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Review

Transition metal phosphide hydroprocessing catalysts: A review

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ABSTRACT

The diminishing quality of oil feedstocks coupled with increasingly more stringent environmental regulations limiting the content of sulfur in transportation fuels have given rise to a need for improved hydroprocessing technology. This review begins with a summary of the major improvements in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) catalysts and processes that have been reported in recent years. It then describes a new class of hydroprocessing catalysts, the transition metal phosphides, which have emerged as a promising group of high-activity, stable catalysts. The phosphides have physical properties resembling ceramics, so are strong and hard, yet retain electronic and magnetic properties similar to metals. Their crystal structures are based on trigonal prisms, yet they do not form layered structures like the sulfides. They display excellent performance in HDS and HDN, with the most active phosphide, Ni_2P, having activity surpassing that of promoted sulfides on the basis of sites titrated by chemisorption (CO for the phosphides, O_2 for the sulfides). In the HDS of difficult heteroaromatics like 4,6-dimethyldibenzothiophene Ni_2P operates by the hydrogenation pathway, while in the HDN of substituted nitrogen compounds like 2-methylpiperidine it carries out nucleophilic substitution. The active sites for hydrogenation in Ni_2P have a square pyramidal geometry, while those for direct hydrodesulfurization have a tetrahedral geometry. Overall, Ni_2P is a promising catalyst for deep HDS in the presence of nitrogen and aromatic compounds.

Contents

1. Introduction

Recently enacted regulations limiting the emissions of pollutants and the continuing decline in the quality of petroleum feedstocks have made sulfur and nitrogen removal one of the paramount problems in the refining industry. Concerning regulations, in 2006 the US sulfur contents in fuels were mandated to be 30 ppm (with an 80 ppm cap) in gasoline and 15 ppm in diesel [1], and similar levels were legislated in Europe and Japan [2–4]. In 2008, the standards effectively require diesel to reach 10 ppm S content and every blend of gasoline sold in the United States to meet the 30 ppm level [5]. Such levels correspond to the removal of +99.99% of sulfur from a typical crude containing 1.5% sulfur, and the removal process has been termed deep or ultra-deep HDS.

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It has been recognized that current hydrotreating catalysts are not adequate to meet the regulated levels, and this has given rise to widespread research efforts to develop a new generation of replacement materials. This review concerns a new class of catalysts for hydroprocessing, transition metal phosphides, and updates a previous review [6].

2. Hydrodesulfurization challenges and advances

Commercial catalysts for HDS are sulfides based on Mo or W and promoted with Ni or Co. The subject has been covered in several treatises [7,8–24], and deep HDS in other reviews [25–28]. More recent coverage of deep desulfurization has been made in reviews by Song [1], Ho [29] and Babich and Moulijn [30] and has been a principal topic in recent conferences [31–33] and the subject of dedicated journal volumes [34–39].

The review by Song [1] comprehensively covers various process options for removal of sulfur including standard hydroprocessing, but also alternative and emerging processes such as catalytic distillation, reactive adsorption, polar molecule adsorption, selective adsorption, selective extraction, selective alkylation, membrane separation, and caustic extraction. In addition to these there is also biodesulfurization, oxidative desulfurization and ultrasound-assisted oxidative desulfurization [40]. These methods will be covered briefly.

The principal findings by Song [1] and Ho [29] are that HDS research has moved to the most refractory sulfur compounds. Earlier studies had already shown that for diesel these were the sterically hindered dibenzothiophenes, i.e. DBT's with alkyl substituents in the 4- and 6-positions [7,41–43] of which the 4,6-dimethyldibenzothiophene (4,6-DMDBT) molecule is archetypal. The compound 4,6-DMDBT has been found to be at least ten times less reactive than DBT itself [44,43]. In addition for gasoline, the content of aromatics and olefins is important for product quality, as their removal by hydrogenation represents a loss of octane, as well as a costly expenditure of valuable hydrogen. The problem of sulfur removal is closely related to nitrogen removal because nitrogen compounds are strong inhibitors of HDS, especially at the high levels of conversion required for deep HDS.

Considerable research in the past 3 years has concentrated on finding more active sulfide catalysts to overcome present limitations. As summarized below, the approaches taken have consisted in optimizing sulfide compositions, using new supports, exploring novel compounds, and improving processes (Table 1).

A recent perspective on the improvement of sulfides has been given by Leliveld and Eijsbouts [159]. The commentary enumerates the economic, technical and environmental motivations for hydroprocessing catalyst development. Improvements of conventional metal sulfide catalysts and the discovery of novel materials and supports are needed to meet the increasing demand for energy. Enhancement of catalyst activity and stability is required to increase refinery throughput and to upgrade low value feedstocks to high value fuels. In addition, broad applicability of hydrotreating catalysts is desired to treat a wide range of feedstocks, as crudes are becoming more viscous and higher in sulfur, nitrogen and heavy metals contents. These improvements must result in a refinery end-product that meets the mandates of environmental legislation and the shift in the automotive industry to high efficiency, low emission engines requiring fuels with low levels of sulfur and aromatics. Achievement of these demands will require catalysts with higher volumetric activity for HDS, HDN and aromatics saturation with minimal hydrogen consumption. In order to treat a wide range of petroleum crudes, various combinations of the staging of HDS and HDN catalysts must be developed to tailor the hydrotreating process to the characteristics of the feed. In addition, the ability to upgrade unconventional crudes extracted from tarsands and shale will require the development of stable, effective guard and demetallization catalysts for processing of heavier crudes (Table 2).

Table 1
Summary of recent advances in hydroprocessing with sulfides.

Improvement of existing sulfides		
Review: Improving dispersion and morphology	+	Chiannelli et al. [45]
Sonochemical and CVD methods for high dispersion	+	Moon [46,47], Okamoto [48,49], Ramos [50]
Ultrasonic spray pyrolysis for high dispersion	+	Suslick [51]
Microwave method for high dispersion	+	Liu et al. [52–54]
Dispersing agents	+	Yoshimura [55], Okamoto [56], Escobar [57], Costa [58], Lélias [59], Rana [60,61]
Activation agents	+	Perot [62], Frizi [63]
Use of non-traditional elements	+	Fierro [64,65], Hubaut [66], Vít [67], Escalona [68], De Los Reyes [69], Giraldo [70], Centeno [71]
New precursors with Mo–S bonds	+	Ishihara [72], Ho [73], Bensch [74,75], Cruz-Reyes [76]
Urea-matrix combustion method	+	Green [77–80]
Use of unsupported trimetallic compositions	+	Fuentes [81], Alonso [82], Huirache-Acuña [83,84], Nava [85]
Alternative or improved supports for sulfides		
Improvement of Al_2O_3 with Ti, and Ga	+	Segawa [86,87], Ramirez [88,89], Vrinat [90,91], Zhao [92]
Improvement of Al_2O_3 with B	+	Okamoto [93–95], Shimada [96], Centeno [97]
Improvement of Al_2O_3 with B and P	+	Ferdous [98]
F^- or PO_4^{3-} bind to Al^{3+} ions and reduce interactions	–	Prins [99], Maity [100], Ding [101], Moon [102]
Basic additives (K, Li) are beneficial	+	Diehl [103], Fan [104], Mizutani [105]
Composite supports (SiO_2-Al_2O_3)	+	van der Meer [106], Mochida [107], Kunisada [108], Ancheyta [109]
Composite supports (TiO_2-SiO_2, ZrO_2-Al_2O_3)	+	Zhou, Zhang [110], Li [111]
Pure TiO_2 supports for FeMo catalysts	+	Kraleva [112]
Hydroxyapatite modified by Zr and/or Al	+	Travert [113–115]
Carbon nanotubes, mesoporous clays	o	Chen [116], Chuan [117], Dalai [118], Shang [119], Song [120,121]
Mesoporous supports (MCM-41, SBA-15, Ti-HMS)	+	[122–136]
Theoretical studies		
Thiophene HDS mechanism	o	Ma [137], Yao [138], Paul [139], Topsøe [140,141], Nørskov [142],
Coordinatively unsaturated sites	o	Dumeignil [143], Paul [139], Aray [144], Wu [145]
General correlations of activity and electronic properties	o	Oviedo-Roa [146], Orita [147], Raybaud [148,149], Borges Jr. [150]
Support and surface structure, organonitrogen, H_2 adsorption	o	Nelson [151–158]

+: positive effect; –: negative effect; o: neutral or not applicable.

