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Supplementary Information

New synthesis method for nickel phosphide nanoparticles: solid phase reaction of nickel cations with hypophosphites

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Characterization: X-ray diffraction (XRD) patterns were collected in ambient atmosphere by a Philips X'Pert powder diffractometer with Cu Kα radiation (λ=1.5418 Å). The 2θ scans covered the range of 10° to 80° with a step of 0.02°. The applied voltage and current were 40 kV and 40 mA, respectively. The scanning electron microscopy (SEM) measurements were carried out using the Leo 1530 Gemini microscope operated at 20 kV. The BET surface areas were measured on the ASAP 2020 instrument at 77.3 K using N_2 as the adsorbate. Thermogravimetric analysis/mass spectroscopy (TG-MS) measurements were carried out on a STA 449C TG/DTA instrument equipped with a mass spectrometer (ThermoStar TM) under N_2 atmosphere. The temperature-programmed rate was 10 K/min up to 773 K. Elemental analysis was performed by inductively coupled plasma/optical emission spectrometry (ICP-OES, Optima 5300, Perkin Elmer) using solutions prepared by dissolving samples in aqua regia.

Catalytic test: The catalysts were tested in a three-phase trickle-bed reactor for the hydrodesulfurization (HDS) of dibenzothiophene (DBT), hydrodenitrogenation (HDN) of quinoline and hydrogenation or dehydrogenation of tetralin. A model diesel containing 3000 ppmw sulfur of DBT, 200 ppmw nitrogen of quinoline, 5 wt% tetralin, 0.5 wt% n-octane (internal standard) and balanced n-nonane (solvent) was used for the catalytic reactions performed at P=3.1 MPa, T=593-613 K, LHSV (liquid hourly space velocity) =2 h^{-1} and H_2/feed=1500 (v/v). Reaction mixtures were analyzed by a gas chromatograph equipped with a flame ionization detector (FID) for hydrocarbons, a flame photometric detector (FPD) for organic sulfurs and a nitrogen and phosphorus detector (NPD) for organic nitrogens. Products were also confirmed by using a gas chromatograph (DB-5 column with 30 m×0.32 mm and 0.25 μm film thickness) connected to a mass spectrograph (GC-MS). The column temperature was linearly programmed from 305 to 523 K at a rate of 10 K/min. A mass selective detector (EI=70 eV) and the NIST+ library were used for the identification of MS signals. The Ni_2P catalyst was activated for 3 hours in H_2 at 673 K before the catalytic test.

Table S1

Hydrotreatment of dibenzothiophene, quinoline and tetralin over Ni_2P catalysts

				Dehydrogenation/hydrogenation of tetralin			
	Temp.	HDS	HDN	Conv.	Selectivity (%)		
Catalyst	(K)	(%)	(%)	(%)	Naphthalin	Trans-decalin	Cis-decalin
Ni_2P^*	613	90.5	97.3	9.9	69.7	18.5	11.8
Ni_2P/SiO_2[19]	643	90	56	31.6	98.2	0.6	1.2

[*] Sample prepared in this work.

Table S2

Conversion and product selectivity of dibenzothiophene (DBT) over Ni_2P ($H_2PO_2^-/Ni^{2+}=3$) prepared at 473 K

Temperature (K)	Conversion (%)	Selectivity (%)	
		Biphenyl	Cyclohexylbenzene
593	64.8	84.0	16.0
613	90.5	72.2	27.8

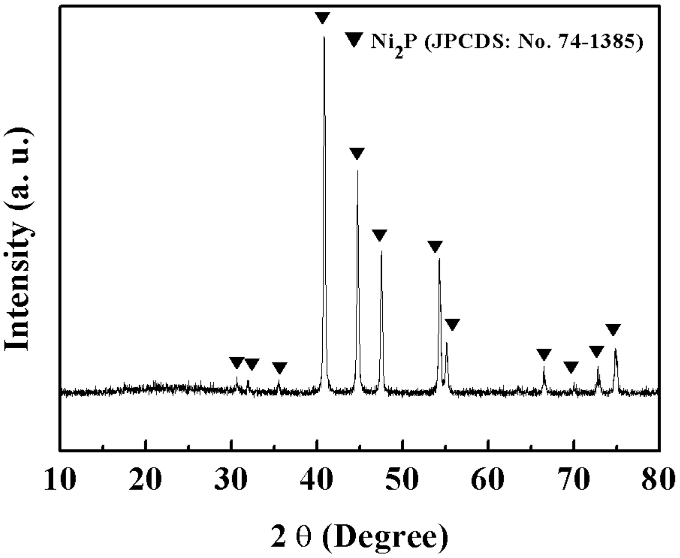

Fig. S1 The XRD patterns for the Ni_2P (473 K, $H_2PO_2^-/Ni^{2+}=3$) after catalytic test.