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Selective hydrodeoxygenation of lignin-related 4-propylphenol into *n*-propylbenzene in water by Pt-Re/ZrO_2 catalysts

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ABSTRACT

Bimetallic Pt-Re/ZrO_2 catalysts were developed for the selective hydrodeoxygenation of 4-propylphenol as a lignin model to *n*-propylbenzene in water. The addition of Re to Pt/ZrO_2 improved the catalyst stability and product selectivity. Reaction temperature greatly affected not only reaction efficiency but also product distribution. *n*-Propylbenzene was obtained in up to 73% yield with ca. 80% selectivity. After the reaction, the catalyst was deactivated possibly due to water-induced wrapping of Pt nanoparticles in ZrO_2. The reaction may involve the hydrogenation of 4-propylphenol to 4-propylcyclohexanol, followed by the dehydration to give 4-propylcyclohexene and the subsequent dehydrogenation to *n*-propylbenzene.

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1. Introduction

The use of renewable biomass for the synthesis of petrochemicals is crucial to reduce the dependency on limited reserves of fossil fuels [1–4]. Due to the structure and availability, lignin is considered as a promising resource of aromatic hydrocarbons which are industrially important feedstock for producing a wide variety of useful chemicals such as polymers, pharmaceuticals, agrochemicals and electronic chemicals [5]. Hydrodeoxygenation (HDO) is an important technology for upgrading of lignin and related chemicals into aliphatic [6–9] and aromatic hydrocarbons [10–16]. For the synthesis of aromatic hydrocarbons, conventional sulfided CoMo catalysts show good activity [17–19]; however, they suffer from the deactivation caused by coke formation and in-situ generated water in the HDO reaction [20]. Ni/SiO_2 was developed for the gas-phase conversion of phenol to benzene in mixed aqueous/methanolic solutions, in which product selectivity was greatly dependent on water content [21]. It should be noted that actual lignin and bio-oils always contain plenty of water. Therefore, the development of highly efficient and water-tolerant catalyst system is desirable for the HDO of lignin and related chemicals into aromatic hydrocarbons.

Aqueous-phase HDO of phenols has been extensively investigated in recent years [22–26]. This process is suitable for the conversion of water-containing lignin-related chemicals, and the easy separation of the organic products from the aqueous phase is also beneficial. Pt/C [27] and Ni-Re/ZrO_2 [28] were evaluated in the HDO of phenols into aromatic hydrocarbons in water. However, the yields and selectivities of aromatic products are still insufficient. We previously reported the aqueous-phase conversion of phenols into aliphatic hydrocarbons by Pt/AC (activated carbon) [29,30]. During our continuous efforts to improve the catalyst efficiency, we found that Pt-Re/ZrO_2 catalysts facilitated the HDO of 4-propylphenol (**1**) into *n*-propylbenzene (**2**) with high yields and selectivities (Scheme 1). Herein, we report the details of characterization and catalytic behavior of Pt-Re/ZrO_2 in the aqueous-phase HDO reaction.

2. Experimental

2.1. General

ZrO_2 (JRC-ZRO-2), 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 and SiO_2 (CAB-O-SIL M-5)

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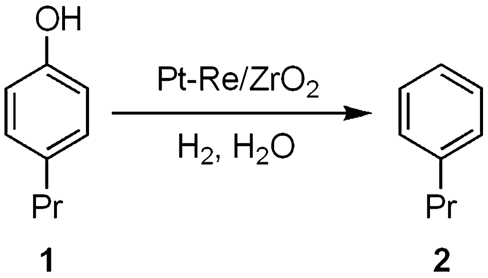

Scheme 1. Selective conversion of 4-propylphenol **1** to *n*-propylbenzene **2**.

from Acros Organics. These metal-oxide supports were calcined in air at 400 °C for 4 h before use. Activated carbon (activated charcoal Norit SX Ultra, denoted as AC) was purchased from Aldrich and used without further treatment. The following chemicals were purchased and used as received: $H_2PtCl_6 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$ from Kanto; NH_4ReO_4, $SnCl_2 \cdot 2H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $PdCl_2$, $Na_2WO_4 \cdot 2H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ from Wako; $Ga(NO_3)_3 \cdot nH_2O$ and $In(NO_3)_3 \cdot 3H_2O$ from Junsei; aqueous solution of H_2IrCl_6 from Furuya Metals; 4-propylphenol, propylbenzene, propylcyclohexane, 4-propylcyclohexanol and 4-propylcyclohexanone from Tokyo Chemical Industry.

