Vapor-phase hydrodeoxygenation of guaiacol over carbon-supported Pd, Re and PdRe catalysts

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ABSTRACT

Vapor-phase hydrodeoxygenation (HDO) of guaiacol was investigated over a commercial Pd/C (A) catalyst (Evonik) and Pd/C (B), Re/C and PdRe/C catalysts prepared by incipient wetness impregnation of Norit SX-1 G activated carbon. The Pd/C catalysts had equivalent dispersions after reduction at 300 °C; however, Pd/C (B) had very low dispersion after reduction at 400 °C. CO chemisorption, Re L_{III} edge extended x-ray absorption fine structure (EXAFS) spectroscopy, and high-angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM) of the Re/C catalyst after reduction at 400 °C evidenced the formation of supported Re clusters. EXAFS spectroscopy of the PdRe/C catalyst after in situ reduction at 300 °C indicated the presence of Pd nanoparticles and Re clusters; a 2.70 Å Pd-Re contribution was required to adequately fit the Re L_{III} EXAFS spectrum. HAADF-STEM with energy-dispersive x-ray (EDX) analysis of the PdRe/C catalyst after reduction at 400 °C revealed Re clusters and Pd nanoparticles, some in intimate contact. In guaiacol HDO at 300 °C and 1 atm, Pd/C (A) was selective to phenol and cyclohexan-one/-ol and did not produce significant yields of benzene and cyclohexane, despite its high activity. Turnover frequencies for phenol (and cyclohexan-one/-ol) formation over the Pd/C catalysts were equivalent. Phenol, benzene and anisole were major products over Re/C after in situ reduction at 400 °C. The highest yield (52%) of fully deoxygenated products was obtained over PdRe/C after in situ reduction at 400 °C. We infer that the bimetallic catalyst combines synergistically the demethoxylation and hydrogenation functions of Pd/C with the capability of Re/C to deoxygenate phenol [Ghampson, et al., Catal. Sci. Technol. 2016].

1. Introduction

Modern transportation relies heavily on liquid fuels derived from petroleum. Concerns over the limited supply of petroleum and global climate change have motivated research on biorenewable transportation fuels [1]. Woody biomass is a viable source of renewable liquid fuels for the near- to mid-term and is, in principle, carbon-neutral [2,3]. Fast pyrolysis oils (bio-oils) derived from lignocellulose are not suitable for direct use as transportation fuels because of their low energy densities, pH values, and shelf lives associated with oxygenated organic constituents (e.g., acids, ketones and aldehydes) [1,2,4,5]. Hydrodeoxygenation (HDO) of bio-oils has been demonstrated using petroleum hydrotreating catalysts (e.g., sulfided CoMo and NiMo/Al$_2$O$_3$); however, these catalysts deactivate via sulfur leaching, coking, and acid attack on the Al$_2$O$_3$ support [6–9]. Carbon-supported noble metal catalysts are promising alternatives that provide higher yields of liquid fuels with lower residual oxygen contents when compared to noble metals on metal oxide supports [10,11].

Guaiacol is a model compound for the phenolic fast pyrolysis products that comprise a significant fraction of bio-oils [12,13]. Guaiacol HDO has been investigated extensively over conventional hydroprocessing catalysts [6,7] and supported noble metals, including Pt, Pd, and Ru/C [12,14–16], Pt/Al$_2$O$_3$ [17,18] and Pt/MgO [19]. Noble metals on non-acidic supports typically show a strong propensity for aromatic ring hydrogenation and demethoxylation of guaiacol to phenol; however, these monofunctional catalysts lack the capacity to fully deoxygenate guaiacol to benzene and cyclohexane [16]. For example, Gao, et al. screened carbon-supported Ru, Rh, Pd, and Pt monometallic catalysts for vapor-phase HDO of guaiacol at 300 °C and 1 atm [14]. Of these catalysts, Pt/C had the highest activity and slowest deactivation rate; the main product was phenol. Similarly, the main products of guaiacol HDO over Pd/C were phenol and cyclohexan-one/-ol [14]. Bifunctional catalysts typically are more effective at complete HDO of guaiacol to benzene and cyclohexane [20]. Metal-zeolite catalysts, such as Ni/H-ZSM-5 [21] and Pt/HY [22,23], have been demonstrated to achieve phenol and guaiacol HDO via synergistic metal (hydrogenation) and acid-catalyzed (dehydration) pathways. Alternatively, a more oxophilic metal may be added to supported noble

