HOKKAIDO UNIVERSITY

Title	Aqueous-phase hydrodeoxygenation of 4-propylphenol as a lignin model to n-propylbenzene over Re-Ni/ZrO2 catalysts
Author(s)	Feng, Bo; Kobayashi, Hirokazu; Ohta, Hidetoshi et al.
Citation	Journal of Molecular Catalysis A : Chemical, 388-389, 41-46 https://doi.org/10.1016/j.molcata.2013.09.025
Issue Date	2014-07
Doc URL	https://hdl.handle.net/2115/57014
Type	journal article
File Information	MOLCAA_R1_0918_clean.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Aqueous-phase hydrodeoxygenation of 4-propylphenol as a lignin model to *n*-propylbenzene over Re-Ni/ZrO_2 catalysts

Bo Feng[a], Hirokazu Kobayashi[a], Hidetoshi Ohta[b], Atsushi Fukuoka[a,*]

[a]*Catalysis Research Center, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan*

[b]*Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan*

**Corresponding author: Tel: +81-11-706-9140; fax: +81-11-706-9139; E-mail address: fukuoka@cat.hokudai.ac.jp*

Abstract: Aqueous-phase hydrodeoxygenation of 4-propylphenol as a lignin model to *n*-propylbenzene was carried out over various Ni based catalysts. Among the catalysts tested, Re-Ni/ZrO_2 showed the best catalytic performance. Addition of Re decreased the Ni particle size and greatly improved the catalytic activity. H_2 pressure, Re to Ni ratio and reaction temperature were tuned in the optimization of reaction conditions for favorable formation of *n*-propylbenzene. Under the conditions of 300 ˚C and 4 MPa H_2, the yield of *n*-propylbenzene reached 54% over Re-Ni/ZrO_2 (Re/Ni ratio 0.33) catalyst. It is suggested that the formation of *n*-propylbenzene proceeds via the hydrogenation of 4-propylphenol to form 4-propylcyclohexanol, followed by the dehydration to give 4-propylcyclohexene and the subsequent dehydrogenation to *n*-propylbenzene.

Keywords: Hydrodeoxygenation, Lignin Model, Ni Catalysts, Water

1. Introduction

Aromatic hydrocarbons are important feedstock for chemical industry, and currently aromatic hydrocarbons are synthesized from petroleum [1]. Under economic and environmental considerations, the replacement of petrochemical-based routes for the production of aromatics with renewable ones has received much attention in recent years. Lignin is the most abundant natural polymer composed of methoxylated phenylpropane units, and has significant potential as a source for the sustainable production of fuels and bulk chemicals [2]. Thus, catalytic transformation of lignin-derived platform chemicals into more valuable aromatic hydrocarbons is promising.

Hydrodeoxygenation (HDO) has been an essential process for the conversion of lignin-derived chemicals, and it generally involves two reaction paths: one leading to aliphatic hydrocarbons and the other to aromatic products [3]. Selective HDO of lignin-related phenols into aliphatic hydrocarbons has been extensively studied [4], but only a limited number of reports have addressed the HDO of phenols into aromatic hydrocarbons [5]. Traditional hydrotreating catalyst, sulfidied CoMo, is active in the gas-phase conversion of phenolics to aromatics, while it suffers from the deactivation caused by the coke formation and in-situ generated water molecules [6]. Mo-based catalysts [7] and Pd catalysts supported on sulfonated carbon aerogel [8] were also developed for the HDO of phenolic compounds to corresponding aromatic hydrocarbons; however, alkanes were used as the reaction solvents. Ni/SiO_2 was effectively used to promote the gas-phase treatment of phenol in mixed aqueous/methanolic solutions, in which product selectivity was strongly dependent on water content [9]. It is worth noting that actual lignin materials and the crude bio-oil always contain a large amount of water, and that water always forms in the HDO reaction. Thus, the conversion of lignin in water is more practical than in organic solvents. Furthermore, easy separation of the products from aqueous phase is the advantage of this approach. Therefore, the development of highly efficient and water-tolerant catalyst system is beneficial for the HDO of lignin and related chemicals into aromatic hydrocarbons. Previously, commercial 5% Pt/C catalyst was used for the conversion of *p*-cresol to toluene with ca. 45% yield in water under the conditions of 300 ˚C and 83 bar H_2 [10]. However, the reaction mechanism was not clearly discussed. For better understanding of the reaction pathway in the aqueous HDO of phenols, further investigation is still required.

Recently, our group reported the highly selective HDO of phenols to cycloalkanes in water by using supported metal catalysts such as Pt/AC (activated carbon) [11]. During this study, we found that 2% Pt/ZrO_2 facilitated the aqueous-phase HDO of 4-propylphenol to *n*-propylbenzene with 47% yield under the conditions of 280 ˚C, 2 MPa H_2 and 1 h. However, it deactivated sharply in the second run (Table S1). Continuing the development of more durable catalysts for the

conversion of lignin related chemicals to aromatic hydrocarbons, we report here the aqueous-phase HDO of 4-propylphenol as a lignin model to *n*-propylbenzene by Ni based catalysts. The reaction pathway is also investigated in detail.

