



The influence of citric acid on the synthesis and activity of high surface area MoP for the hydrodeoxygenation of 4-methylphenol

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ABSTRACT

Unsupported, high surface area MoP was synthesized by adding citric acid (CA) to solutions of ammonium heptamolybdate and diammonium hydrogen phosphate followed by drying (397 K), calcination (773–973 K), and reduction in H₂ (923 K). A tetrameric Mo citrate precursor was formed after drying which decomposed into a monomer of the form, Mo(C₄H₅O₃CN)₂·HPO₄ following calcination. Reduction of this monomer produced CH₄, CO, CO₂, NH₃, H₂O, and MoP. The C content of the reduced MoP-CA catalysts decreased from 12.8 to 4.0 wt% as the calcination temperature increased from 773 to 973 K, whereas the surface area decreased from 136 m²/g to 53 m²/g and the MoP particle size increased from 5 to 9 nm, respectively. The residual C acted as a structural promoter of the calcined samples, limiting agglomeration of the MoP crystallites during reduction so that nanoparticles (5–9 nm) of MoP were produced. The HDO of 4-methylphenol over the MoP-CA catalysts was found to be structure insensitive with an initial turnover frequency (TOF) of 0.079 s^{−1} at 623 K and 4.4 MPa H₂. The ratio of hydrogenation to direct deoxygenation of 4-methylphenol (TOF_{H₂}:TOF_{D₂O} = 0.78:1) was independent of the MoP particle size and greater than that observed over MoS₂.

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1. Introduction

Bio-oils derived from the pyrolysis of bio-mass contain large amounts of oxygen (>10 wt%) that contribute to the low heating value, high viscosity, and instability of these oils [1]. The oxygen can be removed by hydrodeoxygenation (HDO) using supported metal sulfide catalysts such as MoS₂/Al₂O₃ promoted with Ni [2,3], as used in the hydrosulfurization (HDS) of petroleum oils. However, because bio-oils are S free, a sulfiding agent such as CS₂ or H₂S must be fed to the HDO reactor to maintain adequate sulfidation of the catalyst, and this is undesirable [4]. Hence, there is an interest in non-sulfided catalysts for the HDO of bio-oil.

Catalysts such as metal phosphides, that are active and selective for HDS, are also candidates for HDO [5–7]. Studies have shown that MoP/SiO₂ has 4 times the activity (on a mass basis) of MoS₂/Al₂O₃ for the HDS of thiophene [8]. Stinner et al. [9] showed that MoP has a 6 times higher turnover frequency (TOF) for the

hydrodenitrogenation (HDN) of orthopropylaniline than MoS₂/Al₂O₃, based on geometric estimates of surface site density. Several other studies have also reported that metal phosphides are more active and selective than sulfided metals for HDS [6,10,11] and HDN [12].

Previous studies on the HDO of 4-methylphenol demonstrated that unsupported, low surface area MoP has a lower activation energy and higher conversion for the HDO of 4-methylphenol compared to low surface area MoS₂, but the MoP activity was limited by low metal dispersion [13]. The unsupported MoP catalyst is a potential candidate for slurry phase HDO of bio-oil, analogous to the use of unsupported, high surface area MoS₂ catalysts of slurry phase hydroconversion of residue oils [14]. Indeed, the use of an unsupported Fe catalyst for slurry phase bio-oil hydroconversion has been described recently [15].

Wang and Smith [16] have shown that both the surface area and CO uptake of MoP can be increased from 5 m²/g and <1 μmol/g to 139 m²/g and 42.4 μmol/g, respectively, by preparing the catalysts in the presence of citric acid (CA). The increase in MoP surface area corresponded to an increase in 4,6-dimethyldibenzothiophene HDS conversion from 54.5% to 74.7% [16]. Similarly, hydrazine decomposition was found to increase from 55% to 85% for MoP prepared without and with CA, corresponding to MoP surface areas of 8.2 and 122 m²/g, respectively [17]. In the present study, MoP prepared using CA, has been investigated for the HDO of

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