



Hydroprocessing of soybean oil on nickel-phosphide supported catalysts



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HIGHLIGHTS

- Ni₂P supported catalysts display high performance in hydrodeoxygenation of soybean oil.
- Ni₂P/HY hydrocracked and isomerized the paraffinic product.
- Ni₂P/HY hydrocracking activity diminished with time on stream when exposed to water.

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ABSTRACT

Ni₂P/silica and Ni₂P/HY were prepared and for the first time tested in hydroprocessing of soybean oil. The content of Ni₂P in each catalyst was about 25 wt%. The experiments conducted in a trickle-bed reactor operated at conditions normally used in such processes, yielded high hydrodeoxygenation (HDO) activity of both catalysts. No apparent hydrocracking activity was recorded with Ni₂P/silica while Ni₂P/HY displayed high hydrocracking and isomerization activity that diminished with time on stream. Characterization of the fresh and spent Ni₂P/HY indicated that exposing the catalyst to water vapors generated by hydrodeoxygenation reduced the acidity of the catalyst thus reducing its hydrocracking activity. After removal of >99.5% oxygen by HDO of soybean oil and separation of water vapors, the Ni₂P/HY material displayed stable operation during >250 h on stream yielding up to 50 vol% of light fraction boiling out at <250 °C.

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1. Introduction

The production of alternative and renewable liquid fuels for transportation from feedstock other than crude oil is one of the most challenging tasks of the 21st century. Biomass is considered to be a viable feedstock for the short- and mid-term production of renewable fuels, i.e., gasoline, jet-fuel and diesel [1–7]. An ongoing debate on sustainability and other issues related to fuels production from biomass is being conducted [8]. Although it is too early to determine the outcome of this debate, major obstacles need to be overcome before reaching commercial implementation of the so-called second generation biofuels. A recent report [9] reviews the main routes leading to commercial development of biofuels production, classified as biochemical, thermochemical and chemical (catalytic) technologies. Most of the large-scale commercial activities are related to hydroprocessing of vegetable oils or fats to produce green diesel commercialized by Neste Oil [10]. It consists of a two-step process: hydrodeoxygenation of the vegetable or animal oil on a commercial hydrotreating catalyst (Ni–Mo

and Co–Mo) to produce paraffins, which are then further isomerized on Pt–SAPO–11 to produce a mixture that meets the specifications for diesel. The properties of the renewable diesel fuels produced by the two-step process are very similar to those of the gas-to-liquid (GTL) diesel produced from natural gas by the Fischer–Tropsch process. A green diesel with superior properties, close to meeting the commercial specs, known as Isodiesel, produced from animal and vegetable oils in a proprietary one-stage process was developed at the Blechner Center [11–13].

Hydroprocessing is a well-established and widely used technology applied for many years in the refineries. It was natural to apply it to the production of biofuels [14]. Co–Mo and Ni–Mo based catalysts are by far the most widely used commercial catalysts, implemented to production of biofuels. Other metals, including precious metals were tested. Recent reviews and studies [15–22] related to hydroprocessing of vegetable oils provide the status of this intensively researched field. There are three routes for removing oxygen by hydrodeoxygenation (HDO): hydrodewatering (HDW) that yields water vapors, hydrodecarbonylation (HDCO) and hydro-decarboxylation (HDCO₂) that yield CO and CO₂, respectively. The magnitude of each route determines the product distribution and the hydrogen consumption. Furthermore, water

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vapors at high temperature (>350 °C) have a detrimental effect on zeolitic materials as well as supported metals and metal oxides [23–26]. Attempts were made [16,18] to uncover the pathways and to some extent, as claimed by the authors of pertinent publications, the mechanism of the processes. A variety of feedstocks were tested. The effect of the type of vegetable oil was found to be negligible, as expected in such processes.

The supported nickel phosphide (NiP) catalysts display excellent performance in HDS and HDN, with the most active phosphide, Ni₂P, having activity surpassing that of promoted sulfides. A review of the NiP supported catalysts for hydro-processing was published recently [27]. Since hydrodesulfurization is extremely important in commercial applications, most of the published studies focused on this topic. Specifically, the Ni₂P phase was found to be very active in ultradeep desulfurization [28].

The NiP-based catalysts display also high activity in HDO of feedstocks relevant to production of biofuels as follows from the results of experiments conducted mostly with model compounds. A significant advantage of implementation NiP as active compound in catalysts producing biofuels by hydrotreating is its high stability that does not require injection of sulfur compounds to the sulfur-free feedstock.

HDO of methyl laurate to diesel-like hydrocarbons was performed on Ni₂P/SiO₂, Ni₂P/MCM-41, and Ni₂P/SBA-15 catalysts [29]. The catalyst activity decreased in the order Ni₂P/SiO₂ > Ni₂P/SBA-15 > Ni₂P/MCM-41. HDCO was more significant than HDW which was affected by the Brønsted acidity and Ni₂P crystallite size, especially the former. In comparison to Ni/SiO₂, the Ni₂P catalysts had lower activities for methanation and the cracking reaction because of the ligand and ensemble effects of P.

The various phases of NiP supported on inert as well as acidic supports were tested in HDO of methyl laurate [30]. Ni₂P/SiO₂ yielded the highest conversion and selectivity to C₁₁ and C₁₂ hydrocarbons, followed by Ni₃P-Ni₁₂P₅/Al₂O₃, Ni₂P/TiO₂, Ni₂P/SAPO-11, Ni₂P-Ni₁₂P₅/HY and Ni₂P/CeO₂. The C₁₁/C₁₂ molar ratio, which represent (HDCO + HDCO₂)/HDW ratio, followed in the order of Ni₂P/CeO₂ > Ni₃P-Ni₁₂P₅/Al₂O₃ > Ni₂P/SiO₂ > Ni₂P/SAPO-11 > Ni₂P/TiO₂ > Ni₂P-Ni₁₂P₅/HY. The HDO pathways were mainly affected by the electron density of Ni site and the synergism between the Ni site and the acid site or oxygen vacancy. The higher electron density of the Ni site was, the larger the C₁₁/C₁₂ ratio.

