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Highly-Active Nickel Phosphide Hydrotreating Catalysts Prepared In Situ Using Nickel Hypophosphite Precursors

Andrea I. d'Aquino,^{1,2} Samuel J. Danforth,^{1,2} Tess R. Clinkingbeard,^{1,2} Boris Ilic,^{1,2}
Lee Pullan,³ Michael A. Reynolds,⁴ Brendan D. Murray⁴ and Mark E. Bussell^{1,2*}

¹Department of Chemistry, MS-9150
Western Washington University
Bellingham, WA 98225

²Advanced Materials Science and Engineering Center
Western Washington University
Bellingham, WA 98225

³FEI Company
5350 NE Dawson Creek Dr.
Hillsboro, OR 97124

⁴Shell Oil Company
Westhollow Technology Center
3333 Highway 6 South
Houston, TX 77082

*Author to whom correspondence should be addressed.

Correspondence Address

Prof. Mark E. Bussell
Department of Chemistry, MS-9150
Western Washington University
516 High Street
Bellingham, WA 98225

Tel: 360-650-3145

Fax: 360-650-2826

E-mail: Mark.Bussell@wwu.edu

ABSTRACT

An in situ method for the preparation of nickel phosphide (Ni_2P) on silica, alumina, and amorphous silica-alumina (ASA) supports is described. The synthesis avoids the use of nickel and phosphorus salts by employing the reaction between nickel hydroxide ($\text{Ni}(\text{OH})_2$) and hypophosphorus acid (H_3PO_2), allowing the impregnation of nickel hypophosphite ($\text{Ni}(\text{H}_2\text{PO}_2)_2$) onto the oxide supports in the absence of salt byproducts. Temperature-programmed reduction (TPR) in flowing hydrogen at 573-773 K yields phase pure Ni_2P on the supports with small average particle sizes (3-4 nm) as measured using transmission electron microscopy. The conversion of $\text{Ni}(\text{H}_2\text{PO}_2)_2$ to Ni_2P and related reactions were probed using TPR with on-line mass spectral analysis of the gas effluent. Unsupported $\text{Ni}(\text{H}_2\text{PO}_2)_2$ reacts in flowing hydrogen to produce PH_3 and H_2O at 468 and 482 K, respectively; the reaction is shifted to increasingly higher temperatures for $\text{Ni}(\text{H}_2\text{PO}_2)_2$ supported on SiO_2 , Al_2O_3 and ASA. The hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) properties of the Ni_2P catalysts were probed using a mixed feed containing carbazole and benzothiophene. While $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts prepared by the different methods exhibited similar HDN and HDS activities, the in situ prepared $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and $\text{Ni}_2\text{P}/\text{ASA}$ catalysts were substantially more active than their ex situ counterparts prepared from hypophosphite- and phosphate-based precursors.

KEYWORDS

Hydrodenitrogenation, carbazole, hydrodesulfurization, benzothiophene, nickel phosphide, nickel hypophosphite

1. INTRODUCTION

Recent research aimed at the improvement of hydrotreating catalysts has concentrated on the optimization of sulfide-based materials as well as step-out investigations of new classes of materials, many of which have focused on metal phosphides. A growing body of research on the hydrotreating properties of metal phosphides indicates nickel phosphide (Ni_2P) to be the most promising candidate for a new generation of hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) catalysts [1,2]. A recent study showed $\text{Ni}_2\text{P}/\text{SiO}_2$ to be more active (on a mass basis) than a commercial $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ catalyst for the HDN of carbazole, but the Ni_2P catalyst had a lower turnover frequency (TOF) than did the Ni-Mo sulfide catalyst [3]. More recently, an investigation of unsupported Ni_2P -based catalysts showed HDS of a mixed feed to scale with surface area for materials having surface areas in the range 14-45 m^2/g [4]. Not surprisingly given the low surface area of the materials, the Ni_2P -based catalysts were substantially less active than a state-of-the-art Co-Mo/ Al_2O_3 catalyst. Based on an extrapolation of the activities of Ni_2P -based catalysts to that of the Co-Mo/ Al_2O_3 catalyst, the authors concluded that unsupported Ni_2P would need to have a surface area of $\sim 400 \text{ m}^2/\text{g}$ (or a particle size of $\sim 3 \text{ nm}$) to be comparable in activity to a state-of-the-art Co-Mo catalyst [4].

Nickel phosphide catalysts are most often prepared by temperature-programmed reduction (TPR) of precursors prepared by impregnation of aqueous nickel and phosphorus salts (e.g. nickel nitrate and ammonium dihydrogen phosphate) onto an oxide support followed by drying and calcination in air. When supported on silica, a maximum TPR temperature of 873 K or higher is typically needed to reduce the precursor to Ni_2P [2,5]. In addition, an excess of P in the precursor (P/Ni molar ratio > 0.50) is needed to ensure that phase pure Ni_2P is formed on the silica support. Due to the strong interaction of impregnated phosphate with Al-containing supports (leading to formation of AlPO_4 upon calcination), higher reduction temperatures and P contents in the

precursors are needed to produce Ni₂P [5]. In the last few years, new synthetic approaches that use phosphite (H₂PO₃⁻) or hypophosphite (H₂PO₂⁻) in place of phosphate (PO₄³⁻) as the P source have been reported that enable the preparation of Ni₂P and other metal phosphides at substantially lower temperatures [2,6-11]. The lower oxidation state of phosphorus in hypophosphite (P +1) and phosphite (P +3) than in phosphate (P +5) allows reduction of the precursors at lower temperatures than is possible for phosphate-based precursors [2]. The lower reduction temperatures used to prepare Ni₂P catalysts from hypophosphite- and phosphite-based precursors have resulted in smaller particle sizes and higher HDS activities in comparison with Ni₂P catalysts prepared from phosphate-based precursors.

In addition to yielding small particles, an industrially viable synthesis for Ni₂P catalysts should involve as few steps as possible and a reduction temperature that does not exceed the maximum operating temperature of the reactor vessel. Ideally, the Ni₂P catalyst would be prepared in situ and at a temperature of 673 K or lower and the synthesis method should work equally well for aluminum-containing supports as it does for silica. Herein we report a new in situ preparation method that yields highly active Ni₂P catalysts supported on SiO₂, γ-Al₂O₃ and amorphous SiO₂-Al₂O₃ (ASA).

2. EXPERIMENTAL METHODS

2.1 Catalyst Synthesis

The precursors of the nickel phosphide catalysts were prepared by impregnation of aqueous solutions of either nickel hypophosphite or phosphate onto calcined supports followed by drying. Three different oxide supports were used: SiO₂ (Cab-O-Sil, EH-5, 380 m²/g), γ-Al₂O₃ (Engelhard, AL-3945, 186 m²/g) and ASA (Criterion, 5545, 412 m²/g), and were calcined at 773 K in air for 3 h. The reagents used in the catalyst synthesis were nickel hydroxide (Ni(OH)₂, Alfa Aesar, 61% Ni),

Ni(NO₃)₂•6H₂O (Alfa Aesar, Puratronic, 99.9985%), hypophosphorous acid (H₃PO₂, Sigma-Aldrich, 50 wt% in H₂O) and ammonium dihydrogen phosphate (NH₄H₂PO₄, Alfa Aesar, ACS grade). The nominal loadings of the catalysts prepared were 15 wt% Ni₂P/SiO₂, 25 wt% Ni₂P/Al₂O₃, and 25 wt% Ni₂P/ASA.

