Submitted to *Surface Science*, May 29, 2015 revised on October 2, 2015.

Probing Hydrodesulfurization over Bimetallic Phosphides Using Monodisperse Ni_{2-x}M_xP Nanoparticles Encapsulated in Mesoporous Silica

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ABSTRACT

Metal phosphide nanoparticles encapsulated in mesoporous silica provide a well-defined system for probing the fundamental chemistry of the hydrodesulfurization (HDS) reaction over this new class of hydrotreating catalysts. To investigate composition effects in bimetallic phosphides, the HDS of dibenzothiophene (DBT) was carried out over a series of Ni-rich $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ ($\text{M} = \text{Co}, \text{Fe}$) nanocatalysts ($x \leq 0.50$). The $\text{Ni}_{2-x}\text{M}_x\text{P}$ nanoparticles (average diameters: 11-13 nm) were prepared by solution-phase arrested precipitation and encapsulated in mesoporous silica, characterized by a range of techniques (XRD, TEM, IR spectroscopy, BET surface area, CO chemisorption) and tested for DBT HDS activity and selectivity. The highest activity was observed for a $\text{Ni}_{1.92}\text{Co}_{0.08}\text{P@mSiO}_2$ nanocatalyst, but the overall trend was a decrease in HDS activity with increasing Co or Fe content. In contrast, the highest turnover frequency (TOF) was observed for the most Co- and Fe-rich compositions based on sites titrated by CO chemisorption. IR spectral studies of adsorbed CO on the $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ catalysts indicate an increase in electron density occurs on Ni sites as the Co or Fe content is increased, which may be responsible for the increased TOFs of the catalytic sites. The $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts exhibit a strong preference for the direct desulfurization pathway (DDS) for DBT HDS that changes only slightly with increasing Co or Fe content.

GRAPHICAL ABSTRACT

KEYWORDS

Hydrodesulfurization, HDS, dibenzothiophene, nickel phosphide, bimetallic phosphide, nanoparticles encapsulated in mesoporous silica

1. INTRODUCTION

Increasingly stringent regulations on the allowed sulfur content in transportation fuels combined with increased reliance on unconventional crude oil resources containing higher impurity concentrations is motivating researchers to explore new approaches and catalytic materials for processing fossil fuel feedstocks [1-3]. Hydrodesulfurization (HDS) is the industrial hydrotreating process for removing sulfur compounds from crude oil and sulfided Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts are widely used for this purpose [4]. However, the lamellar structure of these molybdenum sulfide (MoS₂) based materials results in metal sites exposed on edge planes only and results in low active site densities. It is unclear whether further engineering of molybdenum sulfide-based catalysts can provide the ultralow sulfur levels required to satisfy future regulatory limits. Metal phosphides such as Co₂P, CoP, Ni₂P, MoP and WP have been found to be active catalysts for HDS and hydrodenitrogenation (HDN) [3,5], attributed in part to the isotropic distribution of metal sites on the particle surfaces resulting in improved catalytic activity. Among the binary phosphides studied, silica-supported nickel phosphide (Ni₂P/SiO₂) has shown the best performance, with high HDS activity and excellent resistance to sulfur poisoning [6-8]. The significance and potential application of phosphide materials for catalysis can be further highlighted by recent studies showing that several binary phosphides act as efficient catalysts for the hydrogen evolution reaction (HER) in acidic media [9-12].

A number of studies have shown that further enhancement of the HDS and HDN properties of nickel phosphide can be achieved by incorporation of a second metal into the Ni₂P structure [13-17]. Bulk and silica-supported nickel cobalt ternary phosphides (Ni_{2-x}Co_xP) have been shown to exhibit higher HDS activities for materials incorporating small amounts of cobalt ($x \approx 0.1$) relative to Ni₂P [13,14]. Silica-supported Ni_{2-x}Fe_xP catalysts also exhibit promising HDS properties, with activities and selectivities dependent upon the metal composition [15,16].

As with the nickel-cobalt phosphide catalysts, an increase in HDS activity was observed for Ni-rich $\text{Ni}_{2-x}\text{Fe}_x\text{P}/\text{SiO}_2$ catalysts ($x \approx 0.03$) for the HDS of thiophene and dibenzothiophene (DBT) [15]. In a different study, Oyama and coworkers observed a substantial shift in product selectivity with metal composition for the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) HDS over a series of $\text{Ni}_{2-x}\text{Fe}_x\text{P}/\text{SiO}_2$ catalysts, with increasing preference for the DDS pathway as the Fe content of the catalysts increased [16,18].

The bimetallic phosphides of interest form solid solutions over broad ranges of composition with $\text{Ni}_{2-x}\text{Co}_x\text{P}$ ($0 \leq x \leq 1.7$) and $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ ($0 \leq x \leq 2$) materials adopting the hexagonal Fe_2P structure type ($\overline{\text{P}}6_2\text{m}$ space group [19]). This hexagonal structure contains two metal sites, M(1) and M(2), coordinated to four (tetrahedral) and five (square pyramidal) P atoms, respectively [19,20]. Neutron diffraction and Mössbauer spectroscopy have shown that there is ordering of the metal atoms in $\text{Ni}_{2-x}\text{Co}_x\text{P}$ and $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ materials [20,21]. Focusing on the $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ System, Fe atoms preferentially occupy M(2) sites in the lattice for Fe-rich compositions, which is expected as Ni atoms are slightly smaller than Fe atoms. However, for the Ni-rich compositions, Mössbauer spectroscopy showed that the Fe atom site preference is reversed with the majority of Fe atoms occupying M(1) sites, leaving an excess of Ni atoms in the square pyramidal M(2) sites in the Ni-rich materials. It was proposed that the anomalous site preferences in $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ (and $\text{Ni}_{2-x}\text{Co}_x\text{P}$) are due to electron transfer from Fe (and Co) to Ni, which could explain why an excess of Ni atoms occupy the square pyramidal M(2) sites in Ni-rich $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ and $\text{Ni}_{2-x}\text{Co}_x\text{P}$ materials instead of the more spatially confined tetrahedral M(1) sites [15,20,22]. Increased electron density around the Ni atoms would result in an increased atomic size and lead to preferential occupation of the M(2) sites.

It has been hypothesized that the distribution of metal atoms in the M(1) and M(2) sites of $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ and $\text{Ni}_{2-x}\text{Co}_x\text{P}$ catalysts plays a role in determining the HDS properties of these

bimetallic phosphides [13-16,18,23]. While the bulk structure of $\text{Ni}_{2-x}\text{M}_x\text{P}$ materials is composed of 50% M(1) and 50% M(2) sites, surface effects become important for nanoscale materials and the distribution of M(1) and M(2) sites need not be equal. For example, the selectivity of 4,6-DMDBT HDS over $\text{Ni}_{2-x}\text{Fe}_x\text{P}/\text{SiO}_2$ catalysts was observed to change from the hydrogenation (HYD) pathway to the direct desulfurization (DDS) pathway with increasing Fe content of the catalysts [16,18]. Based on EXAFS and DFT studies, Oyama and coworkers concluded that Fe preferentially substituted for Ni in M(2) sites at the surfaces of $\text{Ni}_{2-x}\text{Fe}_x\text{P}/\text{SiO}_2$ catalysts, resulting in surfaces that terminate with Ni occupying M(1) sites [18]. In contrast, for Ni-rich $\text{Ni}_{2-x}\text{M}_x\text{P}/\text{SiO}_2$ catalysts, the high HDS activities of the catalysts was attributed to P-rich surfaces that are resistant to S incorporation [14,15]. These P-rich surfaces may arise from a high proportion of Ni(2) sites at the particle surface. Finally, the donation of electron density from Co or Fe to Ni atoms in $\text{Ni}_{2-x}\text{M}_x\text{P}$ catalysts is expected to alter the catalytic properties of surface Ni sites.

In considering the results for silica-supported $\text{Ni}_{2-x}\text{Co}_x\text{P}$ and $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ catalysts, it should be noted that their preparation via conventional impregnation methods and temperature-programmed reduction (TPR) yields samples with polydisperse particle sizes and possibly inhomogeneous compositions, complicating the development of a detailed understanding of how the metal composition of ternary phosphides affects HDS activity and selectivity. In order to develop a detailed understanding of the HDS catalytic properties of $\text{Ni}_{2-x}\text{M}_x\text{P}$ catalysts, mono-disperse and discrete nanoparticles provide an excellent model system for investigation. Solution-phase arrested precipitation reactions enable excellent control of size, shape and composition in the formation of discrete nanoparticles [24-27]. Recently, we reported a protocol to synthesize mono-disperse $\text{Ni}_{2-x}\text{Co}_x\text{P}$ and $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ nanoparticles with different compositions [28,29]. In the present work, Ni-rich $\text{Ni}_{2-x}\text{M}_x\text{P}$ (M = Co, Fe) compositions are encapsulated in

mesoporous silica and their HDS properties are probed using DBT as a model organosulfur compound. These catalytic data are correlated to the surface properties as probed by CO chemisorption capacity measurements and Fourier transform infrared (FT-IR) spectroscopy analysis of adsorbed CO.