Ni₂P/SBA-15 catalyst was also tested for HDO of methyl oleate. It was found to promote both HDCO₂ and HDW reactions [31]. In contrast, Ni/SBA-15 favored cracking reactions, yielding a broader hydrocarbon distribution.

Conversion of vegetable oils to fuels requires HDO as well as isomerization and possibly some mild cracking processes. SAPO-11 supported Ni₂P displayed higher isomerization selectivity than Ni/SAPO-11 in conversion of n-dodecane [32]. This is mainly ascribed to the ligand and ensemble effects of P, which lead to lower hydrogenolysis activity of nickel phosphides. Nickel phosphide based bifunctional catalyst is very promising for hydro-isomerization based of its higher isomerization selectivity and less H₂ consumption than the metallic Ni-based one. The hydrocracking of naphthalene into BTX has been studied over Ni₂P catalysts supported on SiO₂, Beta, USY, or ZSM-5. The Ni₂P/SiO₂ catalyst was found to be active only for the hydrogenation of naphthalene [33]. On the other hand, the zeolite supported Ni₂P catalysts displayed remarkable activity in hydrocracking of BTX (benzene, toluene, xylene) fraction derived by oil refining in the order Ni₂P/Beta > Ni₂P/USY > Ni₂P/ZSM-5, demonstrating the bifunctional catalytic activity.

This information is evident for great potential of implementation NiP-based catalysts both containing and not containing acidic zeolite components in production of green transportation fuels by hydrotreating of vegetable oils. Three functions are essential: HDO,

isomerization and mild cracking, for removal of oxygenates with parallel regulating of the yields of gasoline/jet/diesel fuels and their quality. No information has been published in the scientific literature on the application of supported Ni₂P catalysts for converting of vegetable oils to liquid fuels.

The scope of this study is to prepare, characterize and test the performance of two significantly different catalysts: Ni₂P/silica where the support is inert and Ni₂P/HY where the support is highly acidic thus providing the cracking and possibly the isomerization function. Soybean oil was selected as the feedstock. Other vegetable oils are expected to display a similar behavior.

2. Experimental methods

2.1. Catalysts preparation

Ni₂P/silica and Pt/SAPO-11 were prepared and characterized according to procedures described elsewhere [13,28]. The preparation of Ni₂P/Zeolite HY was based on the same preparation procedure as the Ni₂P/silica, using a commercial Ultrastable Zeolite HY (CBV760, Zeolyst International Inc.). The catalyst was prepared by impregnation of Zeolite HY with an aqueous solution of Ni(NO₃)₂·6H₂O (Fluka, 98%) and NH₄H₂PO₄ (ABCR, 98%) stabilized with HNO₃, keeping a wt. ratio of HY: Ni(NO₃)₂·6H₂O: NH₄H₂PO₄ 1:1.6:0.45, respectively. The catalyst was dried in air at 120 °C for 4 h, and calcined at 500 °C for 6 h. The prepared catalyst powder was pelletized, crushed and sieved to a fraction of 25–60 mesh. The obtained supported amorphous Ni–P–O polyphosphate complex was converted to Ni₂P by reduction in H₂ flow of 500 N ml/min/g, ramping the temperature to 400 °C at 4 °C/min then to 580 °C at 1 °C/min where it was kept for 30 min. The composition of the catalysts based on their chemical analysis is listed in Table 1. It is consistent with the expected components content based on the preparation procedure.

2.2. Catalysts characterization

The crystal and pore structure of the zeolitic component were characterized by XRD and N₂-adsorption–desorption methods, while its acidity was measured by NH₃-TPD. Conventional wide-angle XRD patterns were obtained using software developed by Crystal Logic with a Philips 1050/70 powder diffractometer (Bragg–Brentano geometry), fitted with a graphite monochromator providing a Ka diffracted beam (λ = 1.541 Å) and operating at V = 40 kV and I = 30 mA. The data were collected in a range of 2θ values between 10° and 80°, with a step size of 0.005°. Phase identification was then performed by using Bede ZDS computer search/match program coupled with the ICDD (International Centre for Diffraction Data) Powder Diffraction File database (2006). The relative quantities of crystalline phases (Ni₂P, Ni₁₂P₅, ultrastable faujasite Y) and amorphous phases were estimated by Rietveld refinement of the XRD profile using the DBWS-9807 program. Surface area (total, micro- and mesopores) and pore volume (total and micropores) were derived from N₂ adsorption–desorption isotherms using conventional BET, BJH and t-plot methods. The samples were degassed under vacuum for 2 h at 200 °C. Isotherms were measured using a static-volumetric method with NOVA-2000 (Quantachrome, version 7.02) instrument. The H₂-TPR and NH₃-TPD spectra were recorded using Analyzer Autochem II, Micrometrics Co. equipped with TCD and mass-spectrometer (Cirrus 2, MKS). The H₂-TPR profiles of water evolution were measured by heating the samples gradually up to 650 °C in the 25 ml/min flow of 10% H₂/Ar. The NH₃-TPD procedure was conducted as follows: a sample was heated to 40 °C under 5% NH₃/He at 25 ml/min and kept for

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