



## Effect of loading on the Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts for the hydrotreating reactions

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### ABSTRACT

The 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the phosphidation of corresponding 80%Ni/Al<sub>2</sub>O<sub>3</sub> with triphenylphosphine in liquid phase and compared with the 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> for hydrotreating reactions. Both the 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> and 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> in comparison exhibited the small and uniform Ni<sub>2</sub>P particles (6.3 and 8.4 nm, respectively), high CO uptakes (305 and 345 μmol/g, respectively) and thus high activities for the hydrotreating reactions. After the hydrotreating reactions, the small and uniform Ni<sub>2</sub>P particles were remained, although the CO uptakes on the used 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> and 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> were greatly decreased (to 68 and 95 μmol/g, respectively) due to the incorporation of S into the Ni<sub>2</sub>P surfaces. The 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> was found to be significantly more active than the 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> due to that the 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> possessed more, and more active Ni<sub>2</sub>P sites than the 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub>, probably due to the less S incorporated in the 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> than in the 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> during the hydrotreating reactions.

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### 1. Introduction

The transition metal phosphides were highly active for the hydrodesulphurization (HDS) and hydrodenitrogenation (HDN) reactions [1–3], in which the supported Ni<sub>2</sub>P catalysts might be more active and stable than the traditional NiMoS/Al<sub>2</sub>O<sub>3</sub> and CoMoS/Al<sub>2</sub>O<sub>3</sub> catalysts [4,5], and thus might be used as the next-generation industrial catalysts for the hydrotreating reactions [5].

In industry, alumina is a preferred support since it possesses the strong mechanical strengths, high temperature resistance, appropriate pore structures and large surface areas. The supported Ni<sub>2</sub>P catalysts were frequently prepared using the method of programmed temperature reduction (TPR) of nickel phosphate [1,6–9]. However, only the poorly dispersed Ni<sub>2</sub>P catalysts were prepared with TPR method since it required high temperatures and more phosphates [10–13]. Recently, we phosphided a 60%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst by using triphenylphosphine (PPh<sub>3</sub>) in liquid phase and prepared the 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalyst with highly dispersed Ni<sub>2</sub>P particles [14]. This 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalyst adsorbed great amount of CO (305 μmol/g) and thus exhibited the high activities for the HDS of dibenzothioephene (DBT) and hydrogenation of tetralin to decalin.

In the present work, the Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts with higher Ni loadings (80wt%) were prepared and compared with the 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> for the hydrotreating reactions. It was found that the 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub>

prepared via the pre-reduction at 723 K exhibited the high surface density of Ni<sub>2</sub>P active sites (345 μmol/g) as measured by the adsorption of CO. No higher values than 345 μmol/g were found in the literature so far for the adsorption of CO on Ni<sub>2</sub>P. Our research suggested that the loading and reduction temperature significantly affected the reducibility and dispersion of supported Ni in the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts [15–20], which in turn affected the content and dispersion of supported Ni<sub>2</sub>P in the phosphided Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts [21,22]. The 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> with the higher CO uptake of 345 μmol/g exhibited the higher activities for the HDS of DBT and hydrogenation of tetralin to decalin than the 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> with the relatively lower CO uptake of 305 μmol/g.

### 2. Experimental

#### 2.1. Preparation of catalysts

The 80%Ni/Al<sub>2</sub>O<sub>3</sub> was prepared by the co-precipitation method. The preparation procedure can be found elsewhere [23,24]. Briefly, desired amounts of nickel and aluminum nitrates were dissolved in 100 mL distilled water to form an aqueous solution and another aqueous solution was obtained by dissolved desired amount of sodium carbonate in 100 mL distilled water. The two solutions were simultaneously added dropwise into a beaker containing 200 mL distilled water at 353 K under vigorous stirring. The precipitate was washed thoroughly with deionized water. The filter cake was added into

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200 ml n-butanol which was then evaporated at 353 K. The sample was further dried in an oven at 393 K for 12 h.

The same phosphidation procedure was used as reported previously [22]. Typically, the 80%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was placed in a micro-reactor and pre-reduced in flowing H<sub>2</sub> (0.1 MPa and 40 mL/min) for 2 h at different temperatures (673–823 K). Then, the temperature was lowered to 443 K, at which the catalyst was phosphided with PPh<sub>3</sub> (2% in heptane) for 36 h (LHSV of 2 h<sup>-1</sup> and H<sub>2</sub>/oil of 300 v/v). After the phosphidation, the catalyst was heat-treated in H<sub>2</sub> at 673 K for 3 h and then cooled down to the first reaction temperature (513 K), at which model diesel was introduced into the reactor and the hydrotreating reactions began.

## 2.2. Characterization of catalysts

The adsorption of H<sub>2</sub> and O<sub>2</sub> on the 80%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was carried out in a home-made volumetric apparatus. The catalyst was reduced in H<sub>2</sub> at different temperatures for 2 h and evacuated at the reduction temperature for 1 h before the measurements. The adsorption of H<sub>2</sub> was performed at room temperature. After the adsorption of H<sub>2</sub>, the sample was heated to 673 K at a rate of 10 K/min and evacuated at 673 K for 1 h. The adsorption of O<sub>2</sub> was then performed at 673 K. The uptakes of H<sub>2</sub> and O<sub>2</sub> were obtained by extrapolating the coverage of corresponding isotherms to  $P = 0$ . The degree of reduction (reducibility), dispersion, active surface area and average particle size of supported nickel were calculated based on the amounts of H<sub>2</sub> and O<sub>2</sub> adsorbed and the amount of nickel loaded. The detailed calculation formulae can be found in the literature [23].

