



## Full Length Article

# Bio-oil hydrodeoxygenation catalysts produced using strong electrostatic adsorption <sup>☆</sup>



Yaseen Elkasabi <sup>a,\*</sup>, Qiuli Liu <sup>b</sup>, Yong S. Choi <sup>a</sup>, Gary Strahan <sup>a</sup>, Akwasi A. Boateng <sup>a</sup>, John R. Regalbuto <sup>b</sup>

<sup>a</sup> Eastern Regional Research Center, Agricultural Research Service, U. S. Department of Agriculture, 600 E. Mermaid Lane, Wyndmoor, PA 19038, United States

<sup>b</sup> Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, United States

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## ABSTRACT

Our objective was to synthesize hydrothermally stable metal catalysts with controlled particle size and distribution, with the goal of determining which catalyst(s) can selectively produce aromatics. Both precious and transition metal catalysts (Ru, Pt, Ni, Cu, 2Pt1Ru, NiCu) were deposited on mesoporous alumina (mA) and carbon, respectively, using the strong electrostatic adsorption (SEA) method. Due to the alloying that occurs under SEA, our hypothesis was that controlled bimetallic combinations (precious and/or base metal) could enhance the HDO behavior. As verified by XRD, STEM, and TPR, the SEA method successfully deposited noble metal particles less than 2 nm in size onto alumina. Alloying of bimetallic particles was also confirmed. Hydrodeoxygenation of pyrolysis bio-oil was run for 3 h at 300 °C in an aqueous environment. While partial conversion of mesoporous alumina into boehmite phase occurred, the catalyst particles remained between 2 and 3 nm post-reaction, indicating a high degree of anchoring. Over carbon, base metal particles were initially larger in size (about 3.3 nm) and tended to sinter more. Bimetallic SEA catalysts produced aromatic hydrocarbons at a greater extent than those of Ni/C, or Cu/C, or commercial Ru/Al<sub>2</sub>O<sub>3</sub>, as evidenced by GC–MS and/or NMR. Bimetallic 2Pt1Ru/mA did not exhibit significantly greater activity than Pt or Ru or control catalysts made by dry impregnation (DI), whereas NiCu demonstrated improved oil quality and yields over single-metal Ni and Cu and DI-method control catalysts. With respect to product compounds, the effect of mA support is stronger than that of carbon support.

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## 1. Introduction

Thermochemical methods for conversion of biomass into fuels [1–3] have a potentially carbon-negative environmental impact, in part due to the utilization of carbonaceous solid byproducts which enhance soil quality [4]. In particular, there are well-documented examples [5–7] of how biomass pyrolysis can produce liquid transportation fuel intermediates, especially ones that are amenable to fuel oil applications. However, to meet the annual demand of 36 billion gallons/year of biofuels mandated by the EPA Renewable Fuels Standards [8], the bio-oil must be catalytically hydrotreated to remove oxygen, reduce viscosity and molec-

ular weight, and to hydrogenate bio-oil compounds into combustible hydrocarbons.

Bio-oil upgrading technologies typically utilize processes [9–11] analogous to that of the catalytic hydrotreating processes used in petroleum refineries, i.e. a thermally stable support carries a precious metal catalyst that is deposited by wet/dry impregnation [12]. Due to the inherent problems associated with bio-oil mentioned above, deactivation and coking issues during hydrodeoxygenation (HDO) have fueled significant attempts [13,14] at restructuring a more active and stable catalyst. These efforts include changing the support and/or metal composition and geometry, as well as the deposition method [15]. Unfortunately, many of the structural variables associated with catalyst performance are oftentimes not decoupled from one another, leading to the recurring catalyst problems. For example, metal particle size and geometry constitute examples of variables left unmodified. While wet impregnation is a simple and cheap method for metal deposition, the user cannot exhibit much control over the particle size. Furthermore, metal particles tend to irreversibly sinter [16] through the HDO process, which greatly limits the catalyst lifetime. Most

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\* Corresponding author.

E-mail address: [yaseen.elkasabi@ars.usda.gov](mailto:yaseen.elkasabi@ars.usda.gov) (Y. Elkasabi).

studies on catalyst stability examined reactions on model compounds [13]; those that examined bio-oil reactions primarily look at coke deposition and not the actual catalyst properties, especially not as they relate to their products. Overall, refiners cannot tolerate large variations of reproducibility with catalysis. All the aforementioned issues warrant a fundamentally different method of synthesis that can produce stable and effective catalysts in a tightly controlled manner.

HDO catalysts have yet to benefit fully from the strong electrostatic adsorption (SEA) method of catalyst synthesis [17], which effectively produced active catalysts for aromatic ring hydrogenation [18], ethanol production from syngas [19], and Fischer-Tropsch synthesis [20]. SEA utilizes a precise pH environment for metal deposition, which maximizes the precursor's interaction with the support. In turn, this allows for the formation of small metal particles with relatively narrow size distributions. SEA-derived Ru catalysts for levulinic acid hydrogenation to gamma valerolactone showed a sharp maximum in activity at an average particle size of about 1.5 nm [21].

