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## Surface Modification of a Supported Pt Catalyst Using Ionic Liquids for Selective Hydrodeoxygenation of Phenols into Arenes under Mild Conditions

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Abstract: The selective and efficient removal of oxygenated groups from lignin-derived phenols is a critical challenge to utilize lignin as a source for renewable aromatic chemicals. This report describes that surface modification of a zeolite-supported Pt catalyst using ionic liquids (II s) remarkably increases selectivity for the hydrodeoxygenation (HDO) of phenols into arenes under mild reaction conditions using atmospheric pressure H<sub>2</sub>. Unmodified Pt/H-ZSM-5 converts phenols into aliphatic species as the major products along with a slight amount of arenes (10% selectivity). In contrast, the catalyst modified with an IL, 1-butyl-3-methylimidazolium triflate, keeps up to 76% selectivity for arenes even at a nearly complete conversion of phenols. The IL on the surface of Pt catalyst may offer the adsorption of phenols in an edge-to-face manner onto the surface, thus accelerating the HDO without the ring hydrogenation.

Development of a catalytic process to convert lignin into aromatic fundamental chemicals has emerged as an important challenge to establish biorefinery-based industries.<sup>1</sup> Lignin is a three-dimensional aromatic polymer contained in lignocellulosic biomass, and the lignin-first approach using acids and metal catalysts efficiently converts lignocellulose to phenols.<sup>1a,2</sup> Hydrodeoxygenation (HDO) of the phenols produces arenes that can alternate petrol-based aromatics.<sup>3</sup> However, the HDO reaction suffers from harsh reaction conditions (generally 300 °C or higher under pressurized H<sub>2</sub>) and low selectivity for arenes due to the complete hydrogenation to cycloalkanes.<sup>3,4</sup> Even after recent mechanistic studies on the HDO pathways to show directions to the catalyst design for the selective arene production,<sup>3,5</sup> they have remained serious issues.

We previously reported the selective HDO of phenols into cycloalkanes using a metal-acid bifunctional Pt/H-ZSM-5 catalyst in octane at 110 °C under atmospheric pressure  $H_{2.6}^{6}$  The time course of this reaction indicated that a major reaction

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pathway consisted of the ring hydrogenation, the dehydration of cycloalkanols, and the hydrogenation of cycloalkenes (Scheme 1, path A). However, we found that a small amount of an arene was formed as a transient product in the early stage of the reaction. Among the several possible routes for the arene formation (Scheme S1 in Supporting Information), we assumed that the arene was obtained through the partial hydrogenation-dehydration pathway (Scheme 1, path B). The resulting arene was eventually reduced to the corresponding cyclohexane. These results demonstrate that the catalyst can convert phenols to arenes under the mild conditions but does not show selectivity toward arenes.



Scheme 1. Proposed reaction pathways for the HDO of phenols by ILmodified and unmodified Pt/H-ZSM-5.



**Figure 1.** Presumed adsorption modes of phenols onto a metal surface forming (a) aliphatics and (b) arenes. (c) Schematic images expected for the surface structure of IL-modified Pt/H-ZSM-5 in the HDO of phenols.

In the present study, we aimed for the selective conversion of phenols to arenes (path B) by modifying surface properties of the Pt/H-ZSM-5 catalyst, thereby achieving the arene-selective HDO under mild conditions at 110 °C with atmospheric pressure H<sub>2</sub>. Control of the adsorption mode of phenols onto a metal