EXPERIMENTAL METHODS

2.1 Catalyst Synthesis

Nickel(II) acetylacetonate (95%) was purchased from Alfa Aesar; cobalt(II) acetylacetonate (99%), iron(0) pentacarbonyl (99.99%), triphenylphosphine (TPP) and n-cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich; n-octyl ether (95%), oleylamine (>50%) from TCI America; tri-n-octylphosphine (TOP, 97%) from STREM Chemicals; tetraethylorthosilicate (TEOS) from ACROS; chloroform from Fisher Scientific; and methanol and ethanol (200 proof) from Decon Laboratories. All chemicals were used as received.

The detailed synthetic protocol for the synthesis of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ nanoparticles is described elsewhere [28]. Briefly, in a typical synthesis the corresponding amounts of two metal precursors ($\text{Ni}(\text{acac})_2$ and $\text{Co}(\text{acac})_2$) totaling 2 mmol were combined with 5 mL of oleylamine, 10 mL of octyl ether, and 4 mL of TOP in a Schlenk flask. The mixture was degassed at 383 K for 20 min, followed by purging with argon for 20 min. The temperature was then increased to 503 K and the solution heated for 90 min. As the final step of the synthesis, the temperature was set to 623 K and an additional 6 mL aliquot of TOP was injected, followed by heating for 4.5 h. The black product was isolated by precipitation with ethanol. The product was dispersed in chloroform and sonicated for 5-10 min followed by re-precipitation with ethanol. This precipitation and dispersion procedure were carried out at least three times.

For the preparation of $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ nanoparticles, which has been described in detail elsewhere [29], stoichiometric amounts of nickel(II) acetylacetonate and iron(0) pentacarbonyl were used. In a typical synthesis, $\text{Ni}(\text{acac})_2$ ($2-x$ mmol) was combined with trioctylphosphine (TOP), octylether and oleylamine and heated at 503 K under an argon atmosphere for 30 min. Then $\text{Fe}(\text{CO})_5$ (x mmol) was introduced and heating was continued at 503 K for another 30 min. The temperature of the reaction was raised to 623 K and the reaction was heated for an additional 10 h. After cooling the reaction mixture to room temperature, the nanoparticles were isolated as described for $\text{Ni}_{2-x}\text{Co}_x\text{P}$ nanoparticles.

The procedure for the encapsulation of nanoparticles in mesoporous silica was carried out as previously described for Ni_2P [30]. As-prepared nanoparticles were dispersed in 5 mL of chloroform and added drop-wise to 20 mL of an aqueous 0.1 M CTAB solution. This solution was heated at 348-353 K in order to evaporate the chloroform, during which phase transfer of the nanoparticles from the organic to the aqueous phase occurred. The resultant dispersion was diluted to a final volume of 150 mL with nanopure water and 2.5 mL of 1 M NaOH was added, followed by dropwise injection of 4.6 mL of TEOS to initiate the base catalyzed polymerization. The reaction was completed within 20-30 min and the silica-encapsulated nanoparticles were isolated by centrifugation. The isolated product was washed with water and methanol three times to remove residual NaOH and ethanol formed as the by-product. The purified product was dried under vacuum overnight and then calcined in air at 698 K for 2-3 h to remove the CTAB. The oxidized material formed during calcination was converted back to the phosphide by treatment with TPP, placed up-stream in a furnace, under active flow of 5% H_2/Ar at 673 K.

The preparation of a 10 wt% $\text{Ni}_2\text{P}/\text{SiO}_2$ by incipient wetness and TPR methods has been described in detail elsewhere [8,30].

2.2 Catalyst Characterization

X-ray diffraction (XRD) patterns were collected on either Rigaku RU200B or PANalytical X'Pert Pro diffractometers equipped with monochromatic Cu-K α sources (λ = 1.54050 Å). The patterns were compared to reference patterns from the ICDD database for phase identification. Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) were carried out with a JEOL 2010 electron microscope operating at a voltage of 200 kV and coupled to an EDS detector (EDAX Inc.). Bright field images were captured by Amtv600 software. TEM specimens were prepared by dispersion of as-prepared nanoparticles in chloroform (or silica encapsulated nanoparticles dispersed in methanol) and depositing a drop of solution on a formvar carbon coated 200 mesh Cu grid, followed by drying in air. The metal phosphide loadings (wt%) of the encapsulated samples were evaluated using ICP-MS based on the total metal content (assuming a 2:1 stoichiometry of metal:P) by ICP-MS (Agilent 7700). The samples (2 mg) were digested in concentrated nitric acid (5 mL) over 3-4 days and diluted 48x with nano pure water. A series of external standards were used for calibration over the relevant concentration range.

Surface area and pore size distributions for encapsulated silica samples were collected using a Micromeritics Tristar II surface area/porosimeter. All samples were degassed for 16 h at 423 K under N₂ flow before the analysis. Surface areas were calculated based on the Brunauer-Emmett-Teller (BET) method and pore size distributions were obtained by the Barrett-Joyner-Halenda (BJH) method. Carbon monoxide (CO) pulsed chemisorption measurements were also obtained using a Micromeritics Autochem 2950 instrument equipped with a thermal conductivity detector. Approximately 0.1000 g of catalyst was degassed in 60 mL/min Ar at room temperature for 30 min. Prior to the measurements, the samples were reduced in a 60 mL/min flow of 10.0 mol% H₂/Ar (Praxair) by heating (10 K/h) from room temperature to 673 K and holding at this temperature for 1 h. The catalyst samples were then degassed in 60 mL/min He at

673 K for 30 min prior to the chemisorption measurement. The CO chemisorption measurements were performed by pulsing a 10.0 mol% CO/He mixture (0.6080 mL loop volume) into 60 mL/min of He flowing over the catalyst sample, which was held at 273 K. Pulsing was carried out until the peak areas of three consecutive pulses remained unchanged, after which the chemisorption capacity was calculated.

The IR spectroscopic experiments were conducted in an ion pumped (110 L/s) ultra-high vacuum (UHV) system that has a base pressure of $\sim 5 \times 10^{-9}$ Torr. The UHV system, which has been described in detail elsewhere [31], includes a high-pressure cell outfitted with CaF_2 windows that can be isolated from the main chamber. The system is equipped with a Mattson RS-1 FTIR spectrometer outfitted with a narrow-band MCT detector; the high-pressure cell is situated in the sample compartment of the spectrometer and IR spectra are collected in transmission mode. Catalyst samples were mounted in the UHV system following the procedure described previously [31]. Briefly, ~ 10 mg of the catalyst was pressed at 14 MPa into a nickel metal mesh (50 x 50 mesh size, 0.002 in. wire diameter); the area of the pressed samples was $\sim 0.80 \text{ cm}^2$. A chromel-alumel thermocouple was spot-welded to the nickel mesh in order to monitor the temperature of the sample. This assembly was then mounted onto a sample holder equipped with resistive heating. Following mounting in the UHV system, the catalyst samples were evacuated overnight to a pressure $\leq 10^{-8}$ Torr. The catalyst samples were then reduced in 100 Torr H_2 for 30 min at 700 K. In order to remove weakly bonded species from the surface of the reduced catalysts, the high pressure cell was then evacuated and the sample heated to 700 K in vacuum for 1 min.

Transmission FTIR spectra were acquired in the $4000\text{-}1000 \text{ cm}^{-1}$ range by collecting 128 scans at 2 cm^{-1} resolution. To eliminate the contributions of gas phase CO in the IR spectra, the sample spectrum was ratioed against a spectrum acquired using a blank nickel mesh mounted in the

sample holder in the presence of 1.0 Torr CO. Following pretreatment and degassing, the catalyst sample was cooled to room temperature at a pressure of $\sim 1 \times 10^{-8}$ Torr and a background IR spectrum was acquired. IR spectra of adsorbed CO were then collected at 298 K while the catalyst sample was in the presence of 1.0 Torr CO, and then in UHV following evacuation of the gas phase CO. The IR spectra presented in the figures were prepared by subtracting the background IR spectrum obtained prior to CO exposure from the IR spectrum acquired after CO exposure.

Following HDS measurements, samples of the catalysts were collected from the reactor for X-ray diffraction and bulk carbon and sulfur analyses. Upon completion of an HDS experiment, the flow of liquid feed was stopped while maintaining the H₂ gas flow for 1 h at the reaction temperature. The reactor was then cooled to room temperature, depressurized, and then purged with 60 mL/min He for 30 min. A 1 mol% O₂/He mixture was then flowed over the catalyst for 2 h prior to opening the reactor and recovering the catalyst sample. Bulk carbon and sulfur analyses of HDS-tested catalyst samples were carried out using a LECO SC-144DR Sulfur and Carbon Analyzer. Approximately 0.10 g of catalyst was transferred into a ceramic boat, which was then loaded into a furnace where the sample was combusted in an oxygen-rich environment at ~ 1625 K for 3 min. Combusted carbon (CO₂) and sulfur (SO₂) that evolved from the catalyst sample was quantified via IR detection and reported as wt% C and S. An additional ~ 0.05 g sample of the HDS-tested catalysts was used to acquire an X-ray diffraction pattern as described above.

