



## Full Length Article

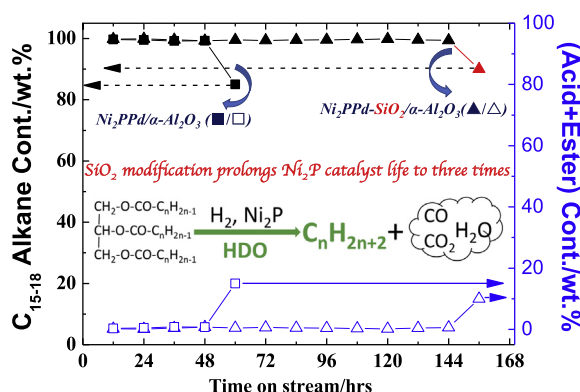
## Improvement of hydrodeoxygenation stability of nickel phosphide based catalysts by silica modification as structural promoter

Xuguang Liu<sup>a</sup>, Zhenyu Li<sup>a</sup>, Baoquan Zhang<sup>a,b,\*</sup>, Maocong Hu<sup>c,\*</sup><sup>a</sup> College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China<sup>b</sup> State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China<sup>c</sup> Department of Chemical, Biological and Pharmaceutical Engineering, New Jersey Institute of Technology, Newark, NJ 07102, USA

## HIGHLIGHTS

- SiO<sub>2</sub> added to Ni<sub>2</sub>P based catalysts as structural promoter.
- Life of catalyst with modification was prolonged to three times of the unmodified one.
- SiO<sub>2</sub> retarded the transformation of the active phase Ni<sub>2</sub>P.
- Carbon deposition originating from metallic nickel was reduced with SiO<sub>2</sub> addition.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 4 March 2017

Received in revised form 9 May 2017

Accepted 16 May 2017

Available online 23 May 2017

## Keywords:

Hydrodeoxygenation

Catalytic stability

Nickel phosphide (Ni<sub>2</sub>P)

Silica promoter

Biodiesel

## ABSTRACT

This study proposed a novel and facile approach to promote the stability of nickel phosphide (Ni<sub>2</sub>P) based catalysts by adding silica (SiO<sub>2</sub>) as structural promoter under hydrothermal condition. Catalytic hydrodeoxygenation (HDO) of triglyceride using soybean oil as model feed over Ni<sub>2</sub>P and palladium supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Ni<sub>2</sub>PPd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) with and without SiO<sub>2</sub> addition was conducted. With SiO<sub>2</sub> modification, the catalyst was stable for 144 h which is three times of that from the unmodified one, while higher than 99.0 wt.% conversion was achieved with green diesel (i.e., C<sub>15-18</sub> alkane) as the main products. H<sub>2</sub>-TPD, NH<sub>3</sub>-TPD, and XRD over fresh catalysts proved that SiO<sub>2</sub> addition exhibited no distinguishing effect on hydrogen chemisorption ability and active phase. XRD, TEM, XPS, EDX, XRF, H<sub>2</sub>-TPR, N<sub>2</sub> physisorption, and TG/IR over fresh or/and spent catalysts demonstrated that SiO<sub>2</sub> was a structural stability promoter (spacer), hindering the transformation of the active phase Ni<sub>2</sub>P. Furthermore, carbon deposition during the HDO process due to exist of metallic nickel was reduced with SiO<sub>2</sub> addition. This work demonstrated that Ni<sub>2</sub>P supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> modified by SiO<sub>2</sub> (Ni<sub>2</sub>PPd-SiO<sub>2</sub>/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) was a promising catalyst for the hydrodeoxygenation (HDO) of triglyceride to produce green diesel. With further work, it may lead to a catalyst capable for HDO in industry.

© 2017 Elsevier Ltd. All rights reserved.

\* Corresponding authors at: Department of Chemical, Biological and Pharmaceutical Engineering, New Jersey Institute of Technology, Newark, NJ 07102, USA (M. Hu).

E-mail addresses: [bqzhang@tju.edu.cn](mailto:bqzhang@tju.edu.cn) (B. Zhang), [mh325@njit.edu](mailto:mh325@njit.edu) (M. Hu).