2. Experimental

2.1 General

ZrO_2 (JRC-ZRO-5), TiO_2 (JRC-TIO-4(2)) and CeO_2 (JRC-CEO-2) were supplied by Catalysis Society of Japan. γ-Al_2O_3 (A-11) was purchased from Nishio Industry. SiO_2 (CAB-O-SIL M-5) was purchased from Acros Organics, and Nb_2O_5 from CBMM (Brazil). These metal-oxide supports were calcined in air at 500 ˚C for 4 h before use. Activated carbon (activated charcoal powder, denoted as AC) was purchased from Wako Pure Chemical Industries and used without further treatment. $Ni(NO_3)_2{\cdot}6H_2O$, NH_4ReO_4, $SnCl_2{\cdot}2H_2O$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ were purchased from Wako, $Ga(NO_3)_3{\cdot}nH_2O$ from Junsei Chemical and $Zn(NO_3)_2{\cdot}6H_2O$ from Kanto Chemical. 4-Propylphenol, *n*-propylbenzene, *n*-propylcyclohexane, 4-propylcyclohexanol, 4-propylcyclohexanone and 2-isopropylphenol were purchased from Tokyo Chemical Industry.

2.2 Preparation of catalysts

All the catalysts were prepared by the incipient-wetness impregnation method and Ni loading was kept at 10 wt%. For example, the procedure for preparing Re-Ni/ZrO_2 (Re/Ni ratio 0.33) was as follows: aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (1.17 g in 2 mL water) and NH_4ReO_4 (0.36 g in 1 mL water) were sequentially dropped onto ZrO_2 (2.0 g) powder with continuous stirring. After the mixture was stirred at room temperature for 15 h, the sample was evaporated to dryness and then dried in vacuum for 15 h. Then the sample was calcined in O_2 flow (50 mL/min) at 400 ˚C for 4 h and reduced in H_2 (50 mL/min) at 500 ˚C for 4 h, based on H_2-temperature-programmed reduction (TPR) measurements. For Re-Ni/AC, it was calcined under He and then reduced under H_2.

2.3 Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku Miniflex with Cu Kα radiation (λ = 0.15418 nm) at 30 kV and 15 mA. TPR was performed using a BELCAT (BEL Japan) with 5 vol% of H_2/Ar (30 mL min^{-1}) at a heating rate of 10 ˚C min^{-1} from 50 to 800 ˚C. Samples were pretreated in Ar flow (30 mL min^{-1}) at 100 ˚C for 1 h. The amounts of consumed H_2 for the samples were measured by a TCD detector and then estimated by referring to the amount obtained from reduction of CuO. NH_3-TPD was measured on the BELCAT equipped with a mass spectrometer.

After pretreatment at 200 ˚C for 2 h under He flow (30 mL min^{-1}), the sample was cooled down to 100 ˚C. Then ammonia saturation was carried out at 100 ˚C using 5 vol% of NH_3/He (30 mL min^{-1}) for 0.5 h, and the excess ammonia was removed by purging with He for 2 h. The desorption was operated at a heating rate of 10 ˚C min^{-1} from 100 to 800 ˚C. Desorbed ammonia was detected by a mass spectrometer (*m/z* = 16). TOC (total organic carbon) analysis was conducted on a Shimadzu SSM-5000A.

2.4 Catalytic HDO of 4-propylphenol in water

A typical reaction was carried out as follows: 4-propylphenol (5 mmol), catalyst (0.2 g) and H_2O (40 mL) were loaded into a batch-type reactor (OM Lab-Tech MMJ-100, SUS316, 100 mL). 4 MPa of H_2 was charged into the reactor, and then the reactor was kept at 300 ˚C for 1 h with stirring at 600 rpm. After reaction, the products were extracted with ethyl acetate and analyzed by GC and GC-MS using 2-isopropylphenol as an internal standard. GC analyses were carried out using a Shimadzu GC-14B equipped with an HR-1 column (0.25 mm × 50 m). GC-MS analyses were measured by a Shimadzu GC-2010/PARVUM2 equipped with the same column. The catalyst was recovered by centrifugation, followed by washing with ethyl acetate and dried at 120 ˚C for 2 h. The recovered catalyst was reused in the next reaction. The errors in yields of products were ca. 1% in reproductive tests.

For the time-course study, many batch reactions at different reaction time were conducted separately. Here, the reaction time “0” was defined as the time when the temperature of reaction mixture just reached the reaction temperature.

3. Results and discussion

3.1 Characterization of catalysts

Powder XRD patterns of the various catalysts were shown in Figure 1. ZrO_2 showed mainly monoclinic structure (Figure 1a), and peaks at 37˚, 43˚ and 63˚ corresponded to (111), (200) and (220) planes of NiO (Figure 1b and d). After H_2-reduction at 500 ˚C, the peaks of NiO disappeared, and a typical face-centered-cubic (fcc) crystalline Ni(0) pattern was formed in which a peak at 45˚ was attributed to (111) plane (Figure 1c and e). No diffraction peak assigned to the phases of Re species was detected on Re-Ni/ZrO_2, suggesting that Re species were well dispersed on the catalyst. Especially, it was worth noting that the peak of Ni(111) for Re-Ni/ZrO_2 was broaden compared with Ni/ZrO_2. Based on the Scherrer equation, it was shown that the Ni particle size was decreased from 11.0 nm to 5.5 nm with Re addition, indicating the strong interaction between Re and Ni species. This result is in accordance with a previous report that Pt particle size in Pt-Re/Al_2O_3

catalyst was reduced from 11 nm to 3.5 nm due to Re addition [12]. Promoting effect of Re addition on the dispersion of metal particles has also been reported on Ru-Re/SiO_2 [13].

