Magnetic Mesoporous Palladium Catalyzed Selective Hydrogenation of Sunflower Oil

Wei Liu1*, Fei Tian1, Jingjing Yu2* and Yanlan Bi1

1 Lipid Chemistry, College of Food Science and Technology, Henan University of Technology, Lianhua Street, Zhengzhou 450001, P. R. CHINA
2 Zhengzhou Tobacco Research Institute of CNTC, Zhengzhou 450001, P. R. CHINA

Abstract: In this paper, a novel magnetic mesoporous Pd catalyst is used to catalyse selective hydrogenation of sunflower oil at a mild temperature of 50°C. Effects of reaction temperature, stirring speed, time, catalyst loading and hydrogen pressure on the reaction activity, trans fatty acid (TFA) and stearic acid formation were studied. Under the condition of 3.2 mg Pd/100 g oil, 50°C, 1300 rpm stirring speed and 19.0 atm of H2, the lowest amount of TFA generated during the reaction (IV = 80) was 14.9 ± 0.4% while 11.4 ± 0.4% of stearic acid was produced. And this magnetic Pd-catalyst can be reused easily for at least six times without significant catalyst deactivation, the amount of TFA almost remained unchanged. Moreover, this Pd-catalyst shows a good magnetic separation, which provides a potential method for the facile oil modification.

Key words: Pd, magnetic mesoporous catalyst, partial hydrogenation, sunflower oil

1 Introduction

The hydrogenation of vegetable oils is a chemical process by which hydrogen is added to a carbon-carbon double bond in the triglycerides of an oil molecule. The catalytic hydrogenation of vegetable oils has a widespread application in the fat and oil industry. The oxidative stability, melting characteristics and plasticity of oils have been successfully modified through this important industrial process, and then the modified vegetable oils can be used in food specialty fats, such as shortenings, margarines, baking fats, spreads, frying fats and so on. And the iodine value (I.V.) needs to be reduced to about 70-80 for all-purpose shortenings. Whereas hydrogenation process can improve performance attributes by lowering the amounts of linoleic and linolenic acid in the oil, it increases the levels of saturated and trans fatty acids (TFA), both undesirable in view of health implications. Research has shown that diets high in saturated fats increase low-density lipoproteins, which tend to promote the deposition of cholesterol on the walls of blood vessels. More recently, dietary consumption of foods high in TFA has also been linked to increased serum cholesterol content1-5. So far, catalysts used widely in this field are heterogeneous metal catalysts or supported metal catalysts, which usually contained cheap Nickel (Ni), Copper (Cu) or noble Palladium (Pd), Platinum (Pt) transition metals1-4. Compared with cheap Ni or Cu metal, Pd catalyst shows a better catalytic activity during the hydrogenation reactions. What’s more, its catalytic activity is the best in the transition metals. Even though the price of noble metal catalysts (eg. Pd) is high, their ability of high catalytic activity and easily reused and recycled is enough to fill the gap. At present, supported Pd catalysts attract many attentions because of its ability of reusable, stability and highly catalytic activity5-9. As one of the most important component, many supporting materials have been investigated in hydrogenation of oil or fatty acid esters, such as SiO25, 8, 9, Al2O37, 10, TiO28, Carbon11, etc.

