Probing the Hydrodesulfurization Properties of Metal Phosphides Using Core-Shell Nanoparticle Catalysts

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Introduction
Transition metal phosphides show excellent promise for hydrotreating reactions and the most active phosphides, Ni2P and Ni-rich bimetallic phosphides, have exhibited higher HDS and HDN activities than commercial sulfided Co-Mo and Ni-Mo catalysts [1,2]. Oxide-supported metal phosphate catalysts are most often prepared by temperature-programmed reduction (TPR), in which phosphate-like precursors are heated in flowing hydrogen to a maximum temperature in the range 823-923 K. TPR methods do not enable size and shape control of the degree needed to probe microstructure-reactivity relationships in transition metal phosphides. In this study, the preparation, characterization and hydrodesulfurization (HDS) properties of mesoporous silica encapsulated metal phosphate nanoparticles (Ni2P, Pd2P2) having narrow polydispersity were investigated.

Materials and Methods
The synthesis of phase-pure Ni2P nanoparticles (5-25 nm) was achieved by solution-phase arrested precipitation methods. Encapsulation in mesoporous silica was carried out by formation of a colloidal micellar assembly of cetyltrimethylammonium bromide (CTAB) incorporating hydrophobic Ni2P nanoparticles, followed by introduction of tetrathylorthosilicate and base to induce hydrolysis and condensation of SiO2; around the polar headgroups of the assembly. After isolation, the Ni2P@mSiO2 particles were calcined to remove the CTAB and organic ligands bound to the Ni2P nanoparticles. The oxidized Ni2P@mSiO2 nanoparticles were then reduced by passing PPh3 vapor (solid PPh3 loaded upstream) and a 5% H2/Ar mixture through the calcined Ni2P@mSiO2 samples at 673 K for 2.5 h. The core-shell nanocatalysts were characterized with a range of physicochemical techniques including X-ray diffraction (XRD), BET surface area, pulsed chemisorption and infrared (IR) spectroscopy. Dibenzothiophene (DBT) HDS activity measurements were carried out using a fixed-bed, continuous flow reactor operating at a total pressure of 3.0 MPa and temperatures in the range 523-623 K using a feed consisting of 3000 ppm DBT in decalin.

Results and Discussion
Shown in Figure 1 (left) is a TEM image of a 9.4 wt% Ni2P@mSiO2 core-shell nanocatalyst, consisting of Ni2P nanoparticles of narrow polydispersity (11.2 ± 0.7 nm) encapsulated in mesoporous silica. The Ni2P@mSiO2 core-shell nanocatalyst had a high BET surface area (608 m2/g) and the pore size distribution, calculated from the adsorption branch of the isotherm, yielded an average BJH pore diameter of 5.0 nm. DBT HDS conversions vs. temperature for the Ni2P@mSiO2 nanocatalyst, Ni2P nanoparticles (10.8 nm) dispersed on silica (Ni2P/SiO2) and a TPR-prepared Ni2P/SiO22 catalyst (Ni2P/SiO2-TPR) that had an average Ni2P crystallite size of 11 nm as determined using the Scherrer equation are plotted in Figure 1 (right).

Figure 1. TEM image (left) of a Ni2P@mSiO2 core-shell nanocatalyst. Dibenzothiophene HDS conversion vs. temperature data (right).

The Ni2P/SiO2-TPR catalyst exhibited the highest DBT HDS conversion, while the Ni2P@mSiO2 nanocatalyst was about twice as active as similarly-sized Ni2P nanoparticles dispersed on silica. For the pre-formed Ni2P particles dispersed on silica (Ni2P/SiO2), sintering of the Ni2P nanoparticles occurred under HDS conditions with the average crystallite size increasing from ~11 to ~25 nm, as determined using the Scherrer equation and XRD peak widths. For the Ni2P@mSiO2 nanocatalyst, on the other hand, the sintering of the Ni2P nanoparticles was minimized, with the average Ni2P crystallite size increasing only slightly from ~11 to ~13 nm. A substantially lower O2 chemisorption capacity was measured for the Ni2P@mSiO2 nanocatalyst (40 μmol/g) compared to the Ni2P/SiO2-TPR catalyst (168 μmol/g), most likely due to lower accessibility of the probe molecules to sites on the encapsulated Ni2P nanoparticles than was the case for the conventionally prepared catalyst. Dibenzothiophene HDS turnover frequencies (TOFs) at 598 K calculated using the O2 chemisorption capacities are within 20% of each other, providing evidence that the active sites on the catalysts are similar.

Significance
Encapsulation of metal phosphate nanoparticles to form core-shell structures (e.g. Ni2P@mSiO2) minimizes sintering of the nanoparticles and enables probing of the microstructural properties of metal phosphate catalysts under the harsh reaction conditions relevant to industrial hydrotreating processes.

References