2.1.1 Ni₂P Catalysts Prepared Using Hypophosphite

The impregnation solutions for the hypophosphite-based precursors were prepared by adding a stoichiometric amount of 50 wt% H₃PO₂(aq) to powdered Ni(OH)₂ with stirring, yielding a light green mixture having a phosphorus-to-nickel mole ratio (P/Ni) = 2. The mixture was then heated to 343 K and water was added as needed to form a clear, green solution of Ni(H₂PO₂)₂(aq). This solution was directly impregnated onto the SiO₂, γ-Al₂O₃, and ASA supports until incipient wetness to give precursors having P/Ni = 2.0. An additional Ni₂P/SiO₂ catalyst having P/Ni = 1.5 was prepared; in this case enough Ni(NO₃)₂•6H₂O was added to the impregnation solution to adjust the P/Ni molar ratio to 1.5 prior to the first impregnation. The HDN/HDS testing for Ni₂P/SiO₂ was carried out using the precursor having P/Ni = 1.5 as this catalyst had a significantly higher activity than the catalyst prepared from a precursor having P/Ni = 2.0. If more than one impregnation was necessary to prepare a precursor, the solution was held at 343 K between impregnations. As an example, the precursor of a 15 wt% Ni₂P/SiO₂ catalyst having P/Ni = 1.5 was prepared by impregnation of a solution containing 0.2812 g Ni(OH)₂, 0.885 mL H₃PO₂ and 0.2940 g Ni(NO₃)₂•6H₂O onto 1.7 g SiO₂, followed by drying at 343 K for 24 h.

The supported Ni(H₂PO₂)₂•6H₂O precursors were reduced via temperature-programmed reduction (TPR) as follows. Approximately 0.5 g of the precursor was transferred to a quartz U-tube and degassed in 60 mL/min He (Airgas, 99.999%) for 30 min. The precursor was then subjected to TPR in H₂ (Airgas, 99.999%) flowed at 100 mL/min by heating from room temperature at a heating rate of 5 K/min to a temperature in the range 573-773 K. After holding for 1 h, the

resulting Ni₂P catalyst was cooled to room temperature in continued H₂ flow, purged for 30 min in 60 mL/min He, and then passivated in 60 mL/min 1 mol% O₂/He (Airgas, 99%) for 2 h. The in situ preparation of the supported Ni₂P catalysts is described in Sections 2.2-2.4. The Ni₂P loadings (15 wt% (SiO₂), 25 wt% (Al₂O₃, ASA)) were selected in order to give catalysts with similar Ni₂P particle sizes (3-4 nm, as determined by TEM).

2.12 Ni₂P Catalysts Prepared Using Phosphate

The impregnation solutions for phosphate-based precursors were prepared by dissolving Ni(NO₃)₂·6H₂O and NH₄H₂PO₄ in water, and has been described in detail elsewhere [3]. The composition of the impregnation solution depended upon the support used: SiO₂ (P/Ni = 0.9), γ -Al₂O₃ (P/Ni = 1.5), ASA (P/Ni = 2.2). The solution was impregnated onto the support until incipient wetness; if more than one impregnation was necessary, the solid was dried at 393 K between impregnations. After the final solution addition, the catalyst precursor was dried for 24 h at 393 K. Approximately 0.5 g of the precursor was transferred to a quartz U-tube and degassed in 60 mL/min He for 30 min. The precursor was then subjected to TPR in H₂ flowed at 150 mL/min by heating from room temperature to 923 K at a heating rate of 1 K/min. Following TPR, the Ni₂P catalyst was cooled to room temperature in continued H₂ flow, purged for 30 min in 60 mL/min He, and then passivated in 60 mL/min 1 mol% O₂/He (Airgas, 99%) for 2 h. The P/Ni molar ratios used corresponded to the amounts needed to achieve phase-pure Ni₂P on each support.

2.2 Catalyst Characterization

Powder X-ray diffraction patterns of the supported Ni₂P catalysts were obtained using a PANalytical X'Pert Pro diffractometer equipped with a monochromatic Cu-K α source (λ = 1.54050 Å). A Micromeritics AutoChem 2950HP instrument outfitted with a thermal conductivity detector was used to carry out carbon monoxide (CO) chemisorption capacity and single-point BET surface area measurements for the catalysts. Approximately 0.050 g of a catalyst precursor or passivated

catalyst was placed in a metal U-tube that was then attached to the instrument. Following degassing in 60 mL/min He for 30 min, the sample was heated to 673 K at 10 K/min in 60 mL/min H₂ and held for 1 h in continued H₂ flow. The sample was then purged in 60 mL/min He for 1 h at 673 K, and subsequently cooled to room temperature in continued He flow. With the sample held at 273 K, 10 mol% CO/He (Praxair) was pulsed over the sample until CO uptake ceased. The CO was desorbed from the catalyst sample by heating to 623 K, after which a single-point BET measurement was carried out at 77 K using 30.03 mol% N₂/He.

Transmission electron microscopy (TEM) measurements were carried out using a FEI Talos F200X high resolution transmission electron microscope operating at 200 keV and outfitted with a FEI Super-X energy dispersive X-ray (EDX) analysis system. Catalyst samples were placed on a 200 mesh copper grid coated with formvar and carbon for the TEM measurements.

X-ray photoelectron spectroscopy (XPS) spectra were acquired of the hypophosphite-based precursors and the supported Ni₂P catalysts prepared ex situ using a SAGE 100 XPS System (SPECS GmbH) outfitted with a Mg K α X-ray source (1253.6 eV) and a 95 mm hemispherical energy analyzer. XPS spectra of the catalysts after HDN/HDS testing were acquired using a Thermo Scientific K-Alpha XPS system outfitted with a Mg K α X-ray source (1253.6 eV) and a 180° double focusing hemispherical analyser-128-channel detector. The XPS spectra were collected with a pass energy of 15 or 50 eV and binding energies were corrected for sample charging using the C(1s) peak at 284.6 eV for adventitious carbon as a reference. Surface compositions were determined for the Ni₂P catalysts using the peak areas in the Ni(2p) and P(2p) regions and the instrument relative sensitivity factors.

2.3 Temperature-Programmed Reduction – Mass Spectrometry

Temperature-programmed reduction – mass spectrometry (TPR-MS) measurements were carried out using a Micromeritics Autochem 2950HP instrument outfitted with a MKS Cirrus 2

mass spectrometer for on-line detection of the gas-phase effluent. Approximately 0.05 g of catalyst precursor (or reference material) was loaded into a metal U-tube and attached to the instrument. Following degassing in 60 mL/min He for 60 min, the sample was heated from 300 to 1023 K at 10 K/min in 50 mL/min 10 mol% H₂/Ar (Praxair) while monitoring mass-to-charge ratios (m/z) of 18 (H₂O), 31 (P) and 34 (PH₃). The mass spectrometer has a temperature calibration that interfaces with the AutoChem 2950 thermocouple signal; this calibration is in good agreement with peak temperatures in the TCD signal, which come directly from thermocouple measurement. There is a 1-2 s delay in the MS signal due to gases entering the capillary to the mass spectrometer, but this corresponds to a temperature offset of < 2 K. Sodium hypophosphite (NaH₂PO₂, Sigma-Aldrich, >99%) was used as a reference compound for TPR-MS measurements.

