



# Optimization of MgO/Al<sub>2</sub>O<sub>3</sub> ratio for the maximization of active site densities in the Ni<sub>2</sub>P/MgAlO catalysts for the hydrotreating reactions

Junen Wang<sup>a,b</sup>, Xiaogan Wang<sup>a</sup>, Yamei Yuan<sup>a</sup>, Abdalla Shuaib<sup>a</sup>, Jianyi Shen<sup>a,\*</sup>

<sup>a</sup>Laboratory of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

<sup>b</sup>College of Chemistry and Materials Science, Huaibei Normal University, Huaibei 235000, Anhui, China

## ARTICLE INFO

### Article history:

Received 26 October 2015

Revised 14 December 2015

Accepted 27 January 2016

Available online 10 March 2016

### Keywords:

Supported Ni<sub>2</sub>P

Liquid phase phosphidation

Triphenylphosphine

Microcalorimetric adsorption of CO

Hydrotreating reactions

## ABSTRACT

The Ni<sub>2</sub>P/MgAlO catalysts with different MgO/Al<sub>2</sub>O<sub>3</sub> ratios were prepared by the phosphidation of corresponding Ni/MgAlO catalysts with triphenylphosphine in liquid phase. It was found that the MgO/Al<sub>2</sub>O<sub>3</sub> ratio affected the Ni<sub>2</sub>P/MgAlO catalysts significantly. The Ni<sub>2</sub>P/MgAlO catalyst with the MgO/Al<sub>2</sub>O<sub>3</sub> ratio of 3 (w/w) exhibited the highly dispersed Ni<sub>2</sub>P particles (~9 nm) with the highest CO uptake (344 μmol/g) and thus the highest activities for the hydrotreating reactions. However, based on the CO uptakes on the used catalysts, the TOF values for the hydrodesulphurization of dibenzothiophene as well as those for the hydrogenation of tetralin on all the Ni<sub>2</sub>P/MgAlO catalysts were respectively similar, indicating that the MgO/Al<sub>2</sub>O<sub>3</sub> ratio did not affect the intrinsic activities of Ni<sub>2</sub>P supported on the MgAlO support for the hydrotreating reactions.

© 2016 Science Press, Published by Elsevier B.V. and Science Press.

## 1. Introduction

The increasingly heavier and worse quality crude oils and severer environmental regulations have made the catalytic hydrotreating very important to the petroleum refining industry [1–4]. The development of more active catalysts is an effective way to produce high quality fuels. The transition metal phosphides, especially Ni<sub>2</sub>P, have been shown highly active for the hydrotreating reactions [5,6]. Thus, the supported Ni<sub>2</sub>P catalysts have attracted the wide attention for both fundamental researches and industrial applications [7,8].

SiO<sub>2</sub> is the most widely used porous supports for Ni<sub>2</sub>P catalysts [9–11], but the weak interaction between SiO<sub>2</sub> and Ni<sub>2</sub>P decreased the dispersion of Ni<sub>2</sub>P [12]. Al<sub>2</sub>O<sub>3</sub> is a preferred support in industry, but it was difficult to prepare the highly dispersed Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> catalysts with the programmed-temperature-reduction (TPR) method, which was frequently used to prepare the transition metal phosphides. The other porous supports reported in literature for the supported metal phosphides include SBA-15 [13–15], MCM-41 [16–18], KUSY [19,20] and carbon materials [21–23]. However, few researches were reported on the Ni<sub>2</sub>P catalysts supported on composite oxides [12,24].

Recently, highly dispersed Ni<sub>2</sub>P catalysts supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, MgAlO (shorted for the composite oxide MgO–Al<sub>2</sub>O<sub>3</sub>)

and ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> were prepared in our group by the phosphidation of corresponding Ni catalysts with triphenylphosphine (PPh<sub>3</sub>) in liquid phase at the relatively low temperature (443 K) [25–28]. It was found that 60%Ni<sub>2</sub>P/MgAlO catalyst (MgO/Al<sub>2</sub>O<sub>3</sub> = 35/5, w/w) prepared in this way exhibited the better performance than the 60%Ni<sub>2</sub>P/SiO<sub>2</sub> and 60%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> for the hydrotreating reactions [26]. However, the composition of the MgAlO mixed oxides has not been optimized. In this work, 60%Ni<sub>2</sub>P/MgAlO catalysts with different MgO/Al<sub>2</sub>O<sub>3</sub> weight ratios were prepared, characterized and evaluated for the hydrotreating reactions. It was found that 60%Ni<sub>2</sub>P/MgAlO catalyst with the MgO/Al<sub>2</sub>O<sub>3</sub> ratio of 3 (w/w) exhibited the highest surface density of Ni<sub>2</sub>P active sites (344 μmol/g) as measured by the adsorption of CO, which was similar to that of the 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> (345 μmol/g), although the loading of Ni in the 60%Ni<sub>2</sub>P/MgAlO was significantly lower than that in the 80%Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> [27]. In addition, this value of CO uptake was higher than that for the catalyst 60%Ni<sub>2</sub>P/ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> (328 μmol/g) [28]. Thus, the addition of MgO for the preparation of Ni<sub>2</sub>P/MgAlO catalysts was quite desirable as compared to the Ni<sub>2</sub>P/Al<sub>2</sub>O<sub>3</sub> and Ni<sub>2</sub>P/ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts.

Since Ni<sub>2</sub>P was formed from the phosphidation of metallic Ni, the higher density of surface active Ni sites (as measured by the adsorption of H<sub>2</sub>) usually resulted in the higher density of surface active Ni<sub>2</sub>P sites. Moreover, since the presence of MgO promoted the reduction while decreased the dispersion of supported nickel, it must be compromised between the reducibility and dispersion of supported nickel to maximize the density of surface active Ni sites, which could be monitored by varying the MgO/Al<sub>2</sub>O<sub>3</sub> ratio.

\* Corresponding author. Tel/Fax: +86 25 89684305.

E-mail address: [jyshen@nju.edu.cn](mailto:jyshen@nju.edu.cn) (J. Shen).

In addition, MgO could be highly porous with high surface areas and strong surface basicity [29]. Thus, the composite supports MgAlO could have the high surface areas favoring the dispersion of supported Ni<sub>2</sub>P and the surface basicity benefiting the catalytic stability by reducing the cracking reactions during the hydrotreating processes.

## 2. Experimental

### 2.1. Preparation of catalysts

The 60%Ni/MgAlO catalysts with different MgO/Al<sub>2</sub>O<sub>3</sub> weight ratios were prepared by the co-precipitation method. The preparation procedure can be found elsewhere [30,31]. In short, an aqueous solution containing nickel, aluminum and magnesium nitrates were added simultaneously with another aqueous solution of sodium carbonate into a beaker containing 200 mL distilled water at 353 K under vigorous stirring. Precipitates were formed and washed with deionized water thoroughly. The filter cakes were then dispersed into 200 mL n-butanol. Water and n-butanol were evaporated sequentially at 353 K. The samples were then dried further in an oven at 393 K for 12 h.

The same phosphidation procedure was used as reported previously [25,26]. Typically, a supported nickel catalyst was loaded into a micro-reactor and pre-reduced in H<sub>2</sub> (0.1 MPa and 40 mL/min) for 2 h at 723 K. Then, the catalyst was phosphided with PPh<sub>3</sub> (2%) in heptane solution (LHSV of 2 h<sup>-1</sup> and H<sub>2</sub>/oil of 300 v/v) at 443 K for 36 h. Afterwards, the catalyst was heat-treated in H<sub>2</sub> at 673 K for 3 h.

### 2.2. Characterization of catalysts

The adsorption of H<sub>2</sub> and O<sub>2</sub> for the 60%Ni/MgAlO catalysts was carried out in a home-made volumetric apparatus. The catalysts were reduced in H<sub>2</sub> at 723 K for 2 h and evacuated at the reduction temperature for 1 h before the measurements. The adsorption of H<sub>2</sub> and O<sub>2</sub> was performed at room temperature and 673 K, respectively. 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 [32–36].

The supported Ni<sub>2</sub>P catalysts were prepared separately for characterizations. The phosphidation process was the same as that described in Section 2.1. After the phosphidation, the catalysts were heat-treated in H<sub>2</sub> at 673 K for 3 h. Then, the catalysts were passivated at room temperature for 12 h under N<sub>2</sub> containing about 0.5 vol% O<sub>2</sub> before they were characterized with different techniques.

N<sub>2</sub> adsorption–desorption measurements were carried out at 77.3 K using a Micromeritics Gemini V 2380 autosorption analyzer. The specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) equation while pore distributions were obtained by the Barret–Joyner–Halenda (BJH) method. Samples were degassed in flowing N<sub>2</sub> at 473 K for 5 h before the measurements.

