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PRIORITY COMMUNICATION

Hydrodesulfurization of Petroleum Feedstocks with a New Type of Nonsulfide Hydrotreating Catalyst

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One member of a new family of catalysts for the removal of sulfur from petroleum feedstocks, nickel phosphide on silica (Ni_2P/SiO_2), is reported. The catalyst is able to effectively treat feeds containing alkylated heteroaromatics, the most tenacious of the sulfur compounds. Tests were conducted with model reagents as well as with real feedstocks, and comparisons were made with optimized commercial sulfide catalysts under realistic conditions of temperature and pressure. The phosphide catalyst showed superior activity, selectivity, and stability over the commercial catalysts. Characterization of the phosphide material by X-ray absorption spectroscopy showed that high activity was associated with Ni–P bonding in the catalyst.

INTRODUCTION

The removal of sulfur from petroleum feedstocks is currently *the* paramount problem in the refining industry because of recently enacted environmental regulations to limit sulfur levels in transportation fuels. For example, in the US sulfur contents have been mandated to be reduced to 30 ppm in gasoline by 2004 (1) and 15 ppm in diesel by 2006 (2), and similar levels have been legislated in Europe and Japan (3). The currently allowed concentrations in gasoline and diesel in the US are 300 and 500 ppm, respectively, and meeting the new standards will require considerable capital investment. It can be calculated that with present activity, hydrotreating reactor volumes would have to be increased 10–20 fold to satisfy the new limits (4). Recognition of this problem has led to a worldwide search for better catalysts (5). Current approaches include the improvement of existing sulfide catalysts and the investigation of new compositions such as bimetallic carbides (6), nitrides (7), and materials containing noble metals (8, 9). We report here a member of a novel class of materials that have substantial promise as next-generation catalysts. The materials are the transition metal phosphides, a group of refractory metallic compounds. Recent work has shown that MoP (10–12), WP (13, 14), Ni_2P, and Co_2P (15, 16) are new catalysts active for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of petroleum feedstocks. This paper concerns nickel phosphide supported on silica, Ni_2P/SiO_2. Studies with model compounds indicate that the material has excellent performance in HDS even with an inhibiting nitrogen compound, and tests with an actual feed confirm its unusually high activity.

Commercial hydrotreating catalysts are molybdenum or tungsten sulfides promoted by cobalt or nickel, and supported on alumina. They have been the standard catalysts since they were reported by researchers at I. G. Farben Industrie more than 70 years ago (17). The most common compositions are $Co–Mo–S/Al_2O_3$ and $Ni–Mo–S/Al_2O_3$ with metal oxide weight loadings of close to 20% on an alumina carrier of about 250 $m^2\,g^{-1}$. The catalysts consist of crystallites of MoS_2 decorated at their crystal edges by Co or Ni atoms (18, 19). The MoS_2 has a layered structure in which the basal planes are largely inactive, and modern improvements have aimed at increasing dispersion and improving the support.

The metal-rich transition metal phosphides are a broad class of compounds which combine metallic properties such as conductivity with refractory properties such as hardness. They adopt many types of structure, but in general are not layered. For example, Ni_2P has the hexagonal Fe_2P structure of space group $P_{\bar{6}2m}$ (Fig. 1, insert) with lattice parameters $a_o = b_o =$ 0.5859 nm and $c_o =$ 0.3382 nm (20, 21).

RESULTS AND DISCUSSION

The phosphides can be prepared readily by the temperature-programmed reduction in H_2 of phosphate

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precursors (22–24). For bulk Ni_2P the reduction occurs in two stages, with maximum temperatures of 610 and 705 K. In the case of supported Ni_2P the precursors (nickel nitrate and ammonium phosphate) are impregnated onto the support, calcined, and then reduced in a similar manner. However, the presence of the support can separate the metal and phosphate components, and higher concentrations of the phosphorus component are desirable for the synthesis reaction. This is reported in detail in a forthcoming publication (25). For this study a Ni_2P/SiO_2 with a starting molar ratio of Ni/P of 1/2 was employed, corresponding to a Ni concentration of 1.15 mmol g^{-1} SiO_2. Silica (Cabosil L90, Cabot corporation, 90 m^2 g^{-1}) was chosen as the carrier to minimize support interactions and allow the intrinsic activity of the phosphide to be determined. After preparation, the catalyst was passivated in 1% O_2/He to protect its surface from bulk oxidation, but was re-reduced prior to characterization or testing.

