Preparation of core-shell structured Ni$_2$P/Al$_2$O$_3$@TiO$_2$ and its hydrodeoxygenation performance for benzofuran

CrossMark

Hua Song [a,*], Jing Gong [a], Hua-Lin Song [b], Feng Li [a], Jian Zhang [a], Yan-Guang Chen [a]

[a] College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, China
[b] Key Laboratory of Cancer Prevention and Treatment of Heilongjiang Province, Mudanjiang Medical University, Mudanjiang 157011, Heilongjiang, China

ARTICLE INFO

ABSTRACT

Highly active Ni$_2$P catalyst supported on core-shell structured Al$_2$O$_3$@TiO$_2$ for hydrodeoxygenation (HDO) of benzofuran (BF) was prepared and the effect of water on the performance for BF HDO over as-prepared catalyst was studied. The hydrophobic TiO$_2$ shell can enhance the catalytic activity, water resistance and HDO stability of the Ni$_2$P/Al$_2$O$_3$ catalyst. The Ni$_2$P/A@T exhibited the highest HDO activity of 95% with O-free products yield of 87%, which is an increase of 40% when compared with that found for Ni$_2$P/Al$_2$O$_3$ (47%).

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The increasing environmental concerns create the need to develop alternative methods of energy production from renewable sources, including biomass. One method of biomass conversion is pyrolysis [1], but unfortunately the liquid products obtained by pyrolysis contain a high fraction of oxygen (35–50 wt.%), which can result in higher viscosity, acidity, and lower heating values [2]. A method for upgrading pyrolysis oil is hydrodeoxygenation (HDO) [3]. Most recently, transition metal phosphides, especially Ni$_2$P catalysts, have been proposed as viable low-cost alternatives to precious metals [4,5].

The macroporous γ-Al$_2$O$_3$ with high thermal stability and large surface area has been extensively used as a support for catalysts. However, phosphorus interacts strongly with γ-Al$_2$O$_3$, in many cases resulting in the formation of aluminum phosphates such as AlPO$_4$ on the surface of the support [6]. Moreover, the Al$_2$O$_3$ is known to cause coke deposition and rapid deactivation in the HDO, particularly in the presence of water [7]. Our previous work showed that TiO$_2$ can inhibit the formation of AlPO$_4$, and act as an electronic promoter for the Ni–P catalyst [8]. Recently, a great deal of interest has been devoted worldwide to studying core-shell structured supports and catalysts due to their unique physical and chemical properties [9]. The shell enhances selectivity for the target products and protects the catalyst from rapid poisoning. The TiO$_2$ has been extensively used in catalytic fields for its unique high activity and specific electronic effect. The use of hydrophobic TiO$_2$ as shell

could be beneficial in maintaining the HDO activity and protecting from rapid poisoning by the HDO product H$_2$O. Therefore, TiO$_2$ might be one of the promising shell materials. However, to the best of our knowledge, no studies have been reported concerning TiO$_2$ shell supports for HDO reactions. Hence, it is interest to investigate the effect of the TiO$_2$ shell which coated on the commercial large surface area Al$_2$O$_3$ core on the HDO performance of nickel phosphide catalysts.

In the present study, the Al$_2$O$_3$@TiO$_2$ core-shell support was prepared by depositing the hydrophobic TiO$_2$ shell on the surface of commercial large surface area Al$_2$O$_3$ core. And the supported Ni$_2$P/Al$_2$O$_3$@TiO$_2$ core-shell catalyst was synthesized according to a previously described method [10] at a relatively low reduction temperature of 673 K. The effect of water on the performance for benzofuran hydrodeoxygenation over as-prepared catalyst was studied.

2. Experimental

2.1. Preparation of core-shell structured supports and catalysts

The commercial γ-Al$_2$O$_3$ beads (Qingdao Haiyang Chemicals Co., Ltd. 257 m^2·g^{-1}) were rinsed with deionized distilled water and alcohol and then calcined in air for 3 h at 823 K before used.

