Ni-Ag Bimetallic Magnetic Catalyst Improves the Performance of the Catalytic Transfer Hydrogenated Soybean Oil

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Abstract: The role of Ni-Ag bimetallic magnetic catalysts in the catalytic transfer of hydrogenated soybean oil was studied. First, a Ni-0.15/PVP-DB-171/SiO₂/Fe₃O₄ magnetic catalyst with a magnetic saturation value of 10.431 emu / g was prepared. It was found that the addition of the metal Ag promoter enhanced the dispersion of Ni on the PVP-DB-171/SiO₂/Fe₃O₄ support. The conditions of the catalytic transfer hydrogenation (CTH) (temperature 80°C, catalyst loading 0.23%, donor concentration 0.32 mol /50 mL H₂O, and time 90 min) showed the effects of the bimetallic catalysts on the soybean oil hydrogenation process. The hydrogenated soybean oil linolenic acid, linoleic acid and oleic acid reaction rate constants were 4.95×10⁻², 8.6×10⁻³ and 7.54×10⁻⁴, respectively. The selectivity of linolenic acid and linoleic acid is as high as 5.75 and 11.4, respectively; the iodine value (IV) of soybean oil after hydrogenation is 102 g I₂/100g and the trans fatty acids(TFAs) content is only 1.7%. The use efficiency of the catalyst decreased to 60% after 8 cycles. Catalytic transfer hydrogenation has important research significance and application prospects for the preparation of low-trans hydrogenated oils and fats. This method also provides a theoretical basis for the development of the oil hydrogenation industry.

Key words: Ni-Ag magnetic catalyst, dispersivity, catalytic transfer hydrogenation, soybean oil, trans fatty acids, selectivity

1 Introduction
Soybean oil consists primarily of triglycerides of saturated and unsaturated fatty acids. The hydrogenation of oils and fats results in the substantial formation of TFAs. When TFAs are ingested in vivo, their consumption will increase the low density lipoprotein (LDL) level and decrease the high density lipoprotein (HDL) level¹. The hydrogenation of soybean oil is an important process in the chemical industry for oils and fats. Hydrogenation increases oxidation resistance, improves shelf life and flavor, changes the thermal behavior of the oil, and makes the oil suitable for specific uses². Therefore, the unsaturated fatty acid and trans fatty acid levels in hydrogenated oils must be reduced as much as possible.

The quantity of TFAs that is produced during oil and fat hydrogenation can be decreased by changing the catalyst composition. According to the role of each component of the catalyst in the catalytic process, it can be divided into the main catalyst, the promoter and the carrier³. Through the preparation of a highly active catalyst, people can reduce the trans fatty acids contents in oil products. The methods include selecting suitable carriers in order to improve the specific surface area of the catalyst and adding promoters in order to improve the selectivity in the preparation of the main catalyst.

γ-Al₂O₃, MCM-41, SBA-15 and magnetic materials are commonly used as supports during catalyst preparation⁴. Goel et al. reported that highly dispersed PVP-supported Ir–Ni bimetallic nanoparticles was high performance catalysts, and PVP could be used as a capping agent⁵. Composite magnetic materials have both magnetic and other special physical properties, and many types of functional magnetic materials have been widely used⁶. Ansari et al. reported that superparamagnetic Fe₃O₄ nanoparticles were used to prepare magnetic carriers⁷. It was found that the magnetic carriers had strong magnetic responsiveness, and could be separated quickly under an external magnetic field in order to achieve targeted mobility. Shafiei et al. reported that under the action of an external magnetic field, the magnetic particles in the magnetic fluidized bed will...
regularly fluidize, which can improve the mass and heat transfer rates of the fluid in the bed\(^1\). The magnetic particles are locked in the magnetic field area and the substrates can continuously contact with magnetic particles and quickly separate, which is helpful for the continuous production of magnetic particles. In particular, a good magnetic response makes magnetic particles efficient at facilitating separation and orientation in practical applications, and has good control performance. The catalyst that is used for the hydrogenation of oils and fats is metal nickel (Ni). At present, the research on single metal catalysts is highly mature at home and abroad. To realize the complementary advantages of catalysts in the catalytic process, researchers have investigated binary metal catalytic systems\(^2\). There is a unique synergistic effect between the two metals in bimetallic nanocatalysts. This synergistic effect can induce the excellent properties of their corresponding monometallic counterparts\(^3,\(^4\)). Common bimetallic catalysts include Cu-Ni, Ni-Cr and more. The low activation temperature of a Cu-Ni catalyst and the low trans fatty acid content in the hydrogenated oil is likely to cause oil oxidation and rancidity. The results showed that a Ni-Ag catalyst had better selectivity for the hydrogenation of linoleic acid and fewer isomers\(^5\). Therefore, more scholars have studied bimetallic catalysts for hydrogenating vegetable oils and fats.