The activity of the catalyst was first tested using a model mixture containing 3000 ppm sulfur (dibenzothiophene), 2000 ppm nitrogen (quinoline), 500 ppm oxygen (benzofuran), 20 wt.% aromatics (tetralin), and the balance aliphatics (tetradecane). The testing conditions were close to industrial, with a temperature of 643 K, a pressure of 3.1 MPa, a liquid feed of 5 cm^3 h^{-1}, a H_2 flow of 150 cm^3 min^{-1}, and reactor operation in three-phase, fixed-bed mode. The stainless steel reactor had a 9.5-mm O.D. (3/8 in.) and was equipped with an internal basket to hold the catalysts, which were loaded to an equal volume of 1 cm^3, with dilution with quartz chips. The catalysts were in the form of pressed pellets, which were crushed and sieved to ∼1 mm size (16/20 mesh). The results in HDS, hydrodenitrogenation (HDN), and hydrodearomatization (HDA) (26) are summarized in Table 1. The HDS level reached 98% and the HDN conversion was 80%, while the undesirable HDA conversion was only 19%. The results compare very well with those of a commercial $Ni–Mo–S/Al_2O_3$ catalyst (Shell 324), which under the same conditions gave 78% HDS, 43% HDN, and 50% HDA (27). The comparison is based on equal active sites loaded in the reactor (70 μmol), as measured by CO chemisorption for the phosphide and low-temperature (dry-ice/acetone) O_2 chemisorption for the sulfide. At this time we do not have information on how CO chemisorbs onto the catalyst, but it is likely that it interacts with exposed metal atoms, not blocked by phosphorus, and thus is a reasonable probe of active sites. The results are notable, not only because of the high activity displayed by the (Ni/P = 1/2) phosphide, but because of the high quinoline HDN levels. Quinoline is one of the most potent inhibitors of HDS (28).

TABLE 1

Hydrotreating Performance at 643 K and 3.1 MPa

Catalyst	HDS/%	HDN/%	HDA[a]/%
Ni_2P/SiO_2 (Ni/P = 1/2)	98	80	19
$Ni–Mo–S/Al_2O_3$	78	43	50

[a] Defined as hydrogenation of quinoline to N-containing compounds.

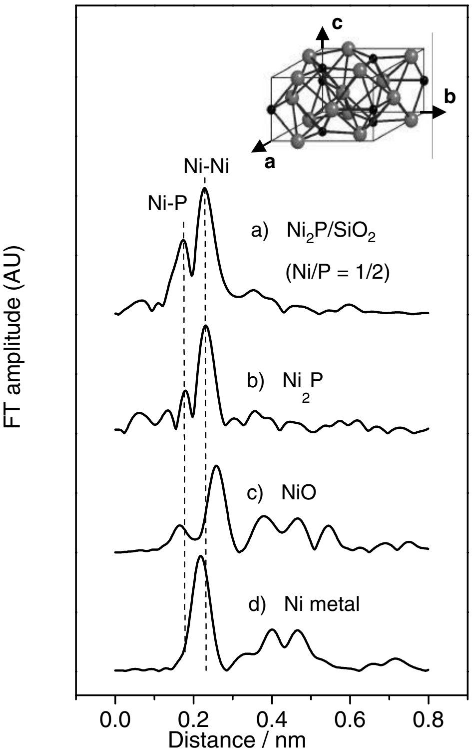

FIG. 1. EXAFS analysis of catalysts and references. The figure presents the Fourier transforms of the Ni *K*-edge region at 8333 eV, not corrected for phase shifts. The catalyst was loaded into a sealed glass cell with Kapton windows. (a) Ni_2P/SiO_2 (Ni/P = 1/2); (b) bulk Ni_2P; (c) bulk NiO; (d) bulk Ni metal. Insert: crystal structure of Ni_2P.

In order to identify the active phase in the catalyst it was examined using extended X-ray absorption fine structure (EXAFS) analysis (29). For the measurement the prepared sample was sealed in a glass cell with Kapton windows to protect it from the atmosphere. Comparisons were made with bulk Ni_2P, NiO, and Ni metal (Fig. 1). The Fourier transform (FT) of bulk Ni_2P shows two prominent peaks corresponding to Ni–P and Ni–Ni distances, respectively (Fig. 1b). The distances in the highly active Ni_2P/SiO_2 sample (Ni/P = 1/2) agree very well with these values, and the absence of other peaks (e.g., NiO) demonstrates that the predominant phase is Ni_2P (Fig. 1a).

The elemental composition of the freshly reduced and passivated catalyst was determined by inductively coupled plasma analysis. It was determined that the measured Ni concentration was 5.67 wt.%, which was close to the original value used in the synthesis of 5.58 wt.%, corresponding to 1.15 mmol Ni g^{-1} SiO_2. However, the measured phosphorus content was only 2.45 wt.%, compared to the value of 11.75 wt.% used in the synthesis. A substantial amount of phosphorus was lost, probably by volatilization during the reduction stage of preparation. Nevertheless, the expected wt.% for a stoichiometric Ni_2P product is only 1.49 wt.%, which means that the catalyst contains 0.96 wt.% extra phosphorus. This gives a gross stoichiometry of $Ni_2P_{1.6}$, with an indeterminate location of the excess phosphorus. Attempts were made to establish the state of the P by measuring the P *K*-edge region by NEXAFS, but this gave inconclusive results, as the samples had to be exposed to the air for this edge measurement, and all the P was observed to be oxidized. However, it is likely that the extra phosphorus probably resides on the surface of the silica in the form of phosphate.

