



Catalytic deoxygenation of methyl laurate as a model compound to hydrocarbons on nickel phosphide catalysts: Remarkable support effect



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ARTICLE INFO

Article history:

Received 19 May 2013

Received in revised form 3 August 2013

Accepted 10 August 2013

Available online xxxx

Keywords:

Methyl laurate
Hydrodeoxygenation
Decarbonylation
Hydrocarbon
Nickel phosphide
Support effect

ABSTRACT

This work investigated the support effect on the deoxygenation of methyl laurate to C11 and C12 hydrocarbons over nickel phosphide catalysts. By the H₂-TPR method from the precursors with Ni/P ratio of 1.0, Ni₂P was produced on SiO₂, CeO₂, TiO₂ and SAPO-11, while Ni₃P and Ni₁₂P₅ were formed on γ -Al₂O₃, and Ni₁₂P₅ and Ni₂P were formed on HY. Ni₂P/SiO₂ had lower electron density of Ni site than other catalysts, where either there were the Ni₃P and Ni₁₂P₅ phases or there was the electron transfer from reduced CeO₂ or TiO₂ to Ni₂P. At 573–613 K and 3.0 MPa, the conversion of methyl laurate and the selectivity to C11 and C12 hydrocarbons tended to decrease in the sequence of Ni₂P/SiO₂ > Ni₃P-Ni₁₂P₅/Al₂O₃ > Ni₂P/TiO₂ > Ni₂P/SAPO-11 > Ni₂P-Ni₁₂P₅/HY > Ni₂P/CeO₂, whereas the C11/C12 molar ratio followed in the order of Ni₂P/CeO₂ > Ni₃P-Ni₁₂P₅/Al₂O₃ > Ni₂P/SiO₂ > Ni₂P/SAPO-11 > Ni₂P/TiO₂ > Ni₂P-Ni₁₂P₅/HY. The effect of supports mainly results from their acidity and reducibility. The catalyst activity, the selectivity to hydrocarbons and the deoxygenation pathway are correlated with the surface density of Ni site, the electron property of Ni site, the Ni₂P crystallite size and the synergism between the Ni site and the acid site or the oxygen vacancy.

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1. Introduction

Nowadays, as the energy demand rapidly increases and the environment pollution becomes more and more serious, to develop clean and sustainable energy has drawn great attention in globe. Vegetable oils and animal fats (complex mixtures of triglycerides) are attractive renewable energy resources. They can be converted to biodiesel (namely fatty acid methyl esters, FAME) via transesterification and to diesel-like hydrocarbons via hydrodeoxygenation. Biodiesel is widely used as a renewable fuel. However, it also has some disadvantageous properties as fuel, such as high oxygen content, high pour point, poor thermal and chemical stability, low energy density and immiscibility with hydrocarbon fuels. To overcome the disadvantages of biodiesel, hydrodeoxygenation has widely been investigated to produce diesel-like hydrocarbons from fatty acids and fatty esters. There is also an advantage for the hydrodeoxygenation that the bio-based feedstock can be processed at refineries using existing equipment and thereby minimizing capital cost.

The deoxygenation of fatty acids or fatty esters can be realized via two pathways, that is, hydrodeoxygenation (HDO) and decarbonylation/decarbonylation. The HDO pathway gives the hydrocarbon with same carbon number to the corresponding fatty acid and oxygen is removed as H₂O. The decarbonylation/decarbonylation pathway leads to

the hydrocarbon that has one carbon atom less than the corresponding fatty acid, and oxygen is released as CO/CO₂. The deoxygenation catalysts mainly include noble metals (Pt [1,2], Pd [2–4]), Ni [2,5,6] and conventional sulfide Ni(Co)-Mo(W)/ γ -Al₂O₃ [7–9]. Noble metals have high activity for deoxygenation and mainly yield decarbonylation/decarbonylation hydrocarbons. However, the limited reserve and high cost inhibit their application. Compared to noble metals, the sulfide catalysts mainly give the HDO hydrocarbons and have been industrialized. To avoid the catalyst deactivation due to S loss, the S-containing agents (such as H₂S and CS₂) are needed to be added to the reactants. However, this leads to the formation of undesirable S-containing products and the increase of operational cost [9,10]. The Ni-based catalysts mainly give the decarbonylation/decarbonylation products [2,5,6], however, they also yield more cracked products. This not only reduces the diesel yield but also increases the H₂ consumption. Therefore, to explore new kind of catalysts is necessary and challengeable.

