



Carbon-supported bimetallic Pd–Fe catalysts for vapor-phase hydrodeoxygenation of guaiacol



Junming Sun^{a,1}, Ayman M. Karim^{a,*}, He Zhang^b, Libor Kovarik^a, Xiaohong Shari Li^a, Alyssa J. Hensley^b, Jean-Sabin McEwen^b, Yong Wang^{a,b,*}

^a Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA 99352, United States

^b The Gene & Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, United States

ARTICLE INFO

Article history:

Received 10 December 2012

Revised 25 March 2013

Accepted 18 May 2013

Keywords:

Pd–Fe

Hydrodeoxygenation

Bimetallic catalysis

Bio-oil upgrading

Alloy catalyst

EXAFS

Carbon support

ABSTRACT

Carbon-supported metal catalysts (Cu/C, Fe/C, Pd/C, Pt/C, PdFe/C, and Ru/C) were characterized and evaluated for vapor-phase hydrodeoxygenation (HDO) of guaiacol (GUA), aiming at the identification/elucidation of active catalysts for high-yield production of completely hydrodeoxygenated products (e.g., benzene). Phenol was found to be the major intermediate on all catalysts. Saturation of the aromatic ring is the major pathway over the precious metal catalysts, forming cyclohexanone and cyclohexanol, followed by ring opening to form gaseous products. Base metal catalysts exhibit lower activity than the precious metal catalysts, but selectively form benzene along with small amounts of toluene, trimethylbenzene (TMB), and cresol without forming ring-saturated or ring-opening products. Compared with Fe/C and Pd/C, PdFe/C catalysts exhibit a substantially enhanced activity while maintaining the high selectivity to HDO products without ring saturation or ring opening. The enhanced activity of PdFe/C is attributed to the modification of Fe nanoparticles by Pd as evidenced by STEM, EDS, EXAFS, TPR, and theoretical calculations.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Fast pyrolysis is potentially an attractive approach for the direct thermo-chemical conversion of lignocellulosic biomass to bio-oils [1–3]. The lignin-derived phenolic compounds (phenols, guaiacols, syringoles) formed during the fast pyrolysis are highly reactive and can undergo secondary reactions during the condensation step to produce oligomers [4,5]. In addition, during bio-oil upgrading, phenolic compounds have been reported to cause fast catalyst deactivation [6,7]. Therefore, it is highly desirable to defunctionalize these phenolic compounds via hydrodeoxygenation (HDO) with minimum H₂ consumption.

Early work indicated that conventional hydrodesulphurization (HDS)/hydrodenitrogenation (HDN) catalysts exhibit promising activity in HDO of phenolic compounds such as phenol, anisole, and guaiacol [8–12]. However, these metal–sulfide catalysts suffer from deactivation in the presence of high water content and the continuous addition of sulfur is required in the reactant stream to maintain the catalysts in the sulfide form. This last factor in

particular can cause serious problems for the downstream processes [11,13,14]. Alternative hydrotreating catalysts have been sought for bio-oil upgrading [6,13,15–20]. Among these, extensive research activities have focused on precious metal catalysts at high H₂ pressures [8–12,16,20–34]. These studies showed the tendency to saturate the aromatic ring before removing the oxygen groups, resulting in a large and costly consumption of H₂.

To date, vapor-phase HDO of biomass fast pyrolysis products have been mostly limited to zeolites [35–41] which suffer from low activity and are highly susceptible to coke formation [7,37]. Only a limited number of studies have been reported using supported metal catalysts [6,15,18,19,42–46]. Zhao et al. compared a group of transition metal phosphides, commercial Pd/Al₂O₃, and CoMoS/Al₂O₃ in HDO of guaiacol [15]. Metal phosphides showed promising HDO activity with benzene, phenol, and anisole being the predominant products, but they suffered from fast deactivation. Pd/Al₂O₃ was more active than the metal phosphides and the commercial CoMoS/Al₂O₃, but it produced mainly catechol [15]. Recently, Gates' group compared Pt/Al₂O₃ and Pt/HY catalysts in the HDO of anisole and guaiacol. Their results showed that the transalkylation activity of the catalyst was significantly affected by the type of acidic site [18,19]. A later study by Zhu et al. further confirmed the effect of acidic sites on the transalkylation activity in the HDO of anisole [17]. A very recent report indicates that Fe/SiO₂ shows a higher hydrodeoxygenation activity without saturation of

* Corresponding authors. Address: Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA 99352, United States (Y. Wang).