Since M41S was first discovered by Mobil scientists in 199212, 13, mesoporous silicas have attracted much attention due to their advantages of high surface area, large pore volume, uniform pore size in the range of 2-30 nm, and tunable surface functional groups14, 15. Several applications have been developed in catalyses, separation, sensors, solar cells, etc.16, 17. In recent years, mesoporous materials have been used as the support of noble metal (eg. Pd) catalysts in the selective hydrogenation of vegetable oils18-20. For example, Belkacemi et al. used mesosstructured silica materials which Pd nanoparticles were highly dispersed as the catalyst for the hydrogenation of vegetable oil, and they reported that the catalytic activity of supported Pd catalyst which Pd loading is 1% was as much as the catalytic activity of Ni catalyst21. However, powder catalysts present difficulty in separation and recovery due to...
high viscosity of vegetable oils. Magnetic materials could be rapidly separated from liquid phase by magnetic field. Magnetic mesoporous materials could combine the property of mesoporous materials and magnetic materials. Since magnetic nanoparticles dispersed in the pores of mesoporous materials were potentially unstable in acid or alkaline system, the core-shell magnetic mesoporous materials showed obvious advantage, and then became an alternative catalyst supports. However, to our knowledge, no example of hydrogenation of vegetable oils catalyzed by magnetic mesoporous Pd-catalyst has been reported until now.

Thus, Pd nanoparticles dispersed on core-shell magnetic mesoporous silica (i.e. Fe3O4@nSiO2@mSiO2/PdNPs) as catalyst was prepared in this work, which was successfully applied to partial hydrogenation of sunflower oil. Different operating conditions, such as reaction temperature, stirring speed, catalyst loading and H2 pressure on the hydrogenation of sunflower oil were discussed. Moreover, the performance of Pd-catalyst reuse and magnetic separation were also evaluated in this work.

2 Experimental

2.1 Materials

Sunflower oil was purchased from a local supermarket (fatty acids composition (wt%): C16:0, 5.9%; C18:0, 5.6%; C18:1, 28.0%; C18:2, 56.9%; C18:3, 0.4%; C20:0, 0.3%; C22:0, 1.0%; L.V. = 123.7). Palladium (II) chloride (Pd ≥ 59%, Shanghai Institute of Fine Chemical Materials, Shanghai, China), Sodium acetate anhydrous (NaOAc, ≥ 99%, Tianjin Fengchuan Chem. Reagents, Tianjin, China), Ferric chloride (FeCl3·6H2O, ≥ 99%), Ethylene glycol and tetraethyl orthosilicate (TEOS, ≥ 98%) all were purchased from Tianjin Kermel Chem. of China. Ammonia solution (≥ 25%), acetone and formaldehyde solution (37 - 40%) were purchased from Luoyang Chem. Reagents of China.

2.2 Catalyst Preparation

Magnetic mesoporous silica material (Fe3O4@nSiO2@mSiO2) was synthesized according to a paper reported by Deng and Zhao. Fe3O4 particles were prepared using FeCl3·6H2O as precursor and ethylene glycol as reductant. Fe3O4@nSiO2 particles were obtained by the hydrolysis of TEOS on Fe3O4 particles. Fe3O4@nSiO2@mSiO2 particles were prepared using CTAB as a template and TEOS as silica source.

Fe3O4@nSiO2@mSiO2/PdNPs catalyst was prepared by impregnating supports (Fe3O4 @nSiO2@mSiO2) with an aqueous solution of palladium chloride (PdCl2). An amount of 0.0167 g PdCl2 was dissolved in deionized water, and then adjusted pH to 2.0 by HCl solution. And 1.0 g supports was added and impregnated for 12 h. After impregnating, the pH value was adjusted with KOH aqueous to 7.0, and then distracted in a three-necked flask. The solution was reduced by formaldehyde at 40 °C for 4 h with a reflux condenser (the amount used was 10 times of theoretical values). The reduced solution was separated with vacuum filtration. And the catalyst was washed with deionized water to remove residual chlorine. Then the Pd-catalyst (3%-Fe3O4@nSiO2@mSiO2/PdNPs) was successfully prepared after dried under vacuum at 80 °C for 5 h.

2.3 N2 Adsorption-Desorption Measurements

The adsorption and desorption experiments of N2 were performed on a Tristar 3020 surface area and pore size analyzer (Micromeritics Instrument Corporation, USA). The average pore diameter distribution was calculated from the desorption branch of the isotherm using the Barrett-Joyner-Halenda method. The surface area was obtained using N2 adsorption isotherm with the BET equation. The total pore volume was evaluated from the amount of N2 adsorbed at a relative pressure of 0.99.