Table 2
Summary of process improvements, new processes and catalyst developments.

Industrial process and catalyst improvements		
Review: Recent developments in industry	o	Babich and Moulijn [30]
Inhibition of deep HDS by H_2S and NH_3	–	[160–162], Vrinat [163], Farag [164], Nørskov [165], Rana [166,167], Perot [168], Song [169], Zeuthen [170], Ho [171]
Removal of H_2S and NH_3 from intermediate stages	+	Adjaye [172], Nava [173], Mochida [174,175]
Biodesulfurization (BDS)	+	Liu [176], Towfighi [177], Kong [178], Xu [179], Huizhou [180], Mohebali [181], Bassi [182], Li [183,184]
Oxidative desulfurization (ODS)	+	Wang [185], Song [186], Sampanthar [187], Corma [188], Lu [189], Green [190], Collins [191], García-Gutiérrez [192,193]
Ultrasound-assisted oxidative desulfurization (UAOD)	+	Doraiswamy [194], Yen [195–197], Zhao [198],
Non-traditional catalytic materials (carbides and nitrides)		
Carbides, nitrides	o	Rodriguez [199,200], Bussell [201], Djéga-Mariadassou [202,203], Al-Megren [204], Zhang [205]
Carbides, nitrides	o	Djega-Mariadassou [206], Nelson [207], Nagai [208,209], Dalai [210]
Review: Carbides and nitrides for hydroprocessing	o	Furimsky [211]

+: positive effect, –: negative effect, o: neutral or not applicable.

Several alternative processes for the removal of sulfur from petroleum crudes have been developed or are being developed. An insightful review of novel sulfur removal processes was recently given by Ito and van Veen [212]. For refractory molecules, the oxidative removal of sulfur from diesel by biodesulfurization, oxidative desulfurization and ultrasound-assisted oxidative desulfurization has been covered extensively in the literature (*vide supra*). Instead of reducing sulfur compounds to form H_2S, these methods oxidize the sulfur species to their corresponding sulfoxides (1-oxides) and sulfones (1,1-dioxides). Refractory sulfur compounds such as DBT and 4,6-DMDBT are only slightly more polar than hydrocarbons of similar structure. However, sulfoxides and sulfones are substantially more polar, thus permitting their selective removal by following the selective oxidation step with solvent extraction or solid adsorption. The development of oxidation methods for sulfur removal is aimed at providing efficient, cost effective, environmentally benign processes alternative to conventional hydroprocessing.

Another option for the removal of sulfur is biocatalytic desulfurization, or biodesulfurization (BDS). Microorganisms require sulfur for growth and several bacteria can utilize the sulfur in thiophenic compounds and thus reduce the sulfur content in petroleum. BDS generally operates under ambient conditions of temperature and pressure and proceeds mainly through two biological pathways. These pathways include partial or complete degradation of the molecule with C–C bond cleavages or a sulfur-specific cleavage of only C–S bonds. The more selective sulfur-specific pathway is preferable to retain the value of fuels. Fig. 1 illustrates the simplified sulfur-specific enzymatic pathway for the BDS of DBT in the presence of oxygen and water to yield 2-hydroxybiphenyl as non-degradable end-product. Although many bacteria can utilize sulfur through the sulfur-specific pathway, the stability and lifetime of the biocatalysts are two major concerns. In addition, cooling of the petroleum feedstock to ambient temperature and subsequent removal of the biocatalyst from the treated feed is costly. Implementation of BDS as an industrial process would require microorganisms with higher sulfur removal activity, hydrocarbon phase tolerance, removal ability at high temperatures and longer stability [182].

The most promising alternative method for achieving deep HDS is sulfur removal via oxidative desulfurization (ODS). Analogous to BDS, the divalent sulfur atoms of thiophenic molecules are oxidized by the electrophilic addition of oxygen atoms to yield sulfones. The sulfones are subsequently removed in a second step by solid adsorption, selective extraction or distillation. Various studies on ODS have employed K_2FeO_4 [185], molecular oxygen [186], air [187], organic hydroperoxides [188], aqueous H_2O_2 [189–193] and many other reagents as oxidizers. However, oxidation of sulfur compounds in the absence of catalysts is slow and several studies have utilized phase-transfer catalysts [185], metal salts [186,190], supported metal catalysts [187,192,193], metal-containing molecular sieves [188], activated carbon [189], metal-ligand activators [191], etc. to accelerate or facilitate the oxidation. Fig. 2 shows the simplified ODS scheme for DBT to DBT sulfone through the intermediate DBT sulfoxide. The ODS method offers several advantages over conven-

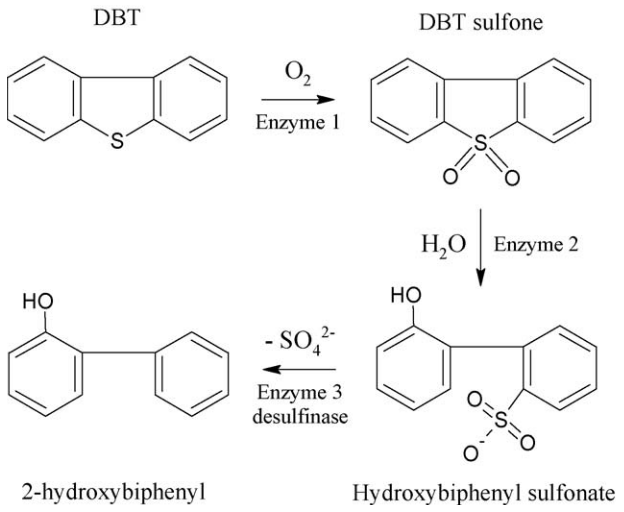

Fig. 1. Simplified sulfur-specific BDS of DBT [212].

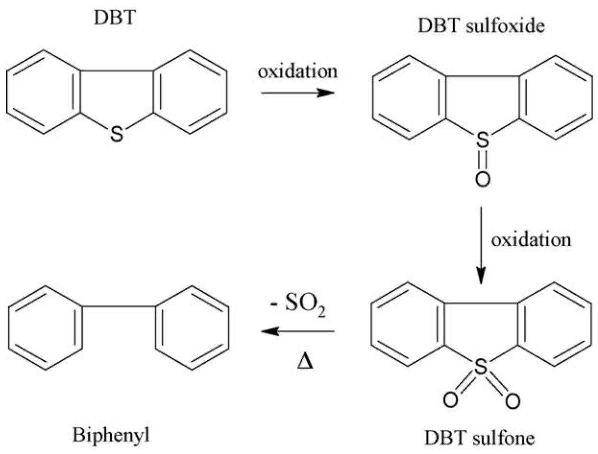

Fig. 2. Simplified network for ODS of DBT [187].

Table 3
Physical properties of metal-rich phosphides.

Ceramic properties		Metallic properties	
Melting point (K)	1100–1800	Electrical resistivity (μΩ cm)	900–25,000
Microhardness (kg/mm^{-2})	600–1100	Magnetic susceptibility (10^6 emu/mol)	110–620
Heat of formation (kJ mol^{-1})	30–180	Heat capacity (J/mol K)	20–50

tional hydroprocessing. The oxidation reactions can be carried out under mild conditions of temperature and pressure and do not require the expenditure of valuable hydrogen. However, the ODS process requires large amounts of oxidizing agent, separation and recovery of the catalysts, and low selectivity and activity towards the sulfur compounds. Both BDS and ODS require long reaction times and the second separation step in the processes leads to expensive waste management issues and oil yield losses of 10–20% [213].

