Preparation of Conjugated Linoleic Acid by Ultrasound-assisted Nanonickel Catalyst
Isomerization of Sunflower Oil

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Abstract: A homemade nanonickel catalyst was made by the ultrasonic liquid-phase reduction method, characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy, and applied to the isomerization reaction of high linoleic acid sunflower oil. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and particle size analysis showed that the homemade nickel particles were spherical, uniformly dispersed, less agglomerated, 20 to 75 nm in size, and nanoscale nickel powder. Compared with commercially available Raney nickel, the homemade nanonickel powder has a larger specific surface area, smaller pore size and higher catalytic activity. The X-ray diffraction spectrum of the homemade nanonickel powder had distinct diffraction peaks at its characteristic peaks which indicated that the powder was pure nickel. The nanometal nickel particles are fully dispersed in high oleic sunflower oil under the action of ultrasound. The results showed that it could effectively reduce the activation reaction time of nanonickel, and the conversion rate of conjugated linoleic acid could reach 86.24%. The process of activating the catalyst is omitted, the number of times of repeated uses of the nanonickel catalyst is increased, and the environmental pollution of the production is avoided. To obtain sunflower oil rich in CLA, it also provides a new idea for the preparation of conjugated linoleic acid.

Key words: ultrasonic, nanonickel, catalyst, conjugated linoleic acid, sunflower oil

1 Introduction

Conjugated linoleic acid (CLA) refers to octadecanoic acid containing a pair of conjugated double bonds. The position of the double bond can be in the 9, 10, and 11 positions, so various CLA isomers are possible. In addition, CLA has different conformations. The conformation of the double bond can be cis-cis (cc), cis-trans (ct), trans-cis (tc), and trans-trans (tt), so the types of CLAs are very rich. CLA has activities that include inhibiting obesity\textsuperscript{1)}, improving immunity\textsuperscript{2) and promoting growth\textsuperscript{3)}, so it is considered a very promising nutritional additive. However, the lack of natural conjugated linoleic acid has become an important obstacle to its development. Sunflower seed oil is rich in linoleic acid\textsuperscript{4). Its linoleic acid content reaches 70\textperthousand, and, is the main source of natural plant linoleic acid. Consuming sunflower oil has the effect of delaying aging, regenerating metabolism and lowering cholesterol levels\textsuperscript{5}). The study found that by adding sunflower oil to goat feed, the content of conjugated linoleic acid in the dairy products produced by the experimental goats was significantly higher than that of the feed without sunflower oil, and improved the quality of goat milk\textsuperscript{6)}.

The current methods for preparing conjugated linoleic acid are roughly divided into two categories: biological methods and chemical methods. Biological methods have a long reaction time, low yield, strict environmental requirements, and difficult product purification\textsuperscript{7)}. The chemical method mainly uses strong alkali, which has a fast reaction and high yield, but the washing of strong alkali severely pollutes the environment, and needs to be reacted at high temperature, which requires high energy consumption\textsuperscript{8)}. Some transition elements such as ruthenium, germanium,
platinum, lead and silver are used as heterogeneous catalysts or organic complexes of their transition metals are used as homogeneous catalysts to catalyze the isomerization of vegetable oil containing linoleic acid to prepare copolnic acid \(^{19, 20}\). Kreich \textit{et al.} \(^{11}\) used silver as a heterogeneous catalyst and silica gel as a carrier to perform isomerization reactions in the presence of hydrogen, with a conversion rate of over 90\%, but the selectivity of CLA was only 60\%, and hydrogenation reactions easily occurred \(^{21}\). The recovery rate of RhCl\((\text{C}_2\text{H}_4)_3\) or RuHCl\((\text{CO})\)(PPh\(_3\)) was 95\% higher. However, these transition metals are expensive, and they must be converted into corresponding complexes, which are uneconomical and highly toxic.

Nickel is widely used as a solid catalyst because of its low price and easy availability. In the hydrogenation of fats and oils, the transition metal nickel is used as a catalyst. The unsaturated double bonds adsorbed on the catalyst surface first undergo positional isomerization to form conjugated double bonds. Then, they undergo an addition reaction with hydrogen \(^{19, 20}\), the product of this process is easy to separate, and the solid catalyst can be recycled, forming an environmentally friendly process.