2.4 Hydrogenation of sunflower oil

Hydrogenation of sunflower oil was performed at set temperature in a 100 mL stainless steel autoclave equipped with a pressure gauge for adjusting the pressure of the reactor, and thermocouples for reactions temperature measurements. Powdered catalyst and sunflower oil (20 g) were weighted to the reactor and hydrogen was filled to replace air in reactor for three times to ensure the system eliminating the air. Maintaining the reaction system under the indicated pressure of H2 (1.0 atm - 19.0 atm). Hydrogenation temperature was maintained at the indicated temperature with an external controller with an agitation rate of 700-1300 rpm. Oil samples were periodically obtained from the hydrogenation reactor and the reaction was stopped when the oil sample was solidified.

2.5 GC Analysis

For the determination of fatty acid composition, the oil sample was converted to fatty acid methyl esters. Typically, 200 μL of 0.5 M methanolic base (CH3ONa) and 30 mg triglyceride oil were mixed together in a screw-capped test tube. The solution was vibrated at room temperature for 10 min. To the sample were added 1 mL hexane and 1 mL brine solution, and the sample was again vortex mixed. The contents separated into organic and aqueous layers; the organic phase was recovered and used directly for GC analysis.

The fatty acid composition of the hydrogenated sunflower oil was analyzed using an Agilent 6890 N gas chromatography equipped with a flame ionization detector (GC-FID). A BPX-70 (120 m × 250 μm × 0.2
μm) capillary column was used. Samples of 1 μl were injected under the following conditions: the carrier gas was nitrogen with a flow rate of 0.6 ml/min, the injector temperature was 210 °C with a split ratio of 50:1, and the detector temperature was 230 °C. The sample was injected at an oven temperature of 120 °C. After an isothermal period of 3 min, the GC oven was heated to 175 °C at a rate of 8 °C/min and held for 28 min, the GC oven was heated to 200 °C at a rate of 3 °C/min and held for 20 min.

The fatty acid methyl esters were identified by their elution times with known standards. The TFA esters consisted of a number of peaks that include esters of trans-mono-enoic acids (such as elaidic acid) and trans-dienoic acids (including conjugated linoleic acids). These values were used in the calculations of fatty acid composition. The I.V. could be calculated from the fatty acid levels from the GC data through Eq. 1:

$\text{IV} = 0.950 \times (C_{16:1}) + 0.860 \times (C_{18:1}) + 1.732 \times (C_{18:2}) + 2.616 \times (C_{18:3}) + 0.785 \times (C_{20:1})$

(“$C_{xy}$” corresponded to the sum of relative percentage concentrations of an unsaturated fatty acid with x total carbon number and y double bonds)

2.6 Iodine Value (I.V.)

The iodine value (I.V.) is defined as the weight in grams of iodine absorbed by 100 g of oil or fat. Experimentally this was obtained by using the Wijs method\(^{20}\). In this method an oil sample was dissolved at 70 °C in 15 mL CCl\(_4\). Wijs solution (25 mL) was added, and the reaction mixture was kept in the dark for approximately 30 min at room temperature to complete the reaction. Finally, 20 mL KI (aq.) and 100 mL distilled water were added, and the excess iodine was titrated with 0.1 M sodium thiosulfate. Note that the Wijs solution contained 0.1 mol/L of iodine monochloride; in this work it was purchased from Sigma-Aldrich as a standardized solution. Spot checks of I.V. values determined from the Wijs method and GC gave good agreement.