2.4 HDN and HDS activity measurements

Carbazole HDN and benzothiophene 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 of 548-673 K. The reactor feed consisted of 3000 ppm benzothiophene, 1000 ppm carbazole, and 500 ppm dodecane in a 39.55 wt% p-xylene/decane solution. The 500 ppm dodecane served as an internal standard for the gas chromatographic analysis of the reactor effluent. The liquid feed (5.4 mL/h) was injected into a 50 mL/min flow of hydrogen, where it was preheated and vaporized prior to entry into the reactor. A sample (0.25 g, 16-20 mesh size) of catalyst precursor or passivated catalyst was diluted with quartz flakes to a total volume of 5 mL and loaded into a reactor tube having a diameter of 1.1 cm and length of 40 cm. The internal reactor temperature was monitored with an axially mounted thermocouple in direct contact with the catalyst bed. The catalyst precursors or passivated catalysts were pretreated by heating from room temperature to 673 K in 1 h in a 60 mL/min flow of H₂ and were held at this temperature for 2 h, then cooled to room temperature in continued H₂ flow. In one experiment, the hypophosphite-based precursor of a

Ni₂P/SiO₂ catalyst was subjected to a sulfidation pretreatment by heating from room temperature to 650 K in 1 h in a 60 mL/min flow of 3 mol% H₂S/H₂, held at this temperature for 2 h, and then cooled to room temperature in continued H₂S/H₂ flow.

Following the pretreatment and cooling to room temperature, the reactor was pressurized to 3.0 MPa with H₂. In a 50 mL/min flow of H₂, the catalyst bed was heated to 548 K and the flow of liquid feed was begun. The reactor was allowed to stabilize under operating conditions for 3 h prior to sampling reactor effluent at 30 min intervals over 2.5 h. The catalyst temperature was then raised 25 K, and the reactor stabilized for 3 h, followed by sampling of the reactor effluent at 30 min intervals. This procedure was repeated until sampling at the maximum catalyst temperature (673 K) was completed. The first effluent sample collected at each temperature was discarded, while the four subsequent effluent samples were analyzed off-line using a gas chromatograph (Agilent 6890N) equipped with an HP-5 column and a flame ionization detector. The GC was calibrated using serial diluted product standard solutions to allow product quantification of reactor effluent samples. Based on this method carbon balances of ~95% were achieved, indicating that the analyses of the reactor effluent accounted for all of the major reaction products. The majority of the HDN and HDS activity measurements were done in duplicate to ensure reproducibility.

3. RESULTS

3.1 Catalyst Synthesis and TPR-MS Measurements

Mixing stoichiometric amounts (P/Ni = 2) of Ni(OH)₂(s) and H₃PO₂(aq) resulted in the formation of a greenish solution containing some undissolved Ni(OH)₂(s). Heating this mixture to 343 K led to complete dissolution of the remaining Ni(OH)₂(s) and the formation of a clear, green solution. Upon cooling to room temperature, green crystals precipitated from solution that were previously identified as Ni(H₂PO₂)₂•6H₂O(s) [12-14]. The Ni(H₂PO₂)₂•6H₂O(s) fully redissolved

upon heating to 343 K to give an approximately 1.2 M $\text{Ni}(\text{H}_2\text{PO}_2)_2(\text{aq})$ solution (see Supplementary Material). The $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}(\text{aq})$ solution was maintained at 343 K between impregnations of the SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and ASA supports to keep the nickel hypophosphite fully dissolved. Heating the $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}(\text{s})$, $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}(\text{aq})$ or impregnated supports to higher drying temperatures in air (e.g. 393 K) resulted in decomposition of the nickel hypophosphite within 24 h (see Supplementary Material).

The reactions of unsupported and oxide-supported $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$, as well as of unsupported NaH_2PO_2 , were investigated using TPR-MS. Shown in Figure 1 are TPR-MS traces for water ($m/z = 18$) and phosphine ($m/z = 34$) for unsupported NaH_2PO_2 in Ar and 10 mol% H_2/Ar over the temperature range 300-1023 K. The decomposition of NaH_2PO_2 in argon shows a large phosphine (PH_3) peak centered at 535 K and a smaller second peak at 579 K. Only a small amount of water is produced, with a very weak peak at 536 K and a somewhat larger peak at 575 K.

Figure 1: TPR-MS traces for NaH_2PO_2 in (a) Ar and (b) 10% H_2/Ar .

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183 Drawing upon thermal gravimetric analysis (TGA) results reported by others [15], the following
 184 reactions are proposed for the two-step decomposition of NaH₂PO₂ in flowing Ar.

187 The observation of PH₃ in the TPR-MS trace at 535 K is assigned to the reaction shown in Equation
 188 1 that involves the disproportionation of NaH₂PO₂ to give PH₃, disodium hydrogen phosphite
 189 (Na₂HPO₃) and sodium dihydrogen phosphate (NaH₂PO₄), but not water. The observation of PH₃
 190 and water at 579 and 575 K, respectively, is assigned to the subsequent reaction of the Na₂HPO₃ as
 191 shown in Equation 2. Sodium phosphate (Na₃PO₄) and sodium pyrophosphate (Na₄P₂O₇) remain as
 192 solid residue upon further heating in Ar flow. The reaction of NaH₂PO₂ in 10 mol% H₂/Ar exhibits
 193 a different TPR-MS trace, with the first PH₃ peak shifted to 558 K as well as being accompanied by
 194 a H₂O peak. It is unclear whether H₂ directly participates in the reaction of the NaH₂PO₂ or simply
 195 leads to a different decomposition pathway resulting in simultaneous evolution of PH₃ and H₂O;
 196 two possible

197 reactions are depicted in Equations 3 [15] and 4 .

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200 The reaction shown in Equation 3 is unlikely to be operative in this case, as the remaining P species
 201 (Na₄P₂O₇) would not be expected to react with H₂ until high temperatures so it is unclear what
 202 species would be reacting to produce PH₃ and H₂O in the 590-680 range. The reaction in Equation
 203 4 seems more likely, as it produces PH₃ and H₂O, but also Na₂HPO₃ that would be expected to

subsequently decompose to form PH_3 and H_2O as shown in Equation 2. The NaPO_3 that is formed in Equation 4 exists as a hexamer species, sodium hexametaphosphate $((\text{NaPO}_3)_6)$, and is not expected to undergo reaction until high temperature.

The replacement of sodium with nickel leads to a substantially different TPR-MS trace, as shown in Figure 2 for the reaction of $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ in 10 mol% H_2/Ar .

Figure 2: TPR-MS traces for $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ in 10% H_2/Ar .

Reaction of the $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ was preceded by the removal of the waters of hydration in a broad peak centered at 387 K in the $m/z = 18$ trace. Evolution of PH_3 occurred in a very sharp peak at 468 K and of H_2O at 482 K, signaling the reaction of $\text{Ni}(\text{H}_2\text{PO}_2)_2$ in 10 mol% H_2/Ar flow at a substantially lower temperature than was observed for NaH_2PO_2 . No further reaction was observed in the TPR-MS traces until the temperature is increased above ~ 750 K with four overlapping H_2O peaks at 870, 928, 962 and 1007 K; these peaks are presumed to be associated with the reaction of phosphate species with H_2 . The observation of only a single, sharp PH_3 evolution peak suggests a

concerted process for the reaction of unsupported $\text{Ni}(\text{H}_2\text{PO}_2)_2$ with H_2 to form Ni_2P , as suggested below in Equation 5.

