



Effect of support-active phase interactions on the catalyst activity and selectivity in deoxygenation of triglycerides

David Kubička^{a,*}, Jan Horáček^a, Michal Setnička^b, Roman Bulánek^b, Arnošt Zukal^c, Iva Kubičková^a

^a Research Institute of Inorganic Chemistry, RENTECH-UniCRE, Chempark Litvínov, Záluží – Litvínov, 436 70, Czech Republic

^b Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

^c J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 182 23 Prague, Czech Republic

ARTICLE INFO

Article history:

Received 14 October 2012

Received in revised form

25 December 2012

Accepted 11 January 2013

Available online 18 January 2013

Keywords:

Deoxygenation

Vegetable oils

Effect of support

Supported NiMo catalysts

ABSTRACT

Three industrially important supports, SiO₂, TiO₂ and Al₂O₃, were used for preparation of NiMo catalysts (3.3 wt.% Ni and 15.0 wt.% Mo) and used in deoxygenation of rapeseed oil in presence of hydrogen (3.5 MPa) at 260–300 °C and liquid feed weight-hourly space velocity in the range 2–8 h⁻¹. Due to the same method of preparation and activation (sulfidation) of the catalysts, the final properties were affected mainly by the differences in the nature of supports as well as their properties, such as specific surface area, pore size distribution or acidity. Most notably the dispersion of the active phase decreased in the following order SiO₂ > Al₂O₃ > TiO₂. As a result, the SiO₂-supported NiMo catalyst exhibited smaller extent of hydrogenation reactions and a larger extent of decarboxylation. On the other hand, the TiO₂-supported NiMo catalyst exhibited increased selectivity to hydrodeoxygenation products, plausible due to the larger active phase cluster size and broad pore size distribution. The results provide clear evidence that even with the conventional hydrotreating active phase, such as sulfided NiMo, the selectivity can be fine-tuned by support selection and modification.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Deoxygenation of triglycerides is one of key processes making possible a convenient production of high quality automotive fuels components (sulfur-, oxygen- and aromatics-free). Various alternative routes for upgrading of triglycerides and related feedstocks, such as free fatty acids, into hydrocarbons have been reported in the literature [1–3]. Three most promising options include (i) catalytic cracking of triglycerides [4–11] under conditions similar to those of fluid catalytic cracking, (ii) decarboxylation using supported Pd catalysts [12–19] and (iii) hydrotreating using conventional hydrotreating catalysts, i.e. supported sulfides of Mo or W promoted by Ni or Co [20–32].

The advantage of catalytic cracking is that deoxygenation can be accomplished without hydrogen consumption. However, the process exhibits rather low selectivity towards diesel fuel components as gaseous and gasoline-range products are formed. The yields vary significantly depending on the catalyst type [4,7–9,11]. The highest yield of diesel cut products were obtained when using hierarchical zeolites (micro-mesoporous materials, such as ZSM-5–MCM-41) [8,33]. Moreover, due to the acid nature of cracking catalysts, cyclization and hydrogen transfer reactions resulting

in formation of aromatics take place in addition to cracking and deoxygenation reactions. Consequently, the diesel fuel properties (cetane number, aromatics content) are worse as compared with hydrodeoxygenation products.

The alternative approach using noble metal catalysts, particularly palladium on carbon, is highly selective, as fatty acids undergo virtually exclusively decarboxylation [12]. Moreover, the reaction does not per se consume hydrogen [12], nonetheless, it has been demonstrated that hydrogen helps in preventing rapid catalyst deactivation by side reactions [14,17,19]. Hydrogen is also needed to saturate any double bonds in the fatty acid moieties to be deoxygenated in order to obtain deoxygenated product having good thermal and oxidation stability. From the industrial perspective point of view, long-term stability and activity of Pd/C catalysts for deoxygenation was not yet demonstrated hindering their widespread application. Recently, another alternative class of catalytic materials has attracted attention for deoxygenation of triglycerides, namely carbides, nitrides and phosphides of molybdenum or nickel [34–36]. These materials offer several advantages for processing of neat triglycerides as these catalysts are stable with time-on-stream [36] and co-feeding of sulfur-containing compounds, which is required for sulfided catalysts to maintain their activity, can be avoided. Since these catalysts are sulfur resistant, co-processing of refinery feeds with triglycerides is possible as well [36].