3 Results and discussion

3.1 N\(_2\) Adsorption-Desorption Measurements

Figure 1 shows the nitrogen adsorption-desorption isotherm for Fe\(_3\)O\(_4\)@nSiO\(_2\)@mSiO\(_2\)/PdNPs catalyst. Figure 2 depicts the corresponding pore size distribution curves. At relative pressure ($p/p_0$) in the range of 0.4 - 0.8, the isotherm of Fe\(_3\)O\(_4\)@nSiO\(_2\)@mSiO\(_2\)/PdNPs gave a sharp rise and produced a hysteresis loop. This is a type IV curve of mesoporous materials\(^{21}\). The BET surface area is calculated to be 49.67 cm\(^2\)/g, and the average pore size is 3.97 nm.

Fig. 1  Adsorption-desorption isotherm for Pd/Fe\(_3\)O\(_4\)@nSiO\(_2\)@mSiO\(_2\). (○ means desorption, ■ means adsorption)

Fig. 2  Pore size distributions for Pd/Fe\(_3\)O\(_4\)@nSiO\(_2\)@mSiO\(_2\).

3.2 Influence factors on reaction rate, TFA and stearic acid content

3.2.1 Effect of reaction temperature

Reaction temperature has an important influence on hydrogenation reactions, such as the reaction rate, hydrogen solubility, viscosity of oil and so on. For Pd catalysts exhibit highly activity in oil hydrogenation at atmospheric pressure of H\(_2\), a set of experiments were conducted at the temperature range of 30 °C to 110 °C under 1.0 atm of H\(_2\). The reaction rate was monitored by the decrease of IV which indicates the level of saturation double bonds. The IV decline curve of hydrogenated sunflower oils at different temperatures is presented in Fig. 3. As expected, the reaction rate was increased when the reaction temperature was increased. The hydrogenation process was very slow at 30 °C, which reached an IV of 73 after 720 mins. And an obvious increase of reaction rate could be observed in Fig. 3 at 50 °C. The hydrogenated sunflower oil at 110 °C reached an IV of 75 after only 60 mins and shown the fastest reaction rate amongst the tested temperatures. In conclusion, the temperature of 50 °C - 90 °C had an approximate reaction rates.

Figure 4 presents the percentage of TFA and stearic acid
formed under different reaction temperatures. Those five experiments were compared when the IV of hydrogenated sunflower oil reached 80. The highest level of TFA (37.3 ± 1.3%) was produced at 110 °C while the contents of TFA were 30.1 ± 1.2%, 24.5 ± 0.6%, 21.7 ± 0.5% and 21.3 ± 0.6% at the reaction temperature of 90 °C, 70 °C, 50 °C and 30 °C, respectively. Compared with those results, a higher reaction temperature led to a higher percentage of TFA generation. These results could be explained by thermodynamics. During the hydrogenation of unsaturated carbon-carbon double bond, with the single increase of temperature, the reaction rate would increase and the selectivity of the reaction would improve which lead more isomers generated. Meanwhile, trans-isomers were more stable than cis-isomers in thermodynamic theory. Therefore, the higher reaction temperature conducted, the more amount of stable trans-isomer produced. Interestingly, the amount of stearic acid generated always maintained at 4.7 ± 0.1% - 6.3 ± 0.2% from 30 to 110 °C, which indicated that this Pd-catalyst exhibited good reaction selectivity. According to Fig. 4, the lowest amounts of TFA (21.3 ± 0.6% vs 21.7 ± 0.5%) and stearic acid (5.6 ± 0.2% vs 6.3 ± 0.2%) were detected at 30 °C and 50 °C. However, semi-solid hydrogenated oil produced as the reaction progress at around 30 °C which would obviously influence its application. What’s more, the hydrogenation reaction rate was too slow to choose it as the condition of this reaction at 30 °C. Thus, 50 °C was chosen as the optimal reaction temperature to investigate the subsequent work and 21.7 ± 0.5% of TFA and 6.3 ± 0.2% of stearic acid were produced in the hydrogenated oil at 50 °C.

3.2.2 Effect of Stirring speed

Under the reaction conditions of 50 °C, 1.0 atm H₂ pressure and 3.2 mg/Pd/100 g Oil catalyst, the effect of stirring speed was investigated. The IV decline curves of hydrogenated sunflower oils at different stirring speeds were shown in Fig. 5.