There has been previous work (15) on Ni phosphide for hydrodenitrogenation (HDN), which showed it to have only moderate activity. Kinetic measurements indicated that it was likely not fully phosphided and susceptible to deactivation. Similar results were observed with a low-P-content (Ni/P = 2/1) catalyst (25) and suggests that control of stoichiometry is important. Although HDS was stable, HDN activity dropped considerably with time. This was not the case with the high-P-content catalyst used here, indicating that phosphide formation was essential for activity and durability.

Results with model compounds often do not correlate with those obtained with real feeds because the interactions between the components are complex, so most catalyst development is carried out with actual feeds. In order to evaluate the potential of the new catalyst it was subjected to a test with a hydrotreated gas oil (designated F-942). This feed was chosen because of its low sulfur (440 ppm) and nitrogen (8 ppm) content and moderate aromatics content (27 wt%), which mimics that which would be used in a second-stage hydrotreating process. The measurements were made again in a trickle-flow system under realistic conditions (593 K and 3.9 MPa) using a stainless steel reactor of 9.5 mm O.D. (3/8 inch). Comparison was made with a current commercial Co–Mo–S/Al_2O_3 catalyst (Ketjenfine 756) of surface area 218 $m^2\,g^{-1}$ and containing 11.2 wt.% Mo and 3.1 wt.% Co (30). The precursor was in oxide form (28/60 mesh) and was sulfided *in situ* at 633 K in 5 mol% H_2S/H_2. In the case of the phosphide a passivated sample was re-reduced *in situ* at 450°C for 2 h. An amount of 1.0 g of each catalyst was used without diluent, and the feed rate of oil was 4.0 g h^{-1} to give a WHSV of 4 h^{-1}.

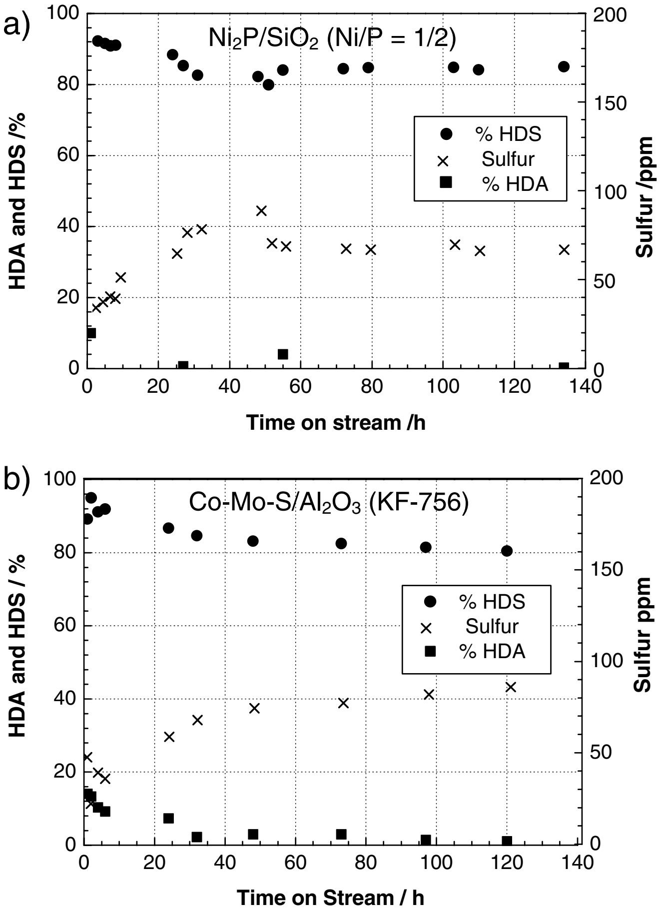

FIG. 2. Real feed results. Reaction conditions were 593 K and 3.9 MPa. The feed was a hydrotreated gas oil with sulfur (440 ppm), nitrogen (8 ppm), and aromatic content (27 wt%). Results for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are based on total elemental analysis, while those for hydrodearomatization (HDA) are based on SFC analysis.