For Al$_2$O$_3$@TiO$_2$ (A@T), the Al$_2$O$_3$ beads was treated in 0.1 M ammonia solution at 373 K and then dried at 313 K. Then, the resulting mixture was dissolved and impregnated in ethanol for 48 h, and dried at 313 K. Finally, calculated amount of the tetra-n-butyl-titanate was dissolved into anhydrous ethyl alcohol, and then dripped into hydrolysis inhibitor of triethanolamine to obtain a uniform and stable emulsion liquid. The treated Al$_2$O$_3$ beads and TiO$_2$ emulsion liquid was transferred

* Corresponding author.
  E-mail address: songhua2004@sina.com (H. Song).

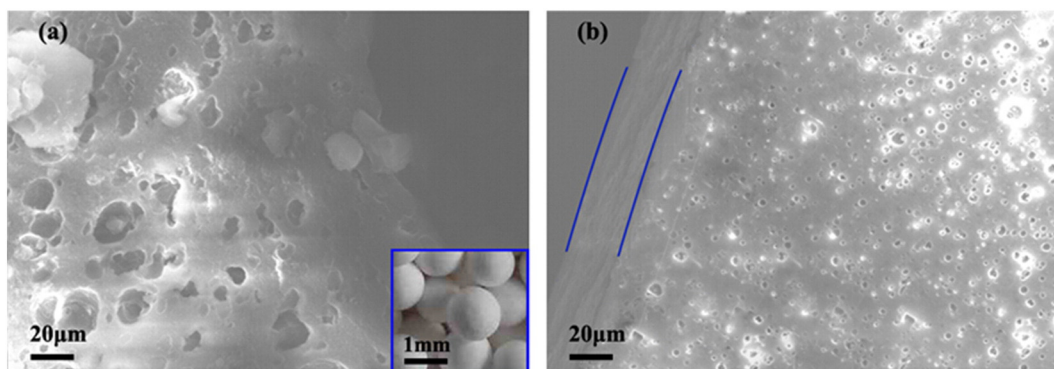**Fig. 1.** SEM cross-sections of catalysts: (a) Ni_2P/Al_2O_3, (b) $Ni_2P/A@T$.

to a Teflon vessel. The mixture was then kept rotating with a rotation speed of 3 rpm for 72 h at 313 K in rotating oven. The obtained sample was dried in air at 393 K and calcined at 823 K. The schematic of the synthetic procedure of the core-shell structured support as detailed in the supplementary information section, Part 1. For comparison, the TiO_2 supports were prepared using the sol–gel method as described previously [11].

The supported Ni_2P catalyst precursor was prepared by impregnating an ammonium hypophosphite ($NH_4H_2PO_2$) and nickel chloride ($NiCl_2 \cdot 6H_2O$) solution with the Al_2O_3 and A@T supports [12]. The precursor, was prepared with Ni loading of 8.8 wt.% and an initial Ni/P molar ratio of 1/2. Finally, the supported Ni_2P catalysts were reduced and surface modification with oxygen as our previous study [12]. The catalysts obtained were named as Ni_2P/Al_2O_3 and $Ni_2P/A@T$, respectively. For comparison test, the Ni_2P/TiO_2 was also prepared.

2.2. Characterization methods

The samples were halved with a clean blade and mounted on a holder for examination under scanning electron microscope (SEM, JSM-5600LV). The XRD analysis was carried out on a D/max-2200PC-X-ray diffractometer using CuKα radiation under the setting conditions of 40 kV, 30 mA. The typical physico-chemical properties of supports and catalysts were analyzed by BET method using Micromeritics adsorption equipment of NOVA2000e. The CO adsorption capacities of catalysts were measured after surface modification with oxygen without re-reduction using a Builder PCA-1200 analyzer.

