ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Metal phosphide catalysts for the hydrotreatment of non-edible vegetable oils

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ARTICLE INFO

Keywords:
Green diesel
Hydrogenation
Vegetable oil
Metal phosphides
Hydrotreatment

ABSTRACT

Silica-supported catalysts of nickel, cobalt, iron, molybdenum, and tungsten metal phosphides (NiP/SiO_2, CoP/SiO_2, FeP/SiO_2, MoP/SiO_2, and WP/SiO_2) with a metal-loading of 15 wt%, were synthesized by reduction of the corresponding phosphite precursors. The catalysts were characterized by N_2 adsorption–desorption, X-ray diffraction (XRD), CO pulse chemisorption, NH_3 temperature programmed desorption (NH_3-TPD), and X-ray photoelectron spectroscopy (XPS). The activity of these catalysts was measured at 573 K, a liquid flow of 0.3 mL min^{-1}, a pressure of 2.0 MPa and a H_2/liquid ratio of 300 in a three-phase, trickle-bed reactor in the hydrotreatment of methyl laurate. The MoP/SiO_2 catalyst was found to exhibit the best catalytic performance based on its higher active phase dispersion as measured by XRD, CO chemisorption and XPS analyses, along with its moderate acidity, which is higher with respect to the other studied catalysts. The reaction conditions using the MoP/SiO_2 catalyst, the most active and selective to C_{12} and C_{11} hydrocarbons, were optimized. Optimal results can be obtained under the following conditions: 573 K, 2.0 MPa, and a liquid flow of 0.3 mL min^{-1}. Moreover, long-run experiments showed that the MoP/SiO_2 catalyst exhibits stable catalytic behavior for at least 96 h.

1. Introduction

The fast development of the global economy is accelerating the consumption of energy resources, while fossil fuel reserves are depleting rapidly, and stringent environmental regulations have led to interest in biomass, being abundant and readily available, as a renewable energy source. The utilization of biomass-derived fuels has several advantages over the use of conventional fuels, such as reduction in greenhouse gas emissions, localized production, and favorable economics of utilization. One very interesting alternative is the use of vegetable oils, oily residues and fats, because these materials have a low oxygen content. Traditionally, the vegetable oils and fats are converted to biodiesel by transesterification [1–4]. An interesting alternative to biodiesel production is the catalytic hydrotreating of oils and fats into hydrocarbon-based fuel (Green Diesel) [4]. Hydrotreatment removes the oxygen of triglycerides, esters and free acids molecules via decarboxylation, decarbonylation or hydrodeoxygenation (HDO) processes to yield mainly n-alkanes [5–12]. Furthermore, isomerization and cracking of the hydrocarbon chains can also be significant, depending on the characteristics of the catalysts, and these reactions contribute to upgrading the fuel properties.

Catalysts employed in the hydrotreatment process are basically constituted by a metal supported on a high surface area oxide support. The metallic function will be responsible of the hydrodeoxygenation of the oil and the hydroisomerization, therefore, selection of the metal is very important. Several kinds of catalysts were employed for this reaction, mainly based on reduced transition metals or sulfided catalysts such as CoMoS or NiMoS, or noble metals. The most active catalysts are based on noble metals, which have a high activity in the hydrotreatment of free acids and methyl esters, but the price of the catalysts is very high. The metal sulfides are a good alternative, and these catalysts show good activity in the hydrotreatment of triglycerides. However, a byproduct of the reaction is water, which makes it necessary to feed a sulfide source to maintain the stability of the metal sulfides [2,13,14]. An interesting alternative is the use of catalysts based on transition metal phosphides. They are very active for hydrotreatment reactions, their electronic structure is quite similar to that of noble metals [15–19], they are quite stable and resistant to the presence of water [16], and they have a lower cost than catalysts based on noble metals. The synthesis of the supported phosphide catalysts

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http://dx.doi.org/10.1016/j.cattod.2017.03.031
Received 29 November 2016; Received in revised form 10 February 2017; Accepted 20 March 2017