2.3 Dibenzothiophene HDS activity measurements

Dibenzothiophene 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 548-648 K. The reactor feed consisted of a decalin solution containing 3000 ppm DBT and 500

ppm dodecane, with the latter used as an internal standard for gas chromatographic analysis of the reactor effluent. The liquid feed (5.4 mL/h) was injected into a 100 mL/min flow of hydrogen and vaporized in-line prior to entry into the reactor. Approximately 0.15 g of catalyst (16-20 mesh size) was diluted with quartz sand 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 reactor temperature was measured with a thermocouple mounted axially in the reactor tube that was in direct contact with the catalyst bed. The $\text{Ni}_{2-x}\text{Co}_x\text{P@mSiO}_2$ and $\text{Ni}_{2-x}\text{Fe}_x\text{P@mSiO}_2$ nanocatalysts were pretreated by heating from room temperature to 673 K in 1 h in a 60 mL/min flow of H_2 and held at this temperature for 2 h, then cooled to room temperature in continued H_2 flow. The He (Airgas, 99.999 mol%) and H_2 (Airgas, 99.999 mol%) were passed through molecular sieve and O_2 removal traps prior to use.

Following pressurization of the reactor with H_2 to 3.0 MPa, the catalyst was heated to 548 K in 100 mL/min H_2 over 1 h after which the flow of liquid feed was begun. The reactor was stabilized for approximately 12 h prior to sampling the reactor effluent at 30 min intervals over 2 h. The catalyst temperature was then raised 25 K, the reactor stabilized for 3 h, followed by sampling of the reactor effluent at 30 min intervals for 2 h. This procedure was repeated until sampling at the highest reaction temperature (648 K) was completed. In an additional experiment, carried out for a $\text{Ni}_{2.00}\text{P@mSiO}_2$ nanocatalyst, the reactor was prepared as described above, but was then stabilized at a single temperature of 623 K. Following stabilization of the reactor for 1 h, the reactor effluent was sampled intermittently over a period of 48 h. The samples of the liquid reactor effluent from the HDS activity measurements were analyzed off-line using a gas chromatograph (Agilent 6890N) equipped with an HP-5 column and a flame ionization detector.

3. RESULTS

3.1 Bulk Characterization

The metal phosphide loadings and bulk compositions of the $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ ($\text{M} = \text{Co}, \text{Fe}$) nanocatalysts, determined by ICP-MS and EDS, respectively, are listed in Table 1. Based on comparison of the XRD patterns (Figure 1) with a reference pattern for Ni_2P (#74-1385) from the JCPDS powder diffraction pattern database, the $\text{Ni}_{2-x}\text{M}_x\text{P}$ nanoparticles are phase pure, except possibly the $\text{Ni}_{1.70}\text{Fe}_{0.30}\text{P@mSiO}_2$ nanocatalyst for which faint peaks assigned to the Ni_{12}P_5 phase (#74-1381) are discernable. The $\text{Ni}_{2-x}\text{M}_x\text{P}$ nanoparticles adopt the Fe_2P -type hexagonal structure characteristic of Ni_2P ; small shifts in the XRD peak positions upon introduction of Co (or Fe) into the Ni_2P lattice are attributed to changes in the lattice constants as determined previously by Rietveld or lattice parameter refinement [28,29].

Table 1: Physicochemical Data for the Nanocatalysts

Nanocatalyst (nominal composition)	Metal phosphide Loading (wt%)	Bulk Composition	P/(Ni+M)	Average Crystallite Size (nm)	BET Surface Area (m ² /g)	BJH average pore diameter (nm)
$\text{Ni}_{2.00}\text{P@mSiO}_2$	10.5	$\text{Ni}_{2.00}\text{P}_{1.08}$	0.54	12	410	3.5
$\text{Ni}_{1.92}\text{Co}_{0.08}\text{P@mSiO}_2$	11.2	$\text{Ni}_{1.89}\text{Co}_{0.11}\text{P}_{1.10}$	0.55	13	938	5.3
$\text{Ni}_{1.75}\text{Co}_{0.25}\text{P@mSiO}_2$	9.8	$\text{Ni}_{1.72}\text{Co}_{0.28}\text{P}_{1.06}$	0.53	11	1270	5.3
$\text{Ni}_{1.50}\text{Co}_{0.50}\text{P@mSiO}_2$	11.6	$\text{Ni}_{1.46}\text{Co}_{0.54}\text{P}_{1.12}$	0.56	13	903	3.4
$\text{Ni}_{1.90}\text{Fe}_{0.10}\text{P@mSiO}_2$	10.3	$\text{Ni}_{1.91}\text{Fe}_{0.09}\text{P}_{1.14}$	0.57	12	806	4.0
$\text{Ni}_{1.80}\text{Fe}_{0.20}\text{P@mSiO}_2$	8.1	$\text{Ni}_{1.82}\text{Fe}_{0.18}\text{P}_{0.98}$	0.49	12	1304	5.2
$\text{Ni}_{1.70}\text{Fe}_{0.30}\text{P@mSiO}_2$	9.5	$\text{Ni}_{1.74}\text{Fe}_{0.26}\text{P}_{0.99}$	0.49	12	787	5.0

Crystallite sizes calculated using the Scherrer equation vary from 11-13 nm as shown in Table 1. TEM images of the $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts (Figure 2) show the dispersion of nanoparticles (small dark spheres) in the mesoporous silica matrix (larger, lower contrast spheres). High-resolution TEM images of the as-prepared $\text{Ni}_{2-x}\text{M}_x\text{P}$ nanoparticles are shown as insets in each TEM image.

Figure 1: XRD patterns of (a) $\text{Ni}_{2-x}\text{Co}_x\text{P@mSiO}_2$ and (b) $\text{Ni}_{2-x}\text{Fe}_x\text{P@mSiO}_2$ nanocatalysts. The compositions noted on the plots are the nominal compositions; the actual compositions are given in Table 1.

Figure 2: TEM images of (a) $\text{Ni}_{2-x}\text{Co}_x\text{P}@m\text{SiO}_2$ and (b) $\text{Ni}_{2-x}\text{Fe}_x\text{P}@m\text{SiO}_2$ nanocatalysts. The insets show high-resolution TEM images of the nanoparticles prior to encapsulation. Particle size histograms for selected compositions are shown in Figure S1.

Lattice planes were observed for all compositions, indicating the crystalline nature of the nanoparticles; d-spacings for the observed lattice planes were approximately 0.5 nm. This d-spacing value corresponds to the $\{100\}$ set of planes in the Ni_2P structure. The Miller indices were assigned for the observed facets of a nanoparticle with the $\text{Ni}_{1.50}\text{Co}_{0.50}\text{P}$ composition. As shown in Figure 3, there is significant exposure of $\{001\}$ planes on the surface of the particle.

Figure 3: An enlarged high-resolution TEM image of a $\text{Ni}_{1.50}\text{Co}_{0.50}\text{P}$ nanoparticle showing lattice fringes corresponding to exposed $\{100\}$ planes with 0.5 nm spacing and the $\{100\}$, $\{001\}$ and $\{101\}$ sets of facets.

The compositions of the non-encapsulated $\text{Ni}_{2-x}\text{M}_x\text{P}$ nanoparticles obtained from EDS measurements are very close to the target compositions (Table 1), with phosphorus-to-metal molar ratios in the range $\text{P}/(\text{Ni}+\text{M}) = 0.49\text{-}0.57$ that are close to the stoichiometric value. As reported previously, the surfaces of the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ nanoparticles are quite P-rich ($\text{P}/(\text{Ni}+\text{Co}) = 2.2\text{-}2.9$), but the surface metal compositions are similar to those of the bulk values [28]. Following HDS measurements, XRD patterns were acquired of the tested catalysts and these are shown in Figures S2-S3. In most cases, only a small increase in average crystallite size was observed for the $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts during HDS testing based on XRD measurements of as-prepared and post-HDS samples. The as-prepared and HDS-tested samples had average crystallite sizes of 12 and 14 nm, respectively. Significant sintering was observed for one sample, $\text{Ni}_{1.70}\text{Fe}_{0.30}\text{P@mSiO}_2$, with the average crystallite size increasing from 12 to 31 nm as a result of HDS testing at 548-648 K. The $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts incorporated minimal amounts of sulfur during HDS testing (Table 2), as indicated by the low sulfur-to-metal mole ratios ($\text{S}/(\text{Ni}+\text{M}) = 0.004\text{-}0.032$) measured for HDS-tested samples of the nanocatalysts.

3.2 Surface Characterization

The BET surface areas and average pore sizes for the $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts are listed in Table 1; nitrogen physisorption isotherms and pore size distributions (calculated from the adsorption branch of the isotherms) are shown in Figures S4-S5. The surface areas of the nanocatalysts are above $400 \text{ m}^2/\text{g}$, reflecting the highly porous nature of the SiO_2 matrix surrounding the $\text{Ni}_{2-x}\text{M}_x\text{P}$ nanoparticles; the average pore diameters lie in the range 3.4-5.3 nm. Active site densities were estimated via CO chemisorption, with the results listed in Table 2. Except for the $\text{Ni}_{1.92}\text{Co}_{0.08}\text{P@mSiO}_2$ nanocatalyst, the CO chemisorption capacities exhibited a decreasing trend with increased Co or Fe content. These results are consistent with trends in CO and O_2 chemisorption capacities reported previously for TPR-prepared $\text{Ni}_{2-x}\text{M}_x\text{P/SiO}_2$ ($\text{M} = \text{Co}, \text{Fe}$) catalysts [14-16,18].