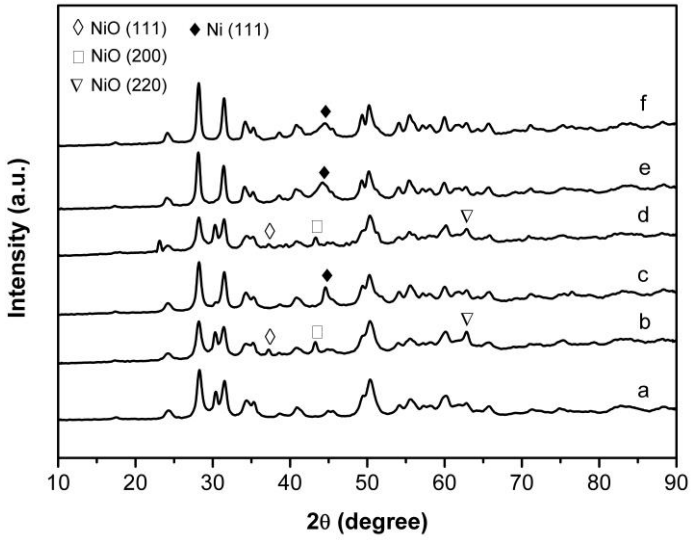


Figure 1 XRD patterns of (a) ZrO_2; (b) Ni/ZrO_2 after O_2 calcination; (c) Ni/ZrO_2 after H_2 reduction; (d) Re-Ni/ZrO_2 after O_2 calcination; (e) Re-Ni/ZrO_2 after H_2 reduction; (f) Re-Ni/ZrO_2 after 3rd run.

For further understanding of the role of Re, H_2-TPR profiles were measured. As shown in Figure 2a, there was no H_2 consumption for ZrO_2. For Re/ZrO_2 after O_2 calcination, the peak around 340 ˚C was attributed to the reduction of Re oxide species (Figure 2b). Ni/ZrO_2 presented a broad peak for NiO reduction in the range of 250-550 ˚C, and the H_2 consumption corresponded to the stoichiometric reduction of Ni^{2+} to Ni(0) (Figure 2c). Compared to Ni/ZrO_2, a sharp peak appeared around 340 ˚C on the Re-Ni/ZrO_2 catalyst (Figure 2d), which clearly showed that Re and Ni species were reduced simultaneously and the NiO reduction peak shifted to lower temperature. The similar phenomenon has been found by Tomishige *et al.* that Re can promote the reduction of Ir species on Re-Ir catalysts [14], which was related to the strong interaction between Re and Ir species. The interaction between Re and metal species has previously been examined on Ru-Re/SiO_2 [13], Pt-Re/NaY zeolite [15] and Pt-Re/TiO_2 [16], in which oxidized Re are attached to metal species. Experimentally, the difference in the H_2 consumption amount between Ni/ZrO_2 and Re-Ni/ZrO_2 was due to the reduction of Re species, and the H_2 consumption amount suggested that Re was reduced from +7 to +4 on the basis that Re was present as +7 after O_2 calcination. Therefore, it is suggested that cationic Re species act as anchors for Ni particles, which induces the decrease of the particle size of Ni.

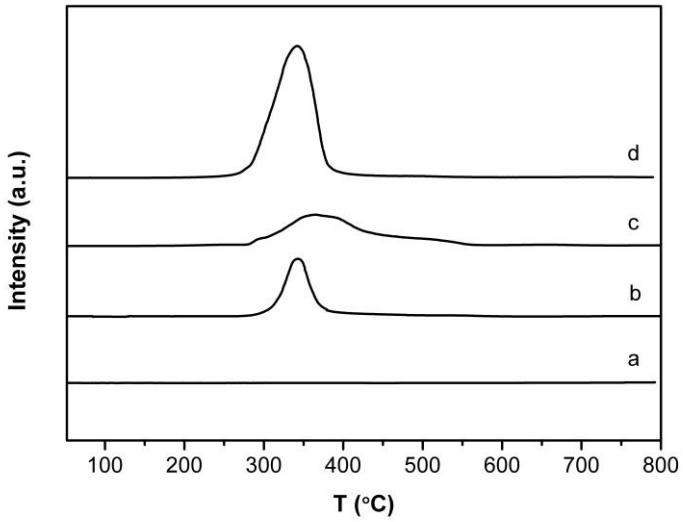


Figure 2 TPR profiles of (a) ZrO_2; (b) Re/ZrO_2 after O_2 calcination; (c) Ni/ZrO_2 after O_2 calcination; (d) $Re\text{-}Ni/ZrO_2$ after O_2 calcination.

NH_3-TPD profiles showed peaks around 300 ˚C for both Ni/ZrO_2 and $Re\text{-}Ni/ZrO_2$, corresponding to weak acid sites of the catalysts (Figure 3). A small peak appeared at around 600 ˚C for $Re\text{-}Ni/ZrO_2$, which suggested the presence of small amount of strong acid sites (0.01 mmol g^{-1}) (Figure 3b). Moreover, the total amount of acid sites for the two catalysts was almost the same (0.13 mmol g^{-1}), indicating that the addition of Re had a little influence on the acidity of the catalysts.