Supercritical fluid hydrogenation, electrochemical hydrogenation and CTH can be used to reduce the TFAs content in the hydrogenation process. The hydrogenation time of soybean oil using supercritical fluid is short, but the reaction is carried out under high pressure and the reaction environment is harsh\(^6\). Electrochemical hydrogenation avoids high pressure and mild reaction conditions, but the hydrogenation rate is slower\(^7\). Therefore, CTH is a hydrogenated soybean oil technology in which hydrogen is replaced by hydrogen donors. This technology can avoid high temperature and pressure, and the reaction rate is fast\(^8\). However, most of the research is on the single metal catalyst CTH in vegetable oil.

In present study, single metal nickel and bimetal nickel silver catalysts were immobilized on PVP-DW-171/SiO\(_2\)/Fe\(_3\)O\(_4\) magnetic particles respectively, and the effect of adding a certain amount of metal silver on the main catalyst was studied. The prepared bimetallic catalysts were applied to the hydrogenation of primary soybean oil in a CTH system. The effects of the donor concentration, catalyst addition and hydrogenation temperature on the hydrogenation process were studied. According to the changing trend of fatty acids in hydrogenated oils and fats, the kinetics of the hydrogenation of oils and fats were studied. The separation effect and reusability of the catalysts were also studied.

### 2 Materials and Methods

#### 2.1 Materials

Refined soybean oil (iodine value, 132 g of I\(_2\)/100 g oil) was obtained from JiisanOils and Grains Industries Group Co., Ltd. Ni(NO\(_3\))\(_2\)-6H\(_2\)O was supplied by Shantou Xilong Chemical Factory Co. Ltd. (China). Silver nitrate was obtained from Tianjin Yinda Noble Metal Chemical Reagent Factory (China). 2, 2'-Azobis(AIBN) was purchased from Kewei New Materials Science and Technical Developing Company of Tianjin University. N-Vinyl-2-pyrrolidone (NVP) was purchased from New Friendship International Industrial and Trading Company. All other chemicals were commercially available and of analytical grade. All chemicals and solvents in the product analysis were of high purity and were used as such without any further processing. The laboratory constructed the stainless steel reactor.

#### 2.2 Methods

##### 2.2.1 Catalyst preparation

SiO\(_2\)/Fe\(_3\)O\(_4\) was prepared following a previously reported procedure\(^9\). PVP-DW-171 was prepared as follows. DB-171 (0.14 g), NVP (3.98 g) and AIBN (0.20 g) were mixed with 80 mL of ethanol. The mixture was refluxed at 75°C for 6 h and then hand-dried at 60°C under vacuum for 24 h. The aqueous solution of 2 g of SiO\(_2\)/Fe\(_3\)O\(_4\), 200 mL of deionized water and 20 mL of 0.05 g/mL PVP-DW-171 ethanol solution were added to the triangular bottle, after which 0.3 g of triethylamine were added. The reflux occurred for 10 h at 70°C. The magnetic separation was conducted, the deionized water was washed three times, and the PVP-DW-171/SiO\(_2\)/Fe\(_3\)O\(_4\) was obtained by magnetic separation while washing. In total, 10 g of aqueous PVP-DW-171/SiO\(_2\)/Fe\(_3\)O\(_4\) solution (0.8%) and 50 mL of deionized water were mixed and dispersed using ultrasonication in a three-necked flask for 30 min, after which 64 g of nickel nitrate and NaBH\(_4\) (0.063 mol/L) aqueous solution were mixed for 4 h in the same three-necked flask. The Ni/PVP-DW-171/SiO\(_2\)/Fe\(_3\)O\(_4\) magnetic NP catalyst was obtained by washing the solid three times with deionized water, which was followed by magnetic separation. In total, 4 g of aqueous PVP-DW-171/SiO\(_2\)/Fe\(_3\)O\(_4\) solution (0.8%) and 25 mL of deionized water were mixed and dispersed using ultrasonication in a three-necked flask, after which 9.2 g of silver nitrate and NaBH\(_4\) (0.2 mol/L) aqueous solution were mixed using ultrasonication in a three-necked flask and reacted for 4 h. Finally, the Ni-Ag/PVP-DW-171/SiO\(_2\)/Fe\(_3\)O\(_4\) catalyst was prepared by placing the powder in a vacuum oven at 60°C for 24 h, and the nickel content was 15 wt. %.

