



Preparation of hydrogenated soybean oil of high oleic oil with supported catalysts



Yue Zhao^a, Yue Ren^a, Ruchun Zhang^a, Lu Zhang^a, Dianyu Yu^{a,*}, Lianzhou Jiang^a, Walid Elfalleh^{b,*}

^a School of Food Science, Northeast Agricultural University, Harbin 150030, China

^b Unité de Recherche Catalyse et Matériaux pour l'Environnement et les Procédés URCMEP (UR11ES85), Faculté des Sciences de Gabès, Université de Gabès, Campus Universitaire Cité Erriadh, Gabès 6072, Tunisia

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ABSTRACT

Cu/SBA15, Cu-Ag/SBA15, Cu-Pd/SBA15, Ni/SBA15, Ni-Ag/SBA15, and Ni-Pd/SBA15 were prepared using a co-impregnation method. The conditions of impregnation (pH4–6, temperature 50–60 °C and time 6.0 h) showed the effects of the supported catalysts on the soybean oil hydrogenation process. The S₁ values of the six catalysts were respectively 32.22, 23.12, 24.26, 29.48, 20.97, and 23.17, under supercritical CO₂ conditions. This clearly indicates that the addition of the precious metals promoter significantly reduced the *trans* fatty acid (TFA) content. When soybean oil was hydrogenated with Cu-Ag/SBA15 catalyst, the selectivity of the linoleic acid was 1.8 times higher than with Cu-Pd/SBA15. When the soybean oil was hydrogenated with Ni-Ag/SBA15 catalyst, the selectivity of the linoleic acid was 1.3 times higher than with Cu-Pd/SBA15. Soybean oil was hydrogenated first with Cu-Ag/SBA15 for 20 min. Then, the hydrogenated soybean oil was purified from the catalyst and hydrogenated again with Ni-Ag/SBA15 for 60 min. The content of oleic acid was up to 50.27% and the content of TFA was lowered to 10.43%.

Practical applications: This paper discusses the preparation process parameters of several representative catalysts for the hydrogenation of soybean oil. The functions of precious metals in hydrogenation reactions are discussed. Kinetic parameters and the selectivity of hydrogenated soybean oil were compared between different supported catalysts. A new method of stepwise hydrogenation is proposed, which can effectively control the unsaturated fat content after hydrogenation. High content of oleic acid in hydrogenated oil was obtained in the current study. This finding will have a wide range of industrial applications in fats and oils industry.

1. Introduction

Hydrogenated oils are often used to overcome the oil unsaturated fatty acid related problems. Hydrogenation increases oxidation resistance, improves shelf life and flavor, changes the thermal behavior of the oil, and makes the oil suitable for specific uses (Alshaihani, Yaakob, Alsobaai, & Sahri, 2017; Fernández, Tonetto, & Damiani, 2009; Simakova, Simakova, Romanenko, & Murzin, 2008). Large amounts of TFA and stearic acid can be produced due to the selectivity and control of catalyst hydrogenation conditions in the oil hydrogenation process. However, excessive amounts of *trans* fatty acids and stearic acid are considered unhealthy. It has been confirmed that the long-term intake of TFA increases the risk of atherosclerosis, thrombosis, coronary heart disease, and other cardiovascular diseases (Oh, Hu, Manson, Stampfer, & Willett, 2005; Stender & Dyerberg, 2004). The studies also showed that obesity and cardiovascular disease are caused by excessive stearic acid intake (Patel, Lecerf, Schenker, & Dewettinck, 2016). Oleic acids

play an important role in preventing high blood pressure and heart disease. Therefore, it is necessary to improve the content of oleic acid in the human diet.