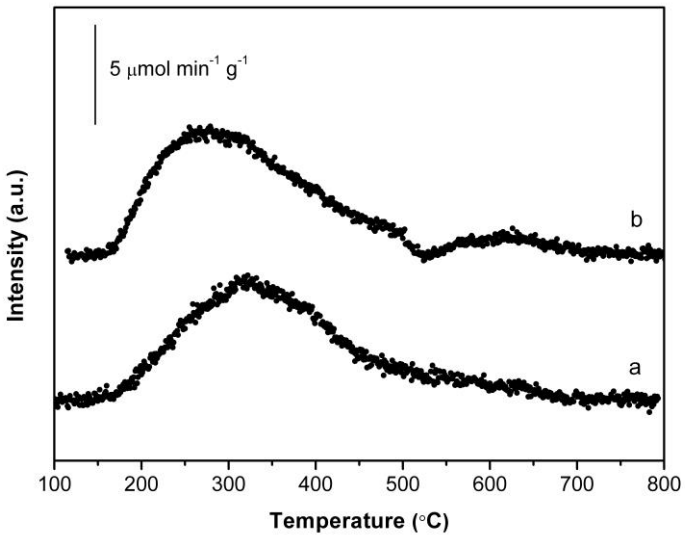


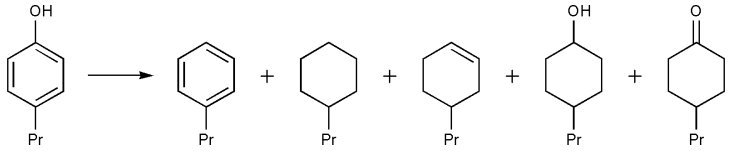
Figure 3 NH_3-TPD profiles of (a) Ni/ZrO_2; (b) $Re\text{-}Ni/ZrO_2$ (Re/Ni ratio: 0.33)

3.2 Catalytic aqueous-phase HDO of 4-propylphenol

Initially, we investigated the HDO of 4-propylphenol using various Ni catalysts in water under the conditions of 300 ˚C, 3 MPa H_2 and 1 h (Table 1). Monometallic catalyst Ni/ZrO_2 converted 4-propylphenol (**1**) into *n*-propylbenzene (**2**), aliphatic hydrocarbons (**3** and **4**), oxygenates (**5** and **6**) and some unidentified products with 41% conversion and 13% HDO degree (Entry 1), while Re/ZrO_2 showed no activity (Entry 2). Addition of different metals gave different catalytic performances. Ga-Ni/ZrO_2, Cu-Ni/ZrO_2 and Zn-Ni/ZrO_2 showed moderate activities and low HDO degrees (Entries 4-6), but Sn, Bi and Mo suppressed the conversion of **1** (Entries 7-9). Particularly, over Re-Ni/ZrO_2 the conversion was greatly improved to 96% compared with Ni/ZrO_2, and 48% of HDO degree was obtained (Entry 3). Thus, Re greatly improved the catalytic performance, which may be ascribed to the decreased particle size by Re addition.

It was also found that supports had a significant influence on the catalytic performance. For Re-Ni/TiO_2, conversion reached 98% with 50% HDO degree and 32% yield of **2** (Entry 10). Re-Ni supported on Al_2O_3 and SiO_2 favored the formation of **5** with high conversions (Entries 11 and 12). When CeO_2 and Nb_2O_5 were used as supports, moderate conversions were obtained (Entries 13 and 14). Re-Ni/AC promoted the reaction in almost 100% conversion, but the HDO degree and the yield of **2** was lower than those of ZrO_2 or TiO_2 supports with more by-products (Entry 15). Among the catalysts tested, Re-Ni/ZrO_2 and Re-Ni/TiO_2 were the most effective for the conversion of **1** into **2** in water. We used Re-Ni/ZrO_2 hereafter because Re-Ni/ZrO_2 gave a higher yield of **2** than Re-Ni/TiO_2 under the optimized conditions (vide infra).

Table 1 HDO of 4-propylphenol **1** by various Ni catalysts in water[a]



Entry	Catalyst	Conversion (%) (HDO degree)[b]	Yield (%)					
			2	**3**	**4**	**5**	**6**	**Others**
1	Ni/ZrO_2	41 (13)	6	6	1	11	0	17
2	Re/ZrO_2	0 (0)	0	0	0	0	0	0
3	$Re\text{-}Ni/ZrO_2$	96 (48)	26	19	3	27	0	21[c]
4	$Ga\text{-}Ni/ZrO_2$	51 (12)	6	5	1	18	0	22
5	$Cu\text{-}Ni/ZrO_2$	42 (9)	2	6	1	20	0	14
6	$Zn\text{-}Ni/ZrO_2$	27 (5)	2	3	0.2	8	0	14
7	$Sn\text{-}Ni/ZrO_2$	9 (1)	0.3	0.4	0.1	1	1	6
8	$Bi\text{-}Ni/ZrO_2$	4 (0.2)	0.1	0.1	0	0.2	0	4
9	$Mo\text{-}Ni/ZrO_2$	1 (0.2)	0.1	0	0.1	0.1	0	1.0
10	$Re\text{-}Ni/TiO_2$	98 (49)	32	14	3	19	0	29
11	$Re\text{-}Ni/Al_2O_3$	96 (14)	9	4	1	62	0	20
12	$Re\text{-}Ni/SiO_2$	91 (39)	12	24	3	27	0	26
13	$Re\text{-}Ni/CeO_2$	52 (3)	2	1	0.1	28	6	16
14	$Re\text{-}Ni/Nb_2O_5$	43 (5)	3	2	0.3	15	3	20
15	Re-Ni/AC	99 (34)	18	16	0.2	25	0	41

[a]Reaction conditions: 4-propylphenol **1** 5.0 mmol, catalyst 0.2 g, 10 wt% Ni loading, M/Ni molar ratio 0.33, water 40 mL, initial H_2 pressure at RT 3 MPa, 300 ˚C, 1 h, 600 rpm. [b]HDO degree was the extent of removed oxygen, defined as the sum of the yields of deoxygenated products **2**, **3** and **4**. [c]Methylcyclohexane (0.3%), ethylcyclohexane (0.6%), toluene (0.6%), ethylbenzene (0.8%), CH_4 (0.4%), and unidentified products (18%). TOC measurement indicated no coke formation on catalyst.

