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# Hydrodeoxygenation of lignin-derived monomers and lignocellulose pyrolysis oil on the carbon-supported Ru catalysts

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ABSTRACT

Five carbon materials, including multi-walled carbon nanotubes (MWCNT), carbon aerogel (CARF), carbon black (Vulcan carbon), activated carbon (AC), and graphite, were used as supports of the carbon-supported Ru catalysts, and the hydrodeoxygenation of lignin-derived monomers and lignocellulose pyrolysis oil was performed. Ru/MWCNT exhibited the highest deoxygenation activity, and the origin of the improved catalytic activity was studied. The metal dispersion, the acidity as measured by means of temperature-programmed desorption, the pore structure, and the surface area were investigated in an effort to understand the catalysis results. We observed that the quantity of accessible Ru nanoparticles on the mesopores determined the hydrodeoxygenation activity.

## 1. Introduction

Lignocellulosic biomass is a potential alternative source for the production of biofuels as a replacement for petroleum [1]. This type of biomass can be converted to the liquefied intermediates through biological [2] or thermochemical [3] degradation. Fast pyrolysis [4] is one of the most promising thermochemical methods for valorizing lignocellulosic biomass to obtain its liquefied product or a bio-oil. Although bio-oil is obtained from a sustainable source of biomass and is predicted to reduce the total amount of $CO_2$ during its life cycle, its high oxygen content limits its direct use in machines which use petroleum. In addition, the instability [5] and difficult storage [6] of oxygenate-rich bio-oil represent the major challenges preventing its wider use. Therefore, the development of processes which stabilize the oil and remove the oxygen content is required to upgrade bio-oils to obtain petroleum-like hydrocarbon fuels.

Hydrodeoxygenation (HDO) is a process which can be used to upgrade bio-oil to deoxygenated hydrocarbons by catalytically removing oxygen atoms as water, alcohols, and other oxygenates [7], producing stable, petroleum-grade fuels [8,9]. In order to develop reliable catalytic HDO processes and highly active catalysts, efforts have been made using bio-oil model compounds including phenol [10], guaiacol [11,12], eugenol [13], and vanillin [14], as bio-oil is a complex mixture whose contents and properties are often difficult to understand. It is well known that reactant–catalyst interactions play a role in the HDO of lignin-derived compounds [15]. When supported catalysts can catalyze the HDO process, the supports may also improve the catalytic activity. Thus, extensive studies of HDO have been performed for the noble metals supported on solid acids, including silica [16], alumina [10,17], silica–alumina [12,18], titania [19], zeolites [20], and other metal oxides. These metal oxides, however, frequently cause coke formation because of their acidity. In addition, the large amount of aqueous acids in the bio-oil leaches the metal oxide supports, deactivating the catalyst. Considering the challenges associated with pyrolysis oil, stable supports with better resistance to water or acidic or basic media are required for the HDO of actual bio-oils.

Carbon is a commonly used support in catalytic applications. It can anchor metal particles on a surface that exhibits weak acid–base properties or catalytic functions [21]. In addition, its structure is stable at high temperatures in an oxygen-free environment. Its amphoteric characteristic improves the adsorption of

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metal nanoparticles as well. It is also less expensive compared to alumina and silica supports, and active noble metals can be recovered by eliminating the support by burning the carbon [22].

In this study, we observed the HDO activity of ruthenium catalysts supported on different carbons, in this case multi-walled carbon nanotubes (MWCNTs), activated carbon (AC), carbon aerogel (CARF), Vulcan carbon, and graphite. Possible descriptors of the HDO catalysis process, including acidity, metal particle size, and pore structure, were studied by analyzing the reaction results.

## 2. Experimental

### 2.1. Materials

All chemicals were used without further purification unless otherwise indicated. Guaiacol (2-methoxyphenol, 98.0%), phenol (99%), cyclohexanone (99.8%), cyclohexanol (99%), (±)-trans-1,2-cyclohexanediol (96%), resorcinol (99%), AC (Darco® G60, −100 mesh, powder), and the MWCNTs (carbon >95%, O.D. × L 6–9 nm × 5 μm) were purchased from Aldrich (Milwaukee, WI, USA). 2-Methoxycyclohexanol (97%), carbon graphite (powder, −325 mesh), and ruthenium chloride (anhydrous, Ru 47.7% min.) were purchased from Alfa (Ward Hill, MA, USA). The formaldehyde solution (37% in water) used here was purchased from Junsei Chemical Co. Ltd. (Tokyo, Japan). Vulcan XC-72 was obtained from Cabot Corp. (Alpharetta, Georgia, USA). Sodium carbonate (99%, anhydrous) was obtained from Daejung Chemicals and Metals Co. Ltd. (Siheung, Korea). Oxygen diluted in nitrogen (1%, v/v), helium, hydrogen diluted in argon (5%, v/v), and nitrogen were purchased from Shinyang Sanso (Seoul, Korea).