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surface may be crucial to improve the selectivity of arenes. Thus, the adsorption of the aromatic ring parallel to a metal surface would promote the formation of aliphatics, whereas the vertical and tilted adsorption may facilitate the partial hydrogenation and finally give arenes (Figure 1, a and b).<sup>7</sup> In addition, the reduction in hydrogenation activity of the metal and the concentration of surface hydrogen species would be effective to suppress the excessive hydrogenation.8 In order to control these factors, we performed the surface modification of Pt/H-ZSM-5 using ILs. It is known that ILs form an ordered structure on a metal surface9 and their physical properties such as viscosity and gas solubility can be regulated by the cation-anion combination.<sup>10</sup> Figure 1c shows the schematic image expected for the surface structure of IL-modified Pt/H-ZSM-5 (denoted as IL/Pt/H-ZSM-5) in the HDO of phenols. Here, the ILs would decrease the hydrogenation activity and the hydrogen concentration by occupying the Pt surface.<sup>11</sup> Furthermore, the loosely ordered ILs on the Pt surface may affect the adsorption mode of phenols.<sup>12</sup> On the basis of the hypotheses, we investigated the HDO of phenols using IL/Pt/H-ZSM-5 catalysts.

The surface modification of 5 wt% Pt/H-ZSM-5 catalyst was performed by impregnating with various ILs in dry MeOH followed by evaporation and drying under vacuum. The prepared catalysts were characterized by several analytical methods, the details of which are available in Supporting Information. Selected analytical data of 30 wt% 1-butyl-3-methylimidazolium triflate ([bmim][OTf])-modified and unmodified Pt/H-ZSM-5 are shown in Figure 2. The <sup>13</sup>C{<sup>1</sup>H} NMR spectra showed that [bmim][OTf] existed on the catalyst surface and remained intact after modification (Figure 2a). In XRD analysis, the modification of Pt/H-ZSM-5 with [bmim][OTf] reduced the intensity of the diffraction peaks at  $2\theta = 7^{\circ}$  to  $18^{\circ}$ , which include the (020) and (200) planes related to the 10-membered ring channel directions of H-ZSM-5 (Figure 2b).13 It is suggested that a part of [bmim][OTf] was located within the pores.14 A large decrease in the BET surface area and the pore volume determined by N2 adsorption measurements after the modification (Table S1) is consistent with the XRD results. TEM analysis confirmed that the average Pt particle size of Pt/H-ZSM-5 did not change by the modification (Figure 2c), whereas the CO adsorption measurements showed that the CO-accessible Pt surface area of Pt/H-ZSM-5 decreased to 16% of the original value (Table S1). These data show that [bmim][OTf] covers Pt surface. In Pt LIIIedge XAFS analysis, [bmim][OTf]-modified and unmodified Pt/H-ZSM-5 provided slightly larger white lines than that of Pt foil in the XANES spectra (Figure 2d). This result shows lower electron density on 5d orbitals due to the  $\delta$ + oxidation state.<sup>15</sup> The average Pt oxidation state in [bmim][OTf]-modified and unmodified Pt/H-ZSM-5 was evaluated in detail by Pt Li-edge XAFS analysis and determined to be 0.44 and 0.56, respectively (Figures S2 and S3).<sup>16</sup>



Figure 2. (a) <sup>13</sup>C{<sup>1</sup>H} NMR spectra of 30 wt% [bmim][OTf]/Pt/H-ZSM-5 (solid-state CP/MAS) and [bmim][OTf] (solution-state, in CDCl<sub>3</sub>). (b) XRD patterns as well as (c) TEM images and Pt particle size distributions of 5 wt% Pt/H-ZSM-5 and 30 wt% [bmim][OTf]/Pt/H-ZSM-5. (d) Pt  $L_{III}$ -edge XANES spectra of PtO<sub>2</sub>, 5 wt% Pt/H-ZSM-5, 30 wt% [bmim][OTf]/Pt/H-ZSM-5, and Pt foil.

