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Effect of a second metal (Co, Fe, Mo and W) on performance of Ni₂P/SiO₂ for hydrodeoxygenation of methyl laurate[☆]

Zhengyi Pan, Rijie Wang, Ziyang Nie, Jixiang Chen*

Tianjin Key Laboratory of Applied Catalysis Science and Technology, Department of Catalysis Science and Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

ABSTRACT

Ni_2P/SiO_2 and bimetallic $NiMP/SiO_2$ (M = Co, Fe, Mo, W; Ni/M atomic ratio=5) catalysts were prepared by the temperature-programmed reduction method. The catalysts and their precursors were characterized by means of UV–Vis DRS, H_2-TPR, XRD, TEM, CO chemisorption and NH_3-TPD. Their performance for the deoxygenation of methyl laurate was tested on a fixed-bed reactor. The results show that the main phase was Ni_2P in all catalysts, and M (M = Co, Fe, Mo, W) entered the lattice of Ni_2P forming solid solution. Different from Fe and Co, the introduction of Mo and W into Ni_2P/SiO_2 reduced the phosphide particle size and increased the acid amount. In the deoxygenation reaction, the turnover frequency of methyl laurate increased on the catalysts in the order of $NiMoP/SiO_2$, Ni_2P/SiO_2, $NiWP/SiO_2$, $NiFeP/SiO_2$ and $NiCoP/SiO_2$, which is influenced by the size of phosphide particles and the interaction between Ni and M (M = Fe, Co, Mo or W). The introduction of the second metal (especially Mo and W) into Ni_2P/SiO_2 promoted the hydrodeoxygenation pathway. This is mainly attributed to the interaction between Ni and the second metal. Finally, the $NiMoP/SiO_2$ catalyst was tested at 340 ℃, 3 MPa, methyl laurate WHSV of 14 h^{-1} and H_2/methyl laurate molar ratio of 25 for 132 h, and its deactivation took place. We found that the catalyst deactivation mainly resulted from carbonaceous deposit rather than the sintering of metal phosphide crystallites.

1. Introduction

Now, the fossil fuel consumption has surged, particularly the petroleum consumption, because of the rise of the automobile industry, although the price of oil has risen substantially. Besides such a swift decline of the limited fossil energy reserve, the fossil energy consumption also results in serious environmental problems. So, to develop clean and renewable alternative energy resource is very urgent. As a kind of renewable and environment-friendly energy resource, biomass has attracted great attention. Through transesterification, triglycerides derived from animal fat and vegetable oil can be converted into the conventional biodiesel (i.e. fatty acid methyl ester). However, the conventional biodiesel has some poor properties because of its high oxygen content, which prevents it from replacing fossil energy entirely. Therefore, to meet the specification as fuel in terms of volatility, thermal stability, corrosiveness and viscosity, the removal of oxygen from

animal fat and vegetable is necessary [1]. The deoxygenation pathways of the fatty acid ester involve hydrodeoxygenation (HDO) and decarboxylation/decarbonylation [2]. The hydrocarbon with the same number of carbon atoms with the corresponding fatty acid can be obtained through the HDO pathway and the oxygen is removed in the form of water. The hydrocarbon with one carbon less than the corresponding fatty acid can be produced through the decarboxylation/decarbonylation reaction while the oxygen is removed as CO/CO_2. Compared with the HDO pathway, the decarboxylation/decarbonylation pathway consumes less hydrogen if the methanation of CO/CO_2 does not occur, but gives lower carbon yield. In the practical application, to tune the hydrocarbon composition is of great significance and can be achieved via regulating the catalyst property.

Nowadays, hydrodeoxygenation catalysts mainly include transition metal sulfide, noble metal, non-noble metal and new types of catalysts (such as metallic carbide, nitride, and phosphide). However, sulfur-containing reagents (e.g. CS_2 or H_2S) have to be added into feedstock to maintain the stability of the metal sulfide catalyst. This results in the formation of sulfur-containing products as well which reduces the quality of the oil products and does not adhere to the standard requirements of clean energy [3]. To develop non-sulfide

catalysts is very significant. For the noble metal catalysts, the high cost hinders their application on a large scale. Non-noble metals also have some disadvantages. For example, metallic Ni has the high activity for decarboxylation/decarbonylation, cracking and methanation, which brings about low hydrocarbon yield, large hydrogen consumption and so high operation cost [1,4–6]. The transition metal nitrides and carbides have been investigated due to their noble-metal-like catalytic properties [7].

As a new type of hydrotreating catalysts, transition metal phosphide catalysts used in the sulfur-free condition have received the widespread attention [7–9]. Based on our previous work [10], Ni_2P had higher activity than Fe, Co, Mo and W phosphides for the deoxygenation of methyl laurate. Recently, bimetallic phosphide catalysts for hydrodeoxygenation have drawn great attention because of the formation of solid solution [11–13]. The formation of solid solution can improve the catalytic performance, which could not be achieved by mono-metal [14]. Although some studies indicate that mono-metal phosphides exhibit interesting hydrodeoxygenation performance [15–17], so far it has not been systematically studied on bimetallic phosphide catalysts for the deoxygenation of fatty ester.

In this study, SiO_2-supported Ni_2P and bimetallic phosphide (NiMP, M = Co, Fe, Mo and W) catalysts were prepared and tested for the deoxygenation of methyl laurate as a model compound to hydrocarbons. Their structure–activity relationship was discussed.