Depending on the role of the catalyst in the catalytic process, the catalysts can be divided into; the main catalyst, the promoter, and the support (Lloyd, 2011). The function of a promoter is to improve the catalytic performance, the selectivity, and the rate of hydrogenation reaction. It has been reported that the addition of Au to Ni-SBA15 catalyst could improve the catalyst activity and the interaction of Ni and SBA15 (He et al., 2015). The choice of the support is very important since it affects the dispersion and the stability of the catalyst, and it may participate in the reaction. Mesoporous materials (e.g. γ-Al₂O₃, MCM41, SBA15) have attracted widespread interest in many areas of catalysis due to their outstanding textural properties. In particular, SBA15, which has a high surface area, good hydrothermal stability, and uniform pore size distribution, is a good carrier for preparing supported metal catalysts (Sareen, Mutreja, Singh, & Pal, 2016; Srivastava et al.,

* Corresponding authors.

E-mail addresses: dyyu2000@126.com (D. Yu), walid.elfalleh@fst.rnu.tn (W. Elfalleh).

2015). A previous study showed that the CeO-Ni-Mo/SBA15 catalyst has good catalytic activity and can prevent carbon deposition (Huang, Benxiong, Zhihua, Chaofeng, & Huang, 2012).

In the oil industry, hydrogenation processes commonly use slurry reactors at high temperatures, low pressures, and long reaction times with Ni catalysts. The carbon double bonds are partially or fully saturated during the hydrogenation. In vegetable oil hydrogenation, the notion of selectivity is important. Usually, hardening linolenic (C18:3) and linoleic acids (C18:2), maintaining oleic acid (C18:1), and minimizing the formation of stearic acid (C18:0) is the desired purpose (Belkacemi, Boulmerka, Hamoudi, & Arul, 2006). However, the selectivity is largely dependent on the residence time in the catalyst pores. A long residence time means higher possibilities of conjugation, isomerization and hydrogenation (De Hault & Demoulin, 1984). In selective hydrogenation, hydrogen atoms selectively add to oil of different unsaturated double bonds. Thus, the composition of fatty acids, the saturation of hydrogenated oil products, and the selection of the double bond position should meet the processing requirement. Bernas et al. (2004) reported that the selective double bond isomerization of linoleic acid to *cis*-9,*trans*-11-conjugated linoleic acid and *trans*-10,*cis*-12-conjugated linoleic acid was more easily performed through γ -Al₂O₃ catalyst treated with Ru(ac)₃ compared with RuCl₃·3H₂O.

Recently, utilizing supercritical fluid conditions for improving the hydrogenation of oils has been advocated. These conditions include the formation of a homogeneous system, reducing the reaction time and lower probability of forming TFA. When vegetable oils, fats, and fatty acids esters were hydrogenated using supercritical solvents such as CO₂, the results showed that higher selectivities and longer catalyst life could be obtained compared to those usually found in conventional reactors (Ramirez, Mayorga, Cuevas, & Recasens, 2011).

In present study, the supported catalysts of Cu/SBA15, Cu-Ag/SBA15, Cu-Pd/SBA15, Ni/SBA15, Ni-Ag/SBA15, and Ni-Pd/SBA15 were prepared by the co-impregnation method. The aim of this paper was to optimize the hydrogenation process in order to obtain oil with high oleic acid content. A series of single-factor experiments were performed to investigate the influence of preparation conditions on the activity of catalysts. Soybean oil was hydrogenated with each catalyst under supercritical CO₂ conditions to investigate the impact of the addition of precious metals on hydrogenated oil isomerization. The kinetics and the selectivity of fatty acids were studied using these catalysts. The reaction time, ratio of the catalyst, and the unsaturated fatty acid composition in hydrogenated oil was controlled using stepwise hydrogenation.

2. Materials and methods

2.1. Materials

Refined soybean oil (Iodine value, 128 g I₂/100 g oil, C16:0 (11.58%), C18:0 (4.52%), C18:1 (21.16%), C18:2 (53.45%), and C18:3 (8.48%) was obtained from the local supermarket. Support SBA15 was obtained from the Nanjing Pioneer Nano Technology Co. Ltd (China). Ni (NO₃)₂·6H₂O and Cu(NO₃)₂·3H₂O were supplied by the Shantou Xilong Chemical Factory Co. Ltd (China). Silver nitrate and palladium nitrate were obtained from the Tianjin Yinda Noble Metal Chemical Reagent Factory (China). C18:0 and all the other reference standards were purchased from Sigma-Aldrich Co. (St Louis, Mo., U.S.A.).