As new hydroprocessing catalysts, nickel phosphides have been widely investigated in recent decades. They exhibit a range of properties with fundamental and commercial interests. For instance, their particles are globular and not layered, providing more well-exposed sites than the sulfide catalysts. The ligand and ensemble effects of P affect the electronic and geometrical properties of Ni site, while the electronic and geometrical properties are determining factors for the catalyst performance. As reported by many researchers, the nickel phosphide catalysts show excellent performances in hydrodenitrogenation [11,12], hydrodesulfurization [13,14], hydrodechlorination [15,16], synthesis gas conversion [17] and hydrazine decomposition [18]. Also, it has

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recently been reported that nickel phosphides are effective for oxygen removal from the molecules in bio-oils (such as guaiacol [19,20], anisole [21], dibenzofuran [22]) and carboxylic esters [5,23]. Compared to metal nickel catalysts, the nickel phosphide catalysts are lower active for hydrogenolysis [5,23,24], inhibiting the formation of cracked compounds.

It is known that support effect is important for the supported catalysts. On one hand, support influences the structure of active phase (such as dispersion and electron property). On the other hand, the surface acid/base site and oxygen vacancy of support may participate in the activation of reactant and affect the product distribution. For instance, the Lewis acidity of alumina can convert carboxylic ester to carboxylic acid [8]. Ni/HY and Ni/HZSM-5 with the strong acidity show much higher selectivity to the isomers as well as to cracked hydrocarbons than Ni/SAPO-11 with weak and medium acidity [25]. The SH⁻ groups more preferentially promote decarbonylation/decarboxylation than hydrodeoxygenation [7,8]. The oxygen vacancies on CeO₂ and ZrO₂ promote the activation of ester group [6,26]. Nickel phosphides themselves are of bifunctional (acid/metal function) nature. The effect of some supports on their reactivities has been investigated for the hydrodeoxygenation of guaiacol [20], hydrodesulfurization [13], and hydrodechlorination [15,16]. However, to our knowledge, it has not been reported for the deoxygenation of fatty ester.

In the present work, to investigate the support effect on the structure and deoxygenation performance of nickel phosphides, six supports (SiO₂, γ-Al₂O₃, TiO₂, SAPO-11, CeO₂ and HY zeolite) with different acidity/basicity and reducibility were adopted. The catalysts and their precursors were characterized by means of H₂-TPR, N₂ sorption, XRD, XPS, CO chemisorption and NH₃-TPD. The deoxygenation of methyl laurate as a model reactant to diesel-like hydrocarbons was used to evaluate the catalyst performance. Correlating the catalyst performance with its structure, we analyzed the support effect on the catalyst activity and the deoxygenation pathway.

2. Experimental

2.1. Catalyst preparation

SiO₂ (Qingdao Haiyang Chemicals Co., Ltd.), γ-Al₂O₃ (Jiangsu Jingjing New Material Co., Ltd.), TiO₂ (CNOOC Tianjin Research & Design Institute of Chemical Industry), SAPO-11 and HY (The Catalyst Plant of Nankai University) were commercial products. CeO₂ was prepared by a modified coprecipitation method (i.e., the surfactant-assisted method) described in the reference [27]. The supported nickel phosphide catalysts were prepared by the temperature-programmed reduction (TPR) [21]. First, the support (0.15–0.25 mm in diameter) was incipiently impregnated with an aqueous solution of NH₄H₂PO₄ and Ni(NO₃)₂, followed by drying at 393 K for 12 h and calcination at 773 K for 4 h, and so the precursor was prepared. The initial Ni/P molar ratios in all precursors were 1.0. Second, the precursor was reduced with a H₂ flow (320 mL·min⁻¹ per gram of precursor) from 293 to 523 K at a rate of 10 K/min and from 523 to 923 K at a rate of 1 K/min, and then maintained at 923 K for 3 h. The prepared catalyst was cooled to room temperature and subsequently passivated in a 0.5 vol.%O₂/N₂ flow for 6 h. The nickel contents in all nickel phosphide catalysts were set at 15 wt.%. The catalysts are denoted on the base of the phases of nickel phosphides (shown in Table 1). In addition, a Ni₃P-Ni₁₂P₅/SiO₂ catalyst was also prepared from the precursor with the Ni/P ratio of 2.5 (XRD pattern shown in Fig. 1S).