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metals to enhance direct deoxygenation (DDO) activity [20]. For example, PdFe/C catalysts have been shown to provide high yields of fully deoxygenated products (benzene and cyclohexane) when operated at 350–400 °C [16].

Recently, supported rhenium catalysts (Re/C and Re/SiO$_2$) were shown to be active for HDO of guaiacol and related phenolics in the liquid phase at 300 °C and 5 MPa [24,25]. Catalytic activity for C−O bond scission resulting in high yields fully deoxygenated products was ascribed to partially reduced rhenium oxide species (ReO$_x$). Addition of Cu to Re/SiO$_2$ was found to facilitate Re reduction and boost guaiacol conversion and selectivity to benzene and cyclohexane [26]. Conversely, rhenium has been demonstrated to enhance selectivity and catalytic activity for selective hydrogenation [27–33] and C−O bond hydrogenolysis [34–38] when paired with a platinum-group metal (PGM). Tomishige and coworkers have studied several supported PGM-Re catalysts for selective hydrogenation of mono- and dicarboxylic acids [27–29] and hydrogenolysis of ethers and polyols [38]. Their results suggest that the catalytically active sites comprise low-valent ReO$_x$ clusters in intimate contact with PGM nanoparticles; however, a role for zero-valent Re clusters cannot be excluded [39]. Koso, et al. described supported Re nanoparticles covered by ReO$_x$ species and low-valent ReO$_x$ clusters attached to Rh metal particles in Re/SiO$_2$ and RhRe/SiO$_2$ catalysts, respectively, after reduction at ∼330 °C [40]. Hakim, et al. concluded that the active sites for selective hydrogenolysis of 2-(hydroxymethyl)tetrahydropyran (HMTHP) to 1,6-hexanediol comprise small noble metal particles (Rh, Pt) adjacent to highly reduced moieties of a more oxophilic metal (Mo, Re) on a Vulcan carbon support [37]. Focusing on RhRe/C catalysts, Chia, et al. reported that Rh-rich nanoparticles with a partial shell of metallic Re are active for selective hydrogenolysis of HMTHP to 1,6-hexanediol and that Re penetration into the core after reduction at 450 °C correlated with a *decrease* in activity for HMTHP hydrogenolysis [36]. Alloy formation is less favorable for PdRe than RhRe because of the larger miscibility gap in the bulk phase diagram [41]. Takeda, et al. proposed that Re^{n+} species on the surfaces of metallic Re clusters and Pd nanoparticles were the active sites in RePd/SiO$_2$ (Re/Pd = 8) catalysts for hydrogenation of stearic [29] and succinic acids [28]; the percentage of Re° clusters and their interaction with the Pd-rich nanoparticles depended on the precise reduction conditions. Shao, et al., however, demonstrated using high-resolution TEM that a PdRe/C (Re/Pd = 0.6) catalyst for succinic acid hydrogenation contained Pd and Pd-Re alloy nanoparticles [31].

In this work, a commercial Pd/C (A) catalyst (Evonik) and Pd/C (B), Re/C and PdRe/C catalysts prepared by incipient wetness impregnation of Norit SX-1 G activated carbon were investigated for vapor-phase HDO of guaiacol at 300 °C and 1 atm. The catalysts were characterized by temperature-programmed reduction (TPR), CO chemisorption, x-ray absorption spectroscopy (XAS), and scanning transmission electron microscopy (STEM) with energy-dispersive x-ray (EDX) analysis. Guaiacol HDO product distributions were evaluated for each catalyst in a continuous flow reactor at integral conversion, and turnover frequencies (TOFs) for primary products were determined at differential conversion.

