. Slioor, and A. O. I. Krause, *Catal. Today* 147, 239 (**2009**).
11. S. Sitthisa and D. E. Resasco, *Catal. Lett.* 141, 784 (**2011**).
12. G. V. Smith and F. Notheisz, Heterogeneous Catalysis in Organic Chemistry, Academic Press, San Diego (**1999**).
13. I. T. Ghampsona, C. Sepulveda, R. Garcia, J. L. G. Fierro, N. Escalona, and W. J. DeSisto, *Appl. Catal. A: Gen.* 435–436, 51 (**2012**).
14. W. Chang, G. Chae, S. R. Jang, J. Shin, and B. J. Ahn, *J. Ind. Eng. Chem.* 18, 581 (**2012**).
15. H. W. Lee, H. J. Cho, J. H. Yim, J. M. Kim, J. K. Jeon, J. M. Sohn, K. S. Yoo, S. S. Kim, and Y. K. Park, *J. Ind. Eng. Chem.* 17, 504 (**2011**).

16. Y. K. Park, H. W. Lee, J. K. Jeon, J. Han, C. U. Kim, S. Y. Jeong, and K. E. Jeong, *J. Nanosci. Nanotechnol.* 13, 714 **(2013)**.

17. K. Soni, K. C. Mouli, A. K. Dalai, and J. Adjaye, *Catal. Lett.* 136, 116 **(2010)**.

18. S. H. Lee, H. S. Heo, K. E. Jeong, J. H. Yim, J. K. Jeon, K. Y. Jung, Y. S. Ko, S. S. Kim, and Y. K. Park, *J. Nanosci. Nanotechnol.* 11, 759 **(2011)**.

19. C. Nie, L. Huang, D. Zhao, and Q. Li, *Catal. Lett.* 71, 117 **(2001)**.

20. Q. Lu, W. Z. Li, D. Zhang, and X. F. Zhu, *J. Anal. Appl. Pyrolysis* 84, 131 **(2009)**.

21. C. R. Lee, J. S. Yoon, Y. W. Suh, J. W. Choi, J. M. Ha, D. J. Suh, and Y. K. Park, *Catal. Commun.* 17, 54 **(2012)**.

22. D. Procházková, P. Zámostný, M. Bejblová, L. Červený, and J. Čejka, *Appl. Catal. A: Gen.* 332, 56 **(2007)**.

23. M. M. Ahmad, M. F. R. Nordin and M. T. Azizan, *Am. J. Appl. Sci.* 7, 746 **(2010)**.