Nanonickel particles usually have a diameter of 1-100 nm, a large specific surface area, multiple active sites, high catalytic efficiency and selective catalytic properties \(^{14, 15}\). Ni/C supports were prepared by Fang \textit{et al.} Using a liquid impregnation method. This type of catalyst contains a small amount of Fe, which can improve the stability of the catalyst in acidic reaction conditions. A homemade catalyst is used for hydrogenation \(^{19, 20}\). Experiments show that the supported Ni-C catalyst can catalyze oleochemistry \(^{17}\). Compared with the commercially available Raney nickel, the homemade nickel powder has higher catalytic activity, selectivity and stability, the content of stearic acid in the product is reduced, and the harmful \textit{trans} fatty acids are almost completely removed \(^{19, 20}\). However, the catalytic process of solid catalysts also has the problems of a low reaction rate and long reaction time. This is due to the weak interaction between liquid and solid catalysts which are insoluble. Therefore, a continuous and powerful mixing effect must be introduced to enhance the solid-liquid mixing contact area. Ultrasound is widely used in various hybrid acceleration tools because of its high efficiency, energy savings and economic characteristics.

Sound waves with a frequency higher than 20 kHz are called ultrasonic waves. When ultrasonic waves propagate in the medium, they will produce a series of effects such as mechanical effects, thermal effects, and cavitation \(^{18}\). They have a good emulsification effect and can promote a reaction \(^{19, 20}\), so ultrasonic assistance can greatly increase a reaction rate. The use of ultrasonic technology instead of the activation of conventional hydrotreatment catalysts also ensures the safety of the conjugate conversion process \(^{20}\). Studies have shown that ultrasound can cause rapid pressure changes \(^{21}\), and a synergistic effect between the catalyst and ultrasound \(^{19, 20}\), paving the way for reactions that are usually not feasible under quiet conditions. This synergy between ultrasound and catalysis is mainly observed in the presence of solid catalysts. Under the action of ultrasound, the reaction conditions for the hydrogenation of fats and oils can be significantly reduced, and the hydrogenation rate and product yield can be improved \(^{22-24}\). In the mechanism test of the conjugation reaction of oils and fats, the role of ultrasound is to promote the dissociation reaction of linoleic acid molecules, generate numerous H free radicals, enhance the effective collision of Ni\([\text{H}^+\]) with intermediates, and reduce H and intermediates. The activation energy of the body reaction promotes the conjugation reaction of grease.

Herein, nanonickel catalysts are used in the conjugation reaction of sunflower oil. Nitrogen is used as a protective gas. Under the action of ultrasound, the reaction temperature can be effectively reduced, the catalysis time is reduced, and the reaction process is faster, safer, and easier to operate. The introduction of ultrasound replaces the catalyst activation link, improves the repeatability of the catalyst, and provides raw material for subsequent in-depth research of the nutrition and functionality of CLA-rich sunflower oil. It also provides new possibilities for catalyst activation. Finally, the fatty acid composition and composition of the developed conjugated sunflower oil product are analyzed to realize the fast and efficient conjugation reaction of the oil and create an efficient, inexpensive and environmentally friendly new method for the preparation of conjugated oil. This study provides a theoretical basis for the industrial production of oils rich in conjugated linoleic acid.

2 Materials and Methods
2.1 Materials
Raney nickel catalyst, British alfa reagent company; Nanonickel catalyst, laboratory homemade; sunflower oil, Jiu San Food Co., Ltd.; other reagents are of analytical purity.

2.2 Preparation of the nanonickel catalyst
The production process of the laboratory nickel powder catalyst is as follows: in 50 mL 0.02 mol/L sodium hydroxide solution, 2 mL 0.4 mol/L hydrazine hydrate and 2 mL 3\% sodium lauryl sulfate were mixed, and then 10 mL 0.2 mol/L nickel sulfate solution was added to the mixed solution, which was heated to 80°C. Then, the mixed solution was stirred ultrasonically for 30 min at a stirring speed of 2400 rpm/min to study the effect of ultrasonic power on the nickel powder catalyst under the condition of 0~250 W, and centrifuged at 10000 rpm/min for 10 min. Wash the sample 3 times with a large amount of distilled water and...
ethanol, and dry it in a drying oven at 80°C for 30 min.