Table 2: Dibenzothiophene HDS Catalytic Data for the Nanocatalysts

Nanocatalyst	CO Chemisorption Capacity ($\mu\text{mol/g}$)	DBT HDS Activity ^a (nmol DBT/g·s)	TOF ^a (s^{-1})	S/(Ni+M) mole ratio ^b
$\text{Ni}_{2.00}\text{P@mSiO}_2$	17	89	0.0052	0.029
$\text{Ni}_{1.92}\text{Co}_{0.08}\text{P@mSiO}_2$	25	117	0.0047	0.024
$\text{Ni}_{1.75}\text{Co}_{0.25}\text{P@mSiO}_2$	13	85	0.0065	0.032
$\text{Ni}_{1.50}\text{Co}_{0.50}\text{P@mSiO}_2$	9	79	0.0088	0.029
$\text{Ni}_{1.90}\text{Fe}_{0.10}\text{P@mSiO}_2$	12	70	0.0058	0.004
$\text{Ni}_{1.80}\text{Fe}_{0.20}\text{P@mSiO}_2$	8	64	0.0080	-----
$\text{Ni}_{1.70}\text{Fe}_{0.30}\text{P@mSiO}_2$	4	36	0.0090	0.004

^aHDS activities and TOFs at a reaction temperature of 623 K.

^bS/(Ni+M) mole ratio for HDS-tested nanocatalysts.

Infrared spectra of adsorbed CO ($T = 298 \text{ K}$, $P_{\text{CO}} = 1.0 \text{ Torr}$) on a $\text{Ni}_{2.00}\text{P@mSiO}_2$ nanocatalyst and a TPR-prepared 10 wt% $\text{Ni}_2\text{P/SiO}_2$ catalyst are compared in Figure 4. The IR spectra are similar in most respects with IR absorbances for adsorbed CO (ν_{CO}) apparent at 2097-

2015 and 2201-2202 cm^{-1} that are assigned to CO terminally bonded on surface Ni and P sites, respectively [33]. A slight rise in the background is discernable at $\sim 1915 \text{ cm}^{-1}$ that is associated with CO bridge bonded to Ni sites; this mode of CO adsorption is suppressed on Ni_2P as surface P atoms disrupt adjacent Ni sites needed for the formation of bridge bonded CO species [33].

Figure 4: Infrared spectra of adsorbed CO on $\text{Ni}_{2.00}\text{P@mSiO}_2$ and TPR-prepared $\text{Ni}_2\text{P/SiO}_2$ catalysts.

Evacuation of the CO gas results in the disappearance of the ν_{CO} assigned to CO adsorbed on P sites, but (a) (b) Two

differences in the IR spectra are the broader ν_{CO} absorbance for CO adsorbed on Ni sites of the $\text{Ni}_{2.00}\text{P@mSiO}_2$ nanocatalyst as well as a higher integrated absorbance ratio for CO adsorbed on Ni and P sites for the $\text{Ni}_{2.00}\text{P@mSiO}_2$ nanocatalyst ($A_{\text{CO(P)}}/A_{\text{CO(Ni)}} = 0.022$) than for the $\text{Ni}_2\text{P/SiO}_2$ catalyst ($A_{\text{CO(P)}}/A_{\text{CO(Ni)}} = 0.016$).

IR spectra of adsorbed CO on the $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts are shown in Figure 5. Incorporation of Co into the Ni_2P lattice to form $\text{Ni}_{2-x}\text{Co}_x\text{P}$ results in a shift of the ν_{CO}

absorbance for terminally bonded CO to lower wavenumbers ($2097 \rightarrow 2089 \text{ cm}^{-1}$), with the extent of the shift dependent on the amount of Co in the bimetallic phosphide phase. A similar trend is observed for the $\text{Ni}_{2-x}\text{Fe}_x\text{P@mSiO}_2$ nanocatalysts, but with a larger shift ($2097 \rightarrow 2084 \text{ cm}^{-1}$) as the Fe content is increased. The trend for the $\text{Ni}_{2-x}\text{Fe}_x\text{P@mSiO}_2$ nanocatalysts is consistent with the observations of Oyama and coworkers for a series of $\text{Ni}_{2-x}\text{Fe}_x\text{P/SiO}_2$ catalysts ($x = 0, 0.5, 1.0, 1.5$) [18].

Figure 5: Infrared spectra of adsorbed CO on (a) $\text{Ni}_{2-x}\text{Co}_x\text{P@mSiO}_2$ and (b) $\text{Ni}_{2-x}\text{Fe}_x\text{P@mSiO}_2$ nanocatalysts.

3.3 Dibenzothiophene HDS Activity and Selectivity

Dibenzothiophene conversions were measured as a function of time on-stream and of reaction temperature. Plotted in Figure 6 are the DBT HDS conversions over a 48 time period for a $\text{Ni}_{2.00}\text{P@mSiO}_2$ nanocatalyst at 623 K. Following an initial decline in DBT conversion over the first 8 h, a steady conversion was measured over the remainder of the 48 h testing period.

Figure 6: Dibenzothiophene HDS conversion vs. time on-stream for a $\text{Ni}_{2.00}\text{P@mSiO}_2$ nanocatalyst.

The DBT conversions as a function of temperature are plotted in Figure 7 for the $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts over the temperature range 548-648 K; the nanocatalysts exhibit measureable DBT conversions at or above 548 K.

Figure 7: Dibenzothiophene HDS conversion vs. temperature for (a) $\text{Ni}_{2-x}\text{Co}_x\text{P@mSiO}_2$ and (b) $\text{Ni}_{2-x}\text{Fe}_x\text{P@mSiO}_2$ nanocatalysts.

The DBT HDS activities (calculated based on DBT conversion to hydrocarbon products) at 623 K for all of the $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts investigated are listed in Table 2. The $\text{Ni}_{1.92}\text{Co}_{0.08}\text{P@mSiO}_2$ nanocatalyst was the most active (on a mass catalyst basis) of the different compositions investigated; in general, the DBT conversions and HDS activities decreased with increasing Co or Fe content. The trends in DBT HDS activity observed for the $\text{Ni}_{2-x}\text{Co}_x\text{P@mSiO}_2$ and $\text{Ni}_{2-x}\text{Fe}_x\text{P@mSiO}_2$ nanocatalysts are similar to those reported previously for thiophene HDS over TPR-prepared $\text{Ni}_{2-x}\text{Co}_x\text{P/SiO}_2$ and $\text{Ni}_{2-x}\text{Fe}_x\text{P/SiO}_2$ nanocatalysts [14,15]. The DBT HDS turnover frequencies (TOFs), calculated using the CO chemisorption capacities as the measure of active site densities, are listed in Table 2 and plotted in Figure 8 as a function of Co or Fe content. For the calculation of the TOFs, a stoichiometry of one CO molecule adsorbed per Ni site is assumed. The TOFs exhibit an increasing trend as the amount of Co or Fe in the $\text{Ni}_{2-x}\text{M}_x\text{P}$ nanoparticles increases; the slight decrease in TOF for the $\text{Ni}_{1.92}\text{Co}_{0.08}\text{P@mSiO}_2$ nanocatalyst (relative to $\text{Ni}_{2.00}\text{P@mSiO}_2$) is within the uncertainty of the measurements.

Figure 8: Dibenzothiophene HDS TOFs vs. Co or Fe content for $\text{Ni}_{2-x}\text{M}_x\text{P}@m\text{SiO}_2$ nanocatalysts.

While the HDS activities (on a mass catalyst basis) decrease with increasing Co or Fe content, the CO chemisorption capacities decrease more quickly, resulting in the increasing trend for the TOFs. A similar trend is observed for the TOFs of the $\text{Ni}_{2-x}\text{M}_x\text{P}@m\text{SiO}_2$ nanocatalysts if they are compared at similar DBT conversions (~20%) instead of at the same temperature.

There are two pathways for sulfur removal in the HDS of DBT as shown in Scheme 1, with this reaction network determined from a study that used a sulfided Co-Mo/ Al_2O_3 catalyst [34].