Future employment of ODS processes will be dependent on the sulfur removal efficiency and capital investment required for implementation. The use of aqueous H_2O_2 – solid catalyst ODS is a low cost and environmentally benign option. However, such processes are typically impractical, requiring long reaction times and generally result in poor sulfur removal efficiency and excessive decomposition of the oxidant. In such biphasic oil–water systems, introduction of phase-transfer catalysts and ultrasonication in conjunction with ODS can be used to greatly increase the overall sulfur removal efficiency [194]. Ultrasound has a mechanical effect on the reaction system by promoting rapid mixing, accelerating dissolution and renewing the surface of the solid catalyst. Several studies have shown improvement in the ODS process upon ultrasound irradiation including +99% sulfur removal efficiency in shorter reaction times [195,197], complete recovery of solid catalysts [196] and minimal decomposition of H_2O_2 [195]. Although oxidative desulfurization processes are viable alternatives they require capital investment for new unit operations. As a result, discovery of novel catalysts and implementation into existing hydrotreating reactors is the most promising option for achieving deep HDS.

3. Transition metal phosphides

3.1. General properties

Phosphorus reacts with most elements of the periodic table to form a diverse class of compounds known as phosphides. The bonding in these materials ranges from ionic for the alkali and alkaline earth metals, metallic or covalent for the transition elements, and covalent for the main group elements. The focus of this review concerns the metal-rich compounds, MP or M_2P, of the transition metals, which have metallic properties. The phosphorus-rich compositions are semiconducting and are considerably less stable than the metal-rich compounds.

The nature, structure and synthesis of phosphides have been described in a number of reviews [214–216]. Basically, the metal-rich phosphides have physical properties similar to those of ordinary metallic compounds like the carbides, nitrides, borides and silicides. They combine the properties of metals and ceramics, and thus are good conductors of heat and electricity, are hard and strong, and have high thermal and chemical stability (Table 3) [217].

Although the physical and chemical properties of phosphides resemble those of carbides and nitrides, they differ substantially in their crystal structure. In the carbides and nitrides, the carbon and nitrogen atoms reside in the interstitial spaces between metal host atoms to form relatively simple lattices. For the phosphides, however, the atomic radius of phosphorus (0.109 nm) is substantially larger than that of carbon (0.071 nm) or nitrogen (0.065 nm) and P does not fit into the ordinary octahedral holes formed by closed-packed metal atoms. For this reason in phosphides (also borides, sulfides, and silicides) the metal atoms form triangular prisms (Fig. 3) where the metal atoms (dark atoms) surround the nonmetal atom (light atoms) [214]. For metal-rich compositions the number of nearest-neighbors increases to form a 9-fold tetrakaidecahedral (TKD) coordination with additional metal atoms placed near the centers of the vertical faces of the prism (Fig. 3).

Different arrangements of these building blocks give rise to different structures. A summary is given in Fig. 4 [218].

The monophosphide MoP is isostructural with WC, with the nonmetal-containing prisms stacked on top of each other. The monophosphide VP has the Ni–As structure with the P-prisms displaced laterally one-half a lattice spacing. The monophosphides NbP and TaP adopt the closely related NbAs structure, which just differs from VP in the way the prisms are stacked. The monophosphides of groups 6–10 adopt the MnP and NiP structures which have distorted NiAs structures where the phosphorus atoms form chains (MnP) or pairs (NiP). Importantly, the phosphides, unlike the sulfides, do not form layered structures, and so potentially permit greater access to active corner and edge sites on the crystallite surfaces. The globular morphology of MoP [219] and Ni_2P [220] has been nicely demonstrated by electron microscopy by the group of Bussell. Phosphides are different from phosphorus-promoted sulfide catalysts, as reviewed by Iwamoto and Grimblot [221].

3.2. Catalytic properties in hydrotreating

The first catalytic studies of phosphides were by the group of Nozaki [222,223] in the 70s and 80s which examined their hydrogenation properties. This was followed 15 years later by a report on HDN by Robinson et al. [224], but the supported materials in that study are likely to have been sulfides. Transition metal phosphides have also been applied to hydrodehalogenation reactions by Chen et al. [225–227]. A first study on simultaneous HDS and HDN showed that MoP could be easily synthesized by temperature-programmed reduction (TPR) of a metal phosphate precursor [228], and this has been confirmed for other transition metal phosphides by the groups of Prins [229,230], Bussell [219,220,231–233], and Li [234–236]. The synthesis method is simple, and requires only moderate temperatures (773–873 K) and uses inexpensive precursors, compared to direct phosphidation with PH_3 [237,238]. Several

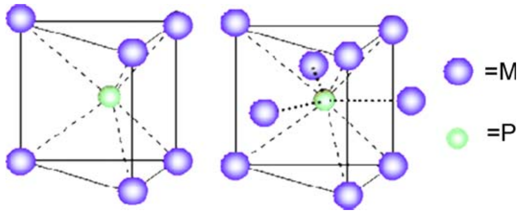

Fig. 3. Triangular prism and tetrakaidecahedral structures in phosphides.

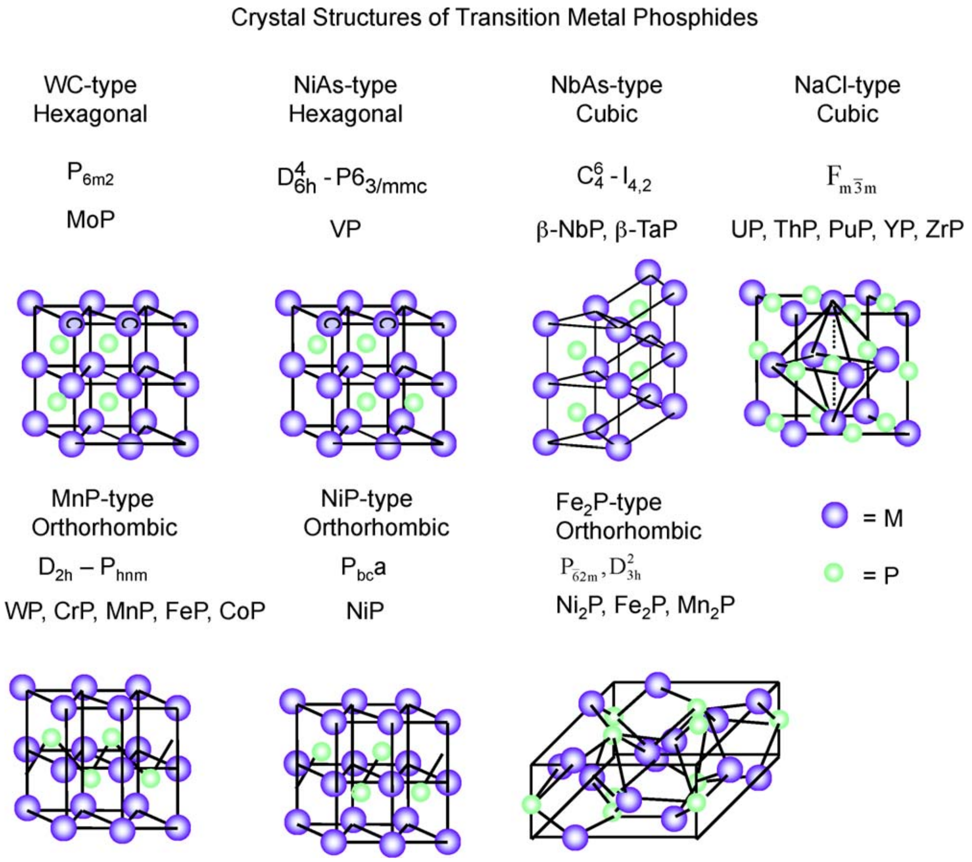

Fig. 4. Crystal structures of metal rich phosphides.

recent studies have investigated novel synthesis methods for unsupported and supported transition metal phosphides. These include metal thiophosphates [239] and amorphous alloys [240] as precursors, citric acid modified precursors [241,242], polymer surfactant assisted synthesis [243], solvothermal synthesis methods [244,245], solution-phase arrested precipitation [246] and novel reducing agents [247]. These methods were aimed at producing monodispersed, high surface area unsupported phosphides and improving the dispersion of supported phosphides.

