Molybdenum Phosphide: A Novel Catalyst for Hydrodenitrogenation

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(Received October 13, 1997; CL-970788)

A single phase molybdenum phosphide, MoP, with a moderate surface area was prepared using temperature programmed reduction of an amorphous phosphate precursor and the so-prepared sample was found to be a good catalyst for hydrodenitrogenation.

Despite the tremendous interest in using transition metal carbides and nitrides as catalysts during the last decade[1], the analogous phosphides have received much less attention. Almost all transition metals form phosphides, with many of the binary phosphides having compositions ranging from M_3P to MP_3[2-5]. In addition there are many ternary mixed-metal phosphides, phosphide nitrides, phosphide sulfides, and phosphide selenides. The flexible metal to phosphorus ratio in metal phosphides offers an excellent opportunity for trying new compositions for catalysts. In this paper we report the preparation of unsupported molybdenum, MoP, of moderate surface area using a temperature-programmed reaction method.

The preparation methods of metal phosphides[6,7] include (1) the direct reaction between metal and phosphorus heated in vacuum or in an inert atmosphere; (2) the isothermal reduction of metal phosphate with carbon or hydrogen at high temperatures; (3) the heating of the metal or metal halide with phosphine compounds; (4) the high temperature electrolysis of molten salt baths containing the metal oxide and an alkali phosphate. These preparation methods usually require very high temperatures (>1000 K)[8-11], resulting in sintered materials of high crystallinity. Indeed it has been reported[8,12] that the materials have low specific surface area, limiting their use as catalysts in unsupported form. Also the use of toxic phosphine compounds raises environmental problem for their disposal[12]. Here we report the first synthesis of single phase molybdenum phosphide, MoP, with a moderate surface area using temperature programmed reduction of an amorphous molybdenum phosphate precursor in hydrogen.

The phosphate precursor was prepared as follows: 17.655 g (0.1 mol Mo) ammonium molybdate (Aldrich) and 13.206 g (0.1 mol P) ammonium phosphate (Aldrich) were dissolved in 300 ml distilled H_2O. The clear solution was stirred overnight at room temperature, and then heated to evaporate H_2O. The resulting material was dried at 393 K for 6 hours, and then calcined at 773 K for 6 h. The material had a glasslike appearance with deep blue color, and had a featureless X-ray diffraction pattern. The material was transformed to the final product by temperature programmed reaction. The method consisted of reducing the phosphate precursor (~2,700 μmol, 0.573 g) in a stream of hydrogen (223 $\mu mol s^{-1}$, 300 $cm^3 min^{-1}$) while raising the temperature in a linear manner at 0.016 $K s^{-1}$ up to 923 K. After the reduction, the black sample was passivated in 0.5% O_2/He before being exposed to air.

The prepared molybdenum phosphide sample was characterized by X-ray diffraction (Scintag, Mg-Kα radiation), BET surface area, ^{31}P magic-angle spinning solid state nuclear magnetic resonance (MAS-NMR) (Bruker, 121.5 MHz) and CO chemisorption (Micromeritics, ASAP 2000) measurements. The XRD pattern of the sample is shown in Figure 1, and it confirms the formation of molybdenum phosphide, MoP. The ^{31}P MAS-NMR spectrum of the sample shows a single peak centered at 144.2 ppm (relative to 85% H_3PO_4), indicating that all P atoms in this sample are equivalent. This is in agreement with the crystal structure of MoP (Hexagonal, P-6m2). Also the observed chemical shift δ (144.2 ppm) is similar to other transition metal phosphides (for ZrP, δ = 128.4, 187.5 ppm)[13]. The surface area of the sample was found to be 15 $m^2 g^{-1}$, while the CO uptake was 18 $\mu mol g^{-1}$.

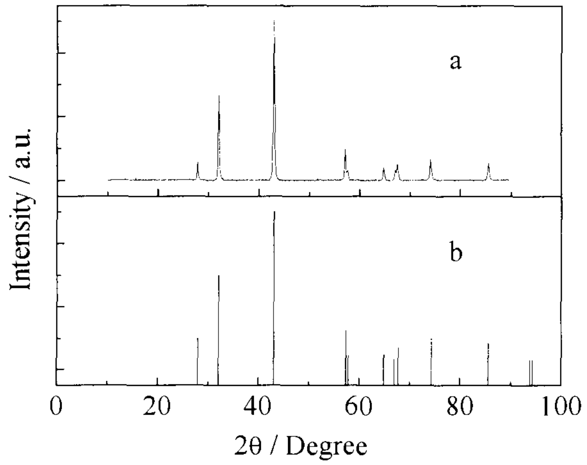

Figure 1. XRD patterns of molybdenum phosphide. **a.** prepared in present work; **b.** MoP, JCPDS 24-771.

The single phase MoP sample was tested in the hydrodenitrogenation (HDN) reaction in the presence of sulfur. The reactivity study was carried out using 30 m^2 catalyst in a high pressure system with a trickle-bed reactor at 3.1 MPa, and 643 K, using model liquid compounds. The details of the reactor system have been given elsewhere[14]. The catalyst was activated in H_2 at 723 K for 2 h at atmospheric pressure prior to reaction. Figure 2 shows the HDN, hydrodesulfurization (HDS), hydrodeoxygenation (HDO), and hydrogenation (HYD) reactivities of the catalyst with on-stream time. Hydrogenation here refers to the saturation of aromatic rings without the removal of a heteroatom (N, S, O). The steady-state HDN conversion (33%) is significantly higher than that of Mo2N (20%), and is comparable to those of Mo_2C (47%) and commercial NiMo-S/Al_2O_3 (38%) under similar reaction conditions[14].

The preparation described provides a simple and environmentally benign way to prepare metal phosphides, because it avoids the use of toxic phosphine compounds. This

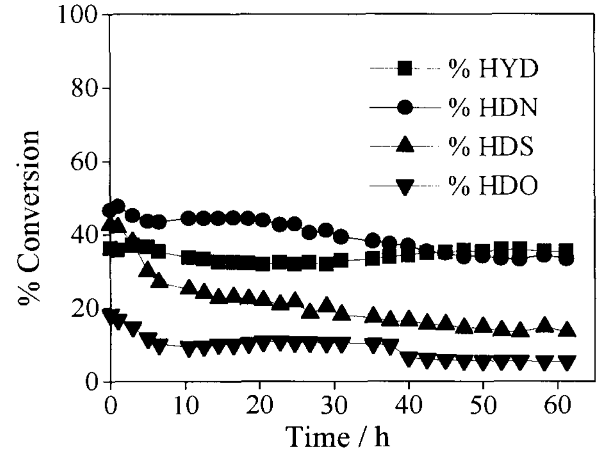

Figure 2. Reactivities of MoP. Feed composition: 3000 ppm S (dibenzothiophene), 2000 ppm N (quinoline), 500 ppm O (benzofuran), 20% tetralin in tetradecane. 30 m^2 catalyst; H_2 150 cm^{-3} min^{-1}; liquid 5 cm^{-3} h^{-1}; 643 K; 3.1 MPa.

method can probably also be generalized to other transition metals. This could open up a whole new class of materials as catalysts. This method can be easily adapted to the preparation of phosphide thin films. Further studies are in progress in this laboratory to explore other transition metal phosphides as well as their applications in other reactions.

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