Scheme 1: Dibenzothiophene HDS reaction network

The direct desulfurization (DDS) pathway involves hydrogenolysis of the C-S bonds without hydrogenation of the aromatic rings and leads to biphenyl (BP) as the hydrocarbon product. The hydrogenation pathway (HYD) proceeds via hydrogenation of one or both aromatic rings prior to C-S bond hydrogenolysis and leads to the formation of cyclohexylbenzene (CHB) and bicyclohexane (BCH) as products. There are a number of intermediates in the HYD pathway, but most are not detected in the reactor effluent under typical operating conditions. The DBT HDS product selectivities as a function of the reaction temperature for $\text{Ni}_{2.00}\text{P@mSiO}_2$ and selected $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts are plotted in Figures 9 and 10, respectively, and the selectivities for all of the nanocatalysts at 623 K are listed in Table 3. The major product was BP in all cases, which is consistent with results reported previously for TPR-prepared $\text{Ni}_2\text{P/SiO}_2$ and $\text{Ni}_{1.97}\text{Fe}_{0.03}\text{P/SiO}_2$ catalysts [15]. As shown for a $\text{Ni}_{2.00}\text{P@mSiO}_2$ nanocatalyst in Figure 9, the BP selectivity holds steady at ~80% over the temperature range 548-648 K.

Figure 9: Dibenzenothiophene HDS product selectivities vs. temperature for a $\text{Ni}_{2.00}\text{P@mSiO}_2$ nanocatalyst.

The only significant changes observed in the product selectivity with temperature are for tetrahydrodibenzothiophene (4H-DBT), a partially hydrogenated DBT, and CHB. At 548 K, 4H-DBT comprises ~10% of the products, but this amount decreases to zero by 648 K. CHB exhibits the opposite behavior in that its selectivity increases with temperature, starting at 5% at 548 K and increasing to 18% of the products by 648 K. The fully hydrogenated product BCH comprises less than 3% of the products at all temperatures. Shown in Figure 10 are the product selectivities for $\text{Ni}_{1.50}\text{Co}_{0.50}\text{P@mSiO}_2$ and $\text{Ni}_{1.70}\text{Fe}_{0.30}\text{P@mSiO}_2$, which had the highest TOFs of the bimetallic phosphide nanocatalysts investigated. The primary differences between the two catalysts are a higher selectivity towards BP for $\text{Ni}_{1.70}\text{Fe}_{0.30}\text{P@mSiO}_2$ (85-87%) than for $\text{Ni}_{1.50}\text{Co}_{0.50}\text{P@mSiO}_2$ (79-82%), while the opposite is observed for CHB selectivity (3-11% for $\text{Ni}_{1.70}\text{Fe}_{0.30}\text{P@mSiO}_2$ vs. 5-18% for $\text{Ni}_{1.50}\text{Co}_{0.50}\text{P@mSiO}_2$).

Figure 10: Dibenzothiophene HDS product selectivities vs. temperature for (a) $\text{Ni}_{1.50}\text{Co}_{0.50}\text{P@mSiO}_2$ and (b) $\text{Ni}_{1.70}\text{Fe}_{0.30}\text{P@mSiO}_2$ nanocatalysts.

The selectivity data summarized in Table 3 show these selectivity differences to hold true for the other Fe and Co containing phosphide nanocatalysts studied here. The DBT HDS product selectivities at similar DBT conversions ($\sim 20\%$) are consistent with those reported in Table 3.

Table 3: Dibenzothiophene HDS Product Selectivities at 623 K

Catalyst	4H-DBT	BP	CHB	BCH
$\text{Ni}_{2.00}\text{P@mSiO}_2$	1.6	80.5	17.3	0.7
$\text{Ni}_{1.92}\text{Co}_{0.08}\text{P@mSiO}_2$	1.7	80.8	16.6	0.9
$\text{Ni}_{1.75}\text{Co}_{0.25}\text{P@mSiO}_2$	1.4	80.2	17.6	0.8
$\text{Ni}_{1.50}\text{Co}_{0.50}\text{P@mSiO}_2$	2.4	79.7	17.2	0.7
$\text{Ni}_{1.90}\text{Fe}_{0.10}\text{P@mSiO}_2$	1.4	85.1	13.4	0.1
$\text{Ni}_{1.80}\text{Fe}_{0.20}\text{P@mSiO}_2$	1.5	86.0	12.4	0.1
$\text{Ni}_{1.70}\text{Fe}_{0.30}\text{P@mSiO}_2$	3.8	86.8	9.5	0.0

4. DISCUSSION

Solution-phase arrested-precipitation methods for preparing metal phosphides enable excellent control of size, shape and composition, producing samples comprising narrowly polydisperse, discrete nanoparticles [25,30,35]. These synthesis methods, which have been extensively applied to binary phosphides, have recently been used to prepare ternary metal phosphide nanoparticles having a range of compositions in the Ni-Co-P and Ni-Fe-P systems [28,29]. In order to investigate the HDS catalytic properties of metal phosphide nanoparticles under industrially relevant conditions, an earlier study showed that encapsulation of the nanoparticles in mesoporous silica was necessary to inhibit sintering [30]. As indicated by the time on-stream data shown in Figure 6, a $\text{Ni}_{2.00}\text{P}@m\text{SiO}_2$ nanocatalyst exhibited excellent stability over a 48 h testing period. In the absence of mesoporous silica shell, Ni_2P nanoparticles dispersed on a high surface area support exhibited significant deactivation under similar HDS testing conditions due to sintering [30]. In the current study, the investigation of the HDS properties of encapsulated $\text{Ni}_{2-x}\text{Co}_x\text{P}$ and $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ nanoparticles has enabled probing of the role of metal composition in determining the HDS properties of Ni-rich bimetallic phosphides.

4.1 Solid-State and Surface Chemical Properties

The solution-phase synthesis of nanoscale $\text{Ni}_{2-x}\text{Co}_x\text{P}$ materials yields nanoparticles having uniform compositions and well defined structures [28]. Elemental mapping showed uniform distribution of Ni, Co and P in the nanoparticles and, as reported in Table 1, the bulk compositions of the nanoparticles closely match the expected values. The high-resolution TEM image of a non-encapsulated $\text{Ni}_{1.50}\text{Co}_{0.50}\text{P}$ nanoparticle shown in Figure 3 reveals surface faceting with $\{001\}$ planes exposed in high proportion at the surface of the particle. Based on DFT studies, it was proposed that the (001) surface of Ni_2P is the most active for HER and HDS [36,37]. It is expected, therefore, that these surface facets contribute significantly to the HDS

activity of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ (and $\text{Ni}_{2-x}\text{Fe}_x\text{P}$) catalysts. The Ni_2P structure consists of alternating layers along the [001] direction having stoichiometries of Ni_3P_2 and Ni_3P with Ni atoms occupying tetrahedral M(1) and square pyramidal M(2) sites, respectively [3,18]. A low energy electron diffraction (LEED) investigation of a $\text{Ni}_2\text{P}(001)$ single crystal revealed both surface terminations to be present, with a P-terminated Ni_3P_2 surface most favored [38]. The proportion of Ni(1) and Ni(2) sites exposed at the surface of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ particles likely depends on a number of factors – including particle size, shape and composition – and influences the catalytic properties of bimetallic phosphides. For the HDS of 4,6-DMDBT, it has been hypothesized that Ni(1) sites are active for desulfurization via the DDS pathway while Ni(2) sites are active for the HYD pathway [18,39].

XPS measurements of the surface compositions of the non-encapsulated $\text{Ni}_{2-x}\text{Co}_x\text{P}$ nanoparticles ($x = 0.0, 0.08, 0.25, 0.5$) showed fairly close agreement between the bulk and surface metal compositions, but the surfaces were highly enriched in phosphorus ($\text{P}/(\text{Co}+\text{Ni}) = 2.0\text{-}2.9$) [28]. Of importance, $\text{Ni}_{2-x}\text{M}_x\text{P}$ catalysts prepared by TPR methods were also observed to have surface P enrichment. Bulk phase $\text{Ni}_{2-x}\text{Co}_x\text{P}$ materials exhibited phosphorus-to-metal ratios in the range $\text{P}/(\text{Ni}+\text{Co}) = 1.2\text{-}4.8$ [13], while Ni-rich $\text{Ni}_{2-x}\text{M}_x\text{P}/\text{SiO}_2$ catalysts had ratios in the range $\text{P}/(\text{Ni}+\text{M}) = 0.51\text{-}0.83$ [14,15]. Phosphorus enrichment of the surfaces of $\text{Ni}_{2-x}\text{M}_x\text{P}$ catalysts has been associated with improved HDS properties, including increased catalyst acidity and enhanced resistance to sulfur incorporation [13-15]. For the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ nanoparticles, a small shift of the $\text{Ni}(2p_{3/2})$ peak to lower binding energies ($852.7 \rightarrow 852.5$ eV) with increased Co content may indicate slight donation of electron density from Co to Ni. A study of bulk $\text{Ni}_{2-x}\text{M}_x\text{P}$ ($\text{M}=\text{Cr}, \text{Fe}, \text{Co}$) materials using XPS and X-ray absorption near-edge spectroscopy

(XANES) indicated that charge transfer from M to Ni does occur and, while small in magnitude, it is larger for Ni-rich $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ than for $\text{Ni}_{2-x}\text{Co}_x\text{P}$ [40].