## 1. Introduction

The so-called green diesel (i.e. sulphur-free C<sub>15-18</sub> alkane) produced by catalytic hydrodeoxygenation (HDO) of triglyceride with

waste vegetable oils, animal fats, or recycled restaurant grease as feed has been gained much attention [1–3], because it can consume waste while simultaneously achieving high valuable products [4,5]. Industrial hydrotreating catalysts (i.e. supported transition metal and their sulfide) were attempted in the HDO of triglyceride in consideration of their successful application experience in the petroleum industry [6–9]. Unfortunately, transition metal sulfide such as supported NiMoS catalysts deactivated rapidly in HDO of triglyceride due to the inherently ultra-low sulphur in feed [10,11]. With the Mars van Krevelen mechanism, this deactivation phenomena can be hindered by adding a small amount of sulphur in the feed [12,13]. Accordingly, the residual sulphur in the products would be an issue for producing sulphur-free green diesel. Moreover, the trace amount of produced water would accelerate the leaching process and severely shorten the lifetime of these sulfided catalysts. The transition metal catalysts, such as Ni, Co, Pd, Pt, and Rh, showed similar deactivation phenomena as a result of carbon deposition [14]. Therefore, it was attractive and critical to develop stable and active non-sulfided catalysts for HDO of triglyceride.

Nickel phosphide ( $\text{Ni}_2\text{P}$ ), an alternative catalyst for catalytic hydroprocessing like hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), was also proved to be active in the HDO process [15–18]. It demonstrated high structural stability under ultra-low sulphur conditions [19,20]. However, deactivation of  $\text{Ni}_2\text{P}$  during the HDO, HDS or HDN were widely reported in many studies due to carbon deposition and loss of phosphorus in  $\text{Ni}_2\text{P}$  crystal, leading to transformation of  $\text{Ni}_2\text{P}$  to  $\text{Ni}_{12}\text{P}_5$  [21–25]. On the other hand, the high reduction temperature for preparation of  $\text{Ni}_2\text{P}$  catalysts may result into active sites aggregation and accordingly activity decrease [26]. One recently developed approach lowering reduction temperature is adding second metals (Pd, Ti, Co, Mo, W, and Y et al.) [27–30]. Surprisingly, to our best knowledge, few public literatures reported on improving the stability of  $\text{Ni}_2\text{P}$  in HDO, which is crucial for developing a promising industrial catalyst [31–33].

In this study, silica ( $\text{SiO}_2$ ) was added to  $\alpha\text{-Al}_2\text{O}_3$  supported nickel phosphide ( $\text{Ni}_2\text{P}$ ) and trace palladium ( $\text{Ni}_2\text{PPd}/\alpha\text{-Al}_2\text{O}_3$ ) catalyst as promoter. The trace Pd was employed to lower the catalysts preparation temperature while the intrinsic macroporous structure of  $\alpha\text{-Al}_2\text{O}_3$  allows it to be suitable for the macromolecule reaction of HDO [34,35]. Catalytic HDO of triglyceride over  $\text{Ni}_2\text{PPd}/\alpha\text{-Al}_2\text{O}_3$  with and without  $\text{SiO}_2$  addition were conducted to investigate the effect of  $\text{SiO}_2$  addition on the catalytic performance including conversion and stability. Characterization techniques including  $\text{H}_2$ -TPD,  $\text{NH}_3$ -TPD, XRD, TEM, XPS, EDX, XRF,  $\text{H}_2$ -TPR,  $\text{N}_2$  physisorption, and TG/IR were carried out over fresh and/or spent  $\text{Ni}_2\text{PPd}/\alpha\text{-Al}_2\text{O}_3$  and  $\text{Ni}_2\text{PPd-SiO}_2/\alpha\text{-Al}_2\text{O}_3$  catalysts to examine physicochemical properties and investigate the promotion effect due to  $\text{SiO}_2$  addition. This work developed a novel and facile approach to promote the stability of  $\text{Ni}_2\text{P}$  based catalysts in catalytic hydroprocessing, which aims to a catalyst capable for industrial HDO in the future.

## 2. Experimental

### 2.1. Synthesis of catalyst

Nickel phosphide ( $\text{Ni}_2\text{P}$ ) supported on  $\alpha\text{-Al}_2\text{O}_3$ , containing few amount of palladium (Pd), was prepared by temperature programmed reduction method with a final temperature of 768 K following the procedures in our previous work [34,36]. Typically,  $\alpha\text{-Al}_2\text{O}_3$  sphere support (with diameter of 2–3 mm, pore volume of  $0.6\text{ cm}^3/\text{g}$ ) was incipient co-impregnated with a mixture solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ , and  $\text{PdCl}_2$ . The molar concentrations

of  $[\text{Ni}^{2+}]$ ,  $[\text{PO}_4^{3-}]$ , and  $[\text{Pd}^{2+}]$  in that mixture solution were adjusted to be 2.0, 1.6, and 0.01 mol/L, respectively. The impregnated sample was subsequently dried at 333 K for 6 h, followed by calcination at 673 K for 3 h. The resulting sample was incipient re-impregnated with above mixture solution, followed by drying and calcination. The obtained precursor was temperature-programmed reduced to nickel phosphides at 768 K. The resulting catalyst, hereinafter, was labeled as  $\text{Ni}_2\text{PPd}/\alpha\text{-Al}_2\text{O}_3$ . Ni and Pd content in  $\text{Ni}_2\text{PPd}/\alpha\text{-Al}_2\text{O}_3$  were determined to be 10 wt.% and 0.1 wt.%, respectively.

