



## Full Length Article

Influence of Si/Al molar ratio on the hydrogenation, isomerization and ring opening of naphthalene over silica-alumina supported Ni<sub>2</sub>P catalyst

Sha Cui, Genggeng Wang, Ying Yang, Baijun Liu\*

State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum, Beijing 102249, People's Republic of China

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## ABSTRACT

Ni<sub>2</sub>P catalysts supported on amorphous silica-alumina (ASA) with various Si/Al molar ratios (*n*) of ∞, 3.40, 1.28, 0.57, 0.21, 0.10 and 0, were prepared using a co-impregnation method followed by temperature-programmed reduction. The resultant Ni<sub>2</sub>P/ASA-*n* catalysts were characterized by means of X-ray diffraction (XRD), N<sub>2</sub> adsorption and desorption, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), temperature-programmed ammonia desorption (NH<sub>3</sub>-TPD) and FTIR spectroscopy of adsorbed pyridine (Py-IR). The catalytic properties were tested towards naphthalene hydrogenation, isomerization and ring opening in a fixed bed reactor under the following reaction conditions of *P* = 4 MPa, *LHSV* = 3 h<sup>-1</sup>, H<sub>2</sub>/oil = 600 volume ratio and *T* = 360 °C. It is found that the superior naphthalene hydrogenation ability was obtained over the Ni<sub>2</sub>P/ASA-0.57 catalyst, while higher isomerization and ring opening activity were achieved using Ni<sub>2</sub>P/ASA-0.21 as the catalyst. It is concluded that the high naphthalene hydrogenation capacity is relevant to the small Ni<sub>2</sub>P particle size and the isomerization and ring opening activity mainly depends on the acid amount of catalyst.

## 1. Introduction

In pace with the diminishing quality of oil feedstocks coupled with increasingly more severe fuel specifications, it has received increased attention recently to produce transportation fuels and non-road fuels with low level of sulfur and aromatics [1,2]. Polycyclic aromatic content is mandated to be reduced to less than 11% in the Europe V standard, and even less than 7% in the coming Europe VI standard. Polycyclic aromatics not only decrease cetane number and combustion efficiency of diesel oil, but also increase particulate matters and pollutant emissions, such as NO<sub>x</sub> emissions and carcinogenic granules [3–6]. Hence, it is highly desirable to remove aromatics from petroleum feedstocks.

Traditionally, polycyclic aromatics can be reduced through hydrogenation and hydrocracking processes [7], leading to the increase of the cetane value (CN). The increase, however, is insufficient through pure aromatic saturation. Hydrocracking may bring a significant CN improvement yet produce a large number of gas leading to a low diesel output. Therefore, ring opening of aromatics without a reduction in carbon number of the product molecular is required.

Phosphides are believed to be promising hydrogenation catalysts because of their intrinsically high catalytic activity, multimetallic forms and easy reduction as well as the lack of layered structure which can lead to a potentially better exposure of surface metal atoms [8].

Transition metal phosphides have been reported as highly active, stable hydroprocessing catalysts [2,9–14], and show excellent heat and electricity conductivity as well as high thermal and chemical stability [10,15,16]. As demonstrated, nickel phosphide (Ni<sub>2</sub>P) was the most active among all phosphides and had been used as the active constituents of catalysts for hydrodesulfurization (HDS) and hydrodenitritication (HDN) [1,8,10,14,15]. Whereas, it is scarcely reported the utilization of transition metal phosphides for aromatic hydrogenation and its isomerization and ring opening reactions [8,17,18], let alone their high catalytic performances.

It has been demonstrated that the support, as a key component of heterogeneous catalyst, can influence the dispersion and morphology of active sites, and thus the catalytic property, and also can render possible metal-support interactions (MSI). And thereby the development of novel supports has received increased interest in recent years [19]. Typically, silica is the most commonly used support for phosphides, due to its relatively inert nature and very weak affiliation to the active species, beneficial to the preparation of phosphide catalyst [8]. However, weaker acidity and MSI in silica supported catalysts are detrimental to catalytic activity, activity stability and sulfur tolerance. Alternatively, utilization of alumina could increase the support interaction with P by the formation of AlPO<sub>4</sub> [20,21], nevertheless, a decrease in the catalytic activity originated from the loss of active components and even the destruction of the surface texture of catalyst

\* Corresponding author.