Effect of ILs-modification of Pt/H-ZSM-5 was evaluated in the HDO of 4-propylphenol **1** in octane at 110 °C under atmospheric pressure H<sub>2</sub> (Table 1). As shown in entry 1, unmodified Pt/H-ZSM-5 gave aliphatics **3** – **5** as the major products and desired arene **2** in 10% selectivity. Bare Pt/H-ZSM-5 was useless for the production of arenes, and thus we performed the HDO using Pt/H-ZSM-5 modified with 30 wt% [bmim]<sup>+</sup>-based ILs having different anions. The ILs having [CI]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, and [BArF]<sup>-</sup> anions just decreased the hydrogenation activity with no improvement on the selectivity for **2** (entries 2 – 5). In contrast, [NTf<sub>2</sub>]<sup>-</sup>, [NPf<sub>2</sub>]<sup>-</sup>, [CPFSA]<sup>-</sup>, [OTf]<sup>-</sup>,

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and [ONf]<sup>-</sup> anions improved the selectivity for **2** (entries 6 – 10). The highest selectivity was obtained by the catalyst having [OTf]<sup>-</sup> anion. In addition, the HDO using the catalysts modified with ILs having other cations gave **2** in lower selectivity (Table S2). The increase in the loading amount of [bmim][OTf] from 30 wt% to 50 wt% improved the selectivity for **2** to 71% (entry 11). Furthermore, nearly complete conversion (94%) was obtained after a two-hour reaction with keeping a good selectivity (76%) for **2**, achieving the highest yield in this study (72%) (entry 12). The use of higher amounts of ILs reduces the reaction rate; in the extreme case, the reaction using Pt/H-ZSM-5 catalyst and [bmim][OTf] as a solvent did not afford any products (Table S2). Thus, 50 wt% [bmim][OTf]/Pt/H-ZSM-5 is the best catalyst for the HDO of **1** under the mild reaction conditions.<sup>17</sup>

Table 1. HDO of 4-propylphenol 1 by IL/Pt/H-ZSM-5.<sup>[a]</sup>

$Pr \stackrel{OH}{1} \xrightarrow{\text{IL/Pt/H-ZSM-5}}_{\text{(1 mol% Pt)}} \xrightarrow{Pr} 2 \stackrel{Pr}{3} \stackrel{Pr}{4} \stackrel{Pr}{5}$						
		Conversion	Selectivity [%]			
Entry	IL	[%]	2	3	4	5
1	None	86	10	17	9	57
2	[bmim][CI]	7	6	3	4	1
3	[bmim][PF <sub>6</sub> ]	19	11	4	19	15
4	[bmim][BF <sub>4</sub> ]	9	8	6	26	2
5	[bmim][BArF]	49	9	8	0	65
6	[bmim][NTf <sub>2</sub> ]	61	37	35	2	2
7	[bmim][NPf <sub>2</sub> ]	51	45	35	2	0
8	[bmim][CPFSA]	38	50	16	0	3
9	[bmim][OTf]	61	56	18	4	2
10	[bmim][ONf]	61	37	23	4	1
11 <sup>[b]</sup>	[bmim][OTf]	66	71	10	0	6
12 <sup>[b,c]</sup>	[bmim][OTf]	94	76	12	6	3

[a] Reaction conditions: 1 (1.0 mmol), 30 wt% IL/Pt/H-ZSM-5 (1 mol% Pt), octane (1 mL), 110 °C, H<sub>2</sub> (balloon, 1 atm), 1 h. [b] 50 wt% [bmim][OTf]/Pt/H-ZSM-5 (1 mol% Pt) was used. [c] The reaction was conducted for 2 h.

The catalytic property of 50 wt% [bmim][OTf]/Pt/H-ZSM-5 was investigated by using various substituted phenols in the HDO (Table 2). Among the *p*-substituted phenols, the increase in the bulkiness of the alkyl moiety from *n*-propyl (1) to *i*-propyl (6), *t*-butyl (8), and *n*-heptyl (10) groups decreased selectivity for the corresponding arenes under the same reaction conditions. The reaction rate was only slightly decreased in these cases. The higher selectivity for less bulky substituents may be