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). The 2 $\theta$  degrees covered the range of 10–80° with a step of 0.02°.

The chemical compositions of catalysts were analyzed by an ARL-9800 X-ray fluorescence spectrometer (XRF).

Transmission electron microscope (TEM) was performed using a JEOL JEM-2100 high-resolution microscope operating at 200 kV.

The samples were dispersed in 5% ethanol solution and dropped onto a copper grid coated with a carbon film.

The microcalorimetric adsorption of CO was performed 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 flowing H<sub>2</sub> at 673 K for 3 h and evacuated at 673 K for 1 h before the measurements. Microcalorimetric adsorption was performed at 308 K.

### 2.3. Catalytic tests

Catalytic tests were carried out for the hydrodesulphurization (HDS) of dibenzothiophene (DBT), hydrodenitrogenation (HDN) of quinoline and hydrogenation of tetralin in a model diesel 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). A fix-bed reactor was used to perform the reactions. The reactions were carried out at 3.1 MPa with LHSV of 2 h<sup>-1</sup> and H<sub>2</sub>/oil ratio of 1500 (v/v). The catalytic activity was measured at different reaction temperatures. The reactant solution was fed into the reactor through a high pressure syringe pump. The products were collected after 24 h when the activity was stabilized and analyzed by gas chromatographs [25].

## 3. Results and discussion

### 3.1. Dispersion and reducibility of Ni supported on MgAlO

Table 1 shows the results of adsorptions of H<sub>2</sub> and O<sub>2</sub> on the catalysts. It is seen that all the Ni/MgAlO catalysts exhibited the high densities of surface Ni sites as titrated by the adsorption of H<sub>2</sub> (889–1040  $\mu$ mol/g), in which the one with the MgO/Al<sub>2</sub>O<sub>3</sub> ratio of 3 (30/10) possessed the highest H<sub>2</sub> uptake (1040  $\mu$ mol/g) and active Ni surface area (81.4 m<sup>2</sup>/g). The average sizes of Ni particles were small (3.5–4.1 nm) in these catalysts, as estimated by the uptakes of H<sub>2</sub> and O<sub>2</sub>. These catalysts were then phosphided at 443 K with PPh<sub>3</sub> in liquid phase, and the corresponding Ni<sub>2</sub>P catalysts were obtained.

### 3.2. Properties of fresh and used Ni<sub>2</sub>P/MgAlO catalysts

The XRD patterns of phosphided samples were shown in Fig. 1(a). The diffraction peaks around 40.7°, 44.6°, 47.4°, 54.2° and 66.4° attributed to Ni<sub>2</sub>P (PDF 65-1989) were clearly observed for all the samples. The intensities of these diffraction peaks increased with the increase of MgO content, due to that the size and content of Ni particles in the Ni/MgAlO catalysts increased with the increase of MgO content (see Table 1). According to the broadening of 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 fresh Ni<sub>2</sub>P/MgAlO catalysts were estimated and found to increase with the increase of MgO content (see Table 2).

Fig. 2(b) shows the XRD patterns of the phosphided catalysts after the hydrotreating reactions. Ni<sub>2</sub>P was the only detected phase

**Table 1.** Uptakes of adsorbed H<sub>2</sub> and O<sub>2</sub> on the 60%Ni/MgAlO catalysts with different MgO/Al<sub>2</sub>O<sub>3</sub> ratios reduced in H<sub>2</sub> at 723 K.

MgO/Al <sub>2</sub> O <sub>3</sub>	5/35	10/30	20/20	30/10	35/5
H <sub>2</sub> adsorption ( $\mu$ mol/g)	889	947	996	1040	925
O <sub>2</sub> adsorption ( $\mu$ mol/g)	3114	3357	3588	3797	3802
Dispersion (%)	28.5	28.2	27.8	27.4	24.3
Reducibility (%)	70.9	76.4	81.7	86.4	86.6
Ni particle size, <i>d</i> (nm)	3.5	3.6	3.6	3.7	4.1
Ni surface area (m <sup>2</sup> /g)	69.6	74.1	78.0	81.4	72.4

Download English Version:

<https://daneshyari.com/en/article/63657>

Download Persian Version:

<https://daneshyari.com/article/63657>

[Daneshyari.com](https://daneshyari.com)