2.3 XRD analysis of catalyst samples
In the present study, X-ray diffraction (XRD) was used to detect the crystal structure of the supported catalyst. A certain amount of dried carrier and catalyst were ground into powder and then analyzed using an X-ray diffractometer (German Bruker) with a Cu target and the following settings: voltage, 35 kV; current, 30 mA; range of 20°= 5°~65°; rate, 5°/min; the scan step, 0.02.

2.4 SEM analysis of catalyst samples
An S-3400N scanning electron microscope was used to observe the loading and dispersion characteristics of the catalyst. Maximum magnification: 600,000 times; secondary electron resolution: 20 kV: 1.0 nm (working distance 4 mm); 1 kV: 1.3 nm; maximum acceleration voltage: 30 kV.

2.5 TEM analysis of catalyst samples
The atoms in the sample were bombarded by electrons and forced to change their orbits, which caused scattering and imaging. An H-7650 transmission electron microscope was used to observe the morphology and structure of the sample. The highest magnification was 600,000 times, and the acceleration voltage was 120 kV.

2.6 Isomerization of sunflower oil after activation of conventional catalysts
Two grams of catalyst were placed into a tube furnace. The tube furnace was continuously filled with nitrogen for 5 min, the air was evacuated, and then a certain amount of H2 flowed into the reactor. The hydrogen flow rate was 120 mL/min, and it was preactivated for 2 h at 240°C. Afterward, the furnace was cooled to room temperature, the gas was discharged, and the catalyst was removed25. Then, 150 mL sunflower oil was placed in a three-necked flask, and 8% catalyst was added. The nitrogen valve was opened, and high-purity nitrogen was poured into the three-necked flask for 10 min to remove the air in the flask. The flask was placed on a magnetic stirrer with a constant temperature oil bath, and the sunflower oil was mechanically stirred and heated under the protection of nitrogen. The stirring rate was 600 rpm, and the conjugation temperature was 170°C. After a reaction time of 4 h, the flask was removed and cooled to room temperature. After cooling, the catalyst was centrifuged from the grease, and the supernatant was the reaction product. The product was methyl esterified, and the composition and content of the existing isomers were detected by gas chromatography.

2.7 Ultrasound-assisted preparation of the sunflower oil isomerization reaction
The conjugation reaction of sunflower oil was performed in a homemade reactor (as shown in Fig. 1) (volume 100 mL), and 40 mL of sunflower oil was heated with magnetic stirring and an oil bath. The effect of a catalyzing temperature on the conversion rate of sunflower oil conjugated linoleic acid was studied at an ultrasonic temperature of 180°C, catalyzing time of 70 min, catalyst addition of 8%, and ultrasonic power of 100~300 W. The effect of an ultrasonic catalytic temperature on the conversion of sunflower oil conjugated linoleic acid was studied at 120~200°C, ultrasonic power of 200 W, and catalyst addition of 8%. The effect of an ultrasonic catalyst time of 40~80 min on the conversion rate of sunflower oil conjugated linoleic acid was studied at 180°C, ultrasonic power of 200 W, catalytic time of 70 min, and 4~12% of catalyst added to sunflower oil conjugate.

2.8 Determination of fatty acid composition
Since fatty acids cannot be directly analyzed in gas chromatography, the product oil samples and fatty acid standard samples need to be methylated according to the literature26. A CP-Sil-88 (100 m × 0.25 nm × 0.2 μm) capillary column was used, split injection, split ratio of 100:1, a sample volume of 1 μL, nitrogen carrier gas, a flow rate of 1 mL/min, hydrogen and air. The flow rates were 30 mL/min and 380 mL/min, respectively. The precolumn temperature was held at 180°C for 50 min, increased to 225°C at a rate of 10°C/min, and held for 15 min. The injection and measurement temperatures were 280°C.