The IR spectra of adsorbed CO on the $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts provide conclusive evidence that Ni and P sites on the encapsulated nanoparticles are accessible to molecules from the gas phase. The ν_{CO} absorbance for CO adsorbed on Ni sites of the $\text{Ni}_{2.00}\text{P@mSiO}_2$ nanocatalyst is broader and shifted to lower wavenumbers than for the TPR-prepared $\text{Ni}_2\text{P/SiO}_2$ catalyst (Figure 4). A similar peak shift and broadening was observed in the IR spectra of CO adsorbed on Pt@mSiO_2 and Pt/SiO_2 , which the authors suggested may be due to the intimate contact of silica with the Pt surface for the core@shell catalyst [41]. Interestingly, a similar peak shift and broadening is not observed for the ν_{CO} absorbance for CO adsorbed on P sites, suggesting that the mesoporous silica shell more strongly affects exposed Ni sites of the $\text{Ni}_{2.00}\text{P@mSiO}_2$. Reflecting the high surface P enrichment of the non-encapsulated $\text{Ni}_{2.00}\text{P}$ nanoparticles measured by XPS, the integrated peak area ratio ($A_{\text{CO(P)}}/A_{\text{CO(Ni)}}$) is substantially higher for the $\text{Ni}_{2.00}\text{P@mSiO}_2$ nanocatalyst than for the TPR-prepared $\text{Ni}_2\text{P/SiO}_2$.

The observed trends for the ν_{CO} absorbances in the IR spectra for adsorbed CO on the $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts (Figure 5) are consistent with the findings of the XPS studies discussed above as well as trends in CO chemisorption capacities (Table 2). The most important observation is the shift of ν_{CO} absorbance observed at 2097 cm^{-1} for CO adsorbed on Ni sites of $\text{Ni}_{2.00}\text{P@mSiO}_2$ shifts to lower wavenumbers with increased Co and Fe content. IR spectral measurements for $\text{Co}_2\text{P/SiO}_2$ and $\text{Fe}_2\text{P/SiO}_2$ catalysts revealed ν_{CO} absorbances for CO terminally bonded to Co and Fe sites at 2063 cm^{-1} (sharp peak) and 2003 cm^{-1} (broad peak), respectively [18,42]. The IR spectrum of adsorbed CO on the $\text{Ni}_{1.50}\text{Co}_{0.50}\text{P@mSiO}_2$

nanocatalyst shows evidence for a second absorbance in the form of a shoulder in the 2040-2060 cm^{-1} region that may be indicative of CO adsorption on surface Co sites on this sample. The shifts of the ν_{CO} absorbance for CO terminally bonded to Ni sites from 2097 to 2089 cm^{-1} for $\text{Ni}_{2-x}\text{Co}_x\text{P@mSiO}_2$ and from 2097 to 2084 cm^{-1} for $\text{Ni}_{2-x}\text{Fe}_x\text{P@mSiO}_2$ with increasing Co and Fe contents, respectively, are consistent with electronic donation from Co and Fe to Ni in the nanocatalysts. Increased electron density on Ni sites would enable increased backbonding between Ni and the CO molecule, resulting in a weakening of the CO bond. Oyama and coworkers observed a similar trend in ν_{CO} absorbances for a series of $\text{Ni}_{2-x}\text{Fe}_x\text{P/SiO}_2$ catalysts and came to a similar conclusion [18]. Shifts observed for XPS binding energies and XANES absorption edges for bulk and nanoscale $\text{Ni}_{2-x}\text{Co}_x\text{P}$ and $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ materials are also consistent with a slight transfer of electron density from M to Ni in these bimetallic phosphides [28,40]. Due to difficulty in preparing pressed samples of uniform thickness and area for the IR spectral measurements, it is difficult compare the peak areas for the different samples. Qualitatively, however, the decreasing peak areas of the ν_{CO} absorbance for CO adsorbed on Ni sites for the $\text{Ni}_{2-x}\text{Co}_x\text{P@mSiO}_2$ nanocatalysts with increasing Co content do mirror the trend in CO chemisorption capacities for these nanocatalysts.

4.2 Dibenzothiophene HDS Properties

The DBT HDS results presented in this study indicate that well-defined nanoparticles encapsulated in mesoporous silica provide an excellent system for probing the effect of metal composition on the HDS properties of metal phosphides. Confirming earlier findings that the active sites on the nanoparticle surfaces are accessible to the reactant molecules [30], DBT HDS was observed over $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts having a range of Co and Fe contents. The major findings include the observation of a strong dependence of the TOF on the metal

composition, but only a weak dependence of the product selectivity for DBT HDS. The DBT conversions plotted in Figure 7 and the HDS activities at 623 K (Table 2) reveal the $\text{Ni}_{1.92}\text{Co}_{0.08}\text{P}@m\text{SiO}_2$ to be the most active of the compositions investigated. At 623 K, the $\text{Ni}_{1.92}\text{Co}_{0.08}\text{P}@m\text{SiO}_2$ was 31% more active for DBT HDS than $\text{Ni}_{2.00}\text{P}@m\text{SiO}_2$ when the activities are normalized on a mass of catalyst basis. This result is consistent with a study of $\text{Ni}_{2-x}\text{Co}_x\text{P}/\text{SiO}_2$ catalysts in which a $\text{Ni}_{1.92}\text{Co}_{0.08}\text{P}/\text{SiO}_2$ catalyst prepared from a P-enriched precursor ($\text{P}/(\text{Ni}+\text{Co}) = 0.80$) was the most active catalyst for thiophene HDS, with an activity 34% higher than that of $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst prepared from a precursor having $\text{P}/\text{Ni} = 0.80$ [14]. A similar finding was observed for unsupported phases, as $\text{Ni}_2\text{Co}_{0.08}\text{P}$ (nominal composition) was found to have an activity 67% higher than that of Ni_2P for the HDS of 4,6-DMDBT [13]. In both studies, it was concluded that a small amount of Co in bulk and supported $\text{Ni}_{2-x}\text{Co}_x\text{P}$ resulted in surface enrichment in P; this enrichment may be due to a restructuring of the surface of the metal phosphide particles that results in a higher proportion of Ni in M(2) sites than in Ni_2P . The $\text{Ni}_{1.92}\text{Co}_{0.08}\text{P}@m\text{SiO}_2$ nanocatalyst had a significantly higher CO chemisorption capacity than $\text{Ni}_{2.00}\text{P}@m\text{SiO}_2$ (25 vs. 17 $\mu\text{mol/g}$) that could be a result of a surface restructuring that yields more exposed Ni sites at the surface of the nanoparticles. With increased Co content, the HDS activities and CO chemisorption capacities of the $\text{Ni}_{2-x}\text{Co}_x\text{P}@m\text{SiO}_2$ nanocatalysts decrease monotonically as the surface concentration of Co increases, which mirrors the trend observed for silica-supported $\text{Ni}_{2-x}\text{Co}_x\text{P}/\text{SiO}_2$ catalysts prepared by the TPR method [14].

The DBT HDS activities of the $\text{Ni}_{2-x}\text{Fe}_x\text{P}@m\text{SiO}_2$ nanocatalysts (on a mass catalyst basis) decreased with increasing Fe content, with all of the Fe containing nanocatalysts less active than $\text{Ni}_{2.00}\text{P}@m\text{SiO}_2$. For silica-supported $\text{Ni}_{2-x}\text{Fe}_x\text{P}$ catalysts, higher thiophene activities were measured for catalysts with a very low Fe content ($\text{Ni}_{1.97}\text{Fe}_{0.03}\text{P}/\text{SiO}_2$) that were prepared from precursors having high P contents ($\text{P}/(\text{Ni}+\text{Fe}) = 0.6\text{-}1.0$) [15]. For example, a $\text{Ni}_{1.97}\text{Fe}_{0.03}\text{P}/\text{SiO}_2$

catalyst prepared from a precursor having $P/(Ni+Fe) = 1.0$ was 41% more active than a Ni_2P/SiO_2 catalyst prepared from a precursor having $P/Ni = 0.80$. The $Ni_{1.97}Fe_{0.03}P/SiO_2$ catalyst had a P-enriched surface and its high HDS activity was traced to a strong resistance to S incorporation and a high site density (as measured by O_2 chemisorption) [15]. For $Ni_{2-x}Fe_xP/SiO_2$ catalysts with higher Fe contents ($x \geq 0.08$) the HDS activity (on a mass catalysts basis) decreased rapidly, which is consistent with the findings for the mesoporous silica encapsulated $Ni_{2-x}Fe_xP$ nanoparticle catalysts. Unfortunately, a very low Fe content nanoparticle catalyst (e.g. $Ni_{1.97}Fe_{0.03}P@mSiO_2$) was not investigated in the current study.