E-mail addresses: ayman.karim@pnnl.gov (A.M. Karim), yong.wang@pnnl.gov (Y. Wang).

¹ Current address: The Gene & Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, United States.

aromatic ring in the GUA conversion. A ~38% selectivity to benzene/toluene was achieved under the best reaction conditions [46]. While the transalkylation activity of the acidic catalyst offers a way to preserve the carbon from being lost as a gas product, the presence of acidic sites interacts strongly with the phenolic compounds, resulting in rapid catalyst deactivation by coking [1,9]. Contrary to the acidic supports, carbon-supported catalysts showed a much higher stability in the HDO of phenolic compounds [9].

In this study, guaiacol was used as a model compound since it is stable under the biomass fast pyrolysis conditions and has the characteristic bonds of phenolic compounds. We compared the vapor-phase HDO of guaiacol on a variety of supported metal catalysts (Pd, Pt, Ru, Fe, Cu, and PdFe). In all cases, activated carbon was used to minimize the support effect on the HDO reactions. We found that Fe/C shows promising HDO activity without saturation of the aromatic ring, forming benzene, toluene, TMB, phenol, and o-cresol as major products. A significant improvement in HDO activity was observed on the palladium-promoted Fe/C catalysts. Scanning transmission electron microscopy (STEM) imaging complemented by energy dispersive spectroscopy (EDS) showed the modification of Fe nanoparticles by Pd. Results from temperature-programmed reduction (TPR), extended X-ray absorption fine structure (EXAFS), and theoretical calculations further confirmed the strong interaction between Pd and Fe, which is responsible for the enhanced catalytic performance in the HDO of guaiacol on the PdFe/C catalysts.

2. Experimental methods

2.1. Materials and synthesis

Coconut shell activated carbon (TA70) was obtained from PICA, Inc. Acetone (99.9+%) and the metal precursors ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98+%), $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (99.9+%), $\text{Pd}(\text{AC})_2$ (99.9+%), $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ (99.995%), Ruthenium (III) nitrosyl nitrate in nitric acid solution (1.5 wt%Ru) were purchased from Sigma–Aldrich.

TA70-supported metal catalysts were prepared using the method of traditional incipient wetness impregnation. Specifically, a calculated amount of metal precursor was first dissolved into a given amount of H_2O (for the synthesis of Pd/C and PdFe/C, acetone was substituted for the H_2O to dissolve the palladium acetate) and then impregnated onto the support with single- or multi-impregnations to achieve the desired metal loadings of 5 wt% for Pd, Pt, and Ru, and 10 wt% for Cu and Fe. The wet solids were dried at 80 °C overnight in air and then calcined at 350 °C for 2 h (ramping rate of 5 °C/min) under flowing Ar (50 SCCM). For the 2 wt% Pd–10 wt% Fe/C, a two-step sequential incipient wetness method was used. An iron precursor solution was first impregnated on TA70, dried at 80 °C overnight, and calcined at 350 °C in flowing Ar (50 SCCM) for 2 h, followed by impregnation with the Pd precursor solution, drying at 80 °C overnight, and a second calcination step at 350 °C. Calcination at 350 °C in flowing Ar (50 SCCM) was used to decompose the metal precursors. The details of the samples and the notions are summarized in Table 1.

2.2. Characterization

XRD patterns were collected on a Philips X'pert MPD (Model PW 3040/00) equipped with a $\text{Cu K}\alpha$ X-ray source operating at 40 kV and 50 mA. Step-sizes of 0.015–0.02 and accumulation times of 0.8–1 s were used during the scanning. Nitrogen adsorption–desorption isotherms were recorded on a Quantachrome Autosorb 6-B gas sorption system. Before adsorption analysis, samples were degassed at 250 °C for 2 h. TEM images were recorded on a

Table 1
Notion and physical properties of the carbon-supported metal catalysts.

