

A new type of nonsulfide hydrotreating catalyst: nickel phosphide on carbon

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Nickel phosphide on carbon is successfully synthesized by temperature-programmed reduction as verified with X-ray diffraction and extended X-ray absorption fine structure measurements; it shows superior activity, selectivity, and stability for sulfur removal from the refractory compound 4,6-dimethyldibenzothiophene with a steady-state conversion of 99%, which is much higher than that of a commercial NiMoS/ γ -Al₂O₃ catalyst of 68%.

Hydrotreating research has become an important subject of environmental catalysis studies worldwide because of more stringent environmental regulations and the decreasing quality of available petroleum feedstocks. Recently a new class of high-activity hydrotreating catalysts, the transition metal phosphides, has been reported.¹ The preparation of highly dispersed phosphide phases on carriers such as SiO₂ and γ -Al₂O₃ has been described.^{2–7} These catalysts have been shown to be effective for sulfur removal from thiophene and dibenzothiophene (DBT). Here we present a new type of supported phosphide catalyst, nickel phosphide on carbon, which is very active for treating 4,6-dimethyldibenzothiophene (4,6-DMDBT), which is representative of the least reactive sulfur fraction in petroleum.^{8–10}

The carbon-supported nickel phosphide (Ni₂P/C) was prepared by the temperature-programmed reduction (TPR) in H₂ of a nickel phosphate precursor.^{3,5,7} The carbon used in this study had a surface area of 250 m²/g (Vulcan 4pc, XC72R). X-ray diffraction (XRD) patterns of the synthesized samples were obtained with a Scintag XDS-2000 powder diffractometer operated at 45 kV and 40 mA, using Cu K α monochromatized radiation. The active phase in the catalyst was further examined using extended X-ray absorption fine structure (EXAFS) spectra, measured at the X-18B beamline in Brookhaven National Laboratory with a 2.5-GeV ring energy and a 400-mA ring current. The fresh sample was pretreated in H₂ flow at 723 K and transferred to a glass cell with Kapton windows. The spent sample was taken from the hydroprocessing reactor, washed with hexane, and then pretreated in He flow at 613 K without exposure to air and similarly transferred to a glass cell.^{5,7} The activity of the catalysts was studied in a three-phase packed-bed reactor operated at 3.1 MPa and 613 K with a model liquid containing 500 ppm sulfur as 4,6-DMDBT, 3000 ppm sulfur as dimethyl disulfide (DMDs), 200 ppm nitrogen as quinoline, 1 wt% tetralin, 0.5 wt% n-octane (internal standard), and balance n-tridecane. Quantities of catalysts loaded in the reactor corresponded to the same amount of *ex situ* chemisorption sites (70 μ mol), as measured by CO chemisorption

for the phosphide and low-temperature O₂ chemisorption for the sulfide. The molar space velocity (moles of 4,6-DMDBT/moles of sites h) was 0.88 h⁻¹ for all the catalysts. Hydrotreating samples were collected in sealed septum vials and were analyzed offline with a gas chromatograph (Hewlett-Packard, 5890A) equipped with a 0.32 mm i.d. \times 50 m fused silica capillary column (CPSIL-5CB, Chrompack, Inc.) and a flame ionization detector.

X-ray diffraction patterns of the fresh Ni₂P/C sample and Ni₂P PDF reference are presented in Fig. 1. The pattern of the Ni₂P/C sample shows a broad feature at $2\theta \sim 25^\circ$ due to the carbon support. At higher angles, peaks due to Ni₂P are visible, indicating the formation of nickel phosphide on carbon.