This reaction would account for the observed evolution of PH_3 and H_2O at 468 and 482 K, respectively, and the subsequent hydrogenation of adsorbed $\text{H}_x\text{PO}_4^{(3-x)-}$ species above 750 K. The reaction expressed in Equation 6, which is similar to one proposed elsewhere [16], seems unlikely as the subsequent reaction of $\text{Ni}(\text{HPO}_3\text{H})_2$ would be expected to be accompanied by the evolution of PH_3 (and H_2O) in a peak at ~ 773 K [7]. In a separate experiment, TPR was carried out for unsupported $\text{Ni}(\text{H}_2\text{PO}_2)_2$ to 500 K (i.e. just beyond the PH_3 and H_2O evolution peaks) and the solid product was collected after passivation in 1 mol% O_2/He . A portion of the solid was rinsed with H_2O and the solution was determined to be acidic (Figure S4c) and the IR spectrum of the viscous liquid residue collected after drying closely matches that of H_3PO_4 (Figure S5). An XRD pattern of the unwashed solid (Figure S6) exhibits strong peaks for Ni_2P and weak peaks at 30.8, 48.2 and 53.1° that indicate the presence of a minor Ni_5P_4 impurity. There is no indication in the XRD pattern for the presence of $\text{Ni}_3(\text{PO}_4)_2$, $\text{Ni}_2\text{P}_2\text{O}_7$ or $\text{Ni}(\text{PO}_3)_2$ as byproducts in the reduction of $\text{Ni}(\text{H}_2\text{PO}_2)_2$. These results provide strong evidence that H_3PO_4 is the P-containing byproduct formed, as proposed in Equation 5. The TPR-MS spectrum (Figure 2) indicates that adsorbed H_3PO_4 on the surface of the Ni_2P particles is reduced above 750 K, as proposed in the following overall reaction: $2\text{H}_3\text{PO}_4 + 5\text{H}_2 \rightarrow 2\text{P} + 8\text{H}_2\text{O}$. The envelope of overlapping H_2O evolution peaks in the 750-1050 K range indicates that this reduction occurs via sequence of hydrogenation steps. This H_2O evolution profile is quite different from that reported previously for unsupported $\text{Ni}_2\text{P}_2\text{O}_7$, for which TPR-MS showed H_2O evolution only starting at ~ 873 with small and large peaks at 953 and 993 K, respectively [17].

TPR-MS traces for SiO_2 -, $\gamma\text{-Al}_2\text{O}_3$ - and ASA-supported Ni hypophosphite precursors are shown in Figure 3. Relative to unsupported $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$, the TPR-MS traces are more complex, showing differences depending on the support material. Removal of the waters of hydration (and adsorbed H_2O) was observed in broad peaks with maxima in the 393-413 K range, while H_2O evolved in peaks at 481-566 K can be assigned to reaction of the supported $\text{Ni}(\text{H}_2\text{PO}_2)_2$.

Figure 3: TPR-MS traces for (a) $\text{Ni}(\text{H}_2\text{PO}_2)_2/\text{SiO}_2$, (b) $\text{Ni}(\text{H}_2\text{PO}_2)_2/\text{Al}_2\text{O}_3$, and $\text{Ni}(\text{H}_2\text{PO}_2)_2/\text{ASA}$ in 10% H_2/Ar .

The quantity and temperature of PH_3 evolution depended strongly on the support, with the largest amount and the lowest temperature observed for SiO_2 , and then progressively lower amounts and higher temperatures observed for $\gamma\text{-Al}_2\text{O}_3$ and ASA in that order. While the PH_3 evolution peaks are broader than for unsupported $\text{Ni}(\text{H}_2\text{PO}_2)_2$, and shifted to higher temperatures, the coincident evolution of H_2O is consistent with the reaction shown in Equation 5. High temperature H_2O evolution peaks with maxima in the 774-958 K range are assigned to the reaction of H_2 with

265 surface-bonded $\text{H}_x\text{PO}_4^{(3-x)-}$ species. The H_2O evolution peak observed at an intermediate
 266 temperature (648 K) for $\text{Ni}(\text{H}_2\text{PO}_2)_2/\text{ASA}$ is more difficult to assign, but the absence of a PH_3 peak
 267 at this temperature suggests that it is not due to reaction of a phosphite species as was assigned in
 268 the case of NaH_2PO_2 in 10% H_2/Ar .

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270 3.2 Catalyst Characterization

271 XRD patterns for the precursors of the supported Ni_2P catalysts subjected to TPR to
 272 increasing temperatures in flowing H_2 are shown in Figure 4; the temperature at which Ni_2P was
 273 observed depends on the support material. Phase purity was determined by comparing the XRD
 274 patterns to those of reference phases in the JCPDS database (Ni_2P : #089-2742, Ni_{12}P_5 : #22-1190

Figure 4: XRD patterns for (a) $\text{Ni}(\text{H}_2\text{PO}_2)_2/\text{SiO}_2$, (b) $\text{Ni}(\text{H}_2\text{PO}_2)_2/\text{Al}_2\text{O}_3$, and $\text{Ni}(\text{H}_2\text{PO}_2)_2/\text{ASA}$ subjected to TPR in flowing H_2 to the indicated temperatures. The average Ni_2P crystallite sizes are noted on the XRD plots.

[18]) and average crystallite sizes were calculated using the Scherrer equation and the {111} peak at 40.8°.

In the case of SiO₂, phase pure Ni₂P having an average crystallite size of ~5 nm was observed by 573 K; increasing the TPR temperature led to the formation of larger Ni₂P crystallites. These results are consistent with the findings of others for the preparation of Ni₂P/SiO₂ catalysts using hypophosphite as the P source, while noting that the catalysts prepared in these other studies utilized H₂O washing steps to remove salt byproducts (e.g. NaCl) formed during catalyst synthesis [9,10,16]. The XRD patterns for the Ni(H₂PO₂)₂/Al₂O₃, and Ni(H₂PO₂)₂/ASA samples subjected to TPR exhibit peaks for Ni₂P at higher temperatures than for the Ni(H₂PO₂)₂/SiO₂, with broad peaks apparent only after TPR at 773 K. The average Ni₂P crystallite sizes determined from the 773 K XRD patterns are small (≤ 5 nm) and, given that the TPR-MS traces indicate Ni(H₂PO₂)₂ undergoes reaction on these supports at 500-575 K, it is likely that smaller Ni₂P crystallites were present at lower temperatures, but in sizes below the detection limit of XRD. Since the XRD peaks for the ex situ prepared Ni₂P/Al₂O₃ and Ni₂P/ASA catalysts are broad, it is not possible to exclude the possibility of minor Ni₁₂P impurities being present in these catalysts. However, the TEM and EDX results described below are consistent with the presence of phase-pure Ni₂P in these catalysts.

Low and high resolution TEM images of ex situ prepared Ni₂P/SiO₂, Ni₂P/Al₂O₃ and Ni₂P/ASA catalysts are shown in Figure 5.

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Figure 5: TEM images of ex situ prepared (a) Ni₂P/SiO₂, (b) Ni₂P/Al₂O₃ and (c) Ni₂P/ASA catalysts.

The low-resolution images reveal even dispersions of the Ni₂P particles on the oxide supports; particle size measurements of 25-50 Ni₂P particles yielded average particle sizes in the 3-4 nm range (Table 1). The average Ni₂P particle size for the Ni₂P/SiO₂ is significantly smaller than the average Ni₂P crystallite size of 9 nm determined for this catalyst using the Scherrer method. This discrepancy is likely due to the fact that only a few of the Ni₂P particles are large enough to be detected by XRD. The high-resolution images for the Ni₂P/Al₂O₃ and Ni₂P/ASA catalysts show lattice fringes having spacings of 0.19 nm that are assigned to the {210} crystallographic planes of Ni₂P, which have a d-spacing of 0.192 nm. The spacing between lattice fringes of the Ni₂P/SiO₂ catalyst was slightly larger (0.20 nm), but the uncertainty was also higher because of the lower quality of the TEM image for this catalyst. The observed d-spacings are consistent with those reported by others for Ni₂P/MCM-41 catalysts prepared using hypophosphite as the P source [9,11]. Particle compositions determined using EDX (averaged for 5-7 particles) for the ex situ prepared Ni₂P/SiO₂, Ni₂P/Al₂O₃ and Ni₂P/ASA catalysts are close to that for Ni₂P (Table 1).

The BET surface areas, CO chemisorption capacities and other characterization data for the supported Ni₂P catalysts prepared from hypophosphite- and phosphate-based precursors are summarized in Table 1.