2.2. Methods

2.2.1. Catalyst preparation

Ni-Ag/SBA15 catalysts with the mass fraction of Ni at 12 wt% were prepared by the co-impregnation method using the support of the mesoporous material SBA15 and the promoter silver nitrate, following the procedures described by (Zhou et al., 2015).

AgNO₃ and Ni (NO₃)₂ × 6H₂O were dissolved in deionized water at a ratio of 0.15 wt% (AgNO₃/Ni (NO₃)₂ 6H₂O). The mixture was vigorously stirred and subjected to impregnation at 40 °C–70 °C, for 4–7 h and pH 2.0–7.0; a small amount of dilute nitric acid was added in the preparation of salt solution to change the pH value of the immersion solution. Then, The resultant solid was dried at 100 °C for approximately 12 h, calcined at 350 °C for 4 h, and then reduced in a 5% H₂–95%N₂ atmosphere at 320 °C (the rate of temperature increasing was 5 °C/min) for 3 h to produce the final catalyst (H₂ flow rate of 40 mL/min). The Cu-Ag/SBA15, Cu-Pd/SBA15, Ni-Pd/SBA15, Cu/SBA15, and Ni/SBA15 catalysts were prepared by the same procedure described above. The final percentages of Cu, Ni, Pd, and Ag of the catalysts were determined by ICP-OES (Leeman Labs Company, USA).

2.2.2. X-ray diffraction (XRD) patterns

The crystal structures of SBA15 support and prepared catalysts were examined by powder X-ray diffraction (XRD, D8 ADVANCE X-ray diffraction) with nickel-filtered Cu K α radiation with the following operating parameters: 40 kV, 30 mA, 2 θ scanning from 10° to 80° for wide-angle XRD at a scanning rate of 12°/min.

2.2.3. Transmission electron microscopy (TEM)

The particle size distribution of catalysts was determined by TEM using a JEM-1200EX (Japanese Electronics Optical Company) instrument operated at 100 kV. The sample was put into ethanol and ultrasonically dispersed for 15 min to form a suspension. A drop of the suspension was placed on a copper grid for direct observation.

2.2.4. Hydrogenation method of soybean oil

Refined soybean oil (90 g) and 0.23% of catalysts (w /w) were placed in a 150 mL high-pressure reactor. The CO₂ was filled in to 8 MPa, and then H₂ was introduced to the reactor. The experiment was conducted at 100 °C in an oil bath, at a total pressure of 12 MPa and a hydrogenation stirring rate of 300 r/min under the supercritical CO₂ system. After the reaction, the catalysts from the products were separated. Products were collected and analyzed.

2.2.5. Analysis of iodine value (IV) of fats and oils

The IV of fats and oils was assayed by AOCs Official Method Cd 1–25 (Society & Firestone, 1989).

2.2.6. Determination of catalysts activity

The soybean oil hydrogenation activity of the studied catalysts was determined. The change of the oil iodine value (IV) with the reaction time was calculated to obtain the conversion percentage according to the expression below (Stanković et al., 2015):

$$\text{Conversion (\%)} = [(IV_0 - IV_t)/IV_0] \times 100$$

Where IV₀ - initial iodine value at time t = 0 min and IV_t-iodine value after t = t min.

2.2.7. Determination of fatty acids

Methyl esters of fatty acids were prepared according to the literature (Li et al., 2010). The compositions of the samples were analyzed by Gas chromatography (GC) using flame ionization detector (FID) and a CP-Sil-88 (100 m × 0.25 mm × 0.2 μ m) column (Agilent Technologies, Palo Alto, CA). The carrier gas was nitrogen at a flow rate of 1 mL min⁻¹. The hydrogen and the combustion-supporting gas (air), respectively, were at a flow rate of 30 mL min⁻¹ and 380 mL min⁻¹. The injection temperature and the measured temperature both were 260 °C. The pressure before columniation was 81.7 kPa, the column temperature was 170 °C, the split ratio was 100:1, and the sample size was 1 μ L.

2.2.8. Statistical methods

All the measurements were carried out in triplicate. The mean

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