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The catalytic activity of $Pd/WO_x/\gamma\text{-}Al_2O_3$ for hydrodeoxygenation of guaiacol

Yoon-Ki Hong[a], Dae-Won Lee[a,*], Hee-Jun Eom[a], Kwan-Young Lee[a,b,**]

[a] Department of Chemical and Biological Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 136-701, Republic of Korea
[b] Green School, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 136-701, Republic of Korea

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ABSTRACT

In this study, $Pd/WO_x/\gamma\text{-}Al_2O_3$ was examined as a catalyst for the catalytic hydrodeoxygenation (HDO) of guaiacol (2-methoxyphenol), which is a model molecule for the bio-oils derived from lignocellulose biomass. The HDO activity of the catalyst was governed by its surface acidity and the physicochemical state of palladium. The surface acidity of the catalyst was closely related to the surface density of tungstate on the alumina support. The density of the tungstate was the highest (3.7–5.0 W/nm^2) when it was mono-layered. The highest HDO activity was obtained with Pd32WA ($Pd/WO_x/\gamma\text{-}Al_2O_3$ containing 2 wt.% Pd and 32 wt.% W) in which the tungstate formed a near-perfect monolayer on the support and the amount of surface acidity reached the highest. Palladium interacted closely with the tungstate, making the tungsten relatively electron-rich (less electron-deficient) due to the electron transfer from Pd to W. The interaction also caused the perimeter of the palladium particle to become partially decorated with a tungstate overlayer. The palladium species on WO_x/Al_2O_3 was more HDO-active than the palladium species supported on other acidic supports (SiO_2/Al_2O_3) similar to WO_x/Al_2O_3 in surface acidity. The results indicated that the catalysis progressed through a bi-functional mechanism in which the aromatic ring of guaiacol was fully hydrogenated by a Pd species to form 2-methoxycyclohexanol, which was subsequently deoxygenated by the acidic sites on the $Pd\text{–}WO_x$ surface to generate cyclohexane. When using Pd32WA, we could achieve a 100% guaiacol conversion and an 88% yield of cyclohexane (C_1-based) under the given reaction conditions.

1. Introduction

As the resources of conventional petroleum crude dwindle, there are increased needs for using unconventional but alternative petroleum resources such as shale oils, oils sands, extra heavy oils, bio-fuels. Before use, such unconventional resources should be chemically processed or upgraded. For example, heavy oil is deficient in hydrogen and high content of sulfur and metallic impurities [1]. It is necessary to lower its viscosity and remove the impurities through the hydrotreating processes such as hydrocracking, hydrodesulfurization (HDS), hydrodemetallation (HDM), etc. Another promising example of unconventional resources is bio-fuel (bio-oil). Bio-oils, obtained from raw biomass through thermochemical processes [2–4], have a low LHV (40–45% of the LHV (weight basis) of commercial petroleum oils), a high viscosity and innate chemical instability due to a high concentration of oxygen (up to 50 wt.%) [5–7]. Bio-oils need *hydrodeoxygenation* (HDO) process to eliminate the oxygen, either totally or partially, and generate a material more suited for use. We focused on the HDO and achieved this end using heterogeneous catalytic system.

We selected guaiacol (2-methoxyphenol) as a model reactant (or probe molecule representing the bio-oil) for the HDO reaction. Guaiacol is an adequate model molecule to investigate the catalysis on HDO because it has two functional groups which contain oxygen (hydroxyl and methoxy groups). Therefore, because many other researchers have utilized guaiacol in their studies about HDO reactions [5,6,8–17], we also selected guaiacol as a model reactant molecule.

The catalysts used in catalytic HDO reactions can be divided into two groups: the sulfided catalysts [5,9–14,18–21] and the noble metal catalysts [6,22–24]. Delmon's group had studied the HDO of guaiacol over sulfided molybdenum catalysts (supported NiMo and CoMo) extensively during the mid-nineties [5,9–14]. The sulfided molybdenum catalysts are well known for their commercial applications in HDS reactions. For the sulfided Mo catalysts, the reaction characteristics of HDO were similar to those of HDS. On the

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* Corresponding author. Tel.: +82 2 3290 3299; fax: +82 2 926 6102.
** Corresponding author at: Department of Chemical and Biological Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 136-701, Republic of Korea. Tel.: +82 2 3290 3299; fax: +82 2 926 6102.
E-mail addresses: stayheavy@korea.ac.kr (D.-W. Lee), kylee@korea.ac.kr (K.-Y. Lee).

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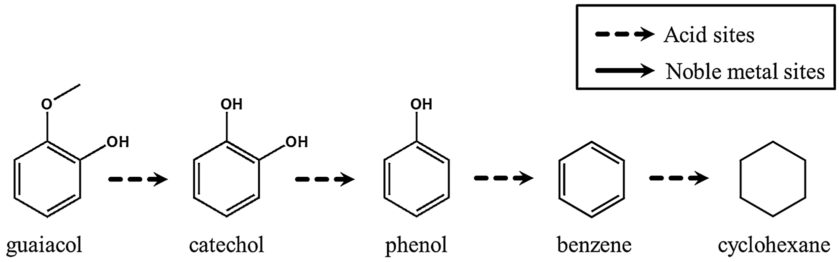
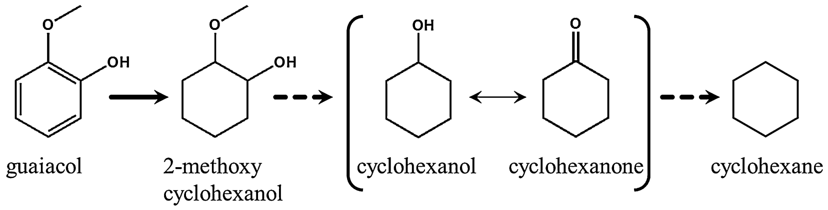