E-mail address: [bjliu2017@163.com](mailto:bjliu2017@163.com) (B. Liu).

cannot be avoided. Apart from the silica and alumina, other supports such as carbon [22], MgO [23], and MCM-41 [25,26], SBA [18,24] and USY zeolite [19] were applied for immobilization of phosphides. Moreover, amorphous silica-alumina (ASA) as a composite carrier possesses more acid sites [27,28] and mezzo metal-support interaction [29] as compared to carbon, magnesia, alumina and silica, and its preparation procedure is simpler and preparation cycle is shorter as opposed to zeolite. Though, the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  support has been used for metal sulfide or reductive metal catalysts, receiving a high hydrogenation activity of aromatic [30–34], no literatures concentrated on silica-alumina supported nickel phosphide catalysts are studied for aromatic hydrogenation and ring opening reactions.

Naphthalene, as a representative polycyclic aromatic, occupies a large proportion in many kinds of oils. Take the high temperature coal tar in Shenmu county of Shanxi for example, the proportion of naphthalene is the range of 8–12%, which is higher than the total amount of other aromatic hydrocarbons content [35]. Inspired by these studies, here we report the amorphous silica-alumina supported  $\text{Ni}_2\text{P}$  catalysts and discusses the effect of Si/Al molar ratio on the physical-chemical properties and hydrogenation, isomerization and ring opening activity of naphthalene.

## 2. Experimental

### 2.1. Support preparation

A series of amorphous silica-aluminum with various Si/Al molar ratio, including  $\infty$  ( $\text{SiO}_2$ ), 3.40, 1.28, 0.57, 0.21, 0.10 and 0 ( $\text{Al}_2\text{O}_3$ ), were prepared by a stepwise precipitation method using  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and water glass as the raw materials, and  $\text{NH}_4\text{-H}_2\text{O}$  as the precipitant. The as-prepared ASA materials have similar specific surface area (Table 1) by controlling the preparation conditions. Before being used as supports, the ASA were tablet compressed, calcined, grounded and screened to obtain 20–40 mesh objective particles and named  $\text{SiO}_2$ , ASA-3.40, ASA-1.28, ASA-0.57, ASA-0.21, ASA-0.10 and  $\text{Al}_2\text{O}_3$  respectively.

### 2.2. Catalyst preparation

The supported nickel phosphide catalysts were prepared using a co-impregnation method followed by temperature-programmed reduction in  $\text{H}_2$  atmosphere. Typically, 5 g of amorphous silica-alumina support (ASA) was impregnated in a solution containing nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and ammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ) dissolved in the presence of several drops of nitric acid. During synthesis, the content of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is fixed to be 10 mmol, while the amount of  $(\text{NH}_4)_2\text{HPO}_4$  is varied, yielding catalyst precursors with diverse Ni/P ratios. After being dried at 120 °C and calcined at 550 °C for 3 h. The catalyst precursor was converted to the active nickel phosphide by temperature-programmed reduction (TPR) in  $\text{H}_2$  (1 atm) at a flow rate of 150 mL/min and at 650 °C for 3 h with a temperature ramp rate of 2 °C/min. After the reduction, the catalyst was naturally cooled to room temperature in  $\text{N}_2$  atmosphere. Then, the supported  $\text{Ni}_2\text{P}$  catalyst was passivated in 0.5%  $\text{O}_2/\text{N}_2$  for 6 h at room temperature. And, the

catalysts with various Si/Al molar ratio were denoted to  $\text{Ni}_2\text{P-Si}$  ( $\text{Ni}_2\text{P}/\text{ASA}-\infty$ ),  $\text{Ni}_2\text{P}/\text{ASA}-3.40$ ,  $\text{Ni}_2\text{P}/\text{ASA}-1.28$ ,  $\text{Ni}_2\text{P}/\text{ASA}-0.57$ ,  $\text{Ni}_2\text{P}/\text{ASA}-0.21$ ,  $\text{Ni}_2\text{P}/\text{ASA}-0.10$  and  $\text{Ni}_2\text{P-Al}$  ( $\text{Ni}_2\text{P}/\text{ASA}-0$ ). And the Ni and P elemental ratio (checked by Inductive Coupled Plasma (ICP) measurements) of all prepared catalysts is shown in Table 1.