The 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared separately for characterizations. The phosphidation process was the same as that described above (Section 2.1). The phosphided catalysts were passivated for 12 h at room temperature under N<sub>2</sub> containing about 0.5 vol% O<sub>2</sub> before they were characterized with different techniques.

The surface area and pore structure were determined with a Micromeritics Gemini V 2380 autosorption analyzer at 77.3 K after the samples were degassed in flowing N<sub>2</sub> at 473 K for 5 h. X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD-6000 powder diffractometer (Japan) using a Cu K $\alpha$  radiation ( $\lambda = 0.1541$  nm) under the setting conditions of 40 kV and 30 mA. The chemical compositions of catalysts were determined by an ARL-9800 X-ray fluorescence spectrometer (XRF). The morphologies of catalysts were performed on a JEOL JEM-2100 transmission electron microscope (TEM) operated at 200 kV.

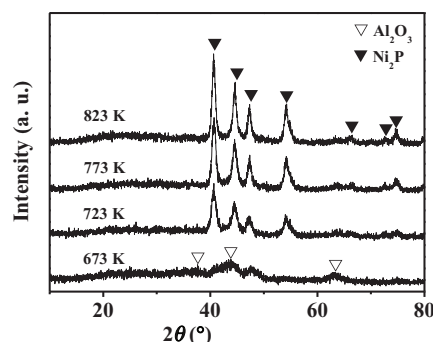
The microcalorimetric adsorption of CO was performed by using a Setaram Tian-Calvet C-80 heat-flux microcalorimeter, connected to a gas-handling system equipped with a Baratron capacitance manometer for precise pressure measurements. Passivated samples were re-reduced in H<sub>2</sub> at 673 K for 3 h and then evacuated at 673 K for 1 h. The microcalorimetric adsorption was performed at 308 K.

**Table 1**

Textural and structural properties of the 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> and 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts phosphided at 443 K with PPh<sub>3</sub> in liquid phase after the 60%Ni/Al<sub>2</sub>O<sub>3</sub> and 80%Ni/Al<sub>2</sub>O<sub>3</sub> were pre-reduced in H<sub>2</sub> for 2 h at different temperatures.

Catalyst	60%Ni <sub>2</sub> P/Al <sub>2</sub> O <sub>3</sub>				80%Ni <sub>2</sub> P/Al <sub>2</sub> O <sub>3</sub>			
	673	723	773	823	673	723	773	823
Pre-reduction temperature (K)	673	723	773	823	673	723	773	823
S <sub>BET</sub> (m <sup>2</sup> /g)	201	154	148	146	158	138	132	111
Pore volume (cm <sup>3</sup> /g)	0.64	0.68	0.61	0.61	0.71	0.69	0.72	0.62
Pore size (nm)	9.9	13.4	12.7	13.1	15.3	15.7	17.1	17.0
XRD phase	Ni <sub>2</sub> P	Ni <sub>2</sub> P	Ni <sub>2</sub> P	Ni <sub>2</sub> P	Ni <sub>2</sub> P	Ni <sub>2</sub> P	Ni <sub>2</sub> P	Ni <sub>2</sub> P
d (nm)	4.1	6.3	6.6	7.2	–	8.4	10.5	11.9
CO uptake ( $\mu$ mol/g)	133	305	251	189	334	345	322	298
CO ads. heat (kJ/mol)	86	95	98	81	96	89	91	93

Note: The particle size (d) of Ni<sub>2</sub>P was estimated by the Scherrer equation according to the full width at half maximum (FWHM) of the peak at 40.7° in the XRD patterns shown in Fig. 1.



**Fig. 1.** XRD patterns for the 80%Ni/Al<sub>2</sub>O<sub>3</sub> catalysts phosphided at 443 K with PPh<sub>3</sub> in liquid phase after the catalysts were pre-reduced in H<sub>2</sub> for 2 h at different temperatures indicated.

## 2.3. Catalytic tests

The reactions of HDS of DBT, HDN of quinoline and hydrogenation of tetralin were performed in a fix-bed reactor using a feed containing 1.72% DBT (3000 ppm S), 0.185% quinoline (200 ppm N), 5% tetralin and 0.5% n-octane (as an internal standard) in balanced n-tetradecane (solvent) at different temperatures (513–613 K) with the fixed pressure (3.1 MPa), LHSV (2 h<sup>-1</sup>) and H<sub>2</sub>/oil ratio (1500 (v/v)). The products were collected after 24 h and analyzed on gas chromatographs.

## 3. Results and discussion

### 3.1. Structural and surface properties of fresh catalysts

The 80%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was pre-reduced at different temperatures (673–823 K) and then phosphided with PPh<sub>3</sub> in heptane at 443 K. Fig. 1 shows the XRD patterns of phosphided samples. When the sample was pre-reduced at 673 K, the diffraction peaks for Ni<sub>2</sub>P were not clear. When the sample was pre-reduced at 723 K, the diffraction peaks around 40.7°, 44.6°, 47.4° and 54.2° for Ni<sub>2</sub>P were clearly seen. The intensities of these diffraction peaks were increased with the further increase of pre-reduction temperatures to 773 and 823 K.

According to the broadening of the Ni<sub>2</sub>P (111) peak at 40.7° and the Scherrer equation, the average particle sizes of Ni<sub>2</sub>P formed in the 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts pre-reduced at different temperatures were estimated. Table 1 shows the results. It is seen that the particle size of Ni<sub>2</sub>P were 8.4 nm in the 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> pre-reduced at 723 K. When the pre-reduction temperature was increased to 773 and 823 K, the particles of Ni<sub>2</sub>P were correspondently increased to 10.5 and 11.9 nm, respectively. The average particle sizes of Ni<sub>2</sub>P

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