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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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 hydrodesulfurization (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-dimethylbenzothiophene 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...