The hydrotreating reaction results for the Ni₂P/C, Ni₂P/SiO₂ and a NiMoS/ γ -Al₂O₃ catalyst in the hydrodesulfurization (HDS) of 4,6-DMDBT, hydrodenitrogenation (HDN) of quinoline, dehydrogenation (DeHYD) and hydrogenation (HYD) of tetralin are summarized in Table 1. The data were taken after 100 h of time on stream. Mass balances were $100 \pm 5\%$ for each reaction type. The reaction of 4,6-DMDBT on the Ni₂P/C occurs with a very high and stable conversion of 99%, which is much higher than that of the Ni₂P/SiO₂ catalyst with 76% or the NiMoS/ γ -Al₂O₃ catalyst with 68%. The Ni₂P/SiO₂ catalyst was previously reported to be the most active among phosphide catalysts for the desulfurization of DBT.¹ There are three major products formed from 4,6-DMDBT on these catalysts: (1) 3,3'-dimethylbiphenyl (DMBP) from direct desulfurization (DDS), (2) 3-(3'-methylcyclohexyl)toluene (MCHT), and (3) 3,3'-dimethylbicyclohexyl (DMBCH) from hydrogenation (HYD) followed by desulfurization. Compared with the NiMoS/ γ -Al₂O₃ and Ni₂P/SiO₂ catalysts, the Ni₂P/C catalyst gave a lower DMBP selectivity of 10% and a

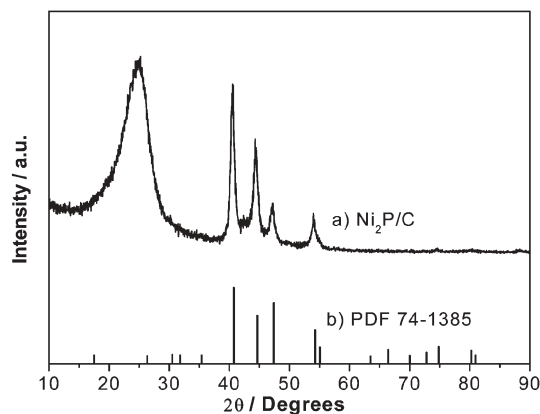


Fig. 1 X-ray diffraction patterns of the synthesized Ni₂P/C sample and a reference Ni₂P (PDF 74-1385).

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Table 1 Hydrotreating performance of Ni₂P/C catalyst and its comparison with commercial NiMoS/γ-Al₂O₃ and Ni₂P/SiO₂^a

Reactants	Type	Conversion (%)			Product	Selectivity (%)		
		Ni ₂ P/C	Ni ₂ P/SiO ₂	NiMoS/γ-Al ₂ O ₃		Ni ₂ P/C	Ni ₂ P/SiO ₂	NiMoS/γ-Al ₂ O ₃
4,6-DMDBT	HDS	99	76	68	3,3'-Dimethylbiphenyl	10	44	24
					3-(3'-Methylcyclohexyl)toluene	51	42	58
					3,3'-Dimethylbicyclohexyl	39	14	18
Quinoline	HDN	100	92	94	Propylcyclohexane	61	52	77
					Propylbenzene	39	41	23
	HYD	0	6	0	<i>ortho</i> -Propylaniline	0	4	0
					5,6,7,8-Tetrahydroquinoline	0	2	0
					1,2,3,4-Tetrahydroquinoline	0	1	0
Tetralin	DeHYD	3	23	7	Naphthalene	21	69	26
					<i>trans</i> -Decalin	51	21	56
	HYD	10	10	19	<i>cis</i> -Decalin	28	10	18