(a) HDO reaction pathway on the acid catalysts



(b) HDO reaction pathway on the noble metal catalysts with acid support

Scheme 1. Pathways for the HDO reaction of guaiacol using an acid catalyst and a bifunctional catalyst (noble metal and acid catalyst) [22].

sulfided catalysts, guaiacol was hydrodeoxygenated via demethylation, demethoxylation and dehydroxylation. The *Lewis* acidic sites, which develop mostly on alumina surface, are primarily responsible for the cleavage of O-methyl bond (i.e., demethylation). The demethylation also takes place preferentially on the sulfided phase, involving a proton (H^+) and a hydride anion (H^-). The proton reacts with the partially negative oxygen atom (δ^-), while the hydride anion adds to the partially positive carbon atom in methoxy group ($-OC^{\delta+}H_3$) [11]. However, when applying the sulfide catalysts to HDO reaction, sulfur leaches from the catalyst and causes serious problems: it not only deactivates the catalyst but also contaminates the reaction products [6,25], making the use of sulfided catalysts challenging.

Another group of catalysts used for the HDO of guaiacol is noble metal catalysts [6,22–24]. In this group of catalysts, a high HDO activity could be obtained when noble metals, such as Pd, Rh, Pt and Ru, were paired with an acidic support, such as γ-Al_2O_3, SiO_2–Al_2O_3, acid-treated carbon and others [22]. Lee et al. suggested that the reaction pathway of HDO over the noble metal-supported acidic oxide catalysts occurred as described in Scheme 1 [22]. The catalytic process progressed through a *step-wise*, *bi-functional* mechanism (Scheme 1(b)): (1) the ring hydrogenation (de-aromatization) of guaiacol into 2-methoxycyclohexanol on the noble metal site; (2) the deoxygenation of 2-methoxy cyclohexanol and its products (demethoxylation, dehydroxylation) on the metal-deposited acid site.

The supported tungsten oxide (WO_x) is a versatile solid acid catalyst used to catalyze various heterogeneous reactions, such as the isomerization of alkenes [26] and alkanes [27], selective catalytic reduction of NO_x with NH_3 [28,29], olefin metathesis, hydrocarbon cracking and most notably, HDS of dibenzothiophenes [30,31] and diesel fuels [32]. Both *Lewis* and *Brønsted* acidic sites are present on WO_x/Al_2O_3 in distributions dependent upon the loading of the tungsten oxide (WO_x) [33–36]. According to other studies, the crystallographic phase of the WO_x species changes along with its surface coverage [37–40]. At low W surface coverage (<2 W atoms/nm^2), the monotungstate species are dominant. These species change to a polytungstate bulk phase as the surface W coverage increases to intermediate values (3–5 W atoms/nm^2). As the W coverage increases higher (>5 W atoms/nm^2), the crystalline WO_3 particulates form on top of the polytungstate layer.

Among the noble metals, palladium has been most widely used as the active metal in selective hydrogenation catalysts [41–45]. In many cases, the electronic and morphological properties of palladium species are influenced by interaction with the support material; both of these properties strongly affect the hydrogenation activity of the catalysts [41–45]. The metal–support interaction also influences the thermal diffusion rate of the metal species, which is directly related to the thermal durability of the catalysts. Several papers have discussed the interactions between the palladium and tungsten oxide in Pd/WO_x supported catalysts [46–49]; it was reported that the degree of the Pd–WO_x interaction critically influenced the catalytic activity in hydrogenation reactions, such as the partial hydrogenation of hept-1-yne [48] or the selective hydrogenation of styrene [49]. The Pd/WO_x is a sort of noble metal-acidic support pair but, in spite of the reports of its good performance in other hydrogenation reactions, there has not been a study detailing its application to the HDO of guaiacol or other bio-oil-related model compounds.

In this study, we examined the activity of Pd/WO_x/Al_2O_3 catalysts for HDO of guaiacol. In particular, we investigated the influences of the acidic properties of the WO_x layer, as well as the Pd–WO_x interaction, on the HDO activity of the Pd/WO_x/Al_2O_3 catalysts. The results strongly suggested that the catalysis occurs through a *bi-functional* HDO mechanism.

2. Experimental

2.1. Preparation of catalysts

Tungsten oxide was impregnated on γ-Al_2O_3 (Sasol, Disperal P2, $V_p = 0.48\ cm^3/g$, $S_a = 264\ m^2\ g^{-1}$) with an incipient-wetness method using aqueous solutions of ammonium metatungstate hydrate (Aldrich, 72.4% W). The sample was dried at 110 °C overnight and calcined at 500 °C for 15 h under an atmosphere of air. The impregnated materials (WO_x/Al_2O_3) were named ○○WA, which indicates that ○○ wt.% of W was loaded onto the Al_2O_3 supports. To compare WA with different acidic support materials, SiO_2–Al_2O_3 supports with different Si/Al ratios were prepared using a previously reported sol–gel method [50]. The prepared SiO_2–Al_2O_3 supports were named SA-X, which X means the atomic molar ratio of Si to Al.