Table 1: Characterization Data for Supported Ni₂P Catalysts

	Catalyst	Precursor P/Ni Ratio	EDX Particle composition	Average Ni ₂ P Crystallite Size (nm) ^a	Average Ni ₂ P particle size (nm) ^c	BET Surface Area (m ² /g)	CO Chemisorption Capacity (μmol/g)
Hypophosphite <i>In situ</i>	Ni ₂ P/SiO ₂	1.5	----	----	----	199	43
	Ni ₂ P/Al ₂ O ₃	2.0	----	----	----	159	57
	Ni ₂ P/ASA	2.0	----	----	----	132	81
Hypophosphite <i>Ex situ</i>	Ni ₂ P/SiO ₂	1.5	Ni _{2.11} P _{1.00}	9	3.2 ± 0.4	202	51
	Ni ₂ P/Al ₂ O ₃	2.0	Ni _{2.07} P _{1.00}	< 5	3.9 ± 0.6	115	46
	Ni ₂ P/ASA	2.0	Ni _{2.16} P _{1.00}	< 5	3.3 ± 0.5	120	55
Phosphate <i>Ex situ</i>	Ni ₂ P/SiO ₂	0.9	----	12 ^b	----	132 ^b	113 ^b
	Ni ₂ P/Al ₂ O ₃	1.5	----	19	----	97	52
	Ni ₂ P/ASA	2.2	----	13	----	153	19

^aCalculated for ex situ prepared catalysts using XRD patterns after TPR to a maximum temperature of 673 K

^bData taken from [3].

^cCalculated for ex situ prepared catalysts using TEM images after TPR to a maximum temperature of 673 K

In the case of the catalysts prepared from hypophosphite-based precursors, data are provided for catalysts prepared in situ as well as ex situ. The ex situ prepared catalysts were passivated after synthesis, transferred through air to the Autochem 2950HP instrument and then reduced at 673 K in flowing H₂ prior to CO chemisorption and BET measurements. The in situ prepared catalysts were loaded into the Autochem 2950HP system in precursor form, and converted to Ni₂P by TPR in flowing H₂ to 673 K just prior to the CO chemisorption and BET measurements.

Except for the Ni₂P/ASA catalysts, the supported Ni₂P catalysts prepared from hypophosphite precursors had higher BET surface areas compared to catalysts prepared from phosphate-based precursors. This same trend was observed for the CO chemisorption capacities, except that for

Ni₂P/SiO₂ the catalyst prepared from the phosphate precursor had the highest chemisorption capacity.

Surface compositions were determined by XPS for the hypophosphite precursors and the Ni₂P catalysts prepared ex situ from them, as well as for some of the in situ and ex situ prepared catalysts after catalytic testing; these compositions are listed in Table 2.

Table 2: Catalyst Surface Compositions determined by XPS

	Catalyst	Surface Composition		
		Precursor	Ex situ Prepared	Post-HDN/HDS Testing
Hypophosphite <i>In situ</i>	Ni ₂ P/SiO ₂	Ni _{2.00} P _{3.14}	----	Ni _{2.00} P _{6.23}
	Ni ₂ P/Al ₂ O ₃	Ni _{2.00} P _{4.57}	----	Ni _{2.00} P _{11.31}
	Ni ₂ P/ASA	Ni _{2.00} P _{2.88}	----	-----
Hypophosphite <i>Ex situ</i>	Ni ₂ P/SiO ₂	Ni _{2.00} P _{3.14}	Ni _{2.00} P _{3.71}	Ni _{2.00} P _{6.04}
	Ni ₂ P/Al ₂ O ₃	Ni _{2.00} P _{4.57}	Ni _{2.00} P _{5.69}	Ni _{2.00} P _{11.84}
	Ni ₂ P/ASA	Ni _{2.00} P _{2.88}	Ni _{2.00} P _{6.33}	----

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Figure 6: XPS spectra for in situ and ex situ prepared Ni₂P/SiO₂ catalysts and (b) Ni₂P/Al₂O₃, with all spectra acquired after HDN/HDS testing.

ed for the hypophosphite precursors, ex situ prepared Ni_2P catalysts, and HDN/HDS-tested catalysts are high relative to the stoichiometry of Ni_2P ($\text{P}/\text{Ni} = 0.5$). Interestingly, the surface P-enrichment increases from the precursor to the ex situ prepared Ni_2P catalysts, and further for the HDN/HDS-tested catalysts. Plotted in Figure 6 are the XPS spectra in the $\text{Ni}(2\text{p}_{3/2})$ and $\text{P}(2\text{p})$ regions for the in situ and ex situ prepared $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalysts after HDN/HDS testing.

Upon completion of an HDN/HDS measurement, the reactor was purged with H_2 for 1 h at the reaction temperature, He for 30 min at room temperature, and then the catalysts were passivated in a 1 mol% O_2/He mixture prior to removal from the reactor for the XPS analyses.

No substantive differences were observed between the XPS spectra of the HDN/HDS-tested samples of the in situ and ex situ prepared catalysts. As reported previously, the most intense peaks in the $\text{Ni}(2\text{p}_{3/2})$ and $\text{P}(2\text{p})$ regions at 856.8-857.7 and 134.3-134.5 eV are assigned to Ni^{2+} and P^{5+} species, respectively, while weaker peaks at 853.0-853.5 and 129.6-129.8 eV are assigned to reduced Ni and P species having oxidation states near zero [5,19]. The low oxidation state species are assigned to Ni and P in Ni_2P . The higher oxidation state species are assigned to Ni and P in the passivation layer at the surface of the Ni_2P particles, but could also be associated with unreduced species (e.g. $\text{H}_x\text{PO}_4^{(3-x)-}$) produced during the synthesis. Such phosphate species would not be expected to be reduced under the synthesis or reaction conditions used in which the temperature did not exceed 673 K. Comparison of the XPS spectra and surface compositions of the hypophosphite-based $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalysts to XPS results published previously for catalysts prepared from phosphate-based precursors reveals some important differences. The ex situ prepared, hypophosphite-based $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst exhibited a surface P/Ni ratio of 1.9, which is substantially higher than values reported for $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts prepared from phosphate based precursors (surface $\text{P}/\text{Ni} = 0.43\text{-}0.68$) [3,5,19]. This difference can be attributed to a dramatically larger $\text{P}(2\text{p})$ peak for oxidized P at 134-134.5 eV for the hypophosphite-based $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst

374 than for the catalysts prepared from phosphate-based precursors. On the other hand, the ex situ
375 prepared, hypophosphite-based $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalyst exhibited a surface P/Ni ratio of 2.8 that is
376 significantly lower than what was observed for a $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalyst prepared from a phosphate-
377 based precursor (surface P/Ni = 4.0) [5]. The surface compositions of the hypophosphite-based
378 catalysts analyzed by XPS after HDN/HDS testing (surface P/Ni = 3.0-3.1 ($\text{Ni}_2\text{P}/\text{SiO}_2$) and 5.7-5.9
379 ($\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$)) indicate dramatic surface P enrichment relative to ex situ prepared catalysts from
380 either hypophosphite- or phosphate-based precursors.

381 *3.3 HDN and HDS Properties*

ASA supports were evaluated using a mixed carbazole/benzothiophene feed and were compared with the properties of phosphate-based Ni_2P catalysts on the same supports. In this study, the carbazole HDN conversion is defined as the conversion of carbazole and hydrogenated carbazoles to hydrocarbon products that do not contain nitrogen; the benzothiophene HDS conversion is

defined similarly. Shown in Figure 7 are the carbazole HDN conversions plotted as a function of the reaction temperature.