As shown in Fig. 5, the faster stirring speeds contributed to the higher reaction rate. The reaction stirring speeds of 1300 rpm and 1500 rpm exhibited the similar reaction rate which were higher than others (700 - 1100 rpm). Under the stirring speed of 1300 rpm and 1500 rpm, the IV of hydrogenated oil were 76 and 74 after 4 h, respectively, which can be explained by mass transfer effect and homogenization. Mass transfer means dissolving hydrogen from ambient of the reactor to the sunflower oil and catalyst. And stirring also corresponds homogenization of the dissolved gas (H₂)-liquid (oil)-solid (Pd catalyst) in the oil. When the mass transfer effects and homogenization reached maximum (1300 - 1500 rpm), the hydrogenation reaction rate was no longer increased.

Figure 6 shows that the percentage of TFA and stearic acid formed at IV of 80 under different stirring speeds. Those experiments at different stirring speeds (700 rpm, 900 rpm, 1100 rpm, 1300 rpm and 1500 rpm), produced TFA were 27.1 ± 0.8%, 25.9 ± 1.1%, 25.1 ± 0.8%, 21.7 ± 0.5% and 21.6 ± 0.8%, respectively. On the whole, a higher stirring speed was contributed to decrease the amount of TFA generated and the percentage of TFA from 1300 rpm to 1500 rpm had not obvious decrease (21.7 ± 0.5% vs 21.6 ± 0.8%). A higher stirring speed was easier to make the hydrogen molecule react with unsaturated carbon-carbon double bonds on the Pd catalyst surface. Moreover, with the stirring speeds increasing from 700 rpm to 1500 rpm, the extra amount of generated stearic acid increased from 3.5 ± 0.1% to 8.2 ± 0.3%. Based on the
amount of TFA and stearic acid formed between 1300 rpm (21.7 ± 0.5%, 6.3 ± 0.2%) and 1500 rpm (21.6 ± 0.8%, 8.2 ± 0.3%), the optimum stirring speed was 1300 rpm for our following study.

3.2.3 Effect of catalyst loading
Catalyst loading has a direct impact on the reaction rate of oil hydrogenation. Under the condition of 50 °C, 1 atm H₂ pressure, different amounts of Pd catalyst (1.6, 3.2, 6.3, 12.6 and 25.2 mg Pd/100 g Oil) were examined in hydrogenation of sunflower oil, respectively. The data presented in Fig. 7 clearly demonstrated the influence of the catalyst amounts on the catalytic hydrogenation rates. Overall, the more amount of catalyst used, the higher hydrogenation rate exhibited. From the economic viewpoint, the least amount of catalyst was used to achieve the best catalytic effect.

The amount of TFA and stearic acid formed under different catalyst loading were shown in Fig. 8. Those five experiments (1.6, 3.2, 6.3, 12.6 and 25.2 mg Pd/100 g Oil respectively) produced 22.9 ± 0.8%, 21.7 ± 0.5%, 21.9 ± 0.8%, 24.3 ± 1.0%, and 26.5 ± 1.2% of TFA, respectively. The lowest percentage of TFA (21.7 ± 0.5% vs 21.9 ± 0.8%) was observed when the catalyst amounts were 3.2
The effect of hydrogen pressure was also investigated. Considering the commonly used H₂ pressure in oil-hydrogenation process, the catalytic hydrogenation at four different hydrogen pressures (1.0, 5.0, 10.0 and 19.0 atm) were studied (Fig. 9). When the IV of hydrogenated oil was 80, the percentage of TFA were 21.7 ± 0.5%, 19.2 ± 0.8%, 17.1 ± 0.7% and 14.9 ± 0.4%, respectively. While the percentage of extra produced stearic acid in the hydrogenated sunflower oil were increased from 6.3 ± 0.2% to 11.4 ± 0.4%.