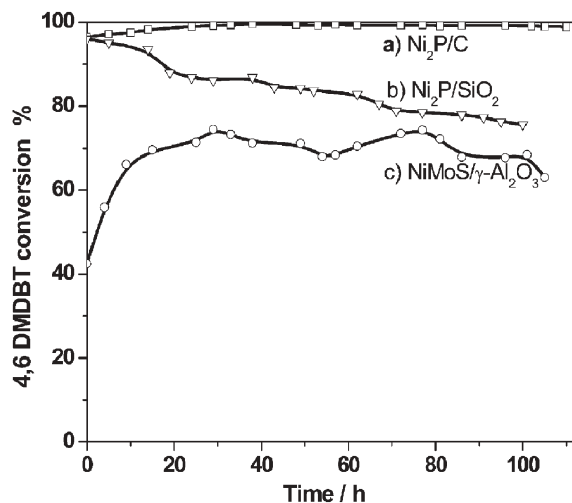
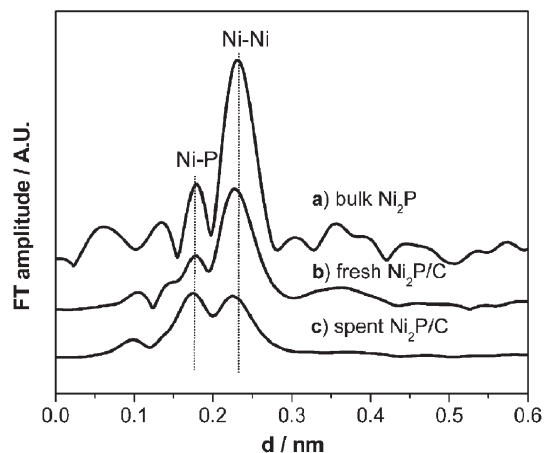
^a Reaction conditions: $T = 613$ K (340 °C), and $P = 3.1$ MPa (450 psig); liquid feed = 5 cm³ h⁻¹; gas flow = 150 cm³ (NTP) min⁻¹.

higher DMBCH selectivity of 39%, indicating that it favors the hydrogenation pathway. The Ni₂P/C catalyst also showed a superior ability for nitrogen removal with an HDN conversion of 100%, which is higher than that of the Ni₂P/SiO₂ of 92% or NiMoS/γ-Al₂O₃ of 94%. The HDN products are propylcyclohexane and propylbenzene. But for the DeHYD and HYD of tetralin, the Ni₂P/C catalyst exhibits less activity with a conversion of 13%.

Fig. 2 presents the time course of HDS activity on the Ni₂P/C, Ni₂P/SiO₂ and NiMoS/γ-Al₂O₃ catalysts. As can be seen, the Ni₂P/C gives 4,6-DMDBT conversions of close to 100% and no deactivation in the prolonged 110 h of time on-stream. The conversions on both the Ni₂P/SiO₂ and NiMoS/γ-Al₂O₃ catalysts are lower. The Ni₂P/SiO₂ catalyst shows deactivation, and the 4,6-DMDBT conversion decreases from an initial 96% to 76%.

The reason for deactivation is probably the loss of active sites as revealed from chemisorption data discussed in our earlier study.⁵ Overall, in terms of activity, selectivity, and stability, the Ni₂P/C was superior to the other catalysts.

To better characterize the nickel phosphide on the carbon support and elucidate the possible active phase involved in the hydrotreating reaction, both the fresh and spent Ni₂P/C samples were analyzed by EXAFS spectroscopy, and the resulting Fourier-transformed Ni K-edge EXAFS spectra are shown in Fig. 3. The

**Fig. 2** Hydrodesulfurization performance of (a) Ni₂P/C, (b) Ni₂P/SiO₂, and (c) NiMoS/γ-Al₂O₃.**Fig. 3** Nickel K-edge EXAFS of the fresh and spent Ni₂P/C samples.

fresh Ni₂P/C sample displays two distinct peaks, whose positions correspond to the Ni–P and Ni–Ni distances in bulk Ni₂P (Ni–P: $R = 0.18$ nm; Ni–Ni: $R = 0.23$ nm). This again demonstrates the formation of the Ni₂P on the carbon support, and is consistent with the XRD results. The spectrum of the spent Ni₂P/C sample is different in comparison with that of the fresh sample, showing a diminution in the intensity of the Ni–Ni peak and a shift to a lower distance. It is likely that another nickel compound is formed as a consequence of the reaction. Earlier studies^{5,7} indicate that the change could be due to development of intensity in the Ni–S distance region in between the Ni–P and Ni–Ni distances. Even though no distinct Ni–S peak is seen, a feature in that region would give rise to the broad signals actually observed.^{5,7} Thus, the active catalyst is probably a Ni–P–S surface phase on the outer region of a Ni₂P crystallite core.

We have thus demonstrated that the nickel phosphide on carbon (Ni₂P/C) is a promising hydrotreating catalyst and is able to effectively remove the sulfur from the tenacious 4,6-DMDBT compound.

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