In previous work it has been shown that MoP, and WP have moderate activity and Ni_2P has excellent activity in hydroprocessing [232,248–249]. The overall activity was found to be in the order: $Fe_2P < CoP < MoP < WP < Ni_2P$ in the simultaneous HDS of dibenzothiophene (3000 ppm S) and HDN of quinoline (2000 ppm N) at 643 K and 3.1 MPa, with the comparison based on equal sites (240 (mol CO/O_2 for phosphides/sulfides) loaded in the reactor [250,248]. Subsequent studies employed advanced techniques such as X-ray absorption fine structure (EXAFS) [251], X-ray absorption near-edge spectroscopy (XANES) [252] and nuclear magnetic resonance (NMR) [253] to characterize the catalysts. Tests were also carried out with a real feed that confirmed their high activity [254].

Early work on supported Ni_2P catalysts had utilized a low surface area silica (90 $m^2 g^{-1}$). The use of high surface area silicas provided an opportunity to investigate the effect of particle size, and interesting results were obtained [255]. Samples of low, medium, and high surface area were denoted as L, M, and H, and X-ray diffraction (XRD) line-broadening and chemisorption analysis duly showed that crystallite size (D_c) decreased with support area (Table 4).

Hydrotreating activities of the samples were obtained in a three-phase, packed-bed reactor operated at realistic conditions of 3.1 MPa and 573–643 K with a model feed liquid.

Fig. 5 illustrates the time course of HDS activities for the various Ni_2P/SiO_2 catalysts. The initial 4,6-DMDBT conversions were uniformly high for all the samples but they declined greatly for the Ni_2P/SiO_2–L, slightly for the Ni_2P/SiO_2–M, and actually grew for the Ni_2P/SiO_2–H. The H catalyst gave a high conversion (99+%) even after 100 h of reaction, the M catalyst gave an intermediate conversion (94%), and the L catalyst gave the lowest conversion (76%). The feed had 500 ppm S as 4,6-DMDBT, 3000 ppm S as dimethyl disulfide, 200 ppm N as quinoline, 1 wt% tetralin, 0.5 wt% *n*-octane (internal standard), and *n*-tridecane (solvent). The high activity of the high surface area Ni_2P catalysts at these conditions indicates that they are effective even in the presence of nitrogen compounds and aromatics, which are usually inhibiting of HDS in sulfides.

The samples were characterized by extended X-ray absorption fine structure spectroscopy (EXAFS). Fig. 6A) shows the Fourier-transfomed Ni K-edge EXAFS spectra of the fresh silica-supported phosphide samples and Fig. 6B) shows the spectra of reference

Table 4
Characteristics of 12 wt% Ni_2P/SiO_2 catalysts.

Sample	Ni_2P/SiO_2–L	Ni_2P/SiO_2–M	Ni_2P/SiO_2–H
Support area/$m^2 g^{-1}$	102	201	333
CO uptake[a]/μmol g^{-1}	59	99	125
CO uptake[b]/μmol g^{-1}	40	72	103
D_c/nm	10.1	7.8	6.5

[a] Before reaction.
[b] After reaction.

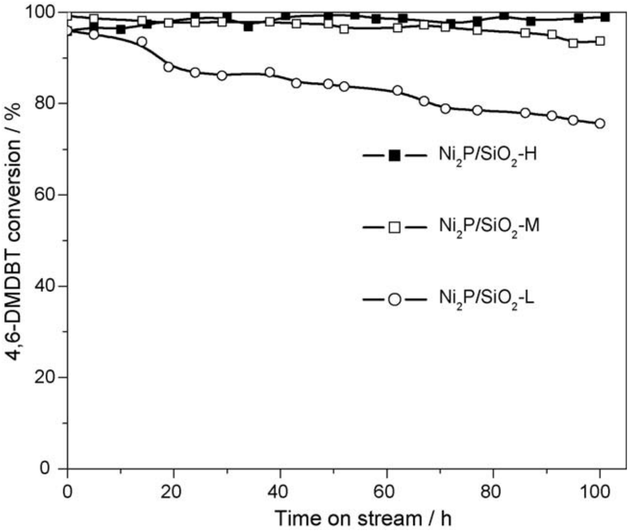

Fig. 5. HDS activity vs. time at 613 K and 3.1 MPa (based on 240 μmol of CO sites loaded in reactor).

standards. The bulk Ni_2P sample has two main peaks at 0.18 nm and 0.23 nm which correspond to Ni–P and Ni–Ni distances (Fig. 6B a). The catalysts all display two distinct peaks at distances close to those of the Ni_2P standard, indicating that the predominant phase in these catalysts is Ni_2P, confirming XRD results. There is no indication of the presence of Ni metal (Fig. 6B b), Ni oxide (Fig. 6B c) or Ni sulfide (Fig. 6B d).

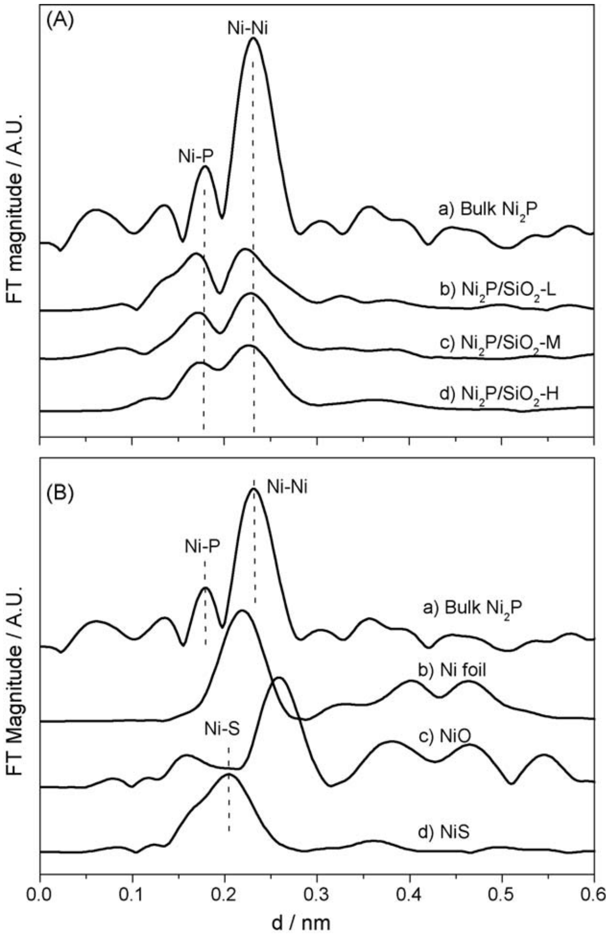

Fig. 6. EXAFS spectra of fresh samples (room temperature, controlled atmosphere cells).

Elemental analysis shows that the high surface catalyst (H) retains more phosphorus than the medium (M) or low area (L) catalysts (Ni/P ratio = 1/0.81 vs. 1/0.62 and 1/0.48). This is confirmed by line-shape analysis which show Ni–P coordination (average number of bonds) to be in the order H > M > L. The smaller crystallites appear to have stronger Ni–P bonding allowing them to retain more phosphorus, and this accounts for their stability and activity. This is also seen in the lower loss of chemisorption sites during the course of hydrotreating (Table 4).

The finding that smaller Ni_2P crystallites have higher activity and stability than larger crystallites is significant, as it suggests using low loadings for making better catalysts. These results were confirmed by Montesinos-Castellanos et al. in the HDS of DBT at 553 K and 3.4 MPa over MoP/Al_2O_3 prepared with different Mo loadings. Phosphides prepared with lower metal loading exhibited higher HDS activity whereas higher loadings resulted in sintering of MoP particles during reduction and lower activities [256]. Lower loadings are beneficial for practical cost reasons. The EXAFS results indicate that the origin of the reactivity difference resides in the electronic structure, as is found in many metallic systems [257,258,259]. This is reflected in the different Ni–P bond strengths and also the different selectivity for products obtained from 4,6-DMDBT (hydrogenation versus direct desulfurization).

Considerable work has been done to understand the state of the working Ni_2P–H catalyst. This was done by extensive analysis of the catalyst after reaction [260–262] and during reaction [263,264]. The results of EXAFS analysis of spent Ni_2P/SiO_2 samples of different loading [260] are shown in Fig. 7.

