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Production of high-grade diesel from palmitic acid over activated carbon-supported nickel phosphide catalysts

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ABSTRACT

A series of activated carbon (AC)-supported nickel phosphide catalysts were prepared; characterized using XRD, XPS, TEM, and NH_3-TPD techniques; and evaluated for the deoxygenation of palmitic acid. The formation of Ni_2P and/or $Ni_{12}P_5$ on the surface of AC could be controlled by controlling the Ni/P molar ratios. With low Ni/P molar ratios from 0.5 to 0.8, only crystalline Ni_2P formed. Both Ni_2P and $Ni_{12}P_5$ formed with Ni/P ratios of 1.0 and 1.5, whereas only $Ni_{12}P_5$ formed with a Ni/P ratio of 2.0. As the Ni/P ratio further increased (Ni/P $\geq$ 3.0), crystalline Ni formed in addition to $Ni_{12}P_5$. The deoxygenation activities of the Ni_xP/AC catalysts were strongly dependent on the types and dispersion of the nickel phosphide. The oil yield and C_{15} selectivity on the catalysts followed the sequence $Ni_{1.5}P/AC > Ni_{2.0}P/AC > Ni_{1.0}P/AC \approx Ni_{3.0}P/AC > Ni_{4.0}P/AC > Ni_{0.5}P/AC \approx Ni_{0.8}P/AC$, $Ni_{1.0}P/AC > Ni_{1.5}P/AC \approx Ni_{0.8}P/AC > Ni_{0.5}P/AC \approx Ni_{2.0}P/AC > Ni_{3.0}P/AC > Ni_{4.0}P/AC$, respectively. The high activity was attributed to the coexistence and high dispersion of Ni_2P and $Ni_{12}P_5$, which were favorable for branched alkanes formation, C_{15} selectivity improvement and oil yield increase. Due to the high-grade diesels (HV = 46.5 MJ kg^{-1}) obtained, Ni_xP/AC can be considered to be a very promising catalyst for transforming fatty acids into high-grade diesel.

1. Introduction

Declining fossil fuels and increasing environmental problems, including global warming and air pollution, are driving our society to search for new sustainable sources of liquid fuels. Fatty acids are produced from the hydrolysis of triglycerides in animal fats and plant oils, which constitute an important renewable biofuel feedstock. Accordingly, biofuel has been proposed as a desirable substitute because it is renewable, carbon-neutral and inexpensive. However, to obtain high-grade fuel, the low stability, high viscosity, and poor calorific value of the feedstock should be improved. These drawbacks are caused by the high oxygen content in their molecular structures [1–4]. Therefore, removing oxygen from the feedstock is becoming one of the most significant issues to obtain high-grade fuel that can potentially serve as or be converted to a drop-in replacement for the fuel currently in use. Currently, three approaches have been used to remove oxygen from fatty acids as shown in Scheme 1 [5–7], in which the degree of H_2 consumption follows the order of decarboxylation < decarbonylation < hydrodeoxygenation (Scheme 1).

There have recently been many reports on the heterogeneous catalytic deoxygenation of fatty acids, and good overviews are available [8–10]. Typically, the most active heterogeneous catalysts are noble metals (Pt, Pd) on a high-surface-area support (carbon-based support) [11,12]. In fact, carbon materials as supports have triggered increasing interest in applications of catalytic deoxygenation due to their uniform mesoporous structures, high surface areas and inert surfaces [11–14]. Fu et al. showed that Pt/C and Pd/C catalysts are highly active for the hydrothermal decarboxylation of different saturated and unsaturated fatty acids [13,14]. Although supported Pd and Pt catalysts have been found to be effective in the conversion of fatty acids and their derivatives into diesel-like hydrocarbons, their high cost has motivated the continuous development of low-cost substitutes. According to the activity trends of Pd > Pt > Ni > Rh > Ir > Ru > Os, Snåre et al. suggested that Ni-based catalysts could be promising candidates [15]. Nickel has been extensively studied for the deoxygenation of fatty acids, but it is not an attractive metal because it favors the cracking reaction [16–18]. Chen et al. demonstrated that Ni_2P/SiO_2 provided higher total selectivity to *n*-C_{11} and *n*-C_{12} in the deoxygenation of methyl

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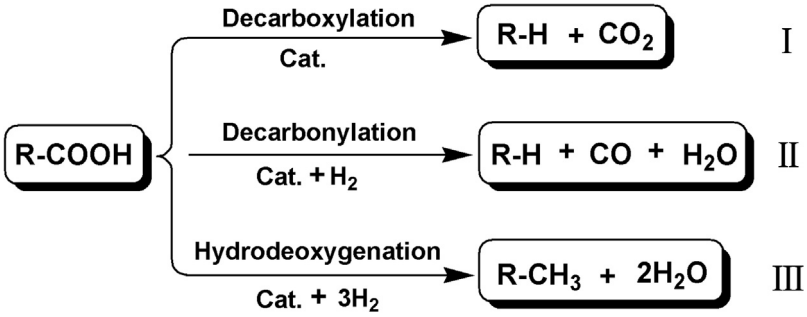

Scheme 1. The three pathways proposed for the deoxygenation of a fatty acid into hydrocarbons. The degree of consumption of H_2 follows the order of decarboxylation (I) < decarbonylation (II) < hydrodeoxygenation (III).

laurate than Ni/SiO_2, whereas Ni produced more cracked products [18a]. Yang et al. comparatively investigated the catalytic performances of Ni_2P/SBA-15 and Ni/SBA-15 toward the deoxygenation of methyl oleate, and they found that Ni_2P/SBA-15 exhibited higher catalytic decarboxylation activity than Ni/SBA-15. Thus, Ni_2P/SBA-15 was suggested to be a promising catalyst for the production of green diesel [17]. In this way, it was determined that transition metal phosphides exhibited particular deoxygenation activity.