##### 2.2.2 EDX/SEM

The particle size distributions of the prepared catalysts were determined by SEM using a JSM-6400 instrument (Japanese Electronics Optical Company, Japan) that was operated at 10 kV. Small amounts of the ground catalysts were evenly coated on the conductive adhesive, and Pt was
sprayed as a pretreatment in order to enhance the conductivity. EDX was used to determine the composition and distribution of the catalysts.

2.2.3 Magnetic properties

The magnetic properties of the products were characterized at room temperature using a BHV-55 VSM (Riken, Japan).

2.2.4 Experimental procedure

Refined soybean oil (90 g), a certain amount of catalyst and an ammonium formate solution were placed in a 150 mL reactor. The reactor is placed in a water bath under magnetic stirring. After the reaction, the catalysts from the products were separated. The products were collected and analyzed.

2.2.5 Iodine value of hydrogenated soybean oil

The IV of the fats and oils were assayed using the AOCS Official Method Cd 1–25 (Society & Firestone, 1989) 20.

2.2.6 Determination of fatty acids

The methyl esters of the fatty acids were prepared according to the literature 21. The compositions of the samples were analyzed by Gas chromatography (GC) using a flame ionization detector (FID) and a CP-Sil-88 (100 m × 0.25 mm × 0.2 μm) 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) were provided at flow rates of 30 mL min⁻¹ and 380 mL min⁻¹, respectively. 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 μL.

2.2.7 Kinetic analysis of CTH soybean oil by bimetallic magnetic catalysts

The CTH soybean oils were hydrogenated with a bimetallic magnetic catalyst in order to study the kinetics of the hydrogenated soybean oils. Albright proposed a reaction procedure based on the Bailey model, as shown below 22:

Linolenic → Linoleic → Oleic → Stearic

With a constant amount of hydrogen in the reaction, the catalyst did not lose activity, based on the first order assumptions and irreversible reactions, which are as follows:

\[
\omega(1) = \omega_{0(1)} \exp(-k_1 t)
\]

\[
\omega(2) = \omega_{0(2)} \left( k_3 \left( k_2 - k_3 \right) \left( k_3 \right) + k_3 \right) \exp(-k_2 t) + \omega_{0(2)} \exp(-k_1 t)
\]

\[
\omega(3) = \omega_{0(3)} \left( k_3 \left( k_2 - k_3 \right) \left( k_3 \right) + k_3 \right) \left( k_3 \right) \exp(-k_3 t) - \omega_{0(3)} \left( k_3 \left( k_2 - k_3 \right) \left( k_3 \right) + k_3 \right) \exp(-k_1 t)
\]

\[
[\exp(-k_2 t) - \exp(-k_3 t)] + \omega_{0(3)} \left( k_3 \left( k_2 - k_3 \right) \left( k_3 \right) + k_3 \right) \exp(-k_3 t)
\]

\[
- \exp(-k_3 t) + \omega_{0(3)} \exp(-k_3 t)
\]

The vector of unknown parameters \( [k_1, k_2, k_3] \) can be identified from Eqs. 1–3 using the nonlinear regression method, where \( \omega(3), \omega(2) \) and \( \omega(1) \) are the compositions on a mole percentage basis for the linolenic, linoleic and oleic acid groups respectively at time \( t \); \( \omega_{0(3)}, \omega_{0(2)} \), and \( \omega_{0(1)} \) are the composition of the linolenic, linoleic and oleic acid groups of the initial oil, respectively; and \( k_n, k_2, k_1 \) are the rate constants for the hydrogenation of the linolenic, linoleic and oleic acids, respectively. The nonlinear regression method is used to solve \((1) - (3)) 3 differential equations and the rate constants of each reaction path are obtained.