Figure 7: Carbazole HDN conversion vs. temperature for (a) $\text{Ni}_2\text{P}/\text{SiO}_2$, (b) $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$, and (c) $\text{Ni}_2\text{P}/\text{ASA}$ catalysts prepared from hypophosphite- and phosphate-based precursors.

The carbazole HDN conversions were highest for the in situ prepared Ni_2P catalysts on the three supports, with the phosphate-based Ni_2P catalysts the least active by a ^(c) substantial margin for the $\gamma\text{-Al}_2\text{O}_3$ and ASA supports. The smallest difference between the in situ and ex situ hypophosphite-based catalysts was observed for the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts, which had similar carbazole HDN conversions as a phosphate-based $\text{Ni}_2\text{P}/\text{SiO}_2$ that were reported elsewhere [3]. The benzothiophene HDS conversions of the Ni_2P catalysts prepared in situ from hypophosphite-based precursors are plotted in Figure 8; Ni_2P on the three different supports exhibited HDS conversions of 94% or higher at 623 K and above.

Figure 8: Benzothiophene HDS conversion vs. temperature for $\text{Ni}_2\text{P}/\text{SiO}_2$, $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$, and $\text{Ni}_2\text{P}/\text{ASA}$ catalysts prepared from hypophosphite-based precursors.

The carbazole HDN and benzothiophene HDS conversions at 623 K for the hypophosphite-based Ni_2P catalysts on the SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and ASA supports are compared in Table 2 with those of phosphate-based Ni_2P catalysts on the same supports. Also listed are the TOFs for each catalyst,

calculated using the CO chemisorption capacities given in Table 1. For comparison purposes, conversions and TOFs for a sulfided Ni-Mo/Al₂O₃ catalyst (Shell 424; 4 wt% NiO, 19.5 wt% MoO₃, 8 wt% P₂O₅) tested using the same feed and reactor conditions are also provided. The Ni₂P/SiO₂ and Ni₂P/Al₂O₃ catalysts prepared in situ from hypophosphite precursors have higher HDN and HDS conversions and TOFs than does the sulfided Ni-Mo/Al₂O₃ catalyst. Lower HDN and HDS activities and TOFs were observed for the Ni₂P catalysts prepared ex situ from hypophosphite-based precursors and from phosphate-based precursors, with the exception of the Ni₂P/SiO₂ catalyst prepared using phosphate as the P source.

Table 3: HDN and HDS Conversions and Turnover Frequencies

	Catalyst	Conversion at 623 K		TOF at 623 K	
		HDN (%)	HDS (%)	HDN (s ⁻¹) x 10 ⁴	HDS (s ⁻¹) x 10 ³
Hypophosphite <i>In situ</i>	Ni ₂ P/SiO ₂	91	96	5.9	2.3
	Ni ₂ P/Al ₂ O ₃	96	97	4.7	1.8
	Ni ₂ P/ASA	58	94	2.0	1.2
Hypophosphite <i>Ex situ</i>	Ni ₂ P/SiO ₂	70	95	3.9	1.9
	Ni ₂ P/Al ₂ O ₃	46	90	2.8	2.0
	Ni ₂ P/ASA	22	84	1.1	1.6
Phosphate <i>Ex situ</i>	Ni ₂ P/SiO ₂	96 ^a	98 ^a	2.4	0.9
	Ni ₂ P/Al ₂ O ₃	1.4	40	0.1	0.8
	Ni ₂ P/ASA	17	71	2.4	3.9
	Sulf. Ni-Mo/Al ₂ O ₃	77 ^a	95 ^a	2.5	1.5

^aCarbazole HDN and benzothiophene HDS data taken from [3].

The Ni₂P/SiO₂ catalysts exhibited the least dependence of the HDS and HDN conversions and TOFs on the preparation method, while the Ni₂P/Al₂O₃ and Ni₂P/ASA catalysts showed a strong dependence. For Ni₂P on the Al-containing supports, the catalysts prepared ex situ (hypophosphite

and phosphate precursors) had significantly lower HDN and HDS conversions than the in situ prepared catalysts. This trend was less pronounced for the TOFs, and was not followed for the $\text{Ni}_2\text{P}/\text{ASA}$ catalysts.

Carbazole HDN over a $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst was investigated previously and the reaction network shown in Scheme 1 was proposed to account for the observed products [3]. The product of the direct denitrogenation (DDN) pathway, biphenyl (BP), was detected in only minor quantities (< 1%) and this pathway does not contribute appreciably to nitrogen removal from carbazole over the Ni_2P catalysts.

Scheme 1: Carbazole HDN reaction network over Ni_2P catalysts.

Three different hydrogenated carbazoles (4H-CARB, 6H-CARB, 12H-CARB) were observed, particularly at low reaction temperatures, and these are intermediates in the hydrogenation (HYD) pathway for carbazole HDN. The HDN product selectivities (i.e. excluding the carbazoles) at similar conversions (14-24%) for the Ni_2P catalysts prepared by the different methods are listed in Table 4.

460

461

462 Table 4: Carbazole HDN Product Selectivities

HDN Product	Sulf. Ni-Mo/Al ₂ O ₃ ^a	Ni ₂ P/SiO ₂			Ni ₂ P/Al ₂ O ₃			Ni ₂ P/ASA		
		Hypo. In situ	Hypo. Ex situ	Phos.	Hypo. In situ	Hypo. Ex situ	Phos.	Hypo. In situ	Hypo. Ex situ	Phos.
BP	0.7	0.5	0.5	0.0	5.2	1.1	1.9	1.1	0.9	0.0
CHB	15.8	45.8	43.6	43.0	47.8	37.9	63.6	50.1	53.4	63.0
BCH	54.0	16.5	11.2	15.6	20.0	17.4	9.1	11.3	10.6	9.8
MCPCH	23.7	32.5	41.3	28.1	14.7	26.5	17.4	23.2	22.9	14.0
HCH	5.8	4.7	3.3	13.2	12.3	17.1	8.0	14.3	12.1	13.1

463 ^aHDN selectivity data taken from [3].

464 For comparison purposes, the HDN selectivity of a sulfided Ni-Mo/Al₂O₃ catalyst tested under the
 465 identical reaction conditions is also provided in Table 4 [3]. Four hydrocarbon products associated
 466 with the HYD pathway for N removal – cyclohexylbenzene (CHB), bicyclohexane (BCH), (2-
 467 methylcyclopentyl)cyclohexane (MCPCH), and hexylcyclohexane (HCH) – were observed in
 468 significant quantities for the supported Ni₂P and sulfided Ni-Mo/Al₂O₃ catalysts. There are
 469 important differences in product selectivities, with the Ni₂P catalysts, regardless of support or
 470 preparation method, producing substantially more of the partially hydrogenated product CHB and
 471 less of the fully hydrogenated product BCH than the sulfided Ni-Mo/Al₂O₃ catalyst. Across
 472 supports, the Ni₂P/ASA catalysts generally produced the most CHB, while the Ni₂P/SiO₂ catalysts
 473 produced the most MCPCH.