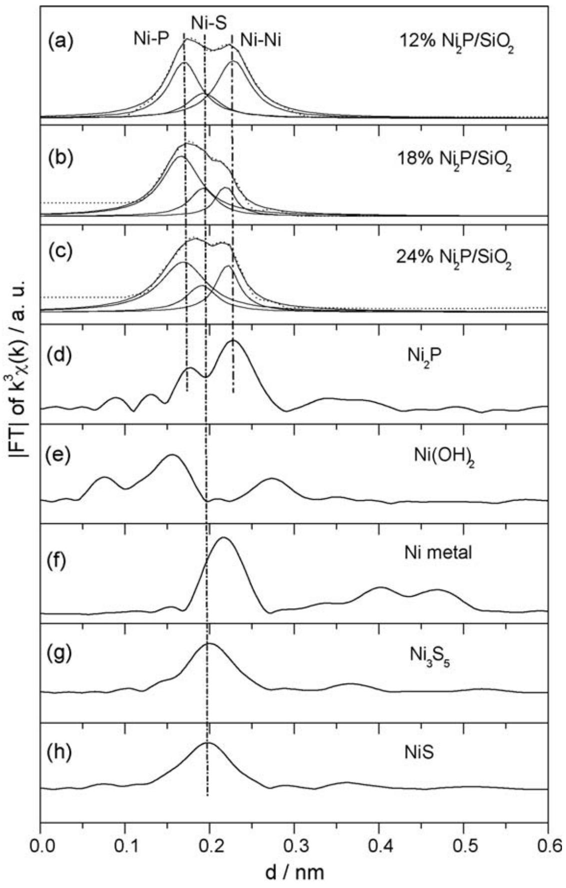

Fig. 7. EXAFS spectra of spent samples (room temperature, controlled atmosphere cells).

The Fourier transforms of the spent samples (Fig. 7a–c) show roughly the two-peak pattern of the fresh samples except that the peaks are broadened and the Ni–Ni distances are less intense, indicating the presence of a new phase. The results were compared with some reference compounds (Fig. 7d–h) to identify the phase. The decrease in the intensity of the Ni–Ni peak was accompanied by a shift to lower distance, while the Ni–P peak itself remained strong. The spectral changes were due to development of intensity in the Ni–S distance region. Even though no distinct Ni–S peak is seen, a feature in that region would give rise to the broad signal actually observed. Fig. 7a–c) shows a fit to three Lorentzian line shapes. The middle peak of each triad fits the position of the Ni–S distance in the sulfide reference compounds (Fig. 7g and h). The spectra of phosphorus deficient compounds like $Ni_{12}P_5$ do not fit the observed pattern [260].

Thus, the EXAFS data strongly suggest that in the catalysts some Ni–Ni bonds are disrupted to form Ni–S linkages. However, the surface is not a pure sulfide, as the reactivity of nickel sulfide is known to be poor [265]. It was deduced that the active phase was a phospho-sulfide in the outer region of a Ni_2P crystallite core. This work was the first to suggest the nature of the active phosphide catalyst. Recent calculations by the group of Nelson [266] confirm the stability of the phosphosulfide overlayer.

Although the post-reaction analysis of the samples gave valuable information about the catalyst, in situ studies were undertaken by Asakura and co-workers to investigate its working state [263,264]. EXAFS has been applied to the investigation of hydrotreating catalysts, but little work has been previously done on structural analysis in the liquid-phase, especially at elevated temperature and pressure [267]. This is because of the strong absorption of X-rays by liquids, and because of the severe stresses on the window material at realistic reaction conditions. Yet, the use of liquid-phase conditions for HDS is important, as it is well known that gas-phase conditions do not reproduce the results that are obtained with liquids [268,269].

A key development for the work was the construction of a low-volume cell with flat windows transparent to X-rays that were chemically, structurally, and thermally stable (Fig. 8) [263,264]. Previous cells could not handle both high temperatures (>600 K) and pressures (>20 bar) for liquids [270–272]. The window was made of cubic boron nitride, an X-ray transparent material superior to beryllium or diamond, because it does not oxidize at high temperatures, and does not give X-ray diffraction peaks.

A measurement at reaction conditions of 12 wt% Ni_2P/SiO_2–H was carried out, and after subtraction of the Ni_2P contribution a single oscillation was isolated (Fig. 8B, dotted line). Curve fitting simulations assuming different bonds such as Ni–P, Ni–S, Ni–C, and Ni–Ni were carried out, and the calculated curve for a Ni–S bond gave a good fit as shown by the dotted curve. The calculated distance of 0.228 ± 0.004 nm is longer than the Ni–P bond of 0.221–224 nm found in phosphides like Ni_2P, NiP, Ni_8P_3, NiP_2 [273,274], but is in the range of 0.225–0.240 nm found in Ni–S bonds in sulfides like NiS [275], NiS_2 [276], and Ni_3S_2 [277]. Therefore, the newly found bond corresponds to a Ni–S bond, which is formed during the reaction, and is consistent with the earlier suggested surface phosphosulfide.

Aside from the silica supported catalysts, various other supports were tested for the phosphides, including carbon [278,279], alumina [262,280], MCM-41 [281–283], SBA-15 [284,285], and USY zeolites [286]. It was found that carbon, MCM-41, SBA-15 and USY zeolites were particularly effective supports.

3.3. Kinetic pathways in HDS and mechanism in HDN

For deep HDS, new catalysts with higher hydrogenation activity are required, and to evaluate these and to design new deep HDS processes, kinetic data for each reaction pathway of 4,6-dimethyldibenzothiophene (4,6-DMDBT) HDS are important. Considerable work was carried out to understand the reaction steps involved in the HDS of this compound by Song and co-workers [287]. The reaction network for dibenzothiophene (DBT) has been studied extensively on sulfides, and an identical network has been suggested for 4,6-DMDBT (Fig. 9) [288,289]. Two main pathways are suggested to dominate: (a) a direct desulfurization route (DDS) and (b) a hydrogenation route (HYD) (Fig. 9). Evidence for these pathways is discussed in several comprehensive articles [7,290–295]. There is also an isomerization route where the methyl rings migrate, but this is likely to operate only with acidic supports [296,297].

The HYD route proceeds through hexahydrodimethyldibenzothiophene (6-H-DMDBT) and forms methylcyclohexyltoluene (MCHT). The DDS route produces 3,3′-dimethylbiphenyl. Interconversion between these products is believed to be slow, and many studies have taken the ratio of these products to be the ratio k_1/k_2 of rate constants for the HYD and DDS routes.

Further hydrogenation of MCHT leads to the ultimate product dimethylbicyclohexane (DMBCH), while the fully hydrogenated 12-hydro-dimethyldibenzothiophene is generally not observed. An accurate determination of the rate constants for the HYD and DDS routes, k_1 and k_2, was obtained by Song and coworkers using batch reactors at low conversions. The concentration data for 4,6-DMDBT fit first-order kinetics and allowed the calculation of $k_1 + k_2$

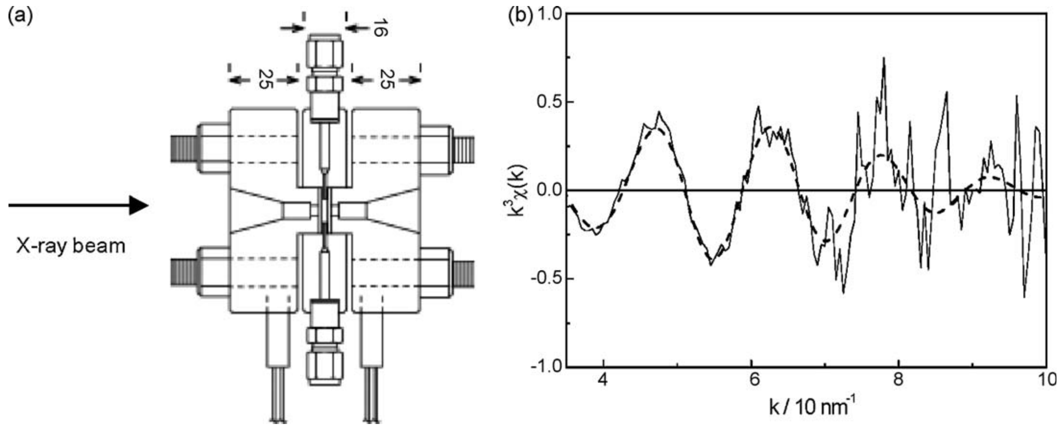

Fig. 8. (A) In situ EXAFS cell (lengths in mm), (B) EXAFS data at reaction conditions (613 K, 3 MPa, 3% DBT in tetradecane).