2.9 Determination of catalyst activity
The CLA peaks of different structures were analyzed qualitatively and quantitatively with conjugated methyl linoleate standard solution. The method used to convert the peak area ratio to a mole fraction and CLA mass content comes from AOCS Ce1f-96. The selectivity of total CLA in the product grape seed oil refers to the ratio of the amount of conjugated linoleic acid produced to the amount of linoleic acid converted, and the expression is shown in (1):
\[ S_{CLA} = \frac{CLA_1 - CLA_0}{LA_0 - LA_1} \]  
where 

- \( S_{CLA} \) —— Selective conversion rate of total CLA (%) 
- \( CLA_1 \) —— mole fraction of total CLA in the reaction product (%) 
- \( CLA_0 \) —— mole fraction of total CLA in the feedstock oil (%) 

The selective conversion rate \( S_{c,t} \) of 9c, 11t-CLA + 10t, and 12c-CLA in the product sunflower seed oil is shown in the following expression (2):

\[ S_{c,t} = \frac{(t,t-CLA)_1 - (c,t-CLA)_0}{LA_0 - LA_1} \]  
where 

- \( S_{c,t} \) —— selective conversion rate of 9c, 11t-CLA + 10t, and 12c-CLA (%) 
- \( (c,t-CLA)_1 \) —— mole fraction of 9c, 11t-CLA + 10t, and 12c-CLA in the reaction product (%) 
- \( (c,t-CLA)_0 \) —— mole fraction of 9c, 11t-CLA + 10t, and 12c-CLA in the feedstock oil (%) 

The selective conversion rate \( S_{t9,t11} \) of 9t, 11t-CLA + 10t, and 12t-CLA in the product sunflower seed oil is shown in the following expression (3):

\[ S_{t9,t11} = \frac{(t,t-CLA)_1 - (t,t-CLA)_0}{LA_0 - LA_1} \]  
where 

- \( S_{t9,t11} \) —— t9, t11-CLA + t10, and t12-CLA selective conversion rate (%) 
- \( (t,t-CLA)_1 \) —— mole fraction of t9, t11-CLA + t10, and t12-CLA in the reaction product (%) 
- \( (t,t-CLA)_0 \) —— mole fraction of t9, t11-CLA + t10, and t12-CLA in the feedstock oil (%) 

The increase in the amount of oleic acid and stearic acid after reacting with the feedstock oil, namely, the hydrogenation selectivity \( S_{H2} \), is expressed as follows (4):

\[ S_{H2} = \frac{O_1 - O_0 + S_t - S_0}{LA_0 - LA_1} \]  
where 

- \( S_{H2} \) —— Hydrogenation selective conversion rate (%) 
- \( O_1 \) —— mole fraction of oleic acid in the reaction product (%) 
- \( O_0 \) —— mole fraction of oleic acid in raw oil (%) 
- \( S_t \) —— mole fraction of stearic acid in the reaction product (%) 
- \( S_0 \) —— mole fraction of stearic acid in raw oil (%) 

### 3 Results and Discussions

#### 3.1 Effect of ultrasonic power on nickel catalyst activity

In 50 mL sodium hydroxide solution, 2 mL of 0.4 mol/L hydrazine hydrate and 2 mL of 3% sodium lauryl sulfate were added and mixed thoroughly, and then 10 mL of 0.2 mol/L nickel sulfate solution to the mixed solution and heated to 80°C. The influence of ultrasonic power on the nickel powder catalyst after 30 min of ultrasonic treatment is shown in Fig. 2.

Figure 2 shows that when the ultrasonic power is 200 W, the prepared catalyst has the highest activity, which can reach 86.4%. With increasing ultrasonic power, the conjugate conversion rate continues to increase and then slowly decreases. Ultrasound significantly increases the generation of cavitation bubbles, increases the cavitation intensity, and ultimately increases the reaction speed. However, when the ultrasonic power is too large, many cavitation bubbles are formed, which produces a certain buffer effect, resulting in a reduction in the energy utilization rate of the cavitation effect and a reduction in the conversion rate of conjugated fatty acids. Compared with the catalyst without ultrasonic treatment, ultrasonic treatment can significantly improve the catalytic activity of the nickel catalyst.