474 *3.4 In situ preparation with H₂S/H₂*

475 While the in situ preparation of supported Ni₂P catalysts was carried out in H₂, the use of a 3
 476 mol% H₂S/H₂ mixture for this purpose was also investigated for Ni₂P/SiO₂. Compared in Figure 9a
 477 are the carbazole HDN conversions vs. temperature for Ni₂P/SiO₂ catalysts prepared in situ using
 478 H₂ (673 K) and H₂S/H₂ (650 K), as well as for a sulfided Ni-Mo/Al₂O₃ catalyst that was pretreated

in $\text{H}_2\text{S}/\text{H}_2$ at 650 K. The $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst prepared from a hypophosphite-based precursor using $\text{H}_2\text{S}/\text{H}_2$ exhibited high HDN activity, with carbazole HDN conversions (623-673 K) about 5% less than those of the same precursor treated in situ in H_2 . Importantly, the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst had HDN conversions 3-5% higher than the sulfided $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ catalyst prepared using the identical pretreatment in $\text{H}_2\text{S}/\text{H}_2$ at 650 K. XRD patterns acquired after HDN/HDS testing for the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts prepared in situ in H_2 or $\text{H}_2\text{S}/\text{H}_2$ are shown in Figure 9b. In both cases, phase pure Ni_2P was observed, providing strong evidence for the successful synthesis of Ni_2P on the SiO_2 support using either H_2 or $\text{H}_2\text{S}/\text{H}_2$, as well as for the stability of the Ni_2P catalysts during HDN/HDS testing. The average Ni_2P crystallite sizes are indicated on the XRD patterns, the larger Ni_2P crystallite size for the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst prepared in $\text{H}_2\text{S}/\text{H}_2$ is likely responsible for the lower HDN activity of this catalyst relative to the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst prepared in H_2 .

Figure 9: (a) Carbazole HDN conversion vs. temperature for $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts prepared in situ using H_2 or $\text{H}_2\text{S}/\text{H}_2$. HDN conversion data for the $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ catalyst taken from [3]. (b) XRD patterns acquired after HDN/HDS testing for $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts prepared in situ using H_2 or $\text{H}_2\text{S}/\text{H}_2$.

4. DISCUSSION

While metal phosphide catalysts have shown substantial promise for use in a new generation of hydrotreating catalysts, significant hurdles will need to be overcome before they can compete with well-established Co-Mo and Ni-Mo sulfide catalysts for use in industrial processing. These hurdles include too many synthetic steps (e.g. ex situ reduction, passivation and then in situ activation) and high TPR temperatures (> 673 K) used in the preparation of metal phosphide catalysts, and low HDN/HDS activities on supports other than SiO_2 . To address these issues, a low-temperature synthesis of oxide-supported Ni_2P has been developed that uses $\text{Ni}(\text{OH})_2$ and H_3PO_2 to prepare catalyst precursors consisting of $\text{Ni}(\text{H}_2\text{PO}_2)_2$ supported on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and ASA, which are subsequently reduced in situ (≤ 673 K) using either H_2 or $\text{H}_2\text{S}/\text{H}_2$ to yield highly active Ni_2P catalysts. Importantly, washing steps to remove salt byproducts from the Ni_2P catalysts are unnecessary when using the supported $\text{Ni}(\text{H}_2\text{PO}_2)_2$ precursors.

Low temperature syntheses of Ni_2P catalysts have been reported by others and these preparation methods have employed a number of strategies to lower the reduction temperature needed to convert the catalyst precursor into the active Ni_2P phase. Syntheses have been reported that use P sources other than phosphate (PH_3 [20-22], $\text{P}(\text{C}_6\text{H}_5)_3$ [23,24], $\text{P}(\text{C}_8\text{H}_{17})_3$ [25], H_2PO_2^- [9,10,16,26,27], H_2PO_3^- [6,7,28,29]), include small amounts of noble metals in the precursors [30], or utilize an H_2 plasma [31]. Focusing on syntheses that use phosphorus oxoacids or their salts as the P source (and without the addition of noble metals), the maximum TPR temperature needed to reduce the catalyst precursors to Ni_2P has been lowered from ≥ 873 K for phosphate-based precursors, to 673-823 K for phosphite-based precursors, and to 473-773 K for hypophosphite-based precursors [2]. The preparation of nickel phosphite ($\text{Ni}(\text{H}_2\text{PO}_3)_2$) based precursors via the stoichiometric reaction of $\text{Ni}(\text{OH})_2$ and phosphorus acid (H_3PO_3) has been reported [6,7] and, while avoiding salt byproducts (e.g. NaCl), the higher oxidation state of P in phosphite required a higher

TPR temperature to successfully reduce the precursor to Ni_2P than is needed for hypophosphite-based precursors.

The use of hypophosphite as the P source enables the reduction of precursors to Ni_2P at low temperatures, but syntheses reported in the literature have utilized nickel salts ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and P salts (NaH_2PO_2 , $\text{NH}_4\text{H}_2\text{PO}_2$) to prepare unsupported or supported $\text{Ni}(\text{H}_2\text{PO}_2)_2$ precursors [9,10,16,26,27]. As a result, the salt byproducts formed during synthesis, and which remain on the catalysts after reduction, must be removed by an H_2O washing step to obtain high activity Ni_2P catalysts. By employing the reaction between $\text{Ni}(\text{OH})_2$ and H_3PO_2 to prepare $\text{Ni}(\text{H}_2\text{PO}_2)_2$ precursors, in an analogous fashion as was done for $\text{Ni}(\text{H}_2\text{PO}_3)_2$, the need for a washing step is eliminated and the precursors can be used for in situ preparation of Ni_2P catalysts at 673 K.

The TPR-MS traces for the reference compound NaH_2PO_2 in Ar and 10 mol% H_2/Ar (Figure 1) reveal that the decomposition/reaction of hypophosphite is a multi-step process. A proposed set of reactions for the decomposition NaH_2PO_2 in Ar (Equations 1-2) involves the sequential disproportionation of NaH_2PO_2 and Na_2HPO_3 to give PH_3 as a gaseous product and, in the case of the second reaction, also produces H_2O . The evolution of PH_3 in peaks at 535 and 579 K from the decomposition of NaH_2PO_2 is consistent with PH_3 being the reactant for conversion of Ni^{2+} (NiCl_2 , $\text{Ni}(\text{NO}_3)_2$, NiO , NiS) to Ni_2P when hypophosphite-based precursors are heated to ~623 K or higher in inert gas (Ar, N_2) [10,16,27]. Phosphine, in the form of 10 mol% PH_3/H_2 or 20 mol% PH_3/He , has been used directly for the conversion of supported Ni and NiO to Ni_2P [20-22], but the toxicity and difficulty in handling of PH_3 make its direct use as a reagent in catalyst synthesis impractical. While the use of hypophosphite salts in preparing Ni_2P catalysts obviates the need to use PH_3 directly, an H_2O washing step is necessary to remove salt byproducts formed during Ni_2P synthesis [2].

The TPR-MS traces for unsupported and supported $\text{Ni}(\text{H}_2\text{PO}_2)_2$ precursors (Figures 2-3), with the $\text{Ni}(\text{H}_2\text{PO}_2)_2$ prepared using $\text{Ni}(\text{OH})_2$ and H_3PO_2 , indicate Ni_2P is formed in the temperature range 468-561 K. The temperature at which $\text{Ni}(\text{H}_2\text{PO}_2)_2$ reacts varies from 468 K for unsupported $\text{Ni}(\text{H}_2\text{PO}_2)_2$ to progressively higher temperatures for $\text{Ni}(\text{H}_2\text{PO}_2)_2$ supported on SiO_2 (476 and 497 K), $\gamma\text{-Al}_2\text{O}_3$ (507 K) and ASA (561 K). The relative amount of PH_3 evolved decreases in the order $\text{SiO}_2 > \gamma\text{-Al}_2\text{O}_3 > \text{ASA}$, which when combined with the increasing reaction temperatures, indicates that the extent of interaction of impregnated P with the supports increases in the order: $\text{SiO}_2 < \gamma\text{-Al}_2\text{O}_3 < \text{ASA}$. These observations are consistent with the preparation of Ni_2P on the three supports using phosphate, as progressively more P was needed in the order: SiO_2 (P/Ni = 0.9), $\gamma\text{-Al}_2\text{O}_3$ (P/Ni = 1.5), ASA (P/Ni = 2.2) to obtain phase-pure Ni_2P . The phosphate-based precursors were not calcined in order to minimize potential reactions with the support (e.g. formation of AlPO_4 [5]), but a TPR temperature of 923 K was needed to form phase-pure Ni_2P on the three supports. The average Ni_2P crystallite sizes determined by XRD (Figure 4 and Table 1) were substantially smaller for the Ni_2P catalysts prepared using hypophosphite-based precursors compared to phosphate-based precursors. The average Ni_2P particle sizes of 3-4 nm determined using TEM (Table 1) underscore the effectiveness of the hypophosphite-based synthesis method for preparing $\text{Ni}_2\text{P}/\text{SiO}_2$, $\text{Ni}_2\text{P}/\text{ASA}$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalysts with high particle dispersions.