### 2.3. Catalyst characterization

XRD analysis was performed using a Bruker AXSD8 Advance X-ray diffractometer with nickel-filtered Cu K $\alpha$ X-ray radiation at 40 kV and 30 mA. The samples were scanned from 10° to 80° with a scanning rate of 2°/min. For the measurements, the sample was pressed into a flatbed sample holder. The assignment of crystalline phases is on the basis of the powder diffraction file cards.

The elemental composition of the catalysts was determined by ICP-OES and taken on an OPTIMA 7300 V analyzer.

Nitrogen adsorption-desorption was performed using a Bilder KuboX1000 system at liquid nitrogen temperature. Prior to the measurement, the samples were outgassed in vacuum at 300 °C for 3 h. The specific surface area is determined based on the theory of BET.

The morphologies, dispersion and particle size of nanoparticles were acquired on a JEM-2100 LaB<sub>6</sub> high resolution transmission electron microscope (TEM) equipped with maximum acceleration voltage of 200 kV, amplification factor of  $50 \times \sim 1500 \times$ , sample maximum inclination angle of  $\pm 35^\circ$  and energy spectrometer element of 5 B  $\sim 92$  U. Prior to analysis, the sample was dispersed in ethanol solution, and then coated on the thin carbon film.

X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Fisher K-Alpha X-ray photoelectron spectrometer with an optimum analytical vacuum of  $5 \times 10^{-9}$  mbar of analysis room. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE). The data obtained are dealt with peak fitting using XPSPEAK software.

Temperature-programmed ammonia desorption ( $\text{NH}_3\text{-TPD}$ ) of the catalysts were measured on a TPD/TPR 5079 analyzer. A total of 200 mg of catalyst was placed in a quartz reactor and pretreated in a He flow and then reduced in  $\text{H}_2$  flow at 400 °C for 1 h. The pretreated catalysts were exposed to ammonia at 30 °C for 20 min to ensure adsorption saturation. When the weakly adsorbed ammonia was removed, the  $\text{NH}_3\text{-TPD}$  profile was recorded from 100 °C to 600 °C at a heating rate of 10 °C/min.

The Fourier transform infrared spectroscopy of adsorbed pyridine (Py-IR) was taken on a Magna-IR 560 ESP spectrophotometer. The catalysts were pretreated at 400 °C for 1 h in a vacuum, and then cooled to 100 °C for pyridine adsorption. Py-IR spectra were recorded in the range of 1600–1400  $\text{cm}^{-1}$  at 200 and 350 °C. The data obtained at 200 °C are categorized as total acid and at 350 °C as the medium and strong acid.

### 2.4. Catalytic activity

The catalytic activity of  $\text{Ni}_2\text{P}/\text{ASA-n}$  catalysts was tested towards the naphthalene hydrogenation and ring opening reactions in a continuous down-flow fixed bed reactor. The feedstock comprised of 5 wt% naphthalene in heptane was introduced by a double plunger pump. Prior to measurement, the calcined catalysts was in situ reduced in flowing pure  $\text{H}_2$  (150 mL/min) from room temperature to 650 °C and maintained at this temperature for 3 h. After reduction, the reactor was cooled in  $\text{H}_2$  atmosphere to the specified reaction temperature. Then 15 mL/h of liquid feed was introduced to the reactor. The products collected were analyzed by GC-MS. Fresh catalysts were used for each operation to ensure no catalyst deactivation.

**Table 1**  
Elemental analysis results.

Catalyst	Si/Al	Ni/(Si + Al)	Ni/P
$\text{Ni}_2\text{P-Si}$	$\infty$	0.120	1.823
$\text{Ni}_2\text{P}/\text{ASA}-3.40$	3.24	0.116	1.789
$\text{Ni}_2\text{P}/\text{ASA}-1.28$	1.29	0.113	1.770
$\text{Ni}_2\text{P}/\text{ASA}-0.57$	0.51	0.108	1.816
$\text{Ni}_2\text{P}/\text{ASA}-0.21$	0.25	0.104	1.790
$\text{Ni}_2\text{P}/\text{ASA}-0.10$	0.13	0.103	1.800
$\text{Ni}_2\text{P/Al}$	0	0.103	1.768

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