Then Re to Ni ratio, reaction temperature and H_2 pressure were further investigated. Table S2 showed the influence of different Re/Ni ratio on the catalytic performance. The conversions were low below the Re/Ni ratio of 0.20, and the yield of **2** decreased at the ratios of 0.50 and 1.0. The catalytic composition of Re/Ni = 0.33 ± 0.15 was the best range for the production of **2**. Reaction temperature showed a significant influence on the selectivity of the product (Table S3). Almost full conversion was obtained and the main product was **5** at 260 ˚C, indicating that the rate-determining

step was the conversion of **5**. At higher temperatures, **3** was obtained in a high yield at 280 ˚C (Entry S9), whereas **2** was the main product at 300 ˚C (Entry S10). High temperature was favorable for the dehydrogenation and selective synthesis of **2**. Table S4 showed that H_2 pressure had an evident influence on the catalytic performance. At low H_2 pressure (2 MPa), the activity was low with **5** as the main product. As the H_2 pressure increased to 3 MPa, conversion reached 96% with complicated product distribution and high H_2 pressure (5 MPa) caused the formation of **3**. 4 MPa H_2 appeared to obtain a high yield of **2**, and under the conditions of 300 ˚C and 4 MPa H_2, the yield of *n*-propylbenzene was boosted to 54% over Re-Ni/ZrO_2 catalyst (Table 2, Entry 16). This yield was higher than the maximum yield obtained by Re-Ni/TiO_2 (42%, Table S5).

We tested the recyclability of Re-Ni/ZrO_2 for HDO of 4-propylphenol in water. As shown in Table 2, the conversion was maintained but the yield of **2** decreased to 32-33% in the second and third runs, and the yield of **5** increased (Entries 16-18). This indicates that the hydrogenation or dehydrogenation ability of Ni particles decreases in the reuse experiments. To study the deactivation of the catalyst, several measurements were conducted. XRD analysis showed that Ni particle size was 5.9 nm after the 3rd run (Figure 1f), showing no obvious aggregation of Ni particles (original size 5.5 nm). TOC analysis of the spent catalyst showed no coke formation. The leaching amount of Ni was only 45 ppm, corresponding to 10wt% of catalyst, and that of Re was less than detection limit (2 ppm). Hence, the deactivation may be due to the slight oxidation of the Ni surface [17].

Table 2 Recyclability of Re-Ni/ZrO_2 for HDO of 4-propylphenol **1** in water[a]

Entry	Conversion (%)	Yield (%)					
		2	**3**	**4**	**5**	**6**	**Others**
16 (1^{st})	100	54	17	1	5	0	23
17 (2^{nd})	100	33	15	2	23	0	27
18 (3^{rd})	100	32	12	1	28	0	26

[a]Reaction conditions: 4-propylphenol **1** 5.0 mmol, Re-Ni/ZrO_2 0.2 g, 10 wt% Ni loading, Re/Ni molar ratio 0.33, water 40 mL, initial H_2 pressure at RT 4 MPa, 300 ˚C, 1 h, 600 rpm.

3.3 Investigation of the reaction pathway

Figure 4 represents the time-course of the conversion of 4-propylphenol over Re-Ni/ZrO_2. Even at 0 h, 99% conversion was obtained with the formation of **2** (yield 5%), **3** (2%) and **5** (87%). This result reveals that the major intermediate is **5** and the hydrogenation of aromatic ring of **1** is rapid. Accordingly, the subsequent steps should be focused in this time-course study. As the

reaction proceeded, the yield of **2**, **3**, and others increased in parallel along with the gradual decrease of the yield of **5**. Moreover, the yield of **4** and **6** did not obviously change during the reaction. **5** is the common intermediate for the formation of **2** and **3**.

