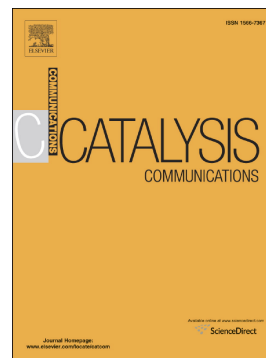


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# Unsupported Transition Metal-Catalyzed Hydrodeoxygenation of Guaiacol

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## Abstract

Unsupported transition metal sulfides with relatively high surface areas were synthesized by using mesoporous silicas as hard templates. The prepared catalysts were characterized by N<sub>2</sub> physisorption, TEM, and NH<sub>3</sub>-TPD method. The products from HDO of guaiacol over the catalysts were analyzed by GC-MS. The analysis results indicated that the acidity of catalysts facilitated the dehydration and transalkylation reactions to yield hydrocarbons and methylated products. Unsupported NiMoW catalyst performed the highest deoxygenation activity among catalysts studied, which were likely attributed to a large number of active sites exposed and the effect of W supplement.

*Keywords:* Unsupported catalysts; NiMoW catalyst; nanocasting method; acid sites; HDO

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## 1. Introduction

The catalysts employed so far for hydrodeoxygenation (HDO) which is the process by which biomass derived pyrolytic oils are converted to fuels [1], have been similar to those used in hydrodesulfurization (HDS) refinery processes [2, 3].

The traditional HDS catalysts are sulfided CoMo or NiMo phases supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. More stringent regulations on fuels sulfur content resulted in a new generation of HDS catalysts exemplified by the NEBULA catalyst [4-6]. The new catalytic materials are constituted of non-supported or highly-loaded CoMo or NiMo, sometimes supplemented with tungsten (CoMoW or NiMoW) showing clear improvement in HDS activity compared to alumina supported catalysts [7, 8]. Wang et al. synthesized unsupported NiMoW sulfide catalysts by a mechanical activation method for the HDO of p-cresol [9]. The catalyst performances showed high conversions and selectivities to hydrocarbons. However, the specific surface area of the non-supported catalysts were not favorable (maximum of 35 m<sup>2</sup>/g).

In the present work we have investigated the use of unsupported CoMo and NiMo with and without W prepared via a nanocasting method in HDO of guaiacol, a model molecule for the phenolic compounds derived from lignin fraction in pyrolysis bio-oils.

## 2. Experimental

### 2.1. Preparation of catalysts

Unsupported catalysts were synthesized by the nanocasting method using SBA-16 as hard template. The synthesis of mesoporous silica SBA-16 has been described elsewhere [10]. The unsupported sulfided catalysts were fabricated as follows. A mixture of metal precursors 0.46 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Alfa Aesar, 99%), 0.64g of (NH<sub>4</sub>)<sub>6</sub>W<sub>12</sub>O<sub>39</sub>·H<sub>2</sub>O (Alfa Aesar, 99%), and 1.51 g of Ni(NO<sub>3</sub>)<sub>2</sub> (Sigma Aldrich, 99%) with a molar ratio 1:1:2 was dissolved in 50ml of water. The aqueous mixture was infiltrated into the channels of 2.0 g of mesoporous silica SBA-16 via a solvent evaporation at 45°C under stirring for 12 hours. The obtained solid was calcined at 550°C for 5 hours (rate 1°C/min), followed by sulfidation under a flow of a mixed gas 10% H<sub>2</sub>S in H<sub>2</sub> at 400°C for 6 hours. Finally, the silica template was removed by treating with a 2M NaOH solution for several times, denoted NiMoW. The same procedure was used to synthesize the unsupported bimetallic Ni(Co)-Mo catalysts denoted NiMo, CoMo. An unsupported trimetallic bulk Ni-Mo-W catalyst was synthesized by a chemical precipitation method described by Liu et al. [7] with the same molar ratio as NiMoW and is thereafter designated as NiMoW bulk. The commercial

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