#### 3.2 XRD characterization analysis of the catalyst

X-ray diffraction analysis can be used to investigate the crystal form and loading of metal particles on the carrier. The content of the crystalline substance in the sample is determined by the number, position and relative intensity of the diffraction lines, and the properties of the homemade nickel catalyst are analyzed through the position and state of the characteristic peaks in the image. The X-ray diffraction characterization analysis of the catalyst is shown in Fig. 3.
Ultrasound Assisted to Improve the Catalytic Activity of Nano-nickel Catalyst

As shown in Fig. 3a, the samples were crystal and no other impurity peaks were observed. The results indicated that the homemade nickel powder was not significantly oxidized under laboratory conditions. The catalyst presents sharp diffraction peaks at 44.42°, 51.75°, and 76.29°, corresponding to Miller indices of 111, 200, and 222 and thus indicating that the obtained sample is pure face-centered cubic nickel. Figure 3b shows that according to the positions of the peaks at 44.416°, 51.779°, and 76.377°, the diffraction pattern corresponding to the homemade nickel particles is usually the same, but the peaks at 37.362°, 65.083°, and 78.389° are characteristic of aluminum. The peak position indicates that the crystal structure of the Raney nickel catalyst has not changed. In addition, this spectrum does not show diffraction peaks of other nickel compounds except for the diffraction peaks of metallic nickel. The shock wave caused by supervibration and the cavitation of microfluidization acoustic waves can effectively remove impurities. This finding shows that the nickel catalyst prepared by the method described in this article is very pure.

3.3 Scanning electron microscope analysis of the catalyst

Figure 4 shows the SEM results of the homemade nickel catalyst and the commercially available Raney nickel catalyst. Figure 4a is a SEM image of a homemade nickel powder catalyst. Figure 4a shows that the homemade nickel powder catalyst is small, uniform, good in spheroidization, and has a large specific surface area, but some nickel will agglomerate, which is related to the small particle size, large surface energy, and magnetism. Figure 4b is a SEM image of commercially available Raney nickel, which shows the irregular shape, uneven particle size, large particles and partial agglomeration of the Raney nickel catalyst. At the same time, because of the unevenness of Raney nickel, its surface area is increased. Comparing the scanning electron micrograph analysis of homemade nickel and Raney nickel, homemade nickel powder forms cavitation in the solution under proper ultrasonic action. When cavitation bubbles collapse, high temperature, high pressure, strong shock waves and jets are generated in a short time. As a result, the diffusion-free path of nickel ions is shortened, the reaction speed is accelerated, and a higher nucleation rate is produced in the dissolution. Then, the crystal nuclei compete with each other to grow, resulting in a smaller diameter and better dispersion of nickel powder.

Fig. 3 Self-made nano-nickel catalyst and commercially available Raney nickel catalyst XRD.

Fig. 4 Self-made catalyst and commercially available Raney nickel catalyst SEM.
In addition, ultrasonication can also play a role in preventing agglomeration, breaking agglomerates and controlling particle reagglomeration so that the diameter of the nickel powder particles prepared under an ultrasonic field is smaller and the particle dispersion is better.

3.4 TEM analysis of the catalyst

TEM is suitable for observing tiny particles. Because the metal particles of the observed sample are very small, the sample was photographed with a transmission electron microscope. Transmission electron microscopy can observe not only the size and morphology of particles but also their distribution, which has an important influence on catalytic performance.

Figure 5 is a TEM image of homemade nickel and Raney nickel. As shown in Fig. 5a, the shape of the nickel particles is mainly spherical, and the particles are relatively uniform in distribution. Using Nano Measurer software, it is found that the size of the homemade nickel particle is between 20 and 75 nm, which is a nanoscale nickel catalyst, and within this particle size range, its catalytic activity is relatively high. The investigation found that the homemade nanonickel has a small amount of agglomeration, the purity is high, and no other impurities are present. Figure 5b shows that all transmission images of Raney nickel are large blocks, with particle sizes ranging from 20 to 100 μm, and a certain agglomeration phenomenon occurs.