Sample information	Sample name	BET surface area (m^2/g)	Particle size (nm) ^a
TA70	C	1479	– ^b
10 wt% Fe/C	10Fe/C	1159	24.0 (± 1.6)
10 wt% Cu/C	10Cu/C	1210	11.6 (± 0.5)
5 wt% Pd/C	5Pd/C	1379	3.3 (± 0.4)
2 wt% Pd 10 wt% Fe/C	2Pd10Fe/C	1208	32 (± 1.7)
5 wt% Pt/C	5Pt/C	1361	– ^b
5 wt% Ru/C	5Ru/C	1207	– ^b

^a Particle size calculated from the XRD spectra using the Scherrer equation.

^b Below detection limit.

JEOL-2010 transmission electron microscope. STEM was performed with an FEI Titan operated at 300 kV. The FEI Titan is equipped with a CEOS GmbH double-hexapole aberration corrector for the probe-forming lens, which allows imaging at a resolution of ~0.1 nm in STEM mode. The images were acquired on a High Angle Annular Dark Field (HAADF) with an inner collection angle of 52 mrad. Compositional analysis was performed with EDAX Si (Li) energy dispersive spectroscopy (EDS) detector and FEI's TIA acquisition and analysis software. The TEM sample preparation involved the mounting of powder samples on copper grids covered with lacey carbon support film and loading into the microscope. Before XRD and TEM characterization, samples were first reduced in H_2/N_2 (1:9 mol; 50 SCCM) at 450 °C with a ramping rate of 5 °C/min for 2 h followed by purging with N_2 for 30 min, the same pretreatment procedure as those used before activity testing, and then cooled down to room temperature and passivated (0.1% O_2 in Ar and He (9:1 mol), 3 h). H_2 -TPR was conducted on a Micromeritics AutoChem II 2920 Chemisorption Analyzer equipped with a TCD detector. 100 mg of sample was loaded in a U-shaped quartz reactor and purged with flowing He (50 SCCM) until a stable base line was reached. The sample was then ramped to a given temperature at a ramping rate of 10 °C/min under flowing 10% H_2/He (50 SCCM). It was found that the temperature where noticeable loss of carbon support by hydrogenation was ~500 °C for noble metals, while it was ~600 °C for base metals or 2Pd10Fe/C in this study, verified by our H_2 -TPR-MS experiments (data not shown).

The 2Pd10Fe/C catalyst was characterized at the Pd K-edge using an in-house built, *in situ* X-ray absorption spectroscopy (XAS) cell with a 4 mm i.d. glassy carbon tubing [47]. The XAS measurements were performed at beamline X-18A at the National Synchrotron Light Source (NSLS) operated by the Synchrotron Catalysis Consortium (SCC) at Brookhaven National Laboratory. The catalyst was reduced in 100% H_2 flow (50 SCCM) at 450 °C with a ramping rate of 10 °C/min for 2 h and then cooled down to room temperature. The extended X-ray absorption fine structure (EXAFS) spectra were collected at room temperature under 100% H_2 flow. EXAFS data processing and analysis was performed using the Athena and Artemis programs of the IFEFFIT data analysis package [48,49]. Three scans were collected and merged after being aligned using a Pd foil spectrum collected simultaneously for each scan. After the normalization of the absorption coefficient, the smooth atomic background was subtracted using the AUTOBKG code to obtain $\chi(k)$ (where k is the photoelectron wave number). The theoretical EXAFS signal for Pd–Pd and Pd–Fe scattering paths was constructed using the FEFF6 code [50]. For Pd–Pd, we used an fcc crystal structure with a lattice constant of 3.89 Å. The Pd–Fe structure was constructed by replacing all the Pd atoms in the first shell of the Pd fcc structure by Fe atoms and changing the lattice constant to 3.7 Å. The theoretical EXAFS signals were fitted to the data in r -space using the Artemis program of the IFEFFIT package. The

Download English Version:

<https://daneshyari.com/en/article/6527641>

Download Persian Version:

<https://daneshyari.com/article/6527641>

[Daneshyari.com](https://daneshyari.com)