attributed to the molecular planarity.<sup>18</sup> We propose that a planar phenol can penetrate into the ordered structure of ILs on the surface of Pt and undergoes selective hydrogenation in the edge-to-face form. Non-planar bulky substituents cannot preserve the ordered structure of ILs in the adsorption and therefore leads to the hydrogenation to cycloalkanes. Next, we studied the effect of o-substitution of phenols on the HDO reaction. 2-t-Butyl-4-methylphenol 12 required a significantly longer reaction time (8 h, 24% conversion) for the HDO reaction than that for 1 (2 h, 94% conversion), and the arene selectivity was moderate as expected in the above discussion. Besides, the o-substitution with methyl groups 14 and 16, possessing good molecular planarity, also decreased the conversion rate of the substrate but maintained good selectivity (65-74%). The effect of the steric hindrance indicates that the HDO reaction requires the hydrogenation of phenolic hydroxyl groups or C=C double bond near from the OH groups, which supports the reaction path B in Scheme 1. Finally, we tested an alkyl guaiacol 18, an important lignin-related phenol, provided 69% conversion after 12 h and gave fully-deoxygenated 2, monodeoxygenated 19 and 1 in selectivity of 44%, 7%, and <1%, respectively. This selectivity is not very high but one of the highest ever reported among the HDO using molecular H<sub>2</sub> in spite of the much lower temperature (110 °C) than those in the previous reports (300 °C or higher).<sup>3a</sup> This is surprising as the formation of arenes are thermodynamically favored at higher temperatures. The HDO by [bmim][OTf]/Pt/H-ZSM-5 still requires further improvement in substrate scope and arene selectivity.<sup>19</sup> However, the catalyst design concept shown in this study would be informative for future development of the HDO under mild conditions.



[a] Reaction conditions: phenols (1.0 mmol), 50 wt% [bmim][OTf]/Pt/H-ZSM-5 (1 mol% Pt), octane (1 mL), 110  $^\circ C,$  H2 (balloon, 1 atm).

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We hypothesize that the HDO of phenols into arenes catalyzed by [bmim][OTf]/Pt/H-ZSM-5 proceeds through path B shown in Scheme 1. As discussed in the introduction part, there are several possibility for the HDO pathway. The most often found mechanism is the hydrogenation of phenols to followed by the dehydration cvcloalkanols and the dehydrogenation (Scheme S1).<sup>3,5c,5h</sup> Therefore, we performed the control experiment using 4-propylcyclohexanol 5 as a substrate (Scheme 2) to reveal whether the HDO by [bmim][OTf]/Pt/H-ZSM-5 proceeded through the pathway. As a result, our catalyst did not give 2 at all, thus indicating that the path B is more plausible for the HDO by [bmim][OTf]/Pt/H-ZSM-5.



Scheme 2. A control experiment for elucidation of reaction pathways.

In summary, we developed the selective HDO of phenols into arenes at 110 °C under atmospheric pressure  $H_2$  by a [bmim][OTf]-modified Pt/H-ZSM-5 catalyst. Unmodified catalyst gave aliphatic species as the major products, whereas the modified one afforded arenes up to 72% yield and 76% selectivity. The type of ILs used for the surface modification greatly affected the reaction progress and product distributions. Although the reaction mechanism is still not clear, we consider that the HDO by [bmim][OTf]/Pt/H-ZSM-5 proceeded through path B shown in Scheme 1. The control of the adsorption mode of phenols onto the catalyst surface and the concentration of surface hydrogen species may be crucial for obtaining high arene selectivity. The detailed mechanistic studies and the development of new catalysts based on the catalyst design concept obtained from this study are currently underway.