3.5 Ultrasonic isomerization of sunflower oil

Using a homemade nanonickel catalyst, when the dose was 8%, the catalytic temperature was 180°C, and the catalytic time was 70 min. The effect of ultrasonic power of 100, 150, 200, 250 and 300 W on the conjugation of sunflower oil was studied. Figure 6a shows that with the increase in ultrasonic power, the conjugate conversion rate first increased and then decreased. The maximum conjugation conversion rate is obtained at 200 W. The reason may be that ultrasound can form a cavitation effect, which generates high temperature, high pressure, strong shock waves and jets in a short time, which increases the contact area between the catalyst and the reactants and accelerates the reaction speed. A further increase in the ultrasonic power forms many cavitation bubbles, which slows down the energy transmission of the ultrasonic power, thereby affecting the conjugation reaction of linoleic acid in sunflower oil. Therefore, the best ultrasonic power is 200 W. Research by Lei Shi et al. showed that ultrasonic treatment can effectively increase the catalyst activity and increase the conjugate conversion rate, but the ultrasonic intensity is too high.

Figure 6b shows results for catalytic temperatures of 120, 140, 160, 180 and 200°C, ultrasonic power of 200 W,
catalytic time of 70 min, and catalyst addition amount of 8%. The effect of the catalytic temperature on the conjugation of grease is discussed, as shown in Fig. 6b. As the temperature of the catalyst increases, the conjugate conversion rate increases rapidly. When the temperature exceeds 180°C, the conversion rate decreases. These results show that the reaction temperature has a great influence on the conjugate conversion rate. At high reaction temperature, linoleic acid is easier to convert to conjugated intermediates. The intermediates meet the nanonickel catalyst carrying hydrogen atoms to form conjugated linoleic acid. When it is high, with the increase in the reaction time and the strengthening of the ultrasonic effect, the temperature will exceed the optimal temperature for isomerization of linoleic acid, and the conjugation conversion rate will decrease. Therefore, the optimal catalytic temperature is between 180°C. However, Zhu et al. studied a Cu ZnO/ZrO2 catalyst for the conversion of CO2 to methyl ester under ultrasonic conditions, and found that the optimal ultrasonic temperature was 240°C.

Figure 6c shows results for a catalytic time of 40, 50, 60, 70, 80 min, ultrasonic power of 200 W, catalytic temperature of 180°C, and the catalyst addition amount of 8%. The effect of the catalytic time on the conjugation effect of the oil is discussed. As shown in Fig. 6c, as the catalysis time is prolonged, the conjugate conversion rate first increases and then decreases, reaching the maximum at 70 min. The reason may be reflected in the results for 40-60 min. The reaction is incomplete, and cavitation bubbles caused by ultrasonic waves do not play a full role. When the ultrasonication time was 70 min, the ultrasonic effect and temperature in the reactor reached the optimal reaction conditions, and the maximum conjugate conversion rate was reached; when the catalysis time continued to increase, the conversion rate decreased. The reason is that the catalytic reaction continues, and the ultrasound effect continues at the same time. Ultrasound will synergize the conversion of linoleic acid in sunflower oil into conjugated linoleic acid, increase the temperature of the reaction system and increase the viscosity of the system. At higher viscosity, the effective collision between the catalyst and grease is weakened, which reduces the conversion rate of the system. Therefore, the best catalysis time is 70 min.

Figure 6d shows the results when the ultrasonic power is 200 W, the catalytic time is 70 min, the catalytic temperature is 180°C, and the catalyst additional amount is 4, 6, 8, 10 and 12%. The influence of the catalyst addition amount on the conjugation conversion rate is discussed. As the amount of added catalyst increases, the conjugate conversion rate slowly increases and then slowly decreases. The catalyst can reduce the activation energy of the reaction and carry H+ to combine with the intermediate. Above a certain amount, the catalytic effect will be reduced or even hinder the progress of the catalytic reaction. The effect is reduced. When the amount of nanonickel catalyst added is less than 8%, the amount of catalyst increases, the contact area between the catalyst and the reactant increases, and the efficiency continues to increase. Above 8%, the amount of catalyst is too high, and it is reduced by easy aggregation and settling of the catalyst. The reduction in specific surface area reduces the contact area between the catalyst and the substrate, resulting in a decrease in catalytic efficiency. Therefore, the optimal catalyst addition amount is between 6-10%. Qiqi Deng et al. determined the optimal catalyst content of a nanonickel-catalyzed conjugation reaction to be 10%, which is basically consistent with this study.

