



## Hydrodeoxygenation of guaiacol over carbon-supported molybdenum nitride catalysts: Effects of nitridding methods and support properties

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### ABSTRACT

Molybdenum nitride catalysts supported on activated carbon materials with different textural and chemical properties were synthesized by nitridding supported Mo oxide precursors with gaseous NH<sub>3</sub> or N<sub>2</sub>/H<sub>2</sub> mixtures using a temperature-programmed reaction. The supports and catalysts were characterized by N<sub>2</sub> physisorption, XRD, chemical analysis, TPD, FT-IR and XPS. Guaiacol (2-methoxyphenol) hydrodeoxygenation (HDO) activities at 5 MPa and 300 °C were evaluated in a batch autoclave reactor. Molybdenum nitrides prepared using a N<sub>2</sub>/H<sub>2</sub> mixture resulted in more highly dispersed catalysts, and consequently more active catalysts, relative to those prepared using ammonolysis. The HDO activity was also related to pore size distribution and the concentration of oxygen-containing surface groups of the different carbon supports. Increased mesoporosity is argued to have facilitated the access to active sites while increased surface acidity enhanced their catalytic activity through modification of their electronic properties. The highest activity was thus attributed to the highest dispersion of the unsaturated catalyst species and the highest support mesoporosity. Surprisingly, addition of Co did not improve the HDO activity.

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### 1. Introduction

Due to long-term economic and environmental concerns, bio-oil derived from pyrolysis of woody biomass has received considerable attention as an alternative renewable feedstock to crude oil for the production of fuels and value-added chemicals [1]. Its utilization as fuel is limited, however, by high viscosity, low heating value, incomplete volatility and thermal instability, which stem from the relative abundance of oxygenated organic compounds [2]. Catalytic hydrodeoxygenation (HDO) reactions are typically performed to refine bio-oil and increase its quality as transportation fuel. There are two significant challenges in this process: (i)

prevention of coke formation/catalyst deactivation and (ii) selective removal of oxygen without excessive hydrogenation of aromatic and olefinic compounds [2,3].

Model compounds have been used to mimic HDO studies of bio-oil components in an effort to understand the role and fate of different functional groups present in the feed, as well as provide additional insight into the development of improved catalysts and processes [3]. Guaiacol (2-methoxyphenol) is commonly used as a model compound for HDO studies to represent the large number of mono- and dimethoxy phenols present in bio-oil [4]; it is known to be a precursor to catechol but it also subsequently forms coke [5,6]. Also, guaiacol possesses two different oxygenated functional groups (–OCH<sub>3</sub> and –OH) which make it challenging to achieve complete deoxygenation [7].

Heterogeneous catalysts commonly studied for HDO of guaiacol (and many other model compounds) are conventional sulfided Co(Ni)Mo/γ-Al<sub>2</sub>O<sub>3</sub> [5,8] and supported noble metal catalysts such as Ru, Rh and Pd [9,10]. The initial interest in the metal sulfides was driven by high cost and lack of selective HDO activity of the noble metal catalysts. Despite the high catalytic activity for

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