2.2.8 Reusability of the catalysts

The Ni-Ag₀.₁₅/PVP-DB-171/SiO₂/Fe₃O₄ catalysts were reused for 10 cycles of soybean oil hydrogenation. After each cycle, the IV of the hydrogenated soybean oil was determined, and the catalysts were magnetically separated and washed several times with 95% ethanol. Finally, the catalysts were dried at 60 °C and reused.

The conversion rate of the catalyst was calculated according to the following formula 23:

\[
\text{Conversion} (\%) = \frac{IV_0 - IV_n}{IV_0} \times 100\%
\]

Among them, IV₀ represents the initial iodine value, and IVₙ is the iodine value after n times.

Furthermore, the use efficiency was defined as the ratio of the conversion rate of catalyst that has been used n times to the conversion rate of the catalyst after being used for the first time.

Therefore, the use efficiency (\%) = \( C_n/C_1 \times 100\% \)

Where \( C_1 \) is the conversion rate of the catalyst that is used for the first time, and \( C_n \) is the conversion rate of the catalyst that has been used n times.

2.2.9 Statistical methods

All of the measurements were carried out in triplicate. The mean values and standard deviations were calculated. The diagrams were drawn out according to the data using Origin 8.5. The data analysis and statistical analysis were done using SPSS software. The kinetic parameters were analyzed using Matlab2016a software.

3 Results and Discussion

3.1 Principle of CTH soybean oil by bimetallic magnetic catalysts

The overall mechanistic insight into catalytic transfer hydrogenation (CTH) using ammonium formate as hydrogen donor can be presented as follows 24:

Main reaction:

\[
\text{HOOCNH}_2 \rightarrow \text{NH}_4^+ + \text{HCOO}^-
\]
HCOO⁻ + H₂O + Ni-Ag→H − Ni-Ag − H + HCO₃⁻
H − Ni-Ag − H + R₁ − CH = CH − R₂→R₁ − CH₂ − CH₂ − R₂ + Ni-Ag
HCO₃⁻→OH⁻ + CO₃²⁻
CO₃²⁻ + H₂O→H₂CO₃→H⁺ + HCO₃⁻
NH₄⁺ + OH⁻→NH₃ + H₂O
HCOONH₄ + R₁ − CH = CH − R₂→R₁ − CH₂ − CH₂ − R₂ + NH₃ + CO₂

side reaction:
H − Ni-Ag − H→Ni-Ag + H₂

3.2 Main characteristics of the Ni-Ag₀.₁₅/PVP-DB-171/SiO₂/Fe₃O₄ magnetic catalyst
3.2.1 EDX/SEM

The EDX spectrum of the Ni-Ag₀.₁₅/PVP-DB-171/SiO₂/Fe₃O₄ magnetic catalyst is shown in Fig. 1. It can be seen from Fig. 1a that Ag and Ni peaks appear in the catalyst spectrum, and the Ag/Ni content (%) ratio is 3/13, which proves that the main component of the catalyst is Ni and Ag is the promoter. From Fig. 1b and 1c, it can be seen that Ni and Ag particles are coated on the surface of PVP-DB-171/SiO₂/Fe₃O₄ and evenly distributed on the carrier.

