

# Hydrodesulfurization of 4,6-dimethyldibenzothiophene over high surface area metal phosphide

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## Introduction

Hydrotreating is an important crude oil refining process that removes S, N, and O from hydrocarbon molecules by reacting them with H<sub>2</sub> over a catalyst. Recently, transition metal phosphides and bi-metal phosphides [1-4] have been investigated as alternatives to metal sulphides, and in some studies, metal phosphides have been shown to be more active than conventional metal sulfides for hydrodesulphurization (HDS). Preparation of unsupported metal phosphides by conventional temperature-programmed reduction (TPR) of metal phosphates leads to low surface area catalysts with relatively low activity [2]. Recently high surface area MoP (122 m<sup>2</sup>/g) was prepared by adding citric acid to the precursor metal salt solution [3].

In the present paper, we report the preparation of high surface area monometallic phosphides (Ni<sub>2</sub>P, MoP) and a series of bimetallic phosphides (Ni<sub>x</sub>MoP) using citric acid as a chelating agent mixed with an aqueous solution of the desired metal salts. The resulting materials are shown to be much more active in the HDS of 4,6-dimethyldibenzothiophene (DMDBT) than the corresponding metal phosphides prepared in the absence of citric acid.

## Materials and Methods

The metal phosphide catalysts were prepared by adding the required amount of citric acid (CA) to de-ionized water containing the corresponding metal salts [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and/or Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] and [(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>]. The resulting solution was aged in a water bath at 363 K, dried at 393 K and calcined at 773 K for 5 h. TPR of the catalyst precursors was done in H<sub>2</sub> (160 ml/min) at a heating rate of 1 K/min to 923 K and this temperature was held for 2.5 h. The HDS of 4,6-DMDBT was measured in a fixed bed reactor at 583 K, 3.0 MPa H<sub>2</sub> and WHSV = 0.78 h<sup>-1</sup>. The product was collected periodically and analyzed using a 3400 Varian GC equipped with a FID.

## Results and Discussion

XRD showed that phase pure MoP was prepared in the presence of the CA. When Ni was added, a NiMoP phase appeared and with increased Ni content of the Ni<sub>x</sub>MoP catalyst, the formation of the NiMoP phase became more evident. Excess P was used in the preparation of Ni<sub>2</sub>P (P/Ni ratio = 1/1 and 2/1), because normally some P loss occurs during TPR. The catalyst with an initial P/Ni ratio of 1/1 contained two phases (Ni<sub>2</sub>P and Ni<sub>8</sub>P<sub>3</sub>) in the reduced product, whereas increasing the P/Ni ratio to 2/1 yielded phase pure Ni<sub>2</sub>P. The addition of citric acid gave rise to a significant increase in the surface area (> 100 m<sup>2</sup>/g) of the monometallic phosphides (MoP, Ni<sub>2</sub>P) compared to those prepared in the absence of CA (< 10 m<sup>2</sup>/g). The Ni<sub>0.25</sub>MoP-CA catalyst also had high surface area (114 m<sup>2</sup>/g), indicating that the bimetallic phosphides could also be prepared with high surface area by adding CA to the precursor salt solutions. There was a gradual decrease in surface area as the Ni content of the Ni<sub>x</sub>MoP (0 < x ≤ 1) catalyst increased.

The TEM micrograph of the MoP-CA sample (Figure 1) showed separate particles of size 6 - 10 nm, whereas MoP prepared without CA showed aggregated particles had formed large nanoclusters with a size of 50 - 60 nm. The TEM micrograph of the Ni<sub>2</sub>P-CA catalyst showed amorphous material, with a wide size distribution and hence the high surface area of the nickel phosphide is mainly from amorphous nickel phosphide.

XPS spectra showed oxidized Ni, Mo and P species as well as reduced species associated with the phosphide phase, due to the presence of a passivation layer on the phosphides. For the MoP-CA catalyst, a transfer of electron density from Mo to P occurred. The addition of Ni led to an increase in the binding energy (BE) of Ni<sub>2p</sub> and a decrease in the BE of Mo<sub>3d</sub>, suggesting that a transfer of electron density from Ni to Mo occurred. This may reflect a strong interaction between Ni and MoP.

The HDS activity data showed that the initial conversions of the catalysts prepared with CA were uniformly high, with 74.7% and 80.9% for MoP-CA and Ni<sub>2</sub>P-CA, respectively. Tests of the MoP and Ni<sub>2</sub>P prepared in the absence of CA yielded much lower conversions (30 - 55%). The HDS turnover frequency (TOF) of the catalysts decreased in order: Ni<sub>2</sub>P-CA > Ni<sub>x</sub>MoP-CA > MoP-CA, and the TOF of the Ni<sub>x</sub>MoP catalysts increased with increased Ni content (Figure 2). Since the LUMO of 4,6-DMDBT is C-S anti-bonding, surfaces that are able to transfer electron density to this orbital facilitate the dissociation C-S bond. The XPS results that showed an increased electron density of the Mo surface over Ni<sub>x</sub>MoP catalysts may account for the higher TOF of Ni<sub>x</sub>MoP compared with MoP. The HDS activity of the metal atoms has been theoretically correlated with the order of density of metal d states near the Fermi level: Ni<sub>2</sub>P > NiMoP > MoP [4] and the results of the present study appear to confirm this trend.

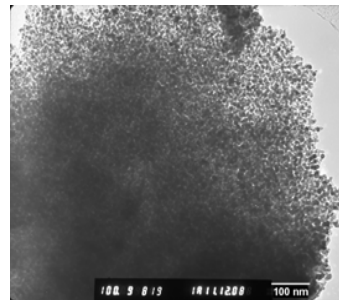


Figure 1. TEM image of MoP-CA catalyst

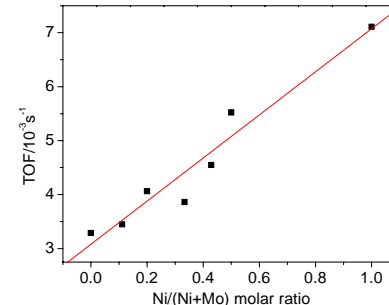


Figure 2. Initial TOF of different catalysts

## References

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