

# Mesoporous carbon supported nickel phosphide catalysts prepared by solid phase reaction

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## Introduction

Transition metal phosphides have received much attention owing to their applications in nanoscale materials and catalysts [1,2]. Nanoparticles of transition metal phosphides exhibited excellent magnetic, electric and optical properties, depending on their sizes and shapes. Supported transition metal phosphides have been tested as catalysts for the hydrotreating reactions [3,4]. Metal-rich phosphides were found to be active for the reactions of hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), and supported  $\text{Ni}_2\text{P}$  might be more active than the commercial sulfide catalysts [4]. A few methods were used to prepare metal phosphides, e.g., solvothermal reactions, reduction of transition metal phosphate, phosphatization of metals or metal oxides by phosphine, decomposition of metal complexes, and the co-reaction of organometallic reagents with phosphine. In the present work, we report a facile and effective way to prepare mesoporous carbon (MC) supported nickel phosphide catalysts. In this method, nickel and ammonium hypophosphites were dissolved in water and added on MC. After heating in  $\text{N}_2$ , a  $\text{Ni}_2\text{P}/\text{MC}$  catalyst was produced, which exhibited high activity for the HDS of dibenzothiophene (DBT) and HDN of quinoline.

## Materials and Methods

A MC ( $1500 \text{ m}^2/\text{g}$  with average pore size of 6.3 nm and pore volume of 2.4 ml/g) was impregnated with an aqueous solution of nickel and ammonium hypophosphites. After drying at 393 K, the sample was linearly heated to 573 K at a rate of 2 K/min and then kept at 573 K for 3 h. After cooled and passivated, the sample was washed thoroughly with aqueous solution of ammonia and deionized water sequentially to remove impurities such as  $\text{H}_3\text{PO}_3$  formed during the solid phase reaction. An unsupported  $\text{Ni}_2\text{P}$  catalyst was prepared in the similar way for comparison.

The catalysts were tested in a three-phase trickle-bed reactor for the HDS of DBT, 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 reaction. The reaction was performed at  $P=3.1 \text{ MPa}$ ,  $T=593\text{--}613 \text{ K}$ ,  $\text{LHSV}=2 \text{ h}^{-1}$  and  $\text{H}_2/\text{feed}=1500 \text{ (v/v)}$ .

## Results and Discussion

Figure 1 shows that the unsupported and MC supported  $\text{Ni}_2\text{P}$  catalysts were successfully prepared by the solid phase reaction between  $\text{H}_2\text{PO}_2^-$  with  $\text{Ni}^{2+}$ . However, the intensity of  $\text{Ni}_2\text{P}$  on MC was much lower than that of the bulk  $\text{Ni}_2\text{P}$ , indicating the high dispersion of  $\text{Ni}_2\text{P}$  on MC.

The data in Table 1 were collected after 36 h on stream for the reaction. 96.1% of DBT and 100% of quinoline were degraded over the  $\text{Ni}_2\text{P}/\text{MC}$  at 593 K, significantly higher

than those over the unsupported  $\text{Ni}_2\text{P}$ . Apparently, the HDS and HDN activities of the  $\text{Ni}_2\text{P}/\text{MC}$  were much higher than those of  $\text{Ni}_2\text{P}/\text{SiO}_2$  reported in literature [5, 6]. The high activities of  $\text{Ni}_2\text{P}/\text{MC}$  for the HDS and HDN might be attributed to the support with high surface area of mesopores and the relatively low temperature of the solid phase reaction for the production of  $\text{Ni}_2\text{P}$  on MC. In addition, the  $\text{Ni}_2\text{P}/\text{MC}$  seemed to catalyze the hydrogenation of tetralin at 593 K, while the  $\text{Ni}_2\text{P}/\text{SiO}_2$  mainly catalyzed the dehydrogenation of tetralin at 643 K [6].

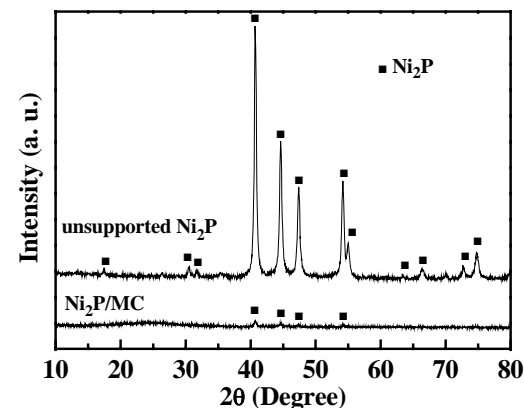


Figure 1. XRD patterns of unsupported and mesoporous carbon supported  $\text{Ni}_2\text{P}$  catalysts.

Table 1. Hydrotreatment of dibenzothiophene, quinoline and tetralin over  $\text{Ni}_2\text{P}$  catalysts

Catalyst	Temp. (K)	HDS (%)	HDN (%)	Conv. (%)	Dehydrogen./hydrogen. of tetralin		
					Selectivity (%)		
					Naphthalin	Trans-decalin	Cis-decalin
Unsupported $\text{Ni}_2\text{P}$	593	64.8	94.1	1.7	69.0	17.2	13.8
$\text{Ni}_2\text{P}/\text{MC}$	593	96.1	100	2.6	54.2	25.0	20.8
$\text{Ni}_2\text{P}/\text{SiO}_2$ [5]	613	82	90	-	-	-	-
$\text{Ni}_2\text{P}/\text{SiO}_2$ [6]	643	90	56	31.6	98.2	0.6	1.2

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