The SEM diagram of the Ni-Ag₀.₁₅/PVP-DB-171/SiO₂/Fe₃O₄ magnetic catalyst is shown in Fig. 2. The prepared catalysts were characterized using SEM imaging in order to obtain information about the Ni dispersion and grain formation on the catalysts. (a) The image shows that the Ni/PVP-DB-171/SiO₂/Fe₃O₄ catalyst has large particles agglomeration, which indicates that the dispersion of the metal nickel is poor. This may be due to the magnetic static interaction between particles. (b) When the molar ratio of silver to nickel is 0.15, the nickel phase is well dispersed on the surface of the carrier and the phenomenon of grain aggregation decreases, thereby indicating that the proper ad-

![Fig. 1](image1.png)

![Fig. 2](image2.png)
dition of silver can promote the dispersion of nickel. Magnetic properties of the catalysts

The magnetic properties of SiO₂/Fe₃O₄, PVP-DB-171/SiO₂/Fe₃O₄, Ni/PVP-DB-171/SiO₂/Fe₃O₄, and Ni-Ag₁₅/PVP-DB-171/SiO₂/Fe₃O₄ were studied using VSM. As shown in Fig. 3, the SiO₂/Fe₃O₄, PVP-DB-171/SiO₂/Fe₃O₄, Ni/PVP-DB-171/SiO₂/Fe₃O₄, and Ni-Ag₁₅/PVP-DB-171/SiO₂/Fe₃O₄ magnetic particles have fairly strong magnetization, and their magnetization saturation (Mₛ) values are approximately 39.637, 20.861, 19.617 and 10.431 emu/g, respectively. There is no hysteresis phenomenon, indicating that the samples are superparamagnetic at room temperature.

3.3.2 Effect of Ni-Ag₁₅/PVP-DB-171/SiO₂/Fe₃O₄ magnetic catalyst on CTH of soybean oil

3.3.1 Effects of formate ion concentration

The effect of the formic acid ion concentration on the iodine value and main fatty acid content of soybean oil during hydrogenation was studied by adding a 0.23 wt.% Ni catalyst at 80°C for 90 min, as shown in Fig. 4.

As seen in Fig. 4, the increases in the concentration of formate ions in the reaction from 0.16 to 0.40 mol/L resulted in a rapid decline in the IV. Meanwhile, almost complete hydrogenation of linolenate (C18:3) was achieved with a concomitant decrease in linoleate (C18:2), which was accompanied by simultaneous increases in the stearate (C18:0) and oleate (C18:1) contents. Use of 0.16 mol/50 mL H₂O and 0.24 mol/50 mL H₂O of ammonium formate resulted in a much slower reaction rate. An increase in the donor quantity to 0.32 mol/50 mL water resulted in the best results, but a further increase to 0.40 mol/50 mL water showed only a marginal difference in the final iodine values that were obtained at the end of the reaction. When the concentration of ammonium formate is 0.40 mol/50 mL H₂O, the final iodine value is 101 g I₂/100g. However, the increase of the donor concentration from 0.32 mol/50 mL H₂O to 0.40 mol/50 mL H₂O resulted in a slight increase in the stearic acid. It can be seen from Table 1 that as the donor concentration increases, TFAS first decreases and then increases and is at its lowest at 0.32 mol/50 mL H₂O. Considering this analysis, 0.32 mol/50 mL H₂O is considered to be the best donor concentration for the further experimental group in order to avoid the formation of more stearic acid.

3.3.2 Effect of catalyst loading

The hydrogenation of soybean oil for 90 min at 80°C with a donor concentration of 0.32 mol/50 mL H₂O was conducted in order to determine which catalyst had a better hydrogenation effect on oil hydrogenation, as shown in Fig. 5.

The figure shows that the iodine value of grease decreases by 20% when the amount of the catalyst is increased from 0.19 to 0.25. The decreasing rate of the

![Fig. 3](image_url) Hysteresis loops of the magnet.

![Fig. 4](image_url) Effect of the formate ion concentration on the hydrogenated soybean oil.