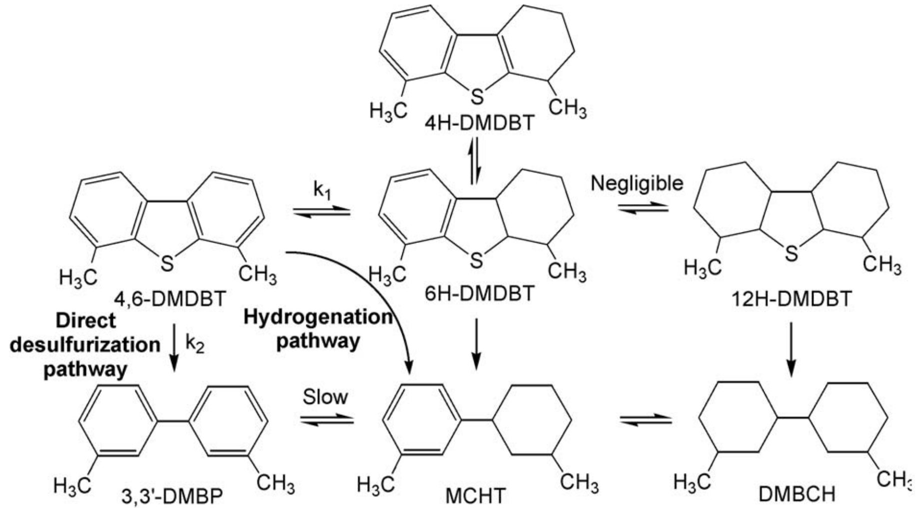

Fig. 9. Reaction network for 4,6-DMDBT desulfurization.

by the following equation:

$$\ln\left(\frac{C_{\mathrm{DMDBT}}}{C_{\mathrm{DMDBT0}}}\right) = -(k_1 + k_2)\cdot t \tag{1}$$

The ratio of rate constants k_1/k_2 was obtained by extrapolating the selectivity as defined by Eq. (2) to zero conversion. The combination of measurements allowed calculation of the individual rate constants.

$$\frac{k_1}{k_2} = \frac{[\text{Initial Selectivity of HDMDBTs}]}{[\text{Initial Selectivity of DMBP}]} \tag{2}$$

Comparison was made to two commercial catalysts, CoMoS/Al_2O_3 (Cr344) and NiMoS/Al_2O_3 (Cr424), obtained from the Criterion Catalyst Co. The rate constants are reported in Table 5 on a weight and (active site) basis.

On a weight basis the overall activity, given by $k_1 + k_2$, followed the order:

$$\mathrm{NiMoS/Al_2O_3} > \mathrm{Ni_2P/SiO_2} > \mathrm{Ni_2P/USY} > \mathrm{CoMoS/Al_2O_3}$$

However, on the basis of active sites the order was

$$\mathrm{Ni_2P/SiO_2} > \mathrm{Ni_2P/USY} > \mathrm{NiMoS/Al_2O_3} > \mathrm{CoMoS/Al_2O_3}$$

The number of active sites was estimated by the chemisorption of CO for the phosphides and the low-temperature chemisorption of O_2 for the sulfides. The CO method is reasonable for counting the number of surface metal atoms in phosphides [252,280] The O_2 method is similarly reasonable for estimating the sites on sulfides [265,298], as it is applied at dry ice/acetone temperatures in a pulse manner, so that corrosive chemisorption is minimized [299]. The result that Ni_2P has higher activity than the sulfides on a site basis is significant, as in the initial stages of catalyst discovery the objective is to find materials with high intrinsic rates. In addition, Ni_2P/SiO_2 gave a very high k_1/k_2 ratio, with a value of 10.1, which is much higher than the value of 1.2 for CoMo sulfide and 3.2 for NiMo sulfide. The indications are that Ni_2P is very effective in the HYD pathway, which is usually slow in the sulfides. Studies on acetonitrile hydrogenation over MoP by Li et al. [300,301] confirmed the high hydrogenation activity of phosphides. In addition, Montesinos-Castellanos et al. reported a direct relationship between hydrogen adsorption capabilities of Al_2O_3-supported MoP and their corresponding HDS activities [302].

A study by the Rodriguez and collaborators of the electronic properties of SiO_2 supported Ni_2P, MoP, and MoS_2 catalysts using density functional calculations [303] has shown that the electron density around the metal followed the order, $MoS_2/SiO_2 < MoP/SiO_2 < Ni_2P/SiO_2$, which correlated well with the thiophene HDS activities of the catalysts. It was suggested that the higher electron density on the metal cation could enhance HDS activity by facilitating the dissociation of H_2 and the adsorption of thiophene [303,304]. The presence of P in Ni_2P prevents the compound from being bulk sulfided and allows it to retain metallic properties for hydrogenation.

Extensive work has also been done [305–308] to study the mechanism of hydrodenitrogenation (HDN). HDN is more difficult than HDS, and generally, for heterocyclic compounds is preceded by the hydrogenation of aromatic nitrogen heterorings, before the hydrogenolysis of C–N bonds [309]. Thus the high hydrogenation activity of phosphides is beneficial, and actually a key to deep HDS, as nitrogen compounds are inhibitors.

The HDN work was carried out using quinoline, pyridine and 2-methyl piperidine as probe reactants. Infrared measurements at reaction conditions showed that pyridine was readily hydrogenated on Ni_2P/SiO_2 but not on NiMoS/Al_2O_3 [310]. The FTIR spectra in He of pyridine adsorbed on the Ni_2P/SiO_2 (Fig. 10a) and NiMoS/Al_2O_3 (Fig. 10c) show the same features due to a pyridinium species with bands at 1604–1608 cm^{-1} assigned to ν_{8a} (CC(N)), 1485–1490 cm^{-1} and 1446–1449 cm^{-1} due to ν_{19b} (CC(N)).

When the flow is switched to H_2 the pyridinium signal for the Ni_2P/SiO_2 (Fig. 10b) is converted to piperidinium (1597, 1575,

Table 5
Comparison of rate constants for sulfides and phosphide s (573 K and 20.4 atm).

Rate Constant 10^{-5} s^{-1} g cat^{-1} or (s^{-1} active $site^{-1}$)	CoMo sulfide	NiMo sulfide	Ni_2P/USY	Ni_2P/SiO_2
$k_1 + k_2$	34.1 (4.0)	83.2 (8.8)	51.5 (15.2)	66.4 (23.7)
k_1/k_2	1.2	3.2	5.2	10.1
k_1	18.8 (2.2)	63.3 (6.7)	43.2 (12.7)	60.4 (21.6)
k_2	15.3 (1.8)	19.9 (2.1)	8.3 (2.5)	6.0 (2.1)

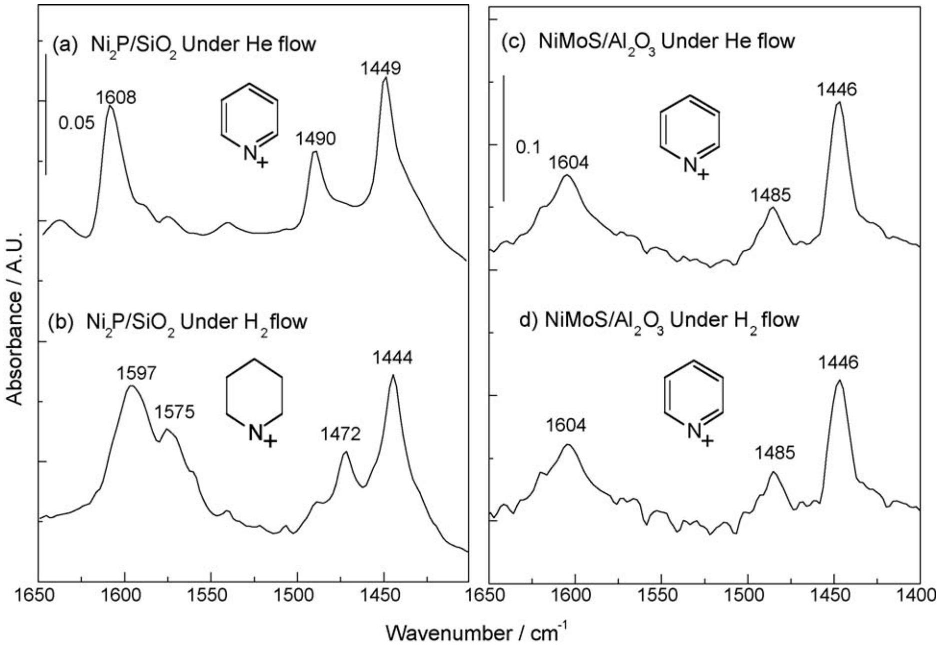

Fig. 10. In situ FTIR spectra of pyridine on Ni2P and NiMo.