In contrast to the HDS activities normalized on a mass basis, the TOFs of the $Ni_{2-x}M_xP@mSiO_2$ nanocatalysts increase with increased Co or Fe content in the bimetallic phosphide nanoparticles. The nanocatalysts with the highest Co and Fe contents, $Ni_{1.50}Co_{0.50}P@mSiO_2$ and $Ni_{1.70}Fe_{0.30}P@mSiO_2$, had the highest TOFs of 0.0088 and 0.0090 s^{-1} , respectively. These TOFs are nearly twice the value for $Ni_{2.00}P@mSiO_2$ (0.0052 s^{-1}). As shown in Figure 8, the TOFs for the $Ni_{2-x}Fe_xP@mSiO_2$ nanocatalysts are higher than for $Ni_{2-x}Co_xP@mSiO_2$ at a similar composition, which could be explained by the extent of electron donation from Co and Fe to Ni in the bimetallic phosphides. Based on careful XPS and XANES measurements, Blanchard et al. concluded that there was increased donation from M to Ni in bulk phase $Ni_{2-x}M_xP$ materials for $M = Co, Fe$ and Cr , with the extent of electron transfer lowest for Co and highest for Cr [40]. The IR spectra shown in Figure 5 are consistent with this conclusion, as the shift to lower wavenumbers of the ν_{CO} absorbance for CO terminally bonded to Ni sites is larger for the $Ni_{2-x}Fe_xP@mSiO_2$ nanocatalysts than for $Ni_{2-x}Co_xP@mSiO_2$, which is indicative of increased electron density on Ni for the Fe-containing nanocatalysts. This is particularly notable because the maximum Fe content investigated ($x = 0.30$) was considerably smaller than for Co ($x =$

0.50). Increased electron density on Ni sites could help facilitate key steps in the HDS process such as the dissociation of H₂ and the adsorption of organosulfur molecules [18].

The DBT HDS selectivity data in Figures 9-10 and Table 3 indicate that Co and Fe have only a minor influence on the product selectivity for the Ni_{2-x}M_xP@mSiO₂ nanocatalysts over the range of metal compositions investigated. It should be noted that for DBT, which does not have alkyl groups at the 4,6 position to hinder adsorption via the S atom, the DDS pathway is the major route for S removal with BP selectivities in the 80-90% range over most catalysts [43]. The Ni_{2.00}P@SiO₂ nanocatalyst exhibited a BP selectivity of ~80% over the temperature range 548-648 K, while the highest Co and Fe content nanocatalysts investigated, Ni_{1.50}Co_{0.50}P@mSiO₂ and Ni_{1.70}Fe_{0.30}P@mSiO₂, had BP selectivities of 79-82% and 85-87%, respectively, over this same temperature range. The selectivity data at 623 K (Table 3) across all nanocatalysts show that there are no significant changes in reaction pathway as a function of Co or Fe content. For Ni_{2-x}Fe_xP/SiO₂ catalysts having a wider range of metal compositions (x = 0, 0.5, 1.0, 1.5, 2.0), Oyama and coworkers measured substantial changes in product selectivity for the HDS of the more demanding organosulfur compound, 4,6-DMDBT [16,18]. A Ni₂P/SiO₂ catalyst exhibited very high selectivity towards the HYD pathway (88%), but the HYD selectivity shifted to favor the DDS pathway with the introduction of substantial amounts of Fe (x ≥ 0.50) into the phosphide catalysts, with a Ni_{1.0}Fe_{1.0}P/SiO₂ catalyst strongly favoring the DDS product, 3,3'-dimethylbiphenyl (85%).

The Ni_{2-x}M_xP@mSiO₂ nanocatalysts exhibited excellent stability under the harsh reaction conditions that are typically used for hydrotreating studies (548-648 K, 3.0 MPa). Except for one case, minimal sintering of the encapsulated nanoparticles was observed and the phase purity of the samples was maintained (Figures S2-S3). In addition, the Ni_{2-x}M_xP@mSiO₂ nanocatalysts

incorporated minimal amounts of sulfur during HDS testing, providing further evidence for the strong resistance of metal phosphides to convert to metal sulfides in sulfur-rich feeds.

5. CONCLUSIONS

Nanoparticles encapsulated in mesoporous silica were investigated as a well-defined model system for probing the fundamental chemistry of the hydrodesulfurization (HDS) reaction over Ni-rich bimetallic phosphides ($\text{Ni}_{2-x}\text{M}_x\text{P}$, $\text{M} = \text{Co}, \text{Fe}$). On a mass of catalyst basis, the highest HDS activity was observed for a $\text{Ni}_{1.92}\text{Co}_{0.08}\text{P@mSiO}_2$ nanocatalyst, which is consistent with the results reported for silica-supported $\text{Ni}_{2-x}\text{Co}_x\text{P}$ catalysts. While the overall trend of HDS activity was a decrease with increasing Co and Fe content, the opposite trend was observed for TOFs based on sites titrated by CO chemisorption. The $\text{Ni}_{2-x}\text{Fe}_x\text{P@mSiO}_2$ nanocatalysts exhibited higher TOFs than did the $\text{Ni}_{2-x}\text{Co}_x\text{P@mSiO}_2$ nanocatalysts, which may be due to increased electron donation from Fe to Ni than for Co to Ni as indicated by IR spectral studies of adsorbed CO. The product selectivity of $\text{Ni}_{2-x}\text{M}_x\text{P@mSiO}_2$ nanocatalysts changed only slightly due to Fe or Co incorporation, and the DDS reaction pathway was strongly favored for all of the compositions investigated. The nanoparticles encapsulated in mesoporous silica exhibited excellent phase stability and resistance to sintering, indicating that this nanoscale architecture provides a robust system for probing the roles of particle size, shape and composition, and of different oxide supports in determining hydrotreating properties of metal phosphides.

6. ACKNOWLEDGEMENTS

This research was supported by the National Science Foundation under grant numbers CHE-1361702 and CHE-1361741. TEM data were acquired on a JEOL 2010 TEM with funds provided by NSF-MRI grant number 0216084. The TEM, BET surface area and porosimetry data, ICP-MS and some of the XRD patterns were acquired at the Lumigen Instrument Center,

Wayne State University. The authors would like to acknowledge Phillips 66 (Ferndale refinery) for providing access to the LECO SC-144DR Sulfur and Carbon Analyzer. We thank P. Cochran (WWU) and D. Bronner (WWU) for carrying out the CO chemisorption and bulk C and S measurements, respectively, and C. Lambert (WSU) for performing ICP-MS analyses.

SUPPORTING INFORMATION

Nitrogen adsorption-desorption isotherms, pore size distributions, XRD patterns of as-prepared and HDS-tested nanocatalysts, and carbon and sulfur analysis data are available in the Supporting Information.

REFERENCES

1. E. Ito, J.A.R. Van Veen, On Novel Processes for Removing Sulphur from Refinery Streams, *Catal. Today*, 116 (2006) 446-460.
2. B. Pawelec, R.M. Navarro, J.M. Campos-Martin, J.L.G. Fierro, Towards Near Zero-Sulfur Liquid Fuels: A Perspective Review, *Catal. Sci. Technol.*, 1 (2011) 23-42.
3. R. Prins, M.E. Bussell, Metal Phosphides: Preparation, Characterization and Catalytic Reactivity, *Catal. Lett.*, 142 (2012) 1413-1436.
4. H. Topsøe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysis, in: J.R. Anderson, M. Boudart (Eds.) *Catalysis: Science and Technology*, Springer-Verlag, Berlin, 1996, pp. 1-310.
5. S.T. Oyama, T. Gott, H. Zhao, Y.-K. Lee, Transition Metal Phosphide Hydroprocessing Catalysts, *Catal. Today*, 143 (2009) 94-107.
6. S.T. Oyama, X. Wang, F.G. Requejo, T. Sato, Y. Yoshimura, Hydrodesulfurization of Petroleum Feedstocks with a New Type of Nonsulfide Hydrotreating Catalyst, *J. Catal.*, 209 (2002) 1-5.
7. S.J. Sawhill, D.C. Phillips, M.E. Bussell, Thiophene Hydrodesulfurization over Supported Nickel Phosphide Catalysts, *J. Catal.*, 215 (2003) 208-219.
8. S.J. Sawhill, K.A. Layman, D.R. Van Wyk, M.H. Engelhard, C. Wang, M.E. Bussell, Thiophene Hydrodesulfurization over Nickel Phosphide Catalysts: Effect of the Precursor Composition and Support, *J. Catal.*, 231 (2005) 300-313.
9. E.J. Popczun, J.R. McKone, C.G. Read, A.J. Biacchi, A.M. Wiltout, N.S. Lewis, R.E. Schaak, Nanostructured Nickel Phosphide as an Electrocatalyst for the Hydrogen Evolution Reaction, *J. Am. Chem. Soc.*, 135 (2013).
10. E.J. Popczun, C.G. Read, C.W. Roske, N.S. Lewis, R.E. Schaak, Highly Active Electrocatalysis of the Hydrogen Evolution Reaction by Cobalt Phosphide Nanoparticles, *Angew. Chem. Int. Ed.*, 53 (2014) 5427-5430.
11. J.F. Callejas, J.M. McEnaney, C.G. Read, J.C. Crompton, A.J. Biacchi, E.J. Popczun, T.R. Gordon, N.S. Lewis, R.E. Schaak, Electrocatalytic and Photocatalytic Hydrogen Production from Acidic and Neutral-pH Aqueous Solutions Using Iron Phosphide Nanoparticles, *ACS nano*, (2014).
12. J.M. McEnaney, J.C. Crompton, J.F. Callejas, E.J. Popczun, C.G. Read, N.S. Lewis, R.E. Schaak, Electrocatalytic hydrogen evolution using amorphous tungsten phosphide nanoparticles, *Chem. Commun.*, 50 (2014) 11026-11028.
13. I.I. Abu, K.J. Smith, The Effect of Cobalt Addition to Bulk MoP and Ni₂P Catalysts for the Hydrodesulfurization of 4,6-dimethyldibenzothiophene, *J. Catal.*, 241 (2006) 356-366.