2. Experimental

2.1. Catalysts

A commercial 5% Pd/C catalyst (Evonik E117), denoted Pd/C (A), was received as a reduced 50% water-wet powder and dried at 110 °C in air prior to use. Carbon-supported Pd, Re, and PdRe catalysts were prepared by incipient wetness impregnation of Norit SX-1 G activated carbon. The catalyst precursors: Pd(NO$_3$)$_2$·H$_2$O (99.9% Pd basis, Strem) and a 76.5 wt% solution of HReO$_4$ (99.99% Re, Acros Organics) were dissolved in 18 MΩ-cm deionized water. After impregnation, the paste was dried at 110 °C in air, the solid was crushed with mortar and pestle,

Table 1
Catalyst metal loadings and CO chemisorption results.

Catalyst	Metal loadings (wt.%)		Reduction temperature[a] (°C)	Strongly bound CO (µmol/g$_{cat}$)[b]	CO/metal[c]	Metal dispersion[d] (%)
	Pd	Re				
Catalysts after in situ reduction						
Pd/C (A)	4.80	–	300	39.3	0.087	17
Pd/C (B)	4.11	–	300	39.3	0.10	20
			400	6.7	0.017	3.5
Re/C	–	7.64	400	222	0.54	54
PdRe/C	3.96	7.50	300	217	0.28	–
			400	224	0.29	–
Catalysts previously reduced ex situ at 400 °C and passivated in air						
Pd/C (B)	4.11	–	300	24.6	0.064	13
			400	4.0	0.010	2.1
Re/C	–	7.64	300	123	0.30	30
			400	178	0.43	43
PdRe/C	3.96	7.50	300	134	0.17	–
			400	147	0.19	–

[a] *In situ* reduction at indicated temperature for 1 h followed by evacuation for 4 h.
[b] Measured by difference isotherm method at 35 °C.
[c] Mols strongly bound CO/mol metal (total).
[d] Stoichiometry factors: 0.5 CO/Pd and 1 CO/Re.

and the resultant powder was stored in a desiccator until use. Metal loadings (Table 1) were determined by inductively coupled plasma-optical emission spectrometry at Eastman Chemical Company, Kingsport, TN.

2.2. TPR

Measurements were performed using a Micromeritics 2920 AutoChem II. Catalyst powder (∼100 mg) was loaded into a quartz U-tube and purged with He (UHP, National Welders) at ∼40 °C. Subsequently, the sample was heated at 10 °C/min in flowing 5% H$_2$/Ar (Certified mixture, Machine and Welding) to a final temperature of 400, 500 or 800 °C. H$_2$ uptake during TPR was monitored using a AgO-calibrated thermal conductivity detector (TCD).

2.3. CO and H$_2$ chemisorption

Volumetric CO chemisorption measurements were made using a Micromeritics 2020c ASAP instrument. Catalyst samples were evacuated for 1 h at 100 °C, reduced in flowing H$_2$ (Research grade, National Welders) at either 300 °C or 400 °C for 1 h, and evacuated at the reduction temperature for 4 h. After a negative leak test, an adsorption isotherm using CO (Research grade, National Welders) was measured at 35 °C. Subsequently, the sample was evacuated to remove weakly bound CO, and then the analysis repeated. A difference isotherm corresponding to strongly bound CO was used in dispersion calculations. Metal dispersions were calculated using surface atom stoichiometry factors of 0.5 CO/Pd [42] and 1 CO/Re [43]. Volumetric H$_2$ chemisorption measurements were performed at 35, 70 and 100 °C on selected samples using an analogous procedure.

2.4. X-ray absorption spectroscopy (XAS)

Pd K (24,350 eV) and Re L$_{III}$ (10,535 eV) x-ray absorption spectra were measured in transmission mode at the National Synchrotron Light Source, Brookhaven National Laboratory using beam lines X-10C and X-11 A. The Si(311) x-ray monochromators were calibrated using Pd foil and Re powder standards. XAS measurements were made on lab-prepared catalysts that had been reduced *ex situ* at 400 °C, cooled to 25 °C, and exposed slowly to air. Powdered samples were pressed into