2.2. Preparation of catalysts

All the catalysts were prepared by the co-impregnation method and Pt loading was kept at 2 wt%. For example, the procedure for preparing Pt-Re/ZrO_2 (Pt/Re molar ratio 3) was as follows: aqueous solutions of H_2PtCl_6 (0.211 mmol in 10 mL water) and NH_4ReO_4 (0.070 mmol in 300 μL water) were sequentially added to a mixture of ZrO_2 (2.00 g) and water (30 mL) with continuous stirring. The reaction mixture was stirred at room temperature for 15 h, evaporated to dryness and dried under vacuum. The sample was calcined in a fixed-bed flow reactor with O_2 (30 mL min^{-1}) at 400 °C for 2 h, then reduced with H_2 (30 mL min^{-1}) at 400 °C for 2 h to give Pt-Re/ZrO_2 catalyst. For Pt-Re/AC, only H_2 reduction was performed after drying the impregnated sample. The prepared catalysts were then exposed to air at room temperature for their passivation.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex using Cu Kα radiation (λ = 0.15418 nm) at 30 kV and 15 mV. N_2 adsorption–desorption analyses were performed at −196 °C with a BEL Japan BELSORP-mini II after heating the samples at 120 °C under vacuum for 2 h. Specific surface areas of samples were calculated according to the Brunauer–Emmett–Teller (BET) method. Pore size distributions were estimated by the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was performed with a JEOL JPC-9010MC using Mg Kα radiation (1253.6 eV) at 100 W and a pass energy of 20 eV. The binding energies were calibrated using adventitious carbon (C_{1s} peak at 284.8 eV). Pt L_3- and Re L_3-edge X-ray absorption fine structure (XAFS) was measured at room temperature in the transmission mode with a synchrotron radiation (ring energy 2.5 GeV, 450 mA) through a Si(1 1 1) double-crystal monochromator at BL-12 C beam line on KEK-PF (Proposal No. 2013G222). The measurement was conducted in the quick XAFS mode (20 s for 1 scan) and repeated 64 times to improve the signal–noise ratio. Transmission electron microscopy (TEM) was conducted with a JEOL JEM-2000ES at an accelerating voltage of 200 kV. Energy dispersive X-ray spectroscopy (EDX) was measured on a Shimadzu Rayny EDX-720. CO chemisorption was carried out with a BEL Japan BELCAT-A. Prior to the chemisorption experiment, a sample was reduced by H_2 at 200 °C for 100 min, followed by cooling to 50 °C under He flow. The chemisorption of CO was performed at 50 °C (with 10% CO in He), where an equilibrium was assumed when no further CO adsorption was observed.

Table 1
Structural parameters of catalysts.

Catalyst	S_{BET} ($m^2 g^{-1}$)[a]	d_p (nm)[b]	d_{TEM} (nm)[c]
ZrO_2	90	3.3	–
Pt/ZrO_2	72	3.7	–[f]
Pt-Re/ZrO_2[d]	74	3.3	–[f]
Pt-Re/ZrO_2 after the reaction[e]	65	3.7	1.7 ± 0.2

[a] BET surface area.
[b] Average pore diameter.
[c] Mean diameter of Pt particle by TEM analysis.
[d] Pt/Re molar ratio 3.
[e] After the reaction in entry 18, Table 3.
[f] Pt nanoparticles were not observed.

2.4. Catalytic HDO of 4-propylphenol in water

A typical procedure: 4-propylphenol (5.0 mmol, 681 mg), catalyst (2 wt% Pt loading, 98 mg) and water (40 mL) were charged in a well dried high-pressure batch reactor (OM Lab-Tech MMJ-100, SUS316, 100 mL). After pressurization with H_2 to 2 MPa at room temperature, the reactor was heated to the desired reaction temperature with continuous stirring at 600 rpm. Then, the reactor was kept at the reaction temperature for 1 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate and the organic layer was 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 integrator (C-R8A) with a capillary column (HR-1, 0.25 mm i.d. × 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 in an oven at 120 °C for 2 h. The recovered catalyst was reused in the next reaction.

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

3. Results and discussion

3.1. Characterization of Pt/ZrO_2 and Pt-Re/ZrO_2 catalysts

Characterization of ZrO_2, Pt/ZrO_2, and Pt-Re/ZrO_2 were performed by N_2 adsorption and XRD analyses. The structural parameters were summarized in Table 1. ZrO_2, Pt/ZrO_2, and Pt-Re/ZrO_2 have BET surface areas of 72–90 $m^2 g^{-1}$ with a pore size of 3.3–3.7 nm. In the XRD patterns of these samples, large peaks of monoclinic ZrO_2 phase and a small peak of tetragonal ZrO_2 phase were observed (Fig. 1(a)–(c)). TEM and XPS measurements of Pt/ZrO_2 and Pt-Re/ZrO_2 were conducted to estimate the metal particle size and the electronic states of the Pt and Re species. The Pt nanoparticles were not observed on the TEM images of Pt/ZrO_2 and Pt-Re/ZrO_2, suggesting the high dispersion of Pt nanoparticles (Fig. 2(a) and (b)). The XPS analyses of Pt/ZrO_2 and Pt-Re/ZrO_2 showed that Pt existed as Pt(0) and oxidized Pt species on the catalyst surface (Fig. 3). The peaks in Pt_{4f} region of Pt-Re/ZrO_2 ($Pt_{4f7/2}$ = 72.7 eV) were observed at higher binding energy than that of Pt/ZrO_2 ($Pt_{4f7/2}$ = 71.7 eV), suggesting the interaction of Pt with Re [31,32]. The Re_{4f} peaks of Pt-Re/ZrO_2 indicate that the major Re species is Re(6+); however, more information was not obtained due

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