Please cite this article as: Alvarez-Galvan, M.C., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.03.031

could be carried out by a standard phosphate method [15] or by a phosphite method [19–21]. The first one has two activation steps in the preparation method: (i) calcination of precursors and (ii) reduction and phosphide formation. While the second method has only one activation step, reduction and phosphide formation without calcination, the phosphorous precursor has a lower oxidation state, and consequently, phosphide formation occurs at a lower temperature [19–21]. The support usually employed in the preparation of supported metal phosphides is based on silica because a low acidity oxide favors the formation of metal phosphides due to the low interaction between the support and the precursors [19], and silica has a high surface area and a mesoporous texture that promotes dispersion [17,22,23].

Several studies of the hydrotreatment of vegetable oils with metal phosphides have been reported, see for instance [16–18,24], but in all of them, the metal phosphides were prepared with the phosphate method. To our knowledge no study has used the phosphite method for catalysts synthesis. In this work, we prepare catalysts using the phosphite method, characterize the catalyst, and test the activity of the phosphide-based catalysts in the hydrotreatment of methyl laureate (a model compound for a vegetable oil) to produce green diesel fraction. The characterization results have been correlated with catalytic activity results to determine those properties that have a role on the catalytic performance.

2. Experimental

2.1. Catalysts preparation

The catalysts were prepared by hydrogen reduction of different transition metals (Ni, Co, Fe, Mo and W) dihydrogen phosphites, using commercial silica cylindrical pellets as the support. As indicated in literature [25], for this preparation method, there is no need for calcination and a lower reduction temperature is required. Moreover, it has been proven to form very active and stable catalysts for hydrotreating reactions.

Catalysts (15 wt% metal) were prepared by successive incipient wetness impregnations of silica, adding stoichiometric amounts of phosphorous acid (H_3PO_3, SIGMA–ALDRICH 99%) and the corresponding transition metal precursors ($Ni(OH)_2$ Sigma–Aldrich, $Co(NO_3)_2{\cdot}6H_2O$ 99% Sigma–Aldrich, $Fe(NO_3)_3{\cdot}9H_2O$ 98% Sigma–Aldrich, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ 99% Merck, $(NH_4)_{10}W_{12}O_{42}{\cdot}5H_2O$ PROLABO) to obtain the following phosphides: Ni_2P, Co_2P, FeP, MoP and WP. The precursors were dissolved in 2 mL of water per gram of silica and added dropwise over commercial pelletized silica (1.5 mm cylindrical pellets, Saint Gobain-NORPRO, SS 61138); this procedure was repeated 5 times. Then, the obtained dihydrogen phosphites ($M(HPO_3H)_x$; M = Ni, Co, Fe, Mo, W; $x = 1$ or 2) were dried in an oven at 333 K overnight.

Impregnation was followed by reduction of the precursors to obtain the corresponding phosphides. The activation was carried out ex situ, in a fixed-bed quartz reactor, using a hydrogen flow (1000 mL (NTP) min^{-1}) at a heating rate of 3 K min^{-1} and kept at the reduction temperature for 2 h. A low heating ramp is critical to avoid the formation of phosphates impurities during reduction [25]. On the other hand, the high flow rate of hydrogen has been chosen because it favors the quick removal of water formed during the reduction process [25,26], leading to the formation of smaller particles as well as favoring diffusion of volatile P species onto nickel the particles to form the phosphide. The reduction temperatures were different for each precursor and were chosen from the reduction data previously published for this systems and preparation method [25,26] being 853 K for the nickel and molybdenum precursors, 873 K for the tungsten one, 993 K for the cobalt one, and 1053 K for the iron counterpart. Subsequently, the phosphides were cooled to room temperature in N_2 (200 mL (NTP) min^{-1}) and passivated in a N_2 stream containing 0.5% O_2 for 2 h.