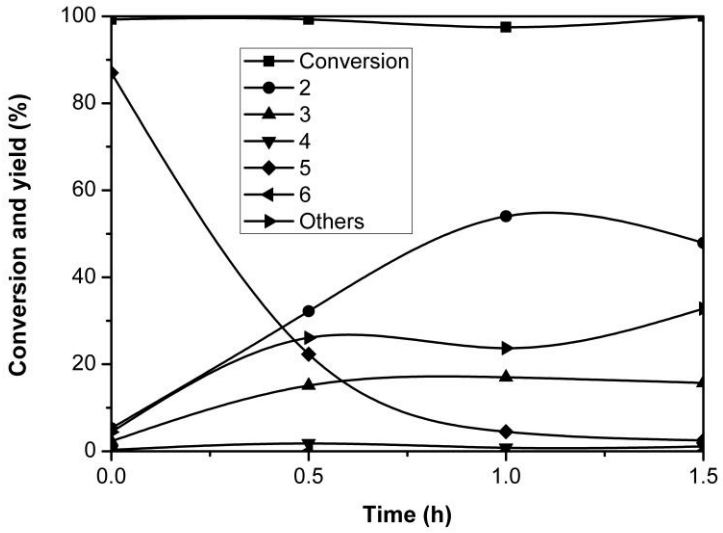


Figure 4 Time-course of the conversion of 4-propylphenol over Re-Ni/ZrO_2. Reaction conditions: 4-propylphenol **1** 5.0 mmol, Re-Ni/ZrO_2 0.2 g, 10 wt% Ni loading, Re/Ni molar ratio 0.33, water 40 mL, initial H_2 pressure at RT 4 MPa, 300 ˚C, 600 rpm.

Next, time-course of **5** over Re-Ni/ZrO_2 was studied. Here, we used 3.7 MPa as the initial H_2 pressure because H_2 was consumed during the temperature rise. Actually, the H_2 pressure at RT was 3.7 MPa at the reaction time 0 in Figure 4. As shown in Figure 5, **5** was gradually converted into **2** and **3** under the conditions of 300 ˚C and 3.7 MPa H_2. Notably, the reaction pathway was similar to that using **1** as a substrate, and it was further indicated that **5** was converted into **2** (52% yield) and **3** (24%) in 1 h, which was in agreement with the previous results in Figure 4. Typically, the formation of **3** from **5** proceeded via the dehydration and subsequent hydrogenation. The pK_w of water is 12 at 300 ˚C [18], suggesting that the dehydration can be catalyzed by *in situ* generated protons and indeed some groups reported the dehydration of alcohols in pure water at high temperature [19]. In our previous work, we also found that without catalyst, **5** was dehydrated to form **4** in 11% yield at 280 ˚C, and the addition of base completed suppressed the dehydration [11a]. Additionally, NH_3-TPD measurement showed the presence of some weak acid sites and a small amount of strong acid sites on Re-Ni/ZrO_2 (Figure 3b). Therefore, in the present system, the dehydration of **5** was catalyzed by the acid sites on Re-Ni/ZrO_2 and *in situ* generated protons.

After the dehydration of **5**, **3** was formed by hydrogenation of **4**. However, the formation of **2** from **5** was intriguing under H_2 pressure, and further experiments were conducted to study this

pathway. Addition of $CaCO_3$ as a base to this reaction greatly suppressed the formation of both **2** and **3** (Table 3, Entries 19 and 20), which indicates these steps need the acid sites. Note that we have confirmed that the catalyst has not been physically covered by $CaCO_3$; the hydrogenation of **1** smoothly takes place in the presence of $CaCO_3$ (Entry 23). The suppression of the formation of **3** by the base was expected, but the suppression of **2** indicated the dehydration may also be involved in this pathway. Furthermore, it was reported that cyclohexene hydrogenation and dehydrogenation strongly depended on the reaction temperature and particle size [20]. Cyclohexene was hydrogenated to cyclohexane at low temperature (<150 ˚C), while simultaneous hydrogenation and dehydrogenation occurred in an intermediate temperature range. Dehydrogenation was the dominated reaction path in a high temperature regime (>300 ˚C); thus benzene can be formed via dehydrogenation even in the presence of H_2. This is in accordance with the temperature influence on favorable formation of **2** at high temperature in our system (Table S3). Smaller particles have lower activation energy and are more active for dehydrogenation, which was the reason why Re-Ni/ZrO_2 showed higher catalytic activity (Table 1, Entries 1 and 3). Accordingly, it is suggested that **2** is formed via hydrogenation of **1** to **5**, rapid dehydration of **5** to **4** and dehydrogenation of **4** to **2**.

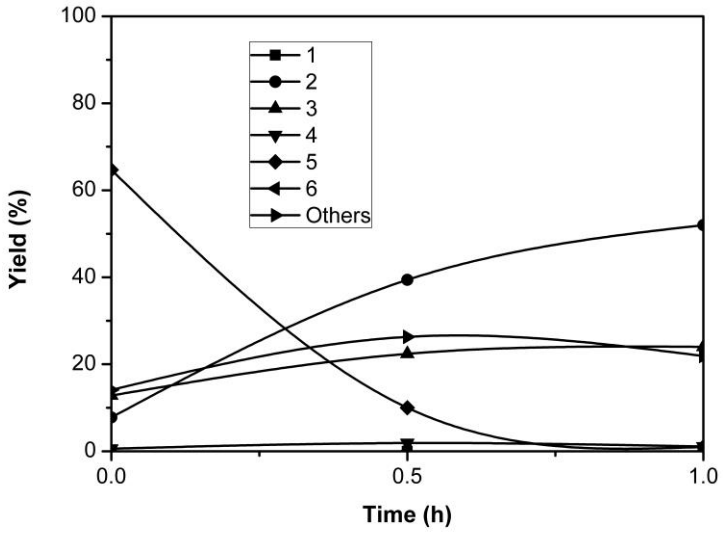


Figure 5 Time-course of the conversion of **5** over Re-Ni/ZrO_2. Reaction conditions: 4-propylcyclohexanol **5** 5.0 mmol, Re-Ni/ZrO_2 0.2 g, 10 wt% Ni loading, Re/Ni molar ratio 0.33, water 40 mL, initial H_2 pressure at RT 3.7 MPa, 300 ˚C, 600 rpm.