#### Acknowledgements

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- For reviews, see: a) Z. Sun, B. Fridrich, A. de Santi, S. Elangovan, K. Barta, *Chem. Rev.* 2018, *118*, 614-678; b) C. Li, X. Zhao, A. Wang, G. W. Huber, T. Zhang, *Chem. Rev.* 2015, *115*, 11559-11624; c) J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* 2010, *110*, 3552-3599.
- [2] a) T. Renders, S. Van den Bosch, S.-F. Koelewijn, W. Schutyser, B. F. Sels, *Energy Environ. Sci.* 2017, *10*, 1551-1557; b) M. D. Kärkäs, *ChemSusChem* 2017, *10*, 2111-2115.
- For reviews, see: a) A. M. Robinson, J. E. Hensley, J. W. Medlin, ACS
  *Catal.* 2016, 6, 5026-5043; b) D. A. Ruddy, J. A. Schaidle, J. R. Ferrell
  III, J. Wang, L. Moens, J. E. Hensley, *Green Chem.* 2014, *16*, 454-490.
- [4] Selected recent papers about the HDO of phenols into arenes: a) P. M. de Souza, R. C. Rabelo-Neto, L. E. P. Borges, G. Jacobs, B. H. Davis, U. M. Graham, D. E. Resasco, F. B. Noronha, *ACS Catal.* 2015, *5*, 7385-7398; b) C. Chen, G. Chen, F. Yang, H. Wang, J. Han, Q. Ge, X. Zhu, *Chem. Eng. Sci.* 2015, *135*, 145-154; c) X. Zhu, L. Nie, L. L. Lobban, R. G. Mallinson, D. E. Resasco, *Energy Fuels* 2014, *28*, 4104-4111; d) J. Sun, A. M. Karim, H. Zhang, L. Kovarik, X. S. Li, A. J. Hensley, J.-S. McEwen, Y. Wang, *J. Catal.* 2013, *306*, 47-57; e) A. L. Jongerius, R. Jastrzebski, P. C. A. Bruijnincx, B. M. Weckhuysen, *J. Catal.* 2012, *285*, 315-323.
- [5] a) C. Wang, A. V. Mironenko, A. Raizada, T. Chen, X. Mao, A. Padmanabhan, D. G. Vlachos, R. J. Gorte, J. M. Vohs, *ACS Catal.* 2018, *8*, 7749-7759; b) N. Duong, Q. Tan, D. E. Resasco, *C. R. Chimie* 2018, *21*, 155-163; c) J. Zhang, L. D. Ellis, B. Wang, M. J. Dzara, C. Sievers, S. Pylypenko, E. Nikolla, J. W. Medlin, *Nat. Catal.* 2018, *1*, 148-155; d) Y. Shao, Q. Xia, L. Dong, X. Liu, X. Han, S. F. Parker, Y. Cheng, L. L. Daemen, A. J. Ramirez-Cuesta, S. Yang, Y. Wang, *Nat. Commun.* 2017, *8*, 16104-16112; e) Z. Luo, Z. Zheng, Y. Wang, G. Sun, H. Jiang, C. Zhao, *Green Chem.* 2016, *18*, 5845-5858; f) Q. Tan, G. Wang, L. Nie, A. Dinse, C. Buda, J. Shabaker, D. E. Resasco, *ACS Catal.* 2015, *5*, 6271-6283; g) S. Kusumoto, K. Nozaki, *Nat. Commun.* 2015, *6*, 6296-6302; h) X. Wang, R. Rinaldi, *Angew. Chem. Int. Ed.* 2013, *52*, 11499-11503; i) P. T. M. Do, A. J. Foster, J. Chen, R. F. Lobo, *Green Chem.* 2012, *14*, 1388-1397.
- [6] H. Ohta, K. Yamamoto, M. Hayashi, G. Hamasaka, Y. Uozumi, Y. Watanabe, *Chem. Commun.* 2015, *51*, 17000-17003.
- [7] a) J. Engelhardt, P. Lyu, P. Nachtigall, F. Schüth, Á. M. García, *ChemCatChem* **2017**, *9*, 1985-1991; b) H. Wan, R. V. Chaudhari, B. Subramaniam, *Top Catal.* **2012**, *55*, 129-139; c) Y. Romero, F. Richard, S. Brunet, *Appl. Catal. B: Environ.* **2010**, *98*, 213-223; d) E.-J. Shin, M. A. Keane, *Ind. Eng. Chem. Res.* **2000**, *39*, 883-892; e) G. Neri, A. M. Visco, A. Donato, C. Milone, M. Malentacchi, G. Gubitosa, *Appl. Catal. A: Gen.* **1994**, *110*, 49-59.
- [8] Z. Luo, C. Zhao, Catal. Sci. Technol. 2016, 6, 3476-3484.
- a) R. Hayes, G. G. Warr, R. Atkin, *Chem. Rev.* 2015, *115*, 6357-6426;
  b) W. Zhou, S. Inoue, T. Iwahashi, K. Kanai, K. Seki, T. Miyamae, D. Kim, Y. Katayama, Y. Ouchi, *Electrochem. Commun.* 2010, *12*, 672-675;
  c) L. Leclercq, A. R. Schmitzer, *Supramol. Chem.* 2009, *21*, 245-263.
- [10] a) Z. Lei, C. Dai, B. Chen, *Chem. Rev.* **2014**, *114*, 1289-1326; b) J. O. Valderrama, W. W. Sanga, J. A. Lazzús, *Ind. Eng. Chem. Res.* **2008**, 47, 1318-1330.
- [11] a) O. Brummel, F. Faisal, T. Bauer, K. Pohako-Esko, P. Wasserscheid, J. Libuda, *Electrochim. Acta* 2016, *188*, 825-836; b) J. Arras, E. Paki, C. Roth, J. Radnik, M. Lucas, P. Claus, *J. Phys. Chem. C* 2010, *114*, 10520-10526; c) J. Arras, M. Steffan, Y. Shayeghi, D. Ruppert, P. Claus, *Green Chem.* 2009, *11*, 716-723; d) C. W. Scheeren, G. Machado, S. R. Teixeira, J. Morais, J. B. Domingos, J. Dupont, *J. Phys. Chem. B* 2006, *110*, 13011-13020.
- [12] C. A. Schoenbaum, D. K. Schwartz, J. W. Medlin, Acc. Chem. Res. 2014, 47, 1438-1445.
- [13] M. M. J. Treacy, J. B. Higgins, Collection of Simulated XRD Powder Patterns for Zeolites, 5th ed., Elsevier, Amsterdam, 2007.
- [14] a) P. He, Y. Lou, H. Song, *Fuel* **2016**, *182*, 577-587; b) H. Wen, Y. Zhou, J. Xie, Z. Long, W. Zhang, J. Wang, RSC Adv. **2014**, *4*, 49647-

