Can Ni phosphides become viable hydroprocessing catalysts?

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ABSTRACT

We prepared higher surface area nickel phosphides than are normally found by reducing nickel phosphate. To do this, we hydrothermally synthesized Ni hydroxy phosphite precursors with low levels of molybdenum substitution. The molybdenum substitution increases the surface area of these precursors. During pretreatment in a sulfiding atmosphere (such as H_2S/H_2) dispersed islands of MoS_2 segregate from the precursor and provide a pathway for H_2 dissociation that allows reduction of the phosphite precursor to nickel phosphide at substantially lower temperatures than in the absence of MoS_2. The results reported here show that to create nickel phosphides with comparable activity to conventional supported sulfide catalysts, one would have to synthesize the phosphide with surface areas exceeding $400 \, m^2/g$ (i.e. with nanoparticles less than 30 Å in lateral dimension).

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1. Introduction

Hydroprocessing catalyst research primarily focuses on Ni, Co/Mo, W sulfide catalysts. Although this comprises a relatively small compositional range, there have been continuous and major advances in this area of catalytic materials discovery, understanding, and deployment over many decades [1]. Catalyst manufacturers arecontinually advertising new, more active catalysts [2]. These advances apparently arise by increasing the number of active sites on MoS_2 sheets by either making the crystallites smaller or having an improved positioning of the promoting Ni or Co atoms. The consensus belief is that isolated Ni or Co atoms decorate positions on the edge of the MoS_2 crystallites or near the basal plane within one sulfur atom of the edge (i.e. brim sites [2]. Because of this limited elemental toolkit, there continues to be an interest in discovering new compositions that could provide alternative catalysts more effective than those that are universally used today. Two alternatives that have received substantial attention in the last number of years are catalysts comprising noble metal sulfides, particularly RuS_2, and variants of nickel phosphide. RuS_2 catalysts can have high activity but only when they contain large crystallites of RuS_2. However small crystallites do not have high activity since the very strong interaction between Ru and S makes

the resulting RuS_2 non-reactive [3]. Only with larger crystallites the Ru–S interaction strength becomes sufficiently weak so that metallic Ru becomes exposed and active. Because of its high cost and especially because of its limited availability, supported Ru at high loadings loses any practical significance. Whereas Mo/W carbides or nitrides also show some catalytic activity, they slowly convert to the corresponding sulfides and therefore do not really represent new materials. A growing body of work reported in the last 15 years describes nickel phosphide as a phase stable catalyst for hydroprocessing reactions. This study addresses issues with nickel phosphide hydroprocessing catalysts.

The Oyama group pioneered the use of nickel phosphides as hydroprocessing catalysts [4]. In their original work they reduced nickel phosphates at high temperature ($\sim$550 °C) to form the nickel rich Ni_2P phase, which had surface areas < 5 m^2/g. They also attempted to disperse low loadings of the nickel phosphate precursor on non-interacting supports, but this provided only slight advantages as it also required high temperature reductions. In the last few years, various researchers have applied nanoparticle preparation methods to increase the number of surface sites [5]. In addition, gas phase phosphidation of small supported nickel particles on silica using phosphine gas has been described [6]. These approaches have been summarized in a recent review [7]. Nonetheless, an industrially viable simple and scalable preparation route to high activity nickel phosphide catalysts remains elusive. It is also probable that in an application of nickel phosphides, there may be a stacked configuration with conventional molybdenum catalysts, so a single activation procedure would be beneficial. In this

study we use a novel route to prepare nickel phosphide/MoS$_2$ composites from single phase molybdenum-substituted nickel hydroxy phosphite precursors. Our data in three phase reactors with real feeds show what improvements are still needed to make nickel phosphides viable hydrotreating catalysts.

2. Experimental

Hydrothermal syntheses were carried out in Teflon lined Parr autoclaves into which nickel carbonate, molybdenum oxide (MoO$_3$) and phosphoric acid were added (typical charge for nominal Ni$_{1.8}$Mo$_{1.6}$P$_1$ molar ratio: 1.38 g of nickel carbonate (0.01163 moles Ni), 1.49 g of MoO$_3$ (0.01035 moles Mo) and 0.75 g of phosphoric acid (0.00651 moles of P) were placed into ~150 cm^3 of water contained in a Teflon liner, which in turn fit into a 300 cm^3 Parr autoclave, which was then heated to 200 °C and held at temperature for 16 h, cooled, filtered and dried at 100 °C. Loadings of 8× compared to the amounts cited above were also confirmed to give the same products. The nominal molar stoichiometry of different reaction mixtures was varied and is shown in the Results section. For several of the samples, analyses of both the liquid filtrate and solid were determined. For the sample containing cobalt, cobalt carbonate was added to the synthesis mix. For the Pt-containing sample, the nickel hydroxy phosphite precursor was impregnated with a solution of Pt tetrammine hydroxide, dried at 100 °C and reduced at 400 °C in hydrogen.

X-ray diffraction spectra using CuK$_\alpha$ radiation were used to identify crystalline phases. Particle sizes were estimated on some samples using the Scherer relationship with background scans of highly crystalline quartz correcting for instrumental line broadening.

Surface areas were measured by a 7 point BET isotherm between p/p_o values of 0.05 and 0.3. TG/DTA data were collected on a Mettler TGA 851 thermal analyzer.