From the above results, it is shown that **1** is first converted into **5** during the temperature rise, and then **5** is converted into **2** and **3**. For further understanding of the reaction pathways, more

control experiments were carried out over Re-Ni/ZrO_2 catalyst (Table 3). **2** converted into **3** (11% yield) and **4** (1% yield) (Entry 21). When **3** was used as a substrate, almost no products formed (Entry 22), indicating that **3** was stable under the reaction conditions. In the presence of a base (Entry 23), **1** was mainly converted to **5** (76% yield), and small amounts of **2** and **3** were formed, which was in agreement with the result of Entry 20. The suppression effect by the base indicates the direct C−O bond hydrogenolysis is not involved in the formation of **2**. In fact, theoretical calculations show that the bond dissociation energy of $C_{aromatic}$−OH bond is 468 kJ/mol, which is higher than that (385 kJ/mol) of the $C_{aliphatic}$−OH bond [21]. Consequently, the direct cleavage of $C_{aromatic}$−OH bond is difficult under the reaction conditions.

Table 3 Control experiments over Re-Ni/ZrO_2 catalyst[a]

Entry	Substrate	Conversion (%)	Yield (%)						
			1	**2**	**3**	**4**	**5**	**6**	**Others**
19[b]	**5**	99	0	52	24	1	−	0	22
20[c]	**5**	16	1	2	1	0.1	−	0	12
21	**2**	50	0	−	11	1	0	0	38
22	**3**	39	0	0	−	0	0	0	39
23[c]	**1**	94	−	2	0.4	0	76	4	11

[a]Reaction conditions: substrate 5.0 mmol, Re-Ni/ZrO_2 0.2 g, 10 wt% Ni loading, Re/Ni molar ratio 0.33, water 40 mL, initial H_2 pressure at RT 4 MPa, 300 ˚C, 1 h, 600 rpm. [b]Initial H_2 pressure at RT 3.7 MPa. [c]$CaCO_3$ (2.0 mmol) was added.

Based on these results, we propose the reaction pathways of the aqueous-phase conversion of 4-propylphenol on Re-Ni/ZrO_2 (Figure 6): (i) the hydrogenation of **1** into **5** during the temperature rise, (ii) dehydrogenation of **5** to **6**, (iii) acid-catalyzed dehydration of **5** to **4**, (iv) hydrogenation of **4** to **3**, (v) dehydrogenation of **4** to **2**, and (vi) hydrogenation of **2** to **3**. The reaction mechanism is different from the typical one for the HDO reaction of phenols, which generally proceeds via two reactions: one is direct hydrogenolysis of C−O bond giving aromatic products and the other is hydrogenation of aromatic ring of phenol to form a cyclohexanol intermediate that rapidly converts to cyclohexane products [3].

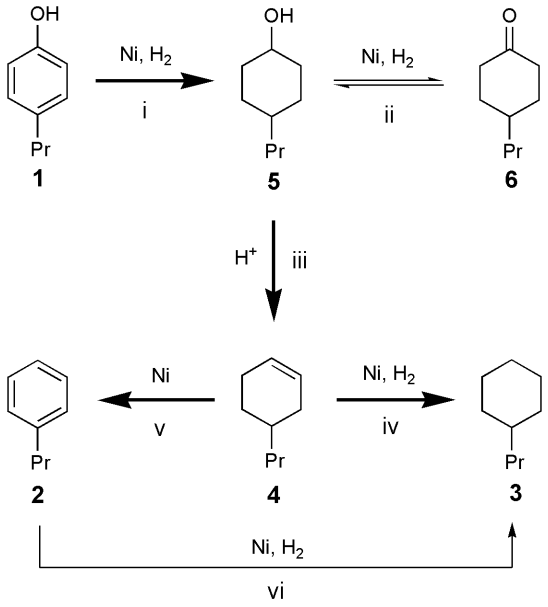


Figure 6 Proposed reaction pathway of the HDO of 4-propylphenol over Re-Ni/ZrO_2 in water. (Other by-products possibly come from all the compounds shown in this scheme.)

4. Conclusions

We have developed a bimetallic catalyst Re-Ni/ZrO_2 for the conversion of 4-propylphenol into *n*-propylbenzene in water. Addition of Re to Ni/ZrO_2 showed great improvement on the catalytic activity. The formation of *n*-propylbenzene was catalyzed via hydrogenation of the phenolic ring followed by rapid dehydration and then dehydrogenation. This provides a new route to convert lignin-related chemicals into aromatic hydrocarbons in aqueous phase. Further improvement of the durability and application of this catalytic system to bio-oil are in progress.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (KAKENHI, 20226016) from the Japan Society for the Promotion of Science (JSPS).

References

[1] S. Matar, L. F. Hatch, Chemistry of Petrochemical Processes, 2nd ed., Gulf Publishing Company, Houston, Texas, 2000.

[2] (a) J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, Chem. Rev. 110 (2010) 3552-3599; (b) M. P. Pandey, C. S. Kim, Chem. Eng. Technol. 34 (2011) 29-41; (c) G. W. Huber, S. Iborra, A. Corma, Chem. Rev. 106 (2006) 4044-4098.