### 2.2. Catalyst preparations

CARF was prepared by the sol–gel polymerization of resorcinol and formaldehyde [23]. Resorcinol (15 g) was dissolved in DI water (35.43 mL). Sodium carbonate (0.0481 g) was then added to accelerate the dehydrogenation of resorcinol. After stirring for 15 min, a formaldehyde solution (22.115 g) was added slowly to the solution to form a sol. The resulting sol was cured in a vial at 80 °C for 24 h to produce a resorcinol–formaldehyde (RF) gel. Solvent exchange was performed with acetone at 50 °C for 2 days. The residual solvent was replaced with fresh acetone every 3 h to remove water thoroughly from the pores of the wet gel. Ambient drying was then performed at 50 °C for 1 day. Carbon aerogel was finally obtained by carbonization of the RF gel at 800 °C for 2 h. 5 wt% Ru on a carbon support was prepared by an incipient wet impregnation method using an aqueous solution of ruthenium chloride. Typically, 0.108 g of ruthenium chloride was dissolved in 20 mL of DI water. After stirring for a few minutes, 1 g of carbon support was mixed into the solution. The mixture was then stirred well at ambient temperatures for 12 h. Excess water was removed using a rotavaporator at 70 °C in a vacuum. The solid residue obtained was subsequently dried in an oven at 105 °C for 12 h, crushed and calcined in air at 400 °C for 2 h, and further reduced in hydrogen diluted in argon (5%, v/v) at 400 °C for 4 h. The obtained catalyst was passivated under oxygen diluted in nitrogen (1%, v/v) at room temperature for 30 min.

### 2.3. Characterizations

Transmission electron micrographs (TEM images) were obtained using a Tecnai G2 F20 device at 200 kV. The powder X-ray diffraction (powder XRD) results were obtained using a Rigaku X-ray diffractometer with a CuK$\alpha_1$ ($\lambda = 0.15406$ nm) radiation source operated at 40 kV and 30 mA. $N_2$ adsorption–desorption isotherms were measured at −196 °C using a Micromeritics ASAP 2020 instrument. The total surface area and pore volume were determined using the BET (Brunauer–Emmett–Teller) equation. The pore size distribution (PSD) curves were calculated by BJH (Barrett–Joyner–Halenda) method. Temperature-programmed desorption analyses coupled with mass-spectroscopy (TPD-MS) were performed using a BELCAT-B catalyst analyzer (BEL Japan, Inc.) with the evolution of $H_2O$ ($m/z = 18$), CO ($m/z = 28$), and $CO_2$ ($m/z = 44$) being monitored by mass spectrometry using a BELMass Gas Analyzer (Osaka, Japan) instrument. The quantities of these compounds were also measured using a thermal conductivity detector (TCD). Prior to the analysis, the sample (ca. 50 mg) was placed in a fixed-bed U-shaped quartz tubular micro-reactor and dried at 150 °C under flowing He for 1 h. The temperature was then increased at a rate of 10 °C/min to 900 °C under a flow of helium (50 mL/min). CO-chemisorption was performed using a BELCAT-B catalyst analyzer. The catalyst powder (30 mg), after being placed in a U-shaped quartz reactor, was heated under a He flow (50 mL/min) to 350 °C at a rate of 10 °C/min. This was followed by a $H_2$ treatment at 350 °C for 1 h. The powder was then cooled to 50 °C under a He flow (50 mL/min) and further treated at 50 °C for 30 min in order to clean the metal surface of the residual adsorbed hydrogen. The powder was subsequently exposed to pulses of 10% (v/v) CO/He at 50 °C under a He flow (30 mL/min). The number of active-surface metal atoms was calculated from the measured CO concentrations of the effluent gas.

### 2.4. Catalysis

The hydrodeoxygenation of guaiacol was performed in a stainless steel autoclave reactor (~100 mL). In a typical reaction procedure, guaiacol (8.96 mmol), water (29 mL), and a solid catalyst (20 mg) were added to the reactor. After flushing with $N_2$ gas, the reactor was pressurized to 40 bar with $H_2$ at room temperature. The reaction was performed at 270–300 °C for 1 h at an agitation rate of 800 rpm. After the reaction, the reactor was cooled to room temperature and the mixture was extracted with ethyl acetate. The catalyst powder was removed and the liquid product was collected. The extracted products were identified using a gas chromatograph–mass spectrometer combination (GC/MS, Agilent 7890A with 5975C inert MS XLD) with a HP-5MS capillary column (60 m × 0.25 mm × 250 μm) and was further quantified using a gas chromatograph with a HP-5 capillary column (60 m × 0.25 mm × 250 μm) equipped with a flame ionized detector (GC/FID, HP Chemstation Series II 5890) using ethyl guaiacol as an internal standard. As observed in our previous study [12,24], guaiacol was hydrogenated to produce 2-methoxycyclohexanol, (including both *cis*- and *trans*-isomers) and further deoxygenated to cyclohexanol, cyclohexanone, and cyclohexane. Phenol and catechol were also obtained via the hydrogenolysis of the methyl–oxygen bond of the methoxy group and the further elimination of the hydroxyl group. Ring-opening reaction products, including cyclopentane and methylcyclopentane, also formed. All of these compounds were then classified into three groups, i.e., compounds containing no oxygen atom (0-Os), those containing one oxygen atom (1-Os), and those containing two oxygen atoms (2-Os). The conversion of guaiacol ($X_{GUA}$), the product yields ($Y_i$), and the oxygen removal (percent of oxygen eliminated during the reaction depicting the efficiency of HDO reaction) were calculated according to a modified method [25], as follows:

$$\text{Conversion}\,(X_{\text{GUA}}, \%) = \frac{n^0_{\text{GUA}} - n^f_{\text{GUA}}}{n^0_{\text{GUA}}} \times 100$$