Hydrodesulfurization of 4,6-dimethyl dibenzothiophene over high surface area metal phosphide

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Introduction
Hydrodesulfurization is an important crude oil refining process that removes S, N, and O from hydrocarbon molecules by reacting them with H₂ 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 m²/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 (Ni₅P, MoP) and a series of bimetallic phosphides (NiₓMoP) 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-dimethyl dibenzothiophene (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 [(NH₄)₆Mo₇O₂₄·4H₂O and/or Ni(NO₃)₂·6H₂O] and [(NH₄)₂HPO₄]. 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 H₂ (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 H₂ and WHSV = 0.78 h⁻¹. 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 NiₓMoP catalyst, the formation of the NiMoP phase became more evident. Excess P was used in the preparation of NiₓP (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 (NiₓP and NiP) in the reduced product, whereas increasing the P/Ni ratio to 2/1 yielded phase pure NiₓP. The addition of citric acid gave rise to a significant increase in the surface area (> 100 m²/g) of the monometallic phosphides (MoP, Ni₅P) compared to those prepared in the absence of CA (< 10 m²/g). The NiₓMoP-CA catalyst also had high surface area (114 m²/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 NiₓMoP (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 NiₓP-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 Ni₅P and a decrease in the BE of Mo₃P₆ 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 NiₓP-CA, respectively. Tests of the MoP and NiₓP prepared in the absence of CA yielded much lower conversions (30 - 55%). The HDS turnover frequency (TOF) of the catalysts decreased in order: NiₓMoP-CA > MoP-CA, and the TOF of the NiₓP prepared in the absence of citric acid.

Figure 1. TEM image of MoP-CA catalyst
Figure 2. Initial TOF of different catalysts

References