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Hydrodeoxygenation of palm oil to hydrocarbon fuels over Ni/SAPO-11 catalysts

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Small particles of SAPO-11 with large surface area and mesoporosity were synthesized hydrothermally. Ni/SAPO-11 catalysts with different Ni loadings were prepared by incipient wetness impregnation, and their physicochemical properties were characterized by X-ray diffraction, scanning electron microscopy, N_2 adsorption-desorption, NH_3 temperature-programmed desorption, Thermogravimetric, and H_2 chemisorption. In the Ni impregnation of SAPO-11, the mesopores of SAPO-11 accommodated the Ni particles and give good dispersions, but with the partial blocking of some micropores. In the hydrodeoxygenation of palm oil, the production of liquid alkanes depends on the competition between hydrodeoxygenation and decarbonylation pathways via the corresponding carboxylic acid intermediates. The weak and medium acidity of SAPO-11 and a good match of the Ni and SAPO-11 functions in the Ni/SAPO-11 catalysts decreased the cracking of primary long chain alkanes and gave a high liquid alkane yield of 70 wt% and isomerization selectivity of >80 mol%.

1. Introduction

Vegetable oil contained in biomass is a vast and easily available renewable carbon resource. Using vegetable oil as the feedstock to produce green fuels for substituting nonrenewable fossil energy has received more attention in the last decade due to increasing concerns over environmental problems induced by burning fossil fuels [1,2]. Catalytic hydrodeoxygenation (HDO) of vegetable oil to hydrocarbon fuels has obvious advantages as compared to their transesterification with methanol because oxygen removal and saturation of C=C bonds during HDO processing result in hydrocarbon fuels with desirable transportation fuel properties such as high heating value, chemical stability, and low freezing point [3,4].

Sulfided W and Mo modified with Ni and Co catalysts were used for obtaining high alkane yields in the HDO of vegetable oil to hydrocarbon fuels. However, sulfur containing reagents are necessary to maintain the catalytic activity and stability during the pretreatment of catalysts and HDO processing, which inevitably causes sulfur contamination of the final products [5–7]. Noble metals including Pt and Pd were also employed to produce hydrocarbon fuel in the diesel range [8,9], but the exorbitant costs limit their applications on a large scale. Recently, metal carbides and phosphides were investigated and high yields of liquid hydrocarbon were obtained. However, the preparation procedures for these catalysts were tedious, and

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change in the active phase was observed during the HDO of vegetable oils, leading to the limited lifetimes of these catalysts [10–12].

In addition, the acid-base properties of the support play an essential role in mediating the product distribution in the HDO of vegetable oil. For example, with basic MgO as the catalyst, heavy alkanes with carbon number larger than 35 were mainly manufactured due to C–C coupling of fatty ester intermediates [13]. In comparison, supports with the appropriate acidity significantly promoted liquid hydrocarbon production by enhancing dehydration/hydrogenation of the alcohol intermediates, but supports with strong acidity cause severe cracking to lighter hydrocarbons [14].

A drawback of the hydrocarbons produced by the HDO of vegetable oil is their poor low temperature properties because the freezing points of *n*-alkanes with long carbon chains are higher than 273 K, and they are unsuitable for cold areas. This problem can be solved by hydro-isomerization of the *n*-alkanes using noble metals supported on acidic zeolite catalysts [15]. However, for good economics and process efficiency, a one-step production of isomerized hydrocarbons by coupling HDO processing and the isomerization of long *n*-alkanes in one reactor is desirable.

SAPO zeolites synthesized by replacing framework Al with Si possess different pore structures with a wide range of pore sizes. They are important members in the family of aluminophosphate molecular sieves. SAPOs mainly have weak and medium acidity from the Si doping and they have shown promising applications in many acid-catalyzed reactions [16,17]. High selectivity in the hydroisomerization of long *n*-alkanes was observed with noble metal Pt and Pd supported on SAPOs as bifunctional catalysts [18]. Owing to their intrinsic acidity and pore structures, SAPOs would be good supports for producing isomerized hydrocarbon in the HDO of vegetable oils. However, the investigation of this was seldom [19,20]. Recently, we compared the catalytic performance of Ni supported on different commercial supports in the HDO of methyl hexadecanoate in an autoclave, in which it was found that a Ni/SAPO-11 catalyst with weak and medium acidity showed > 95% liquid alkane yield with very low isomerization selectivity [21].