1472 cm^{-1}) while that on NiMoS/Al_2O_3 remains unchanged (Fig. 10d). This confirms the high hydrogenation activity of Ni_2P.

Adsorption of CO was also used to characterize the samples. The sulfided NiMoS/Al_2O_3 showed very weak IR peaks (at 2173 and 2117 cm^{-1}) due to physisorbed CO species on cationic sites, as found in previous studies [310–312]. Only at a very low temperature (140 K) did IR bands appear at 2125 cm^{-1} with low intensity [312], indicating a low electron density on the adsorbing metal sites. In contrast to these samples, the Ni_2P/SiO_2 gave a distinctive and stable IR band at 2083 cm^{-1}. After sulfidation the peak reappeared at slightly higher frequency of 2086 cm^{-1} with the intensity being slightly diminished. This was previously observed in studies in Bussell's group on Ni_2P/SiO_2 [231,232] and was attributed to weakening of the Ni–CO bond by electron withdrawal by sulfur. This frequency fell in the region between that of Ni^+–CO and Ni^0–CO, indicating the presence of π back-bonding in a metal-like state. Also, the IR band for bridging CO species was not observed, which is understandable as the bond distance given by EXAFS between Ni–Ni in Ni_2P is not close enough to form bridging CO groups compared to that in Ni metal. Similar results are found for noble metals in a low oxidation state such as Pt and Pd which are well known as hydrogenation catalysts, and display stable IR bands at low frequency ($\sim$2010 cm^{-1}) at room temperature [313,314]. The noble metals are, however, severely deactivated in a sulfur environment with a loss of active sites [314].

An in-depth study was made of the HDN mechanism of 2-methylpiperidine. As shown by the group of Prins [315], this is an ideal probe molecule for distinguishing between elimination and substitution pathways. Piperidine can react by either of two pathways (Fig. 11). The E2 elimination pathway (top) results in the formation of a 6-amino-2-hexene, which is hydrogenated to 1-aminohexane. The S_N2 nucleophilic substitution pathway (bottom) forms 5-amino-1-hexene, which is hydrogenated to 2-aminohexane.

Results of a flow reactor study at 3.1 MPa and 450–600 K were carried out using a Ni_2P/SiO_2 catalyst [306] (Fig. 12). For realistic conditions sulfur (3000 ppm) was included in the feed.

Analysis of the product distribution as a function of contact time showed that the initial product was 2-aminohexane, indicating that the reaction proceeded predominantly by an S_N2 substitution mechanism, as was found on sulfides [315]. FTIR spectroscopy at reaction conditions of the 2-methylpiperidine indicated that a piperidinium ion intermediate was formed [308]. The intermediate was formed on P–OH groups, which showed a clear band at 3668 cm^{-1}. The assignment of the P–OH group on the Ni_2P/SiO_2 had already been addressed in a previous study [306], which showed that the P–OH intensity fell or rose as the piperidine was adsorbed or desorbed. The following reaction sequence (Fig. 13) accounts for the major observations on the reaction, i.e. the occurrence of an S_N2 step and the involvement of a piperidinium ion intermediate.

At the top left is a depiction of the Ni_2P surface. It shows hydroxyl groups associated with phosphorus as shown by FTIR [306], and the coverage of part of the nickel sites with sulfur as shown by EXAFS [260–264] and calculations [266]. A 2-methylpiperidine molecule interacts with this surface to form an adsorbed piperidinium ion, also observed by FTIR. The lone pairs on a suitably positioned sulfur atom carry out a nucleophilic attack on the open side of the ring. This is in agreement with the finding that HDN proceeds by a substitution mechanism. Subsequent steps involve facile C–S bond breaking reactions.

Kinetics indicate that the nucleophilic attack is the likely rate-determining step, and is supported by the observation of the piperidinium ion, as its high concentration is consistent with its participation in a slow reaction. The C–S bond in the resulting amine intermediate is weak and the species can react rapidly in a variety of ways, including elimination, as shown.

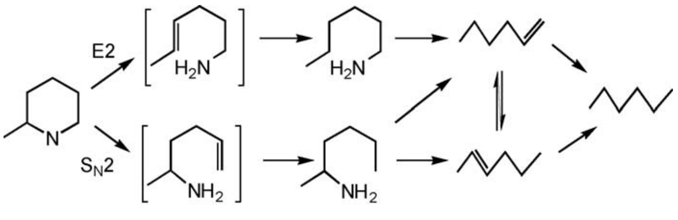

Fig. 11. Reaction network for 2-methylpiperidine HDN.

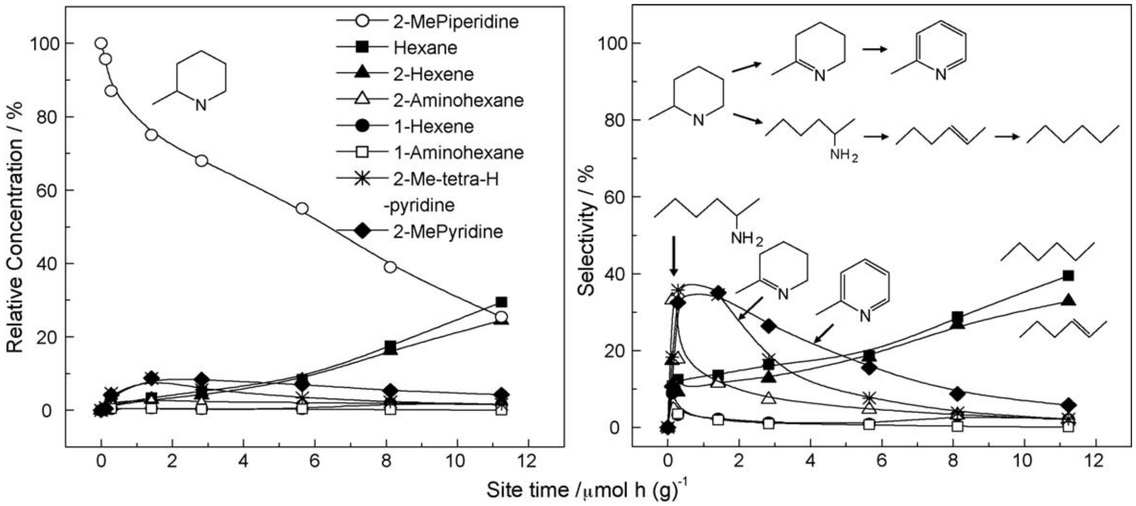

Fig. 12. Relative concentrations and selectivity in the HDN of 2-methylpiperidine.

3.4. Bimetallic systems

As was mentioned earlier, Ni_2P has been found to be the most active among the mono-metallic phosphides. Because of the well known synergism of Co and Ni with Mo in sulfide catalysts, some researchers have investigated mixed metal phosphides like NiMoP and CoMoP [235,316–320]. The surprising finding is that these compositions are poorly active. However, little explanation has been offered, aside from suggestions of alteration of the chemical nature, or interactions with the support. Insight into this unexpected result can be obtained from examining the structure of Ni_2P itself (Fig. 14), as NiMoP has the same structure.