[3] (a) E. Laurent, B. Delmon, Ind. Eng. Chem. Res. 32 (1993) 2516-2524; (b) C. Moreau, C. Aubert, R. Durand, N. Zmimta, P. Geneste, Catal. Today 4 (1988) 117-131; (c) E. O. Odebunmi,

D. F. Ollis, J. Catal. 80 (1983) 56-64; (d) F. E. Massoth, P. Politzer, M. C. Concha, J. S. Murray, J. Jakowski, J. Simons, J. Phys. Chem. B 110 (2006) 14283-14291.

[4] (a) D. Y. Hong, S. J. Miller, P. K. Agrawal, C. W. Jones, Chem. Commun. 46 (2010) 1038-1040; (b) C. Zhao, Y. Kou, A. A. Lemonidou, X. Li, J. A. Lercher, Angew. Chem. Int. Ed. 48 (2009) 3987-3990; (c) N. Yan, Y. Yuan, R. Dykeman, Y. Kou, P. J. Dyson, Angew. Chem. Int. Ed. 49 (2010) 5549-5553; (d) C. Zhao, J. A. Lercher, Angew. Chem. Int. Ed. 51 (2012) 5935-5940; (e) C. Zhao, J. A. Lercher, ChemCatChem 4 (2012) 64-68; (f) Q. Bu, H. Lei, A. H. Zacher, L. Wang, S. Ren, J. Liang, Y. Wei, Y. Liu, J. Tang, Q. Zhang, R. Ruan, Bioresour. Technol. 124 (2012) 470-477.

[5] (a) R. K. M. R. Kallury, W. M. Restivo, T. T. Tidwell, D. G. B. Boocock, A. Crimi, J. Douglas, J. Catal. 96 (1985) 535-543; (b) Y. Yang, A. Gilbert, C. Xu, Appl. Catal. A: Gen. 360 (2009) 242-249; (c) M. Á. González-Borja, D. E. Resasco, Energy Fuels 25 (2011) 4155-4162; (d) R. N. Olcese, M. Bettahar, D. Petitjean, B. Malaman, F. Giovanella, A. Dufour, Appl. Catal. B: Environ. 115-116 (2012) 63-73; (e) H. Y. Zhao, D. Li, P. Bui, S. T. Oyama, Appl. Catal. A: Gen. 391 (2011) 305-310; (f) B. S. Gevert, J. E. Otterstedt, F. E. Massoth, Appl. Catal. 31 (1987) 119-131; (g) P. T. M. Do, A. J. Foster, J. Chen, R. F. Lobo, Green Chem. 14 (2012) 1388-1397.

[6] T. R. Viljava, R. S. Komulainen, A. O. I. Krause, Catal. Today 60 (2000) 83-92.

[7] V. M. L. Whiffen, K. J. Smith, Energy Fuels 24 (2010) 4728-4737.

[8] H. W. Park, U. G. Hong, Y. J. Lee, I. K. Song, Catal. Commun. 20 (2012) 89-93.

[9] E. J. Shin, M. A. Keane, Ind. Eng. Chem. Res. 39 (2000) 883-892.

[10] H. Wan, R. V. Chaudhari, B. Subramaniam, Top Catal. 55 (2012) 129-139.

[11] (a) H. Ohta, H. Kobayashi, K. Hara, A. Fukuoka, Chem. Commun. 47 (2011) 12209-12211; (b) H. Kobayashi, H. Ohta, A. Fukuoka, Catal. Sci. Technol. 2 (2012) 869-883.

[12] S. Rezgui, R. Jentoft, B. C. Gates, J. Catal. 163 (1996) 496-500.

[13] L. Ma, D. He, Catal. Today 149 (2010) 148-156.

[14] (a) Y. Nakagawa, Y. Shinmi, S. Koso, K. Tomishige, J. Catal. 272 (2010) 191-194; (b) Y. Amada, Y. Shinmi, S. Koso, T. Kubota, Y. Nakagawa, K. Tomishige, Appl. Catal. B: Environ. 105 (2011) 117-127.

[15] S. K. Purnell, J.-R. Chang, B. C. Gates, J. Phys. Chem. 97 (1993) 4196-4205.

[16] H. Iida, A. Igarashi, Appl. Catal. A: Gen. 303 (2006) 192-198.

[17] H. Kobayashi, Y. Hosaka, K. Hara, B. Feng, Y. Hirosaki, A. Fukuoka, Green Chem., in press, doi: 10.1039/C3GC41357H.

[18] N. Akiya, P. E. Savage, Chem. Rev. 102 (2002) 2725-2750.

[19] (a) N. Akiya, P. E. Savage, Ind. Eng. Chem. Res. 40 (2001) 1822-1831; (b) B. Kuhlmann, E. M. Arnett, M. Siskin, J. Org. Chem. 59 (1994) 3098-3101; (c) M. J. Antal, Jr., M. Carlsson, X. Xu, D. G. M. Anderson, Ind. Eng. Chem. Res. 37 (1998) 3820-3829.

[20] (a) R. M. Rioux, B. B. Hsu, M. E. Grass, H. Song, G. A. Somorjai, Catal. Lett. 126 (2008) 10-19; (b) A. Fási, I. Pálinkó; T. Katona, M. Bartók, J. Catal. 167 (1997) 215-223; (c) J. M. Cogen, K. E.-Nikpay, R. H. Fleming, S. M. Baumann, W. F. Maier, Angew. Chem. Int. Ed. Engl. 26 (1987) 1182-1184.

[21] E. Furimsky, Appl. Catal. A: Gen. 199 (2000) 147-190.