In this work, we hydrothermally synthesized SAPO-11 as small particles with large surface area and mesoporosity. Ni/SAPO-11 catalysts were prepared by incipient wetness impregnation, and their catalytic performance was tested in a one-step HDO of palm oil to isomerized hydrocarbons. The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption-desorption, NH_3 temperature-programmed desorption (NH_3-TPD), Thermogravimetric (TG), and H_2 chemisorption. The relation between the acid and metal functions of the catalysts and HDO performance was elucidated, and the HDO reaction pathway was discussed.

2. Experimental

2.1. Catalyst preparation

According to the previous report [22], SAPO-11 can be hydrothermally synthesized without using a surfactant. H_3PO_4 (85% of aqueous solution, 26.0 g) and pseudo-boehmite (27.1 g) were dissolved in 124.5 g H_2O and stirred for 90 min. Then 6.5 g tetrapropyloxysilane (TPOS) and 35.1 g *n*-propanol were added, and the mixture was further stirred for 120 min, followed by dropwise addition of an aqueous solution of 23.7 g di-*n*-propylamine to form a homogeneous sol with the molar ratio of H_3PO_4:Al_2O_3·nH_2O:TPOS:di-*n*-propylamine:*n*-propanol: H_2O of 0.226:0.225:0.0246:0.235:0.585:6.917. The sol was transferred to a hydrothermal autoclave (100 mL) lined with Teflon and heated at 458 K for 24 h. The solid product was dried at 393 K and calcined at 873 K for 6 h to obtain the SAPO-11.

The Ni/SAPO-11 catalysts were prepared by impregnating the catalyst support with an aqueous solution of $Ni(NO_3)_2·6H_2O$ with Ni loadings of 2%–9% by weight. The resulting suspension was stirred for 10 h at ambient temperature, followed by evaporating excess water at 353 K. The solid that remained was dried at 393 K and calcined at 823 K for 3 h in air.

2.2. Catalyst characterization

XRD patterns of catalyst were obtained with a X'pert PRO MPD diffraction instrument (PANalytical) operated at 40 kV and 40 mA with Cu K_α (λ = 0.15406 nm) radiation. SEM images of the catalysts were recorded using an S-4800 instrument operated at 2.0 kV. BET surface area and pore size distribution were determined by isothermal adsorption of N_2 at 77 K using a Micromeritics ASAP-2010 automated system. NH_3-TPD experiments were carried out on a homemade instrument equipped with a thermal conductivity detector (TCD). TG analysis of the spent catalyst was performed on a NETZSCH-STA 409PC DSC-SP Thermal analyzer by increasing the temperature from 313 to 1073 K at 10 K/min under air (30 mL/min). H_2 chemisorption measurements were performed on a Quantachrome-ASIQACIV200-2 automated gas sorption analyzer. The catalysts were reduced at 773 K for 2 h with H_2 and further heated at 823 K for 0.5 h under He, followed by cooling down to 323 K for H_2 chemisorption tests. The dispersion of Ni was estimated from the molar ratio of surface metallic Ni to initially introduced Ni species, assuming that one H atom is adsorbed on one Ni atom and no dissolution of H takes place in the Ni particles.

2.3. HDO of palm oil composition

The palm oil (> 99%) was commercially obtained from Yihai (Guangzhou) Food & Oil Industrial Co., Ltd and used without further treatment. The components of the palm oil were determined by transesterification using an alkaline catalyst. Methanol and palm oil with the molar ratio of 6:1 were mixed with KOH in a batch reactor, and the reaction was performed at 338 K for 2 h. After reaction, the supernatant liquid was separated off and washed with distilled water. The methyl esters were diluted with cyclohexane and analyzed on a gas chromatograph (Shimadzu GC-2010) with an FID and a capillary