Figure 9 shows that the percentage of TFA has a noticeable decrease (21.7 ± 0.5% vs. 17.1 ± 0.7%) as hydrogen pressure rises from 1.0 to 10.0 atm, which is reasonably expected as for most oil hydrogenation process. A further decrease of the percentage of TFA levels (17.1 ± 0.7% vs. 14.9 ± 0.4%) has not been obviously observed when the pressure of H₂ was increased from 10.0 to 19.0 atm. The above results can be explained that the concentration of hydrogen, which stay on the surface of Pd-catalyst, was increased with hydrogen pressure rising. However, the increase of concentration of hydrogen is limited. With the dramatic increase of hydrogen pressure, the percentage of TFA could not be further decreased infinitely. Additionally, the increase of H₂ pressure led to increased amount of generated stearic acid (6.3 ± 0.2%/1.0 atm, 8.5 ± 0.4%/5.0 atm, 10.1 ± 0.3%/10.0 atm and 11.4 ± 0.4%/19.0 atm), which was also consistent with the hydrogen pressure effect on saturated acids formation. Based on the experimental range explored in this work and the actual production situation, the optimum H₂ pressure was 19.0 atm.

3.3 Recycle of magnetic mesoporous Pd catalyst

Pd is a noble metal and its price is much higher than Ni and Cu, which typically used for catalytic hydrogenation of oil and fat. From the viewpoint of economic, the recyclable use of supported Pd catalyst for hydrogenation, which can not affect the catalytic activity, is highly desirable. As for the recyclable use, the catalyst was absorbed with a magnet, while hydrogenated oil was dumped from the system at heating temperature. Then, the catalyst was washed with hexane for three times, and dried at 80 °C for 0.5 hour under reduced pressure, which afforded the recycled catalyst. Under the same reaction condition (Fig. 10), the Fe₃O₄@nSiO₂@mSiO₂/PdNPs catalyst was reused for hydrogenation of sunflower oil for at least six times. Those hydrogenated sunflower oils with IV of 80 showed the similar amount of TFA, which were 22.1%, 25.3%, 24.3%, 23.6%, 23.8% and 23.9%, respectively. Compared with the catalyst first used, TFA amount for reused catalyst had slight increase. Notably, as shown in Fig. 11, the Fe₃O₄@nSiO₂@mSiO₂/PdNPs catalyst could be separated from hydrogenated oil easily by a magnet and redispersed quickly with a shake once the magnetic field was removed. Based on the above results, it indicates that this mesoporous
magnetic Pd catalyst has a promising potential for recyclable use with stable catalytic activity in oil hydrogenation.

4 Conclusions

The magnetic mesoporous Pd catalyst was prepared through synthesis of super paramagnetic microspheres with a Fe₃O₄@nSiO₂@mSiO₂ and the metal Pd precursor for impregnation. The magnetic mesoporous Pd catalyst was easy to separate from the hydrogenated oil by a magnet and form a low level of TFA and stearic acid for the selective hydrogenation of sunflower oil, which exhibited good hydrogenation activity and selectivity. The experiments of the hydrogenation of sunflower oil investigated the influence of TFA and stearic acid formation with four factors (temperature, stirring speed, catalyst loading, and pressure of hydrogen). As the results, under the operating conditions of 50 °C, 3.2 mg Pd/100 g oil of catalyst loading, 1300 rpm of stirring speed and 19.0 atm of hydrogen, the hydrogenated sunflower oil (IV = 80) contained the lowest amount of TFA in 14.9 ± 0.4%. Compared with purchased 5% Pd/C catalyst, our magnetic mesoporous Pd catalyst exhibits similar reaction rate and less amount of TFA in hydrogenation process than 5%-Pd/C catalyst. Furthermore, the magnetic catalyst has been successfully reused for the hydrogenation of sunflower oil for six times without the obvious catalyst deactivation.

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