14. A.W. Burns, A.F. Gaudette, M.E. Bussell, Hydrodesulfurization Properties of Cobalt-Nickel Phosphide Catalysts: Ni-rich Materials are Highly Active, *J. Catal.*, 260 (2008) 262-269.
15. A.F. Gaudette, A.W. Burns, J.R. Hayes, M.C. Smith, T. Seda, M.E. Bussell, Mössbauer Spectroscopy Investigation and Hydrodesulfurization Properties of Iron-Nickel Phosphide Catalysts, *J. Catal.*, 272 (2010) 18-27.
16. S.T. Oyama, H. Zhao, H.-J. Freund, K. Asakura, R. Wlodarczyk, M. Sierka, Unprecedented Selectivity to the Direct Desulfurization (DDS) Pathway in a Highly Active FeNi Bimetallic Phosphide Catalyst, *J. Catal.*, 285 (2012) 1-5.
17. R.H. Bowker, B.A. Carrillo, B. Illic, M.A. Reynolds, M.E. Bussell, Carbazole Hydrodenitrogenation over Nickel Phosphide and Ni-rich Bimetallic Phosphide Catalysts, *Appl. Catal. A*, 482 (2014) 221-230.
18. H. Zhao, S.T. Oyama, H.-J. Freund, R. Wlodarczyk, M. Sierka, Nature of active sites in Ni₂P hydrotreating catalysts as probed by iron substitution, *Appl. Catal. B.*, 164 (2015) 204-216.
19. F. Hulliger, Crystal Chemistry of the Chalcogenides and Pnictides of the Transition Elements, *Struct. Bond.*, 4 (1968) 83-229.
20. J.B. Goodenough, Interpretation of Structure and Magnetism in Transition-Metal Pnictides M₂X and (M_{1-x}M'_x)₂X, *J. Solid State Chem.*, 7 (1973) 428-447.
21. M. Artigas, M. Bacmann, D. Boursier, D. Fruchart, R. Fruchart, J.L. Soubeyroux, Formation of diamagnetic metal clusters in the metallic system nickel phosphide (Ni₂P)-cobalt phosphide (Co₂P)., *C. R. Acad. Sci, Paris, Sér 2*, 315 (1992) 29-34.
22. R. Fruchart, A. Roger, J.P. Senateur, Crystallographic and Magnetic Properties of Solid Solutions of the Phosphides M₂P, M = Cr, Mn, Fe, Co and Ni, *J. Appl. Phys.*, 40 (1969) 1250-1257.
23. I.I. Abu, K.J. Smith, HDN and HDS of model compounds and light gas oil derived from Athabasca bitumen using supported metal phosphide catalysts, *Appl. Catal. A*, 328 (2007) 58-67.
24. A.E. Henkes, Y. Vasquez, R.E. Schaak, Converting Metals into Phosphides: A General Strategy for the Synthesis of Metal Phosphide Nanocrystals, *J. Am. Chem. Soc.*, 129 (2007) 1896-1897.
25. E. Muthuswamy, G.H. Layan Savithra, S.L. Brock, Synthetic Levers Enabling Independent Control of Phase, Size, and Morphology in Nickel Phosphide Nanoparticles, *ACS Nano*, 5 (2011) 2402-2411.
26. J. Park, B. Koo, K.Y. Yoon, Y. Hwang, M. Kang, J.-G. Park, T. Hyeon, Generalized Synthesis of Metal Phosphide Nanorods via Thermal Decomposition of Continuously

- Delivered Metal–Phosphine Complexes Using a Syringe Pump, *J. Am. Chem. Soc.*, 127 (2005) 8433-8440.
27. M.H. Mobarok, E.J. Luber, G.M. Bernard, L. Peng, R.E. Wasylshen, J.M. Buriak, Phase-Pure Crystalline Zinc Phosphide Nanoparticles: Synthetic Approaches and Characterization, *Chem. Mater.*, 26 (2014) 1925-1935.
 28. D.R. Liyanage, S.J. Danforth, Y. Liu, M.E. Bussell, S.L. Brock, Simultaneous control of composition, size and morphology in discrete $\text{Ni}_{2-x}\text{Co}_x\text{P}$ nanoparticles, *Chem. Mater.*, accepted for publication, May 2015 (DOI: 10.1021/acs.chemmater.5b00958) (2015).
 29. H. Hitihami-Mudiyanselage, M.P. Arachchige, G. Lawes, T. Seda, S.L. Brock, Synthesis and Characterization of Discrete $\text{Fe}_x\text{Ni}_{2-x}\text{P}$ Nanocrystals ($0 < x < 2$): Compositional Effects on Magnetic Properties, *ACS Nano*, submitted, May 2015.
 30. G.H.L. Savithra, R.H. Bowker, B.A. Carrillo, M.E. Bussell, S.L. Brock, Rational Design of Nickel Phosphide Hydrodesulfurization Catalysts: Controlling Particle Size and Preventing Sintering, *Chem. Mater.*, 25 (2013) 825-833.
 31. A.L. Diaz, M.E. Bussell, An Infrared Spectroscopy and Temperature Programmed Desorption Study of CO on $\text{MoO}_3/\text{Al}_2\text{O}_3$ Catalysts: Quantitation of the Molybdena Coverage, *J. Phys. Chem.*, 97 (1993) 470-477.
 32. E. Muthuswamy, P.R. Kharel, G. Lawes, S.L. Brock, Control of Phase in Phosphide Nanoparticles Produced by Metal Nanoparticle Transformation: Fe_2P and FeP , *ACS Nano*, 3 (2009) 2383-2393.
 33. K.A. Layman, M.E. Bussell, Infrared Spectroscopic Investigation of CO Adsorption on Silica-supported Ni_2P Catalysts, *J. Phys. Chem. B*, 108 (2004) 10930-10941.
 34. Y. Sun, R. Prins, Mechanistic studies and kinetics of the hydrodesulfurization of dibenzothiophene on $\text{Co-MoS}_2/\text{Al}_2\text{O}_3$, *J. Catal.*, 267 (2009) 193-201.
 35. G.H.L. Savithra, R.H. Bowker, B.A. Carrillo, M.E. Bussell, S.L. Brock, Mesoporous Matrix Encapsulation for the Synthesis of Monodisperse Pd_5P_2 Nanoparticle Hydrodesulfurization Catalysts, *ACS Appl. Mater. Interfaces*, 5 (2013) 5403-5407.
 36. P. Liu, J.A. Rodriguez, T. Asakura, J. Gomes, K. Nakamura, Desulfurization Reactions on $\text{Ni}_2\text{P}(001)$ and $\alpha\text{-Mo}_2\text{C}(001)$ Surfaces: Complex Role of P and C Sites, *J. Phys. Chem. B*, 109 (2005) 4575-4583.
 37. P. Liu, J.A. Rodriguez, Catalysts for hydrogen evolution from the $[\text{NiFe}]$ hydrogenase to the $\text{Ni}_2\text{P}(001)$ surface: the importance of ensemble effect, *J. Am. Chem. Soc.*, 127 (2005) 14871-14878.

38. A.B. Hernandez, H. Ariga, S. Takakusagi, K. Kinoshita, S. Suzuki, S. Otani, S.T. Oyama, K. Asakura, Dynamical LEED analysis of Ni_2P (0 0 0 1)-1 x 1: Evidence for P-covered surface structure, *Chem. Phys. Lett.*, 513 (2011) 48-52.
39. S.T. Oyama, Y.-K. Lee, The Active Site of Nickel Phosphide Catalysts for the Hydrodesulfurization of 4,6-DMDBT, *J. Catal.*, 258 (2008) 393.
40. P.E.R. Blanchard, A.P. Grosvenor, R.G. Cavell, A. Mar, Effects of Metal Substitution in Transition-Metal Phosphides ($\text{Ni}_{1-x}\text{M}'_x$)₂P (M' = Cr, Fe, Co) studied by X-ray Photoelectron and Absorption Spectroscopy, *J. Mater. Chem.*, 19 (2009) 6015-5022.
41. X. Liang, J. Li, J.B. Joo, A. Gutiérrez, A. Tillekaratne, I. Lee, Y. Yin, F. Zaera, Diffusion through the Shells of Yolk–Shell and Core–Shell Nanostructures in the Liquid Phase, *Angew. Chem. Int. Ed.*, 51 (2012) 8034-8036.
42. A.W. Burns, K.A. Layman, D.H. Bale, M.E. Bussell, Understanding the Relationship Between Composition and Hydrodesulfurization Properties for Cobalt Phosphide Catalysts, *Appl. Catal. A*, 343 (2008) 68-76.
43. R. Prins, Hydrodesulfurization, in: M. Beller, A. Renken, R.A. Van Santen (Eds.) *Catalysis - From Principles to Applications*, Wiley-VCH Verlag & Co., Weinheim, 2012, pp. 390-398.