2.3. Catalytic activities

The HDO of BF over prepared Ni_2P/Al_2O_3 and $Ni_2P/A@T$ catalysts were performed in a flowing high-pressure fixed-bed reactor (8 mm in diameter, and 400 mm in length), using a feed consisting of a decalin solution of BF (2 wt.%). Catalytic activities were measured at 3.0 MPa, WHSV = 4 h^{-1}, and hydrogen/oil ratio of 500 (V/V). Sampling of liquid products was started 6 h after the steady reaction conditions had been achieved. The feed and reaction product was analyzed by FID gas chromatography with a GC-14C-60 column. The total conversion was calculated from the ratio of converted benzofuran/initial benzofuran. The selectivity to the different reaction products was calculated based on the moles of each chemical.

In order to study the impact of water on the performance of supported Ni_2P catalysts, the mixture of the decalin solution of BF (2 wt.%), and water (1 wt.%) were fed to the fixed-bed reactor separately by using two pumps. They were heated in a pre-heating furnace and mixed before enter the reactor. The effect of water in feed on the HDO of BF over prepared Ni_2P/Al_2O_3 and $Ni_2P/A@T$ catalysts were performed at the same condition.

3. Results and discussion

3.1. SEM

The morphologies of cross-sections of Ni_2P/Al_2O_3 and $Ni_2P/A@T$ were observed by SEM. As can be seen from Fig. 1a, clearly the cross-section of Ni_2P/Al_2O_3 catalyst shows some macroporous. For the $Ni_2P/A@T$ catalyst (Fig. 1b), a uniform TiO_2 shell deposited on the surface of the Al_2O_3 core could clearly be seen. The thickness of this TiO_2 shell layer was about 25 μm. This core-shell structure matched our original intention.

3.2. XRD

The XRD spectra for the γ-Al_2O_3 support, Ni_2P/Al_2O_3 and $Ni_2P/A@T$ catalysts are presented in the supplementary information section, Part 2. All samples showed clear Al_2O_3 peaks at 2θ = 45.59° and 67.37° characteristic of the γ-Al_2O_3 phase. In addition, no distinct diffraction peak corresponding to a crystalline phase of anatase TiO_2 was observed for $Ni_2P/A@T$ catalyst. The result confirmed that the content of anatase TiO_2 particles was well below the detectable limit of XRD (5 nm) or was highly dispersed on the surface. All of the catalysts showed a weak peak at 40.6° corresponding to the characteristic peak of Ni_2P (PDF: 03–0953), showing the presence of highly dispersed Ni_2P particles. No additional phase containing Ni and P was observed, indicating that the active phase formed was mainly Ni_2P for all of the catalysts.

3.3. Textural properties

The structural parameters of the supports and catalysts are shown in Table 1. The surface area and pore volume of the Al_2O_3 bead support used were 257 $m^2 \cdot g^{-1}$ and 0.7 $cm^3 \cdot g^{-1}$, respectively. In comparison to Al_2O_3, the A@T support showed a decrease in specific surface area (S_{BET}) with lower pore volume (V_{BJH}) and lower pore diameter (D). These structural changes could be attributed to the TiO_2 shell layer formed on the surface of the Al_2O_3. It can be seen that both catalysts led to decreases in S_{BET} and V_{BJH} due to blocking of their pores by Ni_2P. The catalyst Ni_2P/Al_2O_3 showed a surface area of 128 $m^2 \cdot g^{-1}$, whereas that of $Ni_2P/A@T$ was higher at 156 $m^2 \cdot g^{-1}$.

Table 1
Textural properties of supports and catalysts.

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	V_{BJH} ($cm^3 \cdot g^{-1}$)	D^a (nm)
Al_2O_3	257	0.70	10.9
A@T	246	0.52	8.5
Ni_2P/Al_2O_3	128	0.33	10.3
$Ni_2P/A@T$	156	0.32	8.2

D^a: pore diameter, $D \approx 4V_{BJH}/S_{BET}$.

دانلود مقاله