To date, some researchers have used Ni_2P as a deoxygenation catalyst [17–22] and found that Ni_2P-based catalysts exhibited excellent catalytic deoxygenation performance. Yang et al. reported that Ni_2P particles can be distributed rather uniformly inside the SBA-15 channels, and the resulting catalyst exhibited an enhanced selectivity for hydrodeoxygenation products compared with Ni/SBA-15 [17]. Moreover, dispersing metal phosphides on mesostructured supports could further enhance their hydrotreating performance, as reported for the HDS of dibenzothiophene and the HDN of methyl aniline over Ni_2P supported on SBA-15 and KIT-6 [23]. In a recent work, we found that unsupported $Ni_{12}P_5$-containing catalysts are more active for the decarboxylation and decarbonylation of palmitic acid, compared with unsupported Ni_2P-containing catalysts [8a].

In the present work, we investigated in detail the effect of the nickel-to-phosphorus molar ratio on the formation and dispersion of different nickel phosphide species and on the deoxygenation performance using palmitic acid as a model compound.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by incipient wetness impregnation. For all catalysts, the content of Ni was fixed at 24.2%. To control the formation of different nickel phosphide species (Ni_2P, $Ni_{12}P_5$, and $Ni_2P/Ni_{12}P_5$ mixture), the molar ratios of Ni/P were changed by adjusting the content of P. The controlled Ni/P molar ratios were 0.5/1, 0.8/1, 1.0/1, 1.5/1, 2.0/1, 3.0/1 and 4.0/1. The AC supports were purchased from the Jiangsun Nantong Activated Carbon Cooperation (China). Prior to impregnation, the AC samples were immersed in 1 M/L $NH_3{\cdot}H_2O$ for 18 h and then washed with distilled water until a neutral pH was achieved. Then, the resulting samples were dried at 373 K for 12 h and calcined at 873 K for 4 h under a nitrogen atmosphere. The dried samples were sieved to 40–60 mesh. The carbon supports (6 g) were impregnated with an aqueous solution containing 9.40 g of $Ni(NO_3)_2{\cdot}6H_2O$ and different amounts of $NH_4H_2PO_4$ for 24 h. Then, the samples were dried at 373 K for 12 h and calcined at 873 K under a nitrogen atmosphere for 4 h. The precursor sample was reduced under flowing H_2 (30 mL/min) to obtain the active phosphide catalyst. The reduction temperature was increased from room temperature to 873 K at a rate of 2 K min^{-1} and was maintained at this temperature for 2 h. Subsequently, the gas was switched to nitrogen, followed by cooling to room temperature. Finally, the carbon-supported catalysts were passivated in an air flow overnight at room temperature. The obtained samples were denoted as Ni_xP/AC catalysts (x = 0.5, 0.8, 1.0, 1.5, 2.0, 3.0, 4.0). The content of Ni was calculated using Eq. (1):

$$\text{Wt.\%Ni} = [\text{weightofNi}/(\text{weightofNi} + \text{weightofAC})] \times 100\%. \quad (1)$$

2.2. Catalyst characterization

X-Ray diffraction (XRD) patterns were recorded using a DX-1000 X-ray diffractometer equipped with Cu-Kα radiation. The X-ray tube was operated at 40 kV and 25 mA. Powder diffraction patterns were recorded over a 2θ range of 30–80 at a scan rate of 0.06 s^{-1}.

N_2 physisorption isotherms of the samples were measured at 77 K on a Micromeritics Tristar II 3020 analyzer. The surface areas were determined by the Brunauer–Emmett–Teller (BET) equation. The pore volumes and average pore diameters were determined by the Barrett–Joyner–Halenda (BJH) method from the desorption branches of the isotherms.

X-Ray photoelectron spectroscopy (XPS) experiments were performed on an AXIS Ultra DLD (KRATOS) spectrometer using a pass energy of 50 eV (0.1 eV per step). A monochromatic Al-Kα X-ray source was used as the excitation source, and the binding energy (BE) was calibrated using C1s at 284.6 eV. A Shirley background was subtracted from all spectra and peak fitting was performed using an 80/20 Lorentz-Gauss function.

Transmission electron microscopy (TEM) images of the samples were obtained on an FEI Tecnai G2 20 TWIN instrument at an acceleration voltage of 200 kV. An energy-dispersive X-ray (EDX) instrument was attached to the TEM system.

The acidities of the catalysts were evaluated by NH_3-temperature-programmed desorption using 1 vol.% NH_3 with He as the carrier gas, a heating rate of 10 K min^{-1} and over the temperature range of 373–773 K. The desorbed NH_3 was detected using a multifunction chemisorption analyzer and detected by a thermal conductivity detector (TCD). The detailed procedure of NH_3-TPD can be found in reference [8a].

Carbon monoxide (CO) chemisorptions and CO-TPD measurements were also performed using the Micromeritics Autochem II 2920 instrument. Approximately 0.1000 g of catalyst was degassed in 60 mL/min He at room temperature for 30 min. Prior to the measurements, samples were heated from room temperature to 650 K in a 60 mL/min flow of H_2 for 2 h. Prior to the chemisorption measurement, all of the samples were then degassed at 650 K in 45 mL/min He for 1 h. CO chemisorption were measured by injecting a calibrated sample volume of CO gas at 1 min intervals into a He flow (45 sccm/min) passing over the catalyst sample until CO uptake ceased. Catalyst samples were maintained at 273 K during