**Table 1** Effect of the formate ion concentration on the trans fatty acids content (TFAs).

<table>
<thead>
<tr>
<th>Formate ion concentration (mol/50 mL H₂O)</th>
<th>TFAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.3 ± 0.2</td>
</tr>
<tr>
<td>0.08</td>
<td>4.6 ± 0.3</td>
</tr>
<tr>
<td>0.16</td>
<td>4.1 ± 0.3</td>
</tr>
<tr>
<td>0.24</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>0.32</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>0.4</td>
<td>3.1 ± 0.2</td>
</tr>
</tbody>
</table>
iodine value is not uniform. This phenomenon could be attributed to the existence of multiple controlling mechanisms in the reaction. It is postulated that, at 0.19-0.23% loadings of the catalyst, the small molecules (formate ions and water) occupied the surface of the catalyst, thereby blocking the triglycerides. Since the formate ions and water acted in bulk, the oil could not be easily dispersed in the aqueous solution. The absence of oil on the surface of the catalyst prevented the hydrogenation reaction from occurring. When the loading of the catalyst is higher than 0.23%, especially 0.23-0.25%, oil can gradually be absorbed onto the surface of the catalyst. This phenomenon could be attributed to the sufficient active sites that are made available by the addition of the catalyst and the subsequent reduction of the rate of desorption of hydrogen atoms on the catalyst surface. It can be seen from Table 2 that as the catalyst loading increases, the TFAs in the oil significantly increase. Therefore, the amount of the catalyst should be controlled at 0.23% during hydrogenation.

3.3.3 Effects of temperature

The 90 g of soybean oil was hydrogenated for 90 min in a 0.32 mol/50 mL ammonium hydrogen formate solution with a catalyst of 0.23 wt.% Ni in oil weight. The effect of the hydrogenation temperature on the iodine value and fatty acid content of the hydrogenated soybean oil is shown in Fig. 6. It can be seen from the figure that the processing temperature increased from 50 to 90°C, and the IV of the oil was found to sharply decrease, which results from the increases in the C18:0 and C18:1 contents and the decreases in both the C18:2 and C18:3 contents. When the temperature rises from 50 to 80°C, it is found that the iodine value rapidly decreases. This finding indicates that the conversion rate of unsaturated fatty acids to saturated fatty acids is higher during this period. When the temperature is higher than 80°C, the decreasing rates of C18:2 and C18:3 become slower. The temperature is also an important parameter to control TFAs production in hydrogenated oil. As can be seen from Table 3, as the temperature increases, the trans fatty acid content decreases first and then rises. Hydrogenation at high temperature can easily lead to TFAs. Therefore, in order to produce low TFAs hydrogenated oil with a high hydrogenation rate, the hydrogenation temperature should be controlled at 80°C.

3.4 Kinetics of the Ni-Ag0.15/PVP-DB-171/SiO2/Fe3O4 magnetic catalyst in the CTH of soybean oil

The results show that the hydrogenation effect is the best when the donor concentration is 0.32 mol/50 mL H2O, the catalyst addition is 0.23% and the hydrogenation temperature is 80°C. The predicted values and experimental values of the fatty acids contents in hydrogenated products using the Ni-Ag0.15/PVP-DB-171/SiO2/Fe3O4 magnetic catalysts are shown in Fig. 7.

It can be seen from the figure that the processing temperature increased from 50 to 90°C, and the IV of the oil was found to sharply decrease, which results from the increases in the C18:0 and C18:1 contents and the decreases in both the C18:2 and C18:3 contents. When the temperature rises from 50 to 80°C, it is found that the iodine value rapidly decreases. This finding indicates that the conversion rate of unsaturated fatty acids to saturated fatty acids is higher during this period. When the temperature is higher than 80°C, the decreasing rates of C18:2 and C18:3 become slower. The temperature is also an important parameter to control TFAs production in hydrogenated oil. As can be seen from Table 3, as the temperature increases, the trans fatty acid content decreases first and then rises. Hydrogenation at high temperature can easily lead to TFAs. Therefore, in order to produce low TFAs hydrogenated oil with a high hydrogenation rate, the hydrogenation temperature should be controlled at 80°C.
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3.5 Reusability

The service life of the catalyst is measured using the conversion rate of hydrogenation, and the experimental results are shown in the diagram.

As shown in Fig. 8, the magnetic nano catalysts that were obtained from magnetic separation were reapplied to the hydrogenation of soybean oil. With the increase in the number of magnetic catalysts that were used, the hydrogenation conversion of the hydrogenated oil gradually decreased, indicating that the catalytic ability of the magnetic nano catalysts gradually decreased with the increase in the number of hydrogenation catalysts that were used in the hydrogenation process. When the magnetic catalyst was reused for the 9th time, the conversion of hydrogenated soybean oil significantly decreased, and the utilization efficiency was less than 60% of that of the newly prepared catalyst. The catalytic performance of the catalyst significantly decreased, and the conversion did not change significantly after that. Therefore, the service life of the magnetic catalyst is 8 times, which reflects a good separation ability and reusability.