For the Ni_2P/SiO_2 (Ni/P = 1/2) the HDS conversion was 85% (±2%) with sulfur content reduced from 440 to 66 ppm (Fig. 2a). This compares favorably with the results obtained with the commercial Co–Mo–S/Al_2O_3 catalyst, which gave a conversion of 80% and sulfur content of 86 ppm (Fig. 2b). The comparison at the same weight-hourly space velocity is important for reactor sizing. A comparison based on surface area would be even more favorable to the Ni_2P/SiO_2, which uses a low surface area (90 $m^2\,g^{-1}$), low density support. The phosphide catalyst shows significant superiority to the sulfide in two other respects. It had a lower HDA conversion (0.7 vs 1.1%). This is desirable in order to limit hydrogen consumption in the final stages of processing, and to avoid disruption of the hydrocarbon structure, which can result in cracking. The phosphide also displayed a more rapid attainment of steady state and no deactivation. If anything, the phosphide showed a mild activation starting at 40 h, while the sulfide showed a slow decline as it approached steady state at 130 h. Overall, in terms of activity, selectivity, and stability the phosphide is superior to the commercial catalyst. This is surprising, since the phosphide is an unpromoted, single-metal catalyst placed on a relatively unattractive support.

Further insight about the unique reactivity of the phosphide catalyst can be derived from examination of the product distribution. Product analysis by sulfur-selective detection at different times in the previous experimental

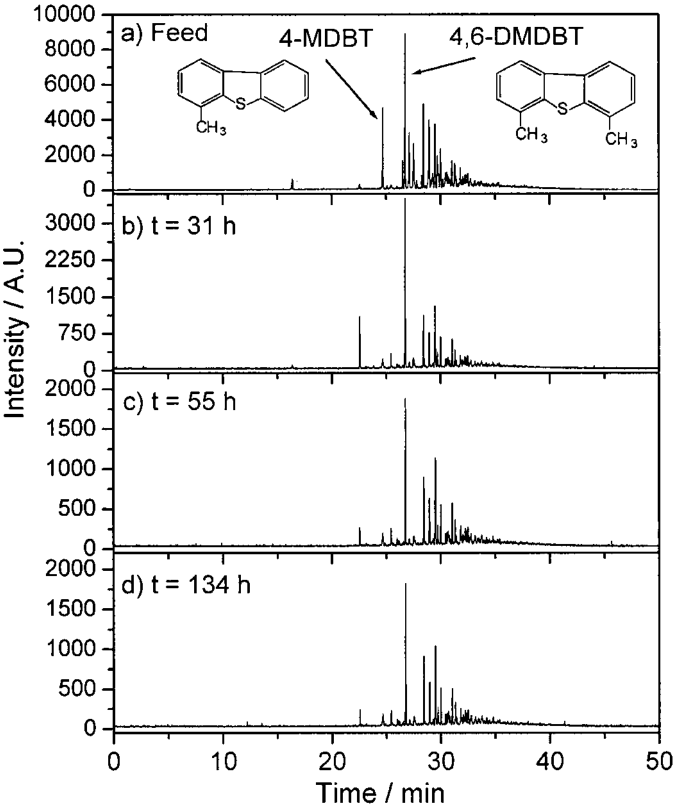

FIG. 3. Detailed analysis of products of Ni_2P/SiO_2. Results are given for the feed and the product at different times, with a scale that is increasing in sensitivity. (a) Feed, full scale 8000; (b) product 31 h, full scale 3000; (c) product, 55 h, full scale 1500; (d) product, 134 h, full scale 1600. Analysis was by sulfur chemiluminescence detection (Sievers, Model 355).

run (Fig. 2a) shows the reduction in the sulfur levels (Fig. 3). The chromatograms display the complex real feed used, with the two peaks for 4-methyldibenzothiophene (MDBT) and 4,6-dimethyldibenzothiophene (DMDBT) indicated. These are the archetypal molecules for the most difficult class of sulfur components to remove (31) and correspond to 6.0 and 11.8% of the total sulfur, respectively. The significant aspect of the results is that the MDBT and DMDBT were removed at levels of 85% (note the increasing scale in going from the feed to the point at 134 h). This is similar to the overall conversion in sulfur removal of 85% (Fig. 2a) and indicates that the phosphide has no particular difficulty in removing these molecules as opposed to others. In comparison, the Co–Mo–S/Al_2O_3 removes MDBT and DMDBT at levels of 77%, substantially lower than the Ni_2P/SiO_2 catalyst. The ability of the phosphide to carry out such deep HDS without excessive hydrogenation (HDA) may be related to its structure, which is not layered. We speculate that in dispersed form, as in the present case, this would expose many crystallite corners and edges. It may be that the highly hindered MDBT and DMDBT molecules are able to approach the surface of the phosphide more easily than the more planar sulfide crystallites.

We believe that phosphides are particularly promising catalysts for many reasons. First, they have an intrinsically high catalytic activity, which may be related to their metallic character. Second, they lack a layered structure, which is important because their entire exposed surface area is potentially active. Third, they can be prepared easily by reduction at moderate temperatures and from inexpensive precursors. Finally, they exist in many multimetallic forms. The compositional and structural chemistry is very rich and as yet unexplored for catalytic activity.

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