The structure of Ni_2P is hexagonal [321] with space group: $P_{\bar{6}2m}$, D^2_{3h}, strucktur-bericht notation: revised C22, and lattice parameters, $a = b = 0.5859$ nm, $c = 0.3382$ nm. The unit cell has two types of Ni and P sites (denoted as Ni(1), Ni(2) and P(1), P(2)), which form two different trigonal prisms.

Although there are equal numbers of Ni(1) and Ni(2) atoms in the unit cell, they have different surroundings. The Ni(1) site has 4 nearest-neighbor P atoms in a near-tetrahedral geometry (2 at 0.2209 nm, 2 at 0.2266 nm) and 8 more distant Ni neighbors (2 at 0.2613 nm, 2 at 0.2605 nm, and 4 at 0.26783 nm). The Ni(2) site has 5 nearest-neighbor P atoms in a square pyramidal arrangement (1 at 0.2369 nm, 4 at 0.2457 nm) and 6 more distant Ni neighbors (2 at 0.2605 nm, 4 at 0.2678 nm).

An EXAFS study indicates that these two Ni sites can be distinguished by line-shape analysis [322]. Expanding on the previous work on Ni_2P/SiO_2–L and Ni_2P/SiO_2–H [255] as discussed in Figs. 6 and 7, a Ni_2P sample supported on a silicious MCM-41 support was characterized and its activity was compared to that of

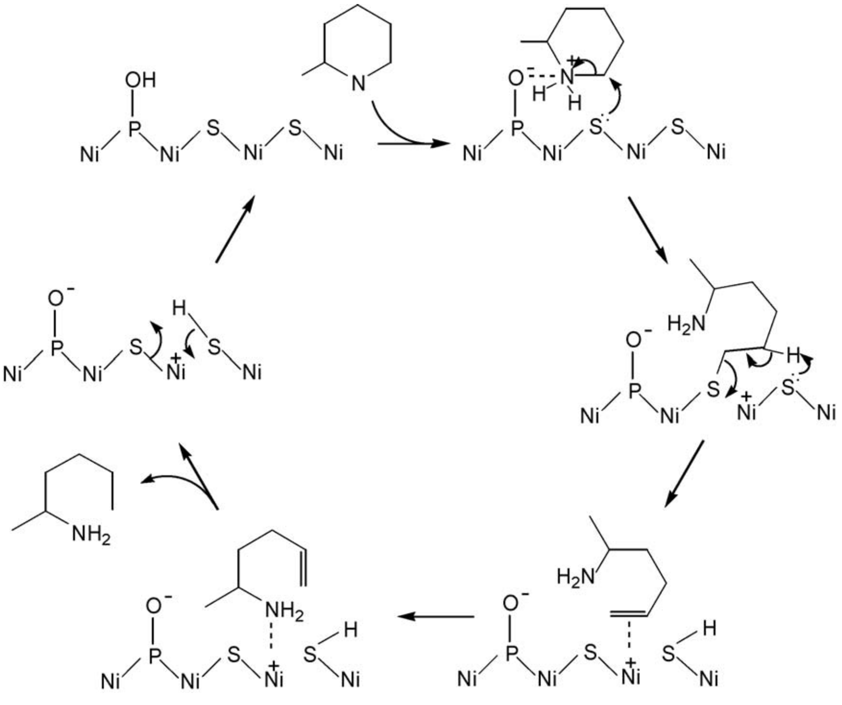

Fig. 13. Scheme for the HDN of 2-methylpiperidine.

Table 6
Correlation between active sites and catalytic performance.

Samples	Surface area ($m^2 g^{-1}$)	D_c (nm)	Ni–P(1)	Ni–P(2)	Conv. at 613 K	Sel. HYD	Sel. DDS
Ni_2P (bulk)	–	–	2.0	1.75	–	–	–
Ni_2P/SiO_2–L	102	10.1	1.99	2.57	62	34	66
Ni_2P/SiO_2–H	333	6.5	1.98	3.19	82	50	50
Ni_2P/MCM–41	487	3.8	1.99	3.48	95	65	35

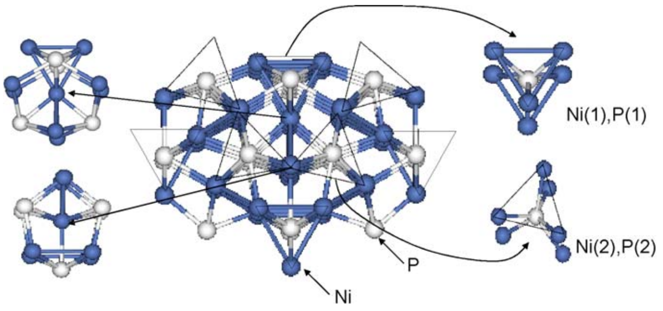

Fig. 14. Structure of Ni_2P showing P (left) and Ni (right) coordination.

the previous samples. The coordination numbers for the first type of Ni(1) are approximately constant, while for the second type of Ni(2) increase as the surface area of the support increases. This shows that Ni(2) is more prevalent in the smaller crystallites.

The feed employed was more severe than that used earlier (Fig. 5) and contained 500 ppm (0.05%) S as 4,6-DMDBT, 6000 ppm (0.6%) S as DMDS, 500 ppm (0.05%) N as quinoline, 1% tetralin, and balance tridecane. The conversion at steady-state at 340 °C was 95% for Ni_2P/MCM-41, 82% for Ni_2P/SiO_2–H, and 62% for Ni_2P/SiO_2–L (Table 6). The catalytic activity of the supported samples was largest for the highest surface area samples:

$$Ni_2P/MCM\text{-}41 > Ni_2P/SiO_2{-}H > Ni_2P/SiO_2{-}L$$

This order follows the number of Ni(2) sites, as deduced from the increasing coordination of Ni–P(2) sites (Table 6). Overall, the changes in coordination numbers suggest that the number of Ni(2) sites is increasing as the crystallite size goes down. This is because coordination numbers are a measure of the number of bonds. The higher coordination numbers for the Ni–P(2) bonds present a picture of crystallites that have more of these groups as they become smaller, but as the crystallite maintains the bulk Ni_2P structure, this could only arise if the Ni–P(2) bonds are at the surface. Thus, the bulk is terminated with the square pyramidal sites in small crystallites. The square pyramidal sites by definition (fivefold coordination vs. tetrahedral) have more P, so the P/Ni ratio increases as crystallite size goes down. The conclusion is that the square pyramidal Ni(II) sites are responsible for the high HDS activity, and constitute the active site.

Returning to the poor activity of NiMoP, it happens that in NiMoP the Mo sites substitute in the Ni(II) sites [323], and this readily accounts for the reduction of activity in this compound. The structure of CoMoP is different [324], but since both CoP and MoP have relatively poor activity, the lack of exceptional activity in CoMoP can be rationalized. That peculiar sites will have enhanced activity is not surprising. Rodriguez and coworkers have examined the role of P sites in single crystal Ni_2P(0 0 1) surfaces and found that they enhance the activity of Ni through a ligand effect [325], and the group of Nelson has identified a stable Ni_3PS site [266].

4. Conclusions

The synopsis presented above described the properties of transition metal phosphides and presented detailed studies of the most active of the catalysts, Ni_2P. The coverage included structural analysis of the active phase during reaction, and mechanistic studies which provide a detailed picture of the properties of nickel phosphide catalysts. It was shown that highly dispersed Ni_2P is particularly active for HDS and resistant to S and N-compounds. It was suggested that a stronger interaction between Ni and P in small particles could enhance the sulfur resistance. Also, the activation of N-compounds is probably related to the acidic properties of the Ni_2P, which provides sites for the formation of the protonated N-compounds as intermediate species in HDN. These results therefore imply that the remarkable activity of the supported Ni_2P catalyst has its origin in the proximity of the Ni and P species which is responsible for the creation of proximal sites of high activity in hydrogenation and the activation of N-and S-compounds.

Acknowledgments

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