2.2. Catalysts characterization

Textural properties were determined from the adsorption–desorption isotherms of nitrogen, recorded at 77 K with a Micromeritics Asap2420. Specific area was calculated by applying the BET method to the relative pressure (P/P^0) range of the isotherms between 0.03 and 0.3, and taking a value of 0.162 nm^2 for the cross-section of an adsorbed nitrogen molecule at 77 K. Pore size distributions were computed by applying the BJH model to the desorption branch of the nitrogen isotherms.

X-ray diffraction profiles of samples were recorded with a X'Pert Pro PANalytical diffractometer equipped with a Cu Kα radiation source ($\lambda = 0.15418$ nm) and X'Celerator detector based on RTMS (Real Time Multiple Strip). The samples were ground and placed on a stainless steel plate. The diffraction patterns were recorded in steps over a range of Bragg angles (2θ) between 4 and 90°, at a scanning rate of 0.02° per step and an accumulation time of 50 s. Diffractograms were analyzed with the X'Pert HighScore Plus software. The mean domain size was then estimated from X-ray line width broadening using the Scherrer equation. Width (t) was taken as the full width at half maximum intensity of the most intense and least overlapped peak.

Metal dispersions were determined by CO pulse chemisorption. CO uptakes were measured using a Micromeritics Autochem II 2920 apparatus. A 100–200 mg portion of reduced and passivated sample was loaded in the reactor and reduced in a H_2 flow (50 mL min^{-1}) at 723 K for 2 h (ramp, 10 K min^{-1}). Afterwards, the sample was cooled to 313 K, while it was flushed with a He flow (50 mL min^{-1}). When the TCD signal was stable, pulses of CO (75 μL) were passed through the samples until the areas of consecutive pulses were constant. The total CO uptake was then calculated.

$$\text{dispersion}(\%) = \frac{\text{CO uptake}\,(\text{mmoles/g})}{\text{Metal loading}\,(\text{mmoles/g})} \tag{1}$$

NH_3-TPD was carried out using a Micromeritics Autochem II 2920 apparatus. A 110–170 mg of sample was reduced with a H_2 flow (50 mL min^{-1}) at 723 K and then cooled to room temperature. Next, an NH_3 (5%)/He flow (15 mL min^{-1}) was passed through the sample for 30 min at 373 K. In the next step, at 373 K, the sample was swept with a He flow (25 mL min^{-1}) for 30 min to remove the physically adsorbed NH_3. Afterwards, NH_3-TPD was performed in a He flow (25 mL min^{-1}) at a heating rate of 15 K min^{-1}, from 373 to 973 K. The desorbed NH_3 was detected by a TCD.

XPS measurements were registered using a VG Scientific Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an Al Kα ($h\nu = 1486.6$ eV, 1 eV = 1.6302×10^{-19} J) 120 W X-ray source. The analyses were performed after an in situ reduction of the samples at 723 K for 2 h. The area of the peaks was estimated by calculating the integral of each peak after smoothing and subtraction of an S-shaped background and fitting of the experimental curve to a mixture of Gaussian and Lorentzian lines of variable proportions. All binding energies (BE) were referenced to the C 1s signal at 284.6 eV from the carbon contamination of the samples to correct for the charging effects. Quantification of the atomic fractions on the sample surface was obtained by integration of the peaks with appropriate corrections for sensitivity factors [27].

2.3. Catalytic activity test

The catalysts were tested for the hydrotreatment of methyl laurate. The reactor operated in trickled-bed mode in parallel flow and at high pressure, ensuring that the three phases, gas–liquid–solid, are in close contact. The reduced/passivated catalyst pellets without dilution was activated by reduction "in situ" at 723 K at atmospheric pressure, then the reactor was cooled to the reaction temperature and pressurized. The reaction conditions employed were: 553–593 K, 1.0–3.0 MPa, liquid flow 0.2–0.4 mL min^{-1}, and H_2/liquid ratio of 300. The gas phase