For comparison, Ni/SiO₂, PO_x/SiO₂ and bulk unsupported nickel phosphate were prepared. Ni/SiO₂ was prepared by the impregnation method. Silica was incipiently impregnated with an aqueous solution of Ni(NO₃)₂ followed by drying at 393 K for 12 h and calcination at 773 K for 4 h, resulting in SiO₂ supported nickel in oxidation state (denoted as NiO/SiO₂). NiO/SiO₂ was then reduced at 723 K for 1 h to obtain Ni/SiO₂. PO_x/SiO₂ was prepared as the following procedure: silica

was incipiently impregnated with an the aqueous solution of NH₄H₂PO₄, followed by drying at 393 K for 12 h and calcination at 773 K for 4 h. To prepare the bulk nickel phosphate, an aqueous mixture of Ni(NO₃)₂ and NH₄H₂PO₄ (nominal Ni/P ratio = 1.0) was first evaporated, followed by drying at 393 K for 12 h and calcination at 773 K for 4 h.

2.2. Catalyst characterization

The reducibility of precursors was characterized by the H₂ temperature-programmed reduction (H₂-TPR). 0.05 g catalyst was loaded to a quartz U-tube reactor (inner diameter of 4 mm). Reduction was conducted at a heating rate of 10 K/min in a 10%H₂/N₂ flow (60 mL/min). The H₂ consumption was determined by a thermal conductivity detector (TCD).

XRD patterns were obtained on a D8 Focus powder diffractometer using Cu-Kα radiation (λ = 0.15406 nm). N₂ adsorption-desorption isotherms were measured on a Quantachrom QuadraSorb SI or a Micromeritics ASAP 2020 apparatus at 77 K. The Brunauer-Emmett-Teller (BET) equation was used to calculate the surface area. For Ni₂P/SAPO-11 and Ni₂P-Ni₁₂P₅/HY, the external surface areas and micropore volumes were calculated by the t-plot method. The pore volume was estimated at a relative pressure of 0.99. The pore volume and the pore distribution were determined by the Barret-Joyner-Halenda (BJH) method using the desorption branch of the isotherm.

CO chemisorption was carried out to determine the surface Ni density of the catalysts, assuming a stoichiometry of 1.0 between CO and Ni atom. It was performed on the same apparatus to H₂-TPR. A 0.1 g portion of the passivated sample was loaded to the reactor and re-reduced with H₂ (60 mL/min) at 723 K for 1 h and was then flushed with a He flow (40 mL/min) at the same temperature for 1 h. Subsequently, the sample was cooled to 303 K. When the TCD signal was stable, the CO pulses (50 μL) were passed through the samples until the effluent areas of consecutive pulses were constant. The total dynamic CO uptake was then calculated.

X-ray photoelectron spectroscopy (XPS) was performed on a PHI-1600 ESCA instrument with Mg Kα radiation (1253.6 eV). Binding energies were determined with adventitious carbon (C1s at 284.6 eV) as the reference. Since the passivation can mask the surface nature electron states of the fresh catalysts, the passivated catalysts were sputter-cleaned with an Ar⁺ ion beam (4 kV, 25 mA) for 1 min.

NH₃-TPD was carried out using the same apparatus as with H₂-TPR. A 0.07 g portion of sample was reduced with a H₂ flow (60 mL/min) at 723 K for 1 h and then cooled to 373 K. After NH₃ adsorption for 30 min, the sample was swept with a He flow to remove the physically adsorbed NH₃. Afterward, NH₃-TPD was performed in a He flow (60 mL/min) at a heating rate of 15 K/min. The desorbed NH₃ was detected by a TCD. To quantify the amount of desorbed NH₃, the equipment was calibrated by measuring the corresponding signal of the thermal decomposition of known amounts of [Ni(NH₃)₆]Cl₂.

2.3. Activity test of catalysts

The deoxygenation of methyl laurate was tested on a stainless-steel fixed-bed reactor (inner diameter of 12 mm). 0.4 g passivated catalyst blended with 3.2 g quartz sand in same diameter was loaded in the reactor. And 2 g quartz sand was placed on the catalyst bed to preheat the reactants. In a H₂ flow (100 mL/min), the passivated catalyst was re-reduced at 723 K for 1 h. After that, the temperature and the H₂ pressure were respectively adjusted to the desired values, and methyl laurate was fed into the reactor using a pump. The weight hourly space velocity (WHSV) of methyl laurate was 10 h⁻¹ and the molar ratio between H₂ and methyl laurate was 50. The reaction was found to operate with negligible mass-/heat-transfer limitations. The liquid products were identified using GC standards and the identification

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