2. Experimental

2.1. Catalyst preparation

Commercial silica (BET surface area of 548 m^2/g) was purchased from Qingdao Haiyang Chemical Co. Ltd., Qingdao, China. The SiO_2-supported Ni_2P and bimetallic phosphide (NiMP, M = Co, Fe, Mo and W) were prepared from the phosphate precursors via the H_2 temperature-programmed reduction (H_2-TPR). First, SiO_2 was incipiently impregnated with a mixture aqueous solution of $NH_4H_2PO_4$ and $Ni(NO_3)_2 \cdot 6H_2O$ or a mixture aqueous solution of $NH_4H_2PO_4$, $Ni(NO_3)_2 \cdot 6H_2O$ and a second metal salt $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $(NH_4)_6W_7O_{24} \cdot 6H_2O$ or $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. To dissolve the salts completely, the pH values of the solution containing Fe or Mo element were adjusted to 0.47 and 2.41 using HNO_3, respectively. The resulting sample was dried at 120 °C for 12 h, and subsequently calcined at 500 °C for 4 h to prepare the precursors with the P/metal (Ni and M) atomic ratio of 1.0. Second, the precursors were reduced from 20 to 650 °C at a rate of 1 °C/min and then maintained at 650 °C for 3 h. The H_2 (>99.9%) flow was set as 320 mL/min per gram of the precursor. The prepared catalyst was cooled to room temperature in the H_2 flow and then passivated in a 0.5 vol% O_2/N_2 flow (320 mL/min) for 4 h, and the Ni_2P/SiO_2 and $NiMP/SiO_2$(M = Co, Fe, Mo, and W) catalysts were obtained. In the catalysts, the mass ratio between Ni and SiO_2 was 12%, and the Ni/M(M = Co, Fe, Mo, W) atomic ratio was 5.

2.2. Catalyst characterization

To distinguish metal-oxygen species in the catalyst precursors, ultraviolet and visible (UV–Vis) spectra were obtained using a Perkin–Elmer Lambda 750S UV–Vis-NIR spectrometer over a wavelength range of 200–800 nm. The catalyst precursors were ground into a powder with a particle size of < 2 μm and loaded into the sample holder with $BaSO_4$ as the white standard.

The reducibility of the catalyst precursors was characterized by the H_2 temperature-programmed reduction (H_2-TPR) on a home-made instrument. The sample (50 mg) was placed in a quartz U-shaped tube (inner diameter of 4 mm) and reduced in a flow of a 10 vol% H_2/N_2 (60 mL/min) at a heating rate of 10 °C/min. The hydrogen consumption was determined by a thermal conductivity detector (TCD).

X-ray diffraction (XRD) patterns were obtained on a D8 Focus powder diffractometer employing Cu $K\alpha$ radiation ($\lambda = 0.1541$ nm) operated at 40 kV and 40 mA. Crystallite size was calculated using the Scherrer equation, $Dc = K\lambda/(\beta \cos \theta)$; where the constant K here is 0.9, λ is the wavelength of the X-ray radiation, β is the width of the peak at half-maximum, and θ is the Bragg angle.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) micrographs were obtained on a JEM-2100F instrument, operated at 200 kV. The powder sample was ultrasonically dispersed in alcohol and then deposited on a carbon-coated copper grid.

N_2 adsorption–desorption was carried out on a Quantachrom QuadraSorb SI instrument at –196 °C. The sample was pretreated in vacuum at 300 °C for 4 h before measurement. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area. 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.

Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) of the fresh and spent $NiMoP/SiO_2$ catalysts were carried out on a Mettler-Toledo TGA 1/SF. The sample was heated from 25 °C to 800 °C with a ramping rate of 10 °C/min in an air flow (100 mL/min).

CO chemisorption uptakes were used to indicate the surface density of exposed metal sites, and were measured on the same equipment as with H_2-TPR. 100 mg passivated catalyst was loaded in the reactor and reduced in a H_2 flow (60 mL/min) at 450 °C for 1 h. And then, the sample was flushed with a He flow (40 mL/min) at 450 °C for 1 h to remove the hydrogen adsorbed on the surface. Afterward, the sample was cooled to 30 °C. When the TCD signal was stable, pulses of CO (50 μL) were passed through the samples until the effluent areas of consecutive pulses were constant. Subsequently, the total dynamic CO uptake was calculated.

The NH_3 temperature-programmed desorption (NH_3-TPD) characterization was executed on the same equipment as with H_2-TPR. 70 mg passivated catalyst was re-reduced with a H_2 flow (60 mL/min) at 450 °C for 1 h and then cooled to 100 °C. After NH_3 adsorption for 30 min, the sample was flushed with a He flow (60 mL/min) to remove the physically adsorbed NH_3. Subsequently, NH_3-TPD was implemented at a heating rate of 15 °C/min with a TCD to detect the desorbed NH_3. Before detection, a trap containing solid NaOH was installed to remove water. To analyze the amount of desorbed NH_3 quantitatively, the apparatus was calibrated by measuring the corresponding signal of the thermal decomposition of known amount of $[Ni(NH_3)_6]Cl_2$.

2.3. Activity test

The reactivities of the catalysts were tested on a continuous-flow stainless-steel fixed-bed reactor (inner diameter of 12 mm). To eliminate the temperature gradient maintaining the isothermal catalyst bed, 0.4 g passivated catalyst (0.15∼0.25 mm in diameter) mixed with 3.2 g quartz sand in the same size to dilute the catalyst was loaded in the reactor. 2 g quartz sand with diameter of 0.43∼0.85 mm was put on the catalyst bed to preheat the reactants. Before the test, the passivated catalyst was re-reduced at 450 °C for 1 h in a H_2 flow (>99.9%, 100 mL/min). And then, the temperature and the H_2 pressure were adjusted to the reaction values. Subsequently, methyl laurate was fed into the reactor with a liquid micro pump. The weight hourly space velocity (WHSV) of methyl laurate was 14 h^{-1} and the H_2/methyl laurate molar ratio was 25. The liquid products were identified using gas