Silica ( $\text{SiO}_2$ ) modified  $\text{Ni}_2\text{PPd}/\alpha\text{-Al}_2\text{O}_3$ , denoted as  $\text{Ni}_2\text{PPd-SiO}_2/\alpha\text{-Al}_2\text{O}_3$ , was prepared by a combination of impregnation and hydrothermal treatment method. Firstly, silica sol ( $\text{SiO}_2$ , 10 wt.%) was obtained by hydrolyzing TEOS (tetraethyl orthosilicate) in TPAOH aqueous solution (25 wt.%) [37], and impregnated with  $\text{Ni}_2\text{PPd}/\alpha\text{-Al}_2\text{O}_3$  precursor (the sample prior to temperature-programmed reduction). The wetting sample was then transferred into a Teflon linked autoclave, and heated for 48 h at 353 K. The resulting sample was recovered and dried for 3 h at 333 K, followed by calcination for 3 h at 673 K. The temperature programmed reduction was further performed with a same procedure as that of  $\text{Ni}_2\text{PPd}/\alpha\text{-Al}_2\text{O}_3$ .  $\text{Ni}_2\text{PPd-SiO}_2/\alpha\text{-Al}_2\text{O}_3$  contained the same Ni and Pd content as those of  $\text{Ni}_2\text{PPd}/\alpha\text{-Al}_2\text{O}_3$  and ca. 2 wt.%  $\text{SiO}_2$  acting as a promoter.  $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$  with trace Pd content of 0.1 wt.% was prepared by impregnation method as the reference.

### 2.2. Characterization

Powder XRD patterns were collected within a range of  $2\theta = 20\text{--}70^\circ$  on a Rigaku D-max2500v/pc X-ray diffractometer equipped with  $\text{Cu-K}\alpha$  radiation. The used step size was  $0.02^\circ$  (step time 1.0 s). Surface elemental composition of samples was analyzed through Energy Dispersive X-ray Spectroscopy (EDX) on an Oxford Instrument. Bulk composition of the samples was analyzed by X-ray fluorescence (XRF) on a FLS920 instrument (Edinburgh Instruments). Transmission electron microscopy (TEM) images of the passive fresh catalysts were taken with a JEM-100CXII microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were collected using a Thermo ESCALAB 250Xi with non-monochromatic Al KR radiation (300 W, 15 kV, and 1486.6 eV) equipped with a multi-channel detector. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). Fresh and spent samples were passivated before XPS analysis.  $\text{H}_2$ -Temperature programmed reduction ( $\text{H}_2$ -TPR) experiment was performed on an AutoChem 2920 (Micromeritics). Samples of weight  $50 \pm 5\text{ mg}$  were loaded in an U type reactor, and heated to 1123 K with a ramp of 5 K/min in a 50 mL/min  $\text{H}_2/\text{Ar}$  (10 v.%) flow [38].  $\text{H}_2$ -Temperature programmed desorption ( $\text{H}_2$ -TPD) profile was gained on the same equipment. Typically, the obtained catalysts of weight  $50 \pm 5\text{ mg}$  were loaded in the U type reactor and reduced in a 50 mL/min  $\text{H}_2/\text{Ar}$  (10 v.%) flow at 623 K, followed by cooling to room temperature.  $\text{H}_2$ -TPD subsequently was performed with a ramp of 5 K/min in a 20 mL/min Ar (99.999%) flow.  $\text{NH}_3$ -Temperature programmed desorption ( $\text{NH}_3$ -TPD), after adsorbing  $\text{NH}_3$  for 30 min at 323 K, was carried out in a 20 mL/min He (99.999%) flow following the same temperature program of the  $\text{H}_2$ -TPD. Nitrogen physisorption measurements were performed on an AutoChem 2020 Analyzer (Micromeritics). Before analysis, samples were dried at 473 K for 3 h in  $\text{N}_2$  (99.999%) atmosphere. The surface area was calculated using a BET method on the basis of adsorption branch in a 0.05–0.30 partial pressure range. A Non-Local Density Functional Theory (NLDFT) method was used to reveal the pore size and pore volume. Thermogravimetric (TG, NETZSCH TG 209) analysis coupled with Infrared (IR) spectra was performed in an air flow (10 mL/min), with a heating ramp of 20 K/min. Effluent of the TG analysis was correspondingly mea-

Download English Version:

<https://daneshyari.com/en/article/4768659>

Download Persian Version:

<https://daneshyari.com/article/4768659>

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