Production of aromatics via HDO is desirable, as this indicates that the catalyst(s) deoxygenate the oil more efficiently with less hydrogenation, resulting in less hydrogen consumption. One-ring aromatic compounds are also a valuable commodity chemical. Computational studies on the HDO of model bio-oil compounds like guaiacol and phenol demonstrated that the reaction mechanisms do not require fully saturated compounds to be intermediate compounds, especially for platinum single metal catalysts [22]. Hence, the selective formation of aromatic compounds could occur over a controlled metal loading and size. It was also proposed that oxophilic nickel could efficiently deoxygenate bio-oil compounds, despite it being a base metal. Building on these proposed metals with SEA-based catalysts, this paper discusses the results of our selected catalysts post-HDO, with respect to both precious and base metal catalysts synthesized by SEA. We also investigate the effect of nanostructured bimetallic alloys on catalyst activity, as alloying could fundamentally alter the metal reactivity.

## 2. Experimental section

### 2.1. Bio-oil production

Fast pyrolysis bio-oils were produced from a pilot-scale mobile combustion-reduction integrated pyrolysis system (CRIPS), as described previously [23]. Briefly, 40 kg/hr of ground dried mixed hardwoods (MESA Reduction Engineering & Processing, Inc.) was fed into a dual-fluidized bed pyrolysis-combustion system, wherein fluidized sand from the pyrolysis bed is augered directly into the adjacent combustion bed. The reheated sand overflows into a chute that returns it to the pyrolysis bed. The pyrolysis bed (~550 °C reaction temperature) was fed with nitrogen and biomass, while the combustion bed was fed with air and cool sand

from the pyrolysis bed. Pyrolyzed vapors then entered a cyclone which removed solid char particles; combusted ash from the combustion bed accumulates in a bin underneath the cyclone. Subsequently, the vapors passed through four condensers in series, cooled by air. After condensation, the oil suspended in the uncondensed gas was collected using an electrostatic precipitator (ESP). The ESP fraction oil was filtered through 8 µm Büchner filtration and subsequently used for all experiments.

### 2.2. Catalyst preparation

The noble metal catalysts were prepared by the method of SEA. The detailed experimental procedure is explained in the supporting information. In brief, potassium hexacyanoruthenate (RuHCN) and hexachloroplatinic acid (PtHC) were used as metal precursors; commercial carbon Timrex (C) and self-synthesized mesoporous alumina (mA) were used as supports. Supported noble metal catalysts (Ru/mA, Pt/mA, and PtRu/mA) were synthesized around their optimal pHs of 3 using HCl, and the metal loading was determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

For the base metal catalysts (Ni/C, Cu/C and NiCu/C, Ni/mA, Cu/mA and NiCu/mA) a method derived from SEA known as “Charge Enhanced Dry Impregnation (CEDI) [24,25] was employed. Nickel nitrate hydrate and copper nitrate hydrate were used as metal precursors as-purchased. Citric acid was used to buffer the bulk pH in the solution significantly below the PZC and form anionic metal complexes so as to maximize electrostatic interaction. Before thorough mixing with support powder, a certain amount of nickel and copper precursors, along with citric acid (1:1 M ratio), were first dissolved into a pore volume's worth of deionized water. The wet paste was then dried in an oven at 80 °C for overnight to remove excess water. Catalysts were characterized and evaluated after being reduced in 10% H<sub>2</sub>/He for 1 h at the optimal temperature determined by TPR (shown later). Metal loadings are presented in Table 1. The molar ratio of two components in bimetallic ratio is 1:1. Table 1 lists the catalysts made for this study along with their physical properties.

### 2.3. Hydrodeoxygenation experiments

Batch hydrodeoxygenation reaction experiments were carried out in a Parr Series 4598 100 mL bench-top reactor, as described previously [26]. HDO catalysts used were either that described above or ones commercially purchased (5% Ru/Al<sub>2</sub>O<sub>3</sub>, 5% Pt/Al<sub>2</sub>O<sub>3</sub>, Johnson Matthey, Inc., UK). HDO experiments consisted of catalyst and bio-oil in 20–30 g of deionized water. For data comparison, the catalyst: bio-oil loading is defined as:

$$CL_l = \left( \frac{x_{cat} W_{cat}}{W_{oil}} \right) \times 100$$

**Table 1**  
HDO catalysts tested, with composition and properties noted.

metal support	Ru mA	Pt mA	PtRu mA	Ni mA	Cu mA	NiCu mA	Ni C	Cu C	NiCu C
loading ratio (wt%)	3.0	4.2	2.0/1.0	2.0	2.0	1.0/1.0	2.0	2.0	1.0/1.0
surface area (m <sup>2</sup> /g)	245	245	237	226	226	226	280	280	280
particle size(s) (nm)	<1.5	<1.5	<1.5	4.2 (NiO) 5.6 (NiAl)	3.7	4.4	3.7	3.8	3.3
metal support	Ru Al <sub>2</sub> O <sub>3</sub> (Comm.)	Pt Al <sub>2</sub> O <sub>3</sub> (Comm.)	PtRu mA (DI)	NiCu mA (DI)	NiCu C (DI)				
loading ratio (wt%)	5.0	5.0	2.0/1.0	1.0/1.0	1.0/1.0				
surface area (m <sup>2</sup> /g)	245	245	226	226	226				
particle size(s) (nm)	5.6	4.7	7.5 (Pt) 4.5 (Ru)	2.4–4.6	5.9 (Ni) 8.6 (Cu)				

mA = mesoporous alumina.

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