4 Conclusions

Bimetallic Ni-Ag/PVP-DB-171/SiO2/Fe3O4 magnetic catalysts with good dispersibility were prepared. The hydrogenated soybean oil in the CTH system had a fast mass transfer rate of the H⁺ that was supplied by the hydrogen donor, and low TFAs contents were found in the hydrogenated oil without the hydrogen addition. It was found that the addition of Ag prevented the aggregation of nickel in the PVP-DB-171/SiO2/Fe3O4 nanoparticles and had good magnetic properties. The CTH of soybean oil has a low reaction temperature, fast reaction rate constants of linolenic acid, linoleic acid and oleic acid in the hydrogenation process of soybean oil; and considerably higher selectivity than conventional hydrogenation. This finding indicates that the mass transfer rate of the H⁺ that was supplied by the ammonium formate solution as a hydrogen donor is

Fig. 7 Predicted values and experimental values for hydrogenated oil.

Fig. 8 Reusability of the catalysts.

The different letters (A-F) marked on the histogram indicate significant (p < 0.05) differences at different uses.
faster, the hydrogenation time is shortened, and the conversion in oils and fats is faster. The low fatty acids content avoids the safety problems that are caused by the conventional hydrogenation of hydrogen. The Ni-Ag\textsubscript{0.15}/PVP-DB-171/SiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} bimetallic magnetic catalysts are easy to separate and have good reusability, which provides a theoretical basis for their application in magnetic fluidized beds in order to achieve continuity.

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**Conflict of interest**

The authors declare no conflicts of interest.

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<table>
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<tr>
<th>Table 2</th>
<th>Effect of the catalyst loading on the trans fatty acids content (TFAs).</th>
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<td>TFAs</td>
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<tr>
<td>0.19</td>
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<tr>
<td>0.21</td>
<td>8.4 ± 0.1</td>
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<tr>
<td>0.23</td>
<td>6.3 ± 0.1</td>
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<tr>
<td>0.25</td>
<td>11.2 ± 0.2</td>
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<tr>
<th>Table 3</th>
<th>Effect of the temperature on the trans fatty acids content (TFAs).</th>
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<tbody>
<tr>
<td>Temperature (℃)</td>
<td>TFAs</td>
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<tr>
<td>50</td>
<td>20.3 ± 0.4</td>
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<tr>
<td>60</td>
<td>14.4 ± 0.5</td>
</tr>
<tr>
<td>70</td>
<td>9.7 ± 0.6</td>
</tr>
<tr>
<td>80</td>
<td>5.6 ± 0.5</td>
</tr>
<tr>
<td>90</td>
<td>8.2 ± 0.7</td>
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</table>

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<th>Table 4</th>
<th>Kinetic parameters and fatty acid content of the soybean oil samples under CTH conditions.</th>
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<tbody>
<tr>
<td>Time (min)</td>
<td>Fatty acid content (%) k_{3} k_{2} k_{1} S_{ln} S_{L}</td>
</tr>
<tr>
<td>0</td>
<td>8.1</td>
</tr>
<tr>
<td>20</td>
<td>2.5</td>
</tr>
<tr>
<td>40</td>
<td>1.6</td>
</tr>
<tr>
<td>60</td>
<td>0.7</td>
</tr>
<tr>
<td>80</td>
<td>0.3</td>
</tr>
<tr>
<td>100</td>
<td>0.1</td>
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</tbody>
</table>

S_{ln} is the ratio of the hydrogenation rate of linolenic acid to that of linoleic acid.

S_{L} is the ratio of the hydrogenation rate of linoleic acid to that of oleic acid.

S_{ln}=k_{3}/k_{2}; S_{L}=k_{2}/k_{1}
20) AOCs. Office methods and recommended practices of the American Oil Chemist’s Society. Oc 1c-85. Champaign, IL, USA (2004).
27) Sanchez, S.V.; Gogate, P.R. Ultrasound assisted selective catalytic transfer hydrogenation of soybean oil using 5% Pd/C as catalyst under ambient conditions in water. Ultrason. Sonochem. 38, 161 (2017).