In contrast to the previous two alternatives, sulfided hydrotreating catalysts have been shown as active and selective catalysts and

* Corresponding author.

E-mail address: david.kubicka@vuanch.cz (D. Kubička).

have been also employed commercially [37,38]. While diesel fuel components are obtained selectively, the only by-products being water, carbon oxides and propane, even at total conversion, and the catalysts are well-known and widely used in the industry, there are several disadvantages to this approach. They include higher consumption of hydrogen than in decarboxylation or cracking [1], need of an external sulfur source to keep the sulfided catalyst in active state [30] and possible formation of sulfur species in the final product [39]. Generally, the formation of new sulfur-containing species is rather limited not threatening the diesel fuel specification limits and hydrogen-sulfide-containing hydrogen streams are readily available in conventional refineries. Hence, the most significant challenge, both from the environmental as well as economical point of view, is the high hydrogen consumption caused by the high oxygen content of triglycerides and fatty acids (ca. 11 wt.%).

The issue can be, in principal, tackled by varying the selectivity of the two main reaction pathways, namely hydrodeoxygenation (HDO) and decarboxylation (HDC). Assuming a model triglyceride consisting exclusively of C₁₈ fatty acids moieties, then in HDO is oxygen eliminated as water and *n*-octadecane (*n*-C₁₈) is formed while in HDC oxygen is removed primarily as CO₂ and *n*-heptadecane (*n*-C₁₇) is formed. Looking at the different stoichiometric requirements for hydrogen consumption in the just described reaction pathways, it becomes obvious that hydrogen consumption could be reduced if one could steer the selectivity towards the HDC pathway. Another aspect that needs to be noted is that by favoring decarboxylation pathway, the yield of diesel fuel range products will be decreased (approximately by 5–6%), as there will be one carbon atom less in the final products than in the case of HDO reaction pathway.

The aim of the work is to investigate the effect of catalyst support on its deoxygenation performance, in particular on the selectivity towards HDO and HDC, respectively. Hence three NiMo catalysts having the same active phase composition were prepared using different industrially relevant supports (Al₂O₃, SiO₂, TiO₂). The deoxygenation performance focusing on deoxygenation products distribution was investigated under typical deoxygenation conditions reported previously [24,32] using rapeseed oil as model feedstock.

2. Experimental

2.1. Catalyst preparation and characterization

NiMo catalysts having the same loading of active components (Ni–3.3 wt.% and Mo–15 wt.%) and different support (Al₂O₃, SiO₂ and TiO₂) were prepared by incipient wetness. The commercial supports were crushed and the fraction 0.25–0.50 mm was used in catalyst preparation. Aqueous solutions of Ni(NO₃)₂·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O were used as the source of nickel and molybdenum, respectively. A two-step procedure was applied. At first the catalyst was impregnated with (NH₄)₆Mo₇O₂₄·4H₂O to contain 15 wt.% Mo and dried at 95–100 °C. Then it was calcined in an oven at 400 °C. Subsequently, the Mo-containing support was impregnated with Ni(NO₃)₂·6H₂O to contain 3.3 wt.% of Ni and dried again at 95–100 °C. Finally, the catalyst was calcined at 400 °C. The same procedure was used for all three supports.

The catalysts were characterized by several physico-chemical methods to assess their relevant catalytic properties. The methods included N₂ physisorption isotherm, DR UV–vis and FTIR spectroscopy, H₂ TPR and NH₃ TPD, and elemental composition (C, S). Nitrogen physisorption method was used to determine textural properties of catalysts (specific surface area and pore size distribution) using a Micromeritics ASAP 2020 volumetric instrument at –196 °C, for details see [40]. The BET surface area was evaluated

using adsorption data in a relative pressure range from 0.05 to 0.25 and mesopore size distributions were calculated using BJH algorithm using Harkins–Jura equation calibrated to accurately determine the pore diameter and volume.