49654; c) M. Milanesio, G. Artioli, A. F. Gualtieri, L. Palin, C. Lamberti, *J. Am. Chem. Soc.* **2003**, *125*, 14549-14558.

- [15] a) Y. Yazawa, H. Yoshida, T. Hattori, *Appl. Catal. A: Gen.* 2002, 237, 139-148; b) A. N. Mansour, J. W. Cook Jr., D. E. Sayers, *J. Phys. Chem.* 1984, *88*, 2330-2334.
- [16] T. Yamamoto, A. Yukumoto, Bunseki Kagaku 2013, 6, 555-563.
- [17] This catalyst system does not selectively provide arenes under pressurized H<sub>2</sub>. As shown in the Supporting Information (Table S2, entry S7), the reaction of **1** under 10 atm H<sub>2</sub> gave aliphatic alcohol **5** as a predominant product.
- [18] J. D. Holbrey, W. M. Reichert, M. Nieuwenhuyzen, O. Sheppard, C. Hardacre, R. D. Rogers, *Chem. Commun.* 2003, 476-477.
- [19] The reaction of 4'-hydroxypropiophenone, a phenol containing carbonyl group, was also examined under the conditions shown in Table 2. As a result, full conversion was achieved after 8 h. However, the reaction gave low yields of HDO products (2 in 3% and 1 in 7%) along with a mixture of unidentifiable products. The presence of the carbonyl group may have caused undesired side reactions.

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Surface modification of a zeolitesupported Pt catalyst using ionic liquids enabled the selective hydrodeoxygenation of phenols into arenes at 110 °C under atmospheric pressure  $H_2$ , which are extremely milder reaction conditions than those generally used (300 °C or higher under pressurized  $H_2$ ).



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