X-ray photoelectron spectroscopy (XPS), and X-ray absorption near edge spectroscopy (XANES) were used to identify oxidation states and structures of the samples. The XPS measurements were made in a Kratos Axis-165 with a working pressure of <3 E-9 torr, a monochromatic Al-Kα (1486.7 eV) source, and a constant-analyzer-energy (CAE) detection mode. Samples were mounted by dispersion of powders on sticky double-sided carbon tape. The XANES measurements were done at sector 9 (XSD) of the Advanced Photon Source (APS) in Argonne National Laboratory. Data were acquired at Mo L$_{III}$ edge, S, P, and Ni K-edges for oxides and sulfide samples.

A three phase fixed bed reactor system with three separate reactors operating in an up flow mode was used to measure HDS activities on a straight run gas oil containing 1.3% S and 160 ppm N. Catalyst powder was pelletized, crushed and sieved to 35/60 mesh (250–500 μm) chips. 3 cm^3 of these chips were mixed with 6 cm^3 of 40–60 mesh quartz chips and loaded into the reactor. Hard sulfur species total approximately 1200–1400 ppm S (based on 2D GC analysis) with aromatics at ~29%. Initial boiling point was 202 °C and the final boiling point is 415 °C. Pressure was maintained at 650 psi and temperature at 338 °C. Apparent rate constants were calculated using 1.5 order kinetics. The three reactors are heated in a common sand bath. The Mo-containing hydroxy nickel phosphite precursors were pretreated ex situ in H$_2$S/H$_2$ and the Pt-containing catalyst in pure H$_2$ to guarantee what phases were present at the start of the reaction. The samples then went through an activation in DMDS (2.5%) with a primary sulfiding hold at 250 °C for 12 h and then with a final treatment at 343 °C for 24 h. The phase composition of the spent catalysts was checked by x-ray diffraction.
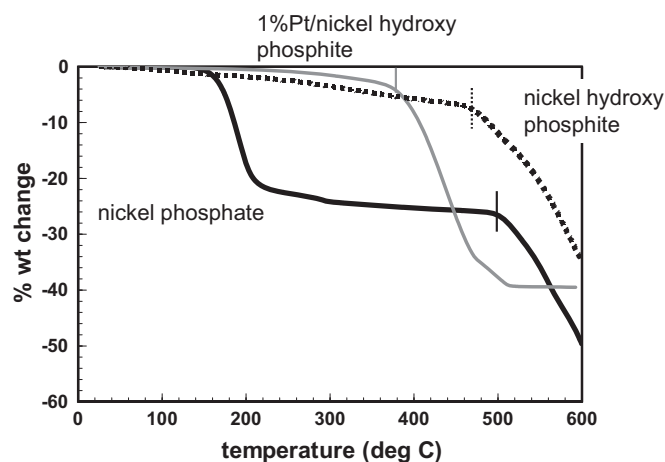

Fig. 1. Reduction of nickel phosphate, nickel hydroxy phosphite and Pt impregnated nickel hydroxyl phosphite. The vertical ticks show the approximate reduction onset temperature.

3. Results and discussion

Based on the approach outlined in the introduction, we have attempted to find an alternative pathway to create a higher surface area bulk nickel phosphide than is possible with high temperature H$_2$ reduction of low surface area nickel phosphates. The hydroxy nickel phosphite precursors have higher surface areas than the conventional nickel phosphates. To capture this benefit we tried to find ways of reducing them at temperatures lower than the ~550 °C used for nickel phosphate reduction. Initially, we examined the effect of adding Pt. As is well known, Pt group metals can promote reduction of mixed metal oxides by a spillover mechanism. However, Pt is poisoned by sulfur which inhibits its ability to dissociate hydrogen. Consequently for Pt to promote the reduction of the nickel precursor to nickel phosphide, the reduction needs to occur in a sulfur-free feed. As we show in Fig. 1, the nickel hydroxyl phosphite does reduce at lower temperatures in H$_2$ with Pt present, although the surface area of the resulting nickel phosphide is only marginally higher. Also, it would be advantageous to be able to reduce the precursors with a conventional hydroprocessing startup (i.e. in both a reducing and sulfiding environment). This would allow them to be run in a mixed bed together with conventional supported Ni–Mo or Co–Mo catalysts. We found that molybdenum substitution into the hydroxy phosphite precursor allowed this. Molybdenum substitution has two effects. It increases the surface area of the precursor, and in H$_2$/H$_2$S, some fraction of the Mo in the substituted Ni hydroxy phosphite segregates as MoS$_2$. This phase in turn dissociates hydrogen which promotes precursor reduction to nickel phosphide.

In Fig. 1 we show a TGA in hydrogen for the classical reduction pattern of nickel phosphate to nickel phosphides. The reduction onset temperature is near 500 °C and substantive reductions in an isothermal mode require temperatures near 550 °C. We also show the reduction patterns of nickel hydroxyl phosphite both with and without added Pt. With the Pt present, the reduction onset temperature is lowered by ~90 C.

We found that hydrothermally reacting mixtures of nickel carbonate and phosphoric acid would produce a crystalline phase (hydroxy nickel phosphite) whose crystal structures had been reported about 15 years ago [8]. The X-ray spectrum of a 200 °C synthesis of nickel carbonate and phosphoric acid in which the mole ratio of Ni/P was 1.8/1 is shown in Fig. 2.

The crystalline pattern in Fig. 2 shows an excellent match to the Ni$_{11}$(HPO$_3$)$_8$(OH)$_6$ phase fully characterized by a solved crystal structure [8], as shown in Fig. 3.