The UV–vis diffuse reflectance spectra of dehydrated samples were measured using Cintra 303 spectrometer (GBC Scientific Equipment, Australia) equipped with a Spectralon-coated integrating sphere using a Spectralon coated discs as a standard. The spectra were recorded in the range of the wavelength 190–850 nm. Before the spectra measurement the samples were dehydrated and oxidized in the glass apparatus under static oxygen atmosphere (15 kPa) in two steps: 120 °C for 30 min and 450 °C for 60 min and subsequently cooled down to 250 °C and evacuated for 30 min. After the evacuation the samples were transferred into the quartz optical cuvette 5 mm thick and sealed under vacuum. This procedure guaranteed complete dehydration and defined oxidation state of all NiMoO_x particles on the catalyst surface. The obtained reflectance spectra were transformed into the dependencies of Kubelka–Munk function $F(R_{\infty})$ on the wavenumber [41].

Redox behavior and dispersion of NiMoO_x surface species was investigated by the temperature programmed reduction by hydrogen (H₂-TPR) using the AutoChem 2920 (Micromeritics, USA). A 100 mg sample in a quartz U-tube microreactor was oxidized in oxygen flow at 450 °C for 60 min prior the TPR measurement. The reduction was carried out from 50 °C to 1050 °C with a temperature gradient of 10 °C/min in flow (25 ml/min) of reducing gas (5 vol% H₂ in Ar). The changes of hydrogen concentration were monitored by the TCD detector and simultaneously hydrogen consumption and water formation was also detected on a quadrupole mass spectrometer OmniStar™ GDS 300 (Pfeiffer vacuum, Germany).

Acidity of supported NiMoO catalysts was investigated by the temperature programmed desorption of ammonia (NH₃-TPD). NH₃-TPD experiments were carried out on the same instrument as H₂-TPR. Before each experiment a 100 mg of sample were pre-treated in a flow of dry oxygen at 450 °C for 60 min and after that the sample was exposed to NH₃ (5 vol% NH₃ in He) at 75 °C for 30 min. The physically adsorbed ammonia was removed by purging with a helium flow for 30 min. Then the TPD was performed in He flow (25 ml/min) with a temperature gradient of 10 °C/min and the desorbed NH₃ was monitored by a TCD detector and by mass spectrometer which allow a monitoring other products of desorption as well.

2.2. Catalytic experiments

The catalytic experiments were carried out in an electrically-heated fixed bed reactor (inner diameter 17 mm) using rapeseed oil as a feedstock (food grade quality, without addition of sulfiding agent) in presence of hydrogen (3.5 MPa) at 260–300 °C. The sulfiding agent was not used to have a clear view on the effect of support only. The liquid feed weight-hourly space velocity was varied in the range 2–8 h⁻¹, while the hydrogen to liquid feed ratio was kept constant at 50 mol/mol. A wide range of LHSV was used in order to evaluate the selectivity changes over a wide range of conversions and degrees of deoxygenation. The conversion and degree of deoxygenation is defined in Eqs. (1) and (2), respectively:

$$\text{Conversion} = \frac{C_{\text{TG}_0} - C_{\text{TG}}}{C_{\text{TG}_0}} \times 100 \quad (1)$$

$$\text{Degree of deoxygenation} = \frac{C_{\text{Ox}_0} - C_{\text{Ox}}}{C_{\text{Ox}_0}} \times 100 \quad (2)$$

where C_{TG_0} and C_{Ox_0} are the concentration of triglycerides and oxygen, respectively, in the feedstock, and C_{TG} and C_{Ox} are the concentration of triglycerides and oxygen in products.

Download English Version:

<https://daneshyari.com/en/article/45312>

Download Persian Version:

<https://daneshyari.com/article/45312>

[Daneshyari.com](https://daneshyari.com)