The surface compositions of the Ni_2P catalysts (prepared ex situ) and of the HDN/HDS-tested catalysts (prepared in situ and ex situ) were highly enriched in P relative to the nominal bulk and measured surface compositions of the hypophosphite-based precursors (Table 2). The XPS spectra acquired after HDS/HDN testing of in situ prepared $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalysts (Figure 6) show the surface P to be almost exclusively P^{5+} species in the form of phosphate. While passivation of the HDS/HDN-tested catalysts in 1 mol% O_2/He forms an oxidized surface layer on the Ni_2P particles, the extent of surface enrichment of P in the form of phosphate is substantially

564 higher than reported previously for phosphate-based $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalysts [5]. The
 565 reaction proposed for the conversion of $\text{Ni}(\text{H}_2\text{PO}_2)_2$ to Ni_2P (Equation 5) yields H_3PO_4 as a product,
 566 and the XPS results suggest that some of this P remains on the catalyst surface as unreduced
 567 $\text{H}_x\text{PO}_4^{(3-x)-}$ species. The extent of surface P enrichment was observed to increase for the
 568 HDS/HDN-tested $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalysts relative to the ex-situ prepared catalysts. The
 569 fact that no significant catalyst deactivation was observed suggests that this high surface P
 570 concentration does not have a deleterious effect on catalytic properties. Surface enrichment of P
 571 has been observed previously by XPS of unsupported Ni_2P and $\text{Co}_x\text{Ni}_2\text{P}$ catalysts, and on the basis
 572 of acidity measurements carried out using n-propylamine, these surface P species were assigned to
 573 $\text{H}_x\text{PO}_4^{(3-x)-}$ [32]. The most active $\text{Co}_x\text{Ni}_2\text{P}$ for HDS of 4,6-dimethyldibenzothiophene, $\text{Co}_{0.08}\text{Ni}_2\text{P}$,
 574 had the highest surface P enrichment and Brönsted acid site density, but also the lowest CO
 575 chemisorption capacity [32]. As described earlier, H_3PO_4 was identified as the P-containing
 576 byproduct formed during the reduction of unsupported $\text{Ni}(\text{H}_2\text{PO}_2)_2$ and it is expected to remain
 577 adsorbed on the surface of the catalyst particles as $\text{H}_x\text{PO}_4^{(3-x)-}$ species following in situ preparation.
 578 The enrichment of Ni_2P particle surfaces with $\text{H}_x\text{PO}_4^{(3-x)-}$ species could also explain why the
 579 $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalysts prepared from hypophosphite-based precursors have similar or
 580 lower CO chemisorption capacities than the catalysts prepared from phosphate-based precursors
 581 (Table 1), despite the hypophosphite-based Ni_2P catalysts having significantly smaller average Ni_2P
 582 crystallite sizes. The CO chemisorption capacities of the $\text{Ni}_2\text{P}/\text{ASA}$ catalysts do not follow the
 583 same pattern, but this could be due to the large excess of P needed to prepare the phosphate-based
 584 Ni_2P catalyst on ASA, resulting in an anomalously low CO chemisorption capacity in this case.

585 The Ni_2P catalysts prepared in situ from hypophosphite-based precursors had the highest
 586 HDS/HDN conversions and TOFs for the different preparation methods on the $\gamma\text{-Al}_2\text{O}_3$ and ASA
 587 supports. For SiO_2 , the catalyst prepared in situ from hypophosphite had similar HDN/HDS

conversions as did a phosphate-based catalyst reported previously [3], but had significantly higher TOFs. The phosphate-based $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst had a higher Ni_2P loading (25 wt%) than did the hypophosphite-based $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst (15 wt%), so the most useful comparison of HDN/HDS activities is the TOFs in this case. For each support, the in situ prepared Ni_2P catalysts significantly outperformed the ex situ prepared Ni_2P catalysts; the disparity is most clearly seen for the $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and $\text{Ni}_2\text{P}/\text{ASA}$ catalysts for which the hypophosphite-based precursors reduced in situ had carbazole HDN conversion 2-3 times higher than the same precursors reduced ex situ and then activated in the reactor. These results highlight the importance of a preparation method that allows low temperature synthesis of the active Ni_2P catalyst directly in the hydrotreating reactor. Finally, the in situ prepared $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalysts had higher HDN/HDS TOFs than did a commercial $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ catalyst, and the high activity of a $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst could be achieved using $\text{H}_2\text{S}/\text{H}_2$ to convert the $\text{Ni}(\text{H}_2\text{PO}_2)_2$ precursor to phase-pure Ni_2P on the support. The ability to use $\text{H}_2\text{S}/\text{H}_2$ for in situ preparation of Ni_2P catalysts at low temperatures may prove to be a particularly attractive feature of the catalyst preparation method described herein as it would enable a Ni_2P -based catalyst to be prepared from a hypophosphite-based precursor in the same catalyst bed as a conventional Co-Mo or Ni-Mo sulfide catalyst.

The most highly active Ni_2P catalysts identified in this study, in situ prepared $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$, had favorable product selectivities relative to a commercial $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ catalyst. The Ni_2P catalysts produced nearly three times more of the partially hydrogenated hydrocarbon CHB than did the $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ catalyst, while the sulfide catalyst produced substantially more of the fully hydrogenated hydrocarbon BCH (Table 4). This product selectivity difference is important as it indicates a lower demand for H_2 for the Ni_2P catalysts while maintaining high HDN (and HDS) conversion.

5. CONCLUSIONS

The in situ preparation of $\text{Ni}_2\text{P}/\text{SiO}_2$, $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ and $\text{Ni}_2\text{P}/\text{ASA}$ catalysts from hypophosphite-based precursors formed by the reaction of $\text{Ni}(\text{OH})_2$ and H_3PO_2 yields highly active catalysts for HDN and HDS of a mixed carbazole/benzothiophene feed. TPR-MS measurements reveal the reaction of $\text{Ni}(\text{H}_2\text{PO}_2)_2$ to form Ni_2P occurs at 468-561 K, with unsupported $\text{Ni}(\text{H}_2\text{PO}_2)_2$ reacting at the low end of this temperature range and $\text{Ni}(\text{H}_2\text{PO}_2)_2$ on the Al-containing supports reacting at the high end of this range. The surface compositions of the ex situ prepared catalysts and of HDN/HDS-tested catalysts are highly enriched in P, with much of this surface P in the form of $\text{H}_x\text{PO}_4^{(3-x)-}$ species. In situ prepared $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ catalysts had higher TOFs than did a commercial Ni-Mo/ Al_2O_3 catalyst, and high catalytic activity could be achieved using $\text{H}_2\text{S}/\text{H}_2$ for the in situ conversion of the $\text{Ni}(\text{H}_2\text{PO}_2)_2$ precursor to phase-pure Ni_2P .

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GRAPHICAL ABSTRACT