3.6 Analysis of the characteristics of oil isomerization products
3.6.1 Catalyst selectivity analysis
To further verify the catalytic effect of the abovementioned experimental homemade catalyst, using sunflower
oil as the raw material, nanonickel was tested under conventional conjugation and ultrasonic isomerization conditions to explore the selectivity of the nanonickel catalyst in the oil isomerization process as shown in Table 1.

It can be concluded from Table 1 that the conjugated linoleic acid selectivity of the nanonickel catalyst is higher than 50%. Conventional isomerization and ultrasonic-assisted isomerization are compared, and the ultrasonic-assisted catalyst has higher conjugation selectivity. This is because ultrasound reduces the activation energy of the catalyst to activate the C-H bond on the adjacent carbon on the semi-hydrogenated intermediate product, which is more prone to isomerization reaction\(^3\), and ultrasound is added during the preparation process, thereby improving the dispersion of nickel, exposing the active site, and increasing the isomerization selectivity. Notably, from the comparison of isomerization methods, the \(S_{\text{CLA}}\) of the ultrasound-assisted nanonickel catalyst is the lowest, only 12.6%, which means that only a small part of the fatty acid is hydrogenated during the catalysis of the isomerization of sunflower oil. Most of the linoleic acid in the oil is isomerized into conjugated products.

3.6.2 Analysis of the fatty acid composition of conjugated sunflower oil

After methylation, the fatty acid composition of sunflower oil was analyzed by GC-MS, and the results are shown in Table 2.

Table 2 shows that nine fatty acids are mainly separated from conjugated sunflower oil. Among them, all conjugated linoleic acid are formed by isomerization of linoleic acid, with a maximum content of 54.34%, followed by an oleic acid content of 20.79%. Unsaturated fatty acids accounted for 88.21% of the total fatty acid content in conjugated sunflower oil. Conjugated isomerized sunflower oil differs from the original sunflower oil in fatty acid content. The content of stearic acid in conjugated sunflower oil is higher than that of crude oil. Linoleic acid is in the process of isomerization. However, as the catalytic time and temperature increase, a small amount of linoleic acid is not converted to conjugated linoleic acid. Instead, \(H_2\) is added to convert linoleic acid to oleic acid and finally to stearic acid. Conjugated oil has a higher stearic acid content.

### Table 1

| Method                 | \(S_{\text{CLA}}\) /% | \(S_{\text{CLA}}\) /% | \(S_{\text{CLA}}\) /% | \(S_{\text{CLA}}\) /% |
|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| conventional          | 60.2 ± 0.15\(^a\)     | 40.13 ± 0.83\(^b\)    | 16.12 ± 0.69\(^c\)    | 21.47 ± 0.50\(^d\)    |
| Ultrasound assisted    | 79.6 ± 1.06\(^a\)     | 59.22 ± 0.72\(^b\)    | 20.73 ± 0.53\(^c\)    | 12.64 ± 0.41\(^d\)    |

Note: The values marked with different superscript letters (a-d) in the same column are significantly different \((p < 0.05)\).

### Table 2

| Number | Retention time/min | Fatty acid     | Molecular formula | Fatty acid content /% |
|--------|--------------------|----------------|-------------------|-----------------------|
| 1      | 21.316             | Myristic acid  | \(C_{14}H_{28}O_2\) | 0.070                 |
| 2      | 24.483             | Palmitic acid  | \(C_{16}H_{30}O_2\) | 5.922                 |
| 3      | 27.753             | Stearic acid   | \(C_{18}H_{36}O_2\) | 10.357                |
| 4      | 28.731             | Oleic acid     | \(C_{18}H_{34}O_2\) | 20.795                |
| 5      | 30.217             | Linoleic acid  | \(C_{18}H_{32}O_2\) | 7.072                 |
| 6      | 30.846             | Arachidic acid | \(C_{20}H_{40}O_2\) | 0.253                 |
| 7      | 31.926             | Linolenic acid | \(C_{18}H_{30}O_2\) | 0.131                 |
| 8      | 33.893             | Behenic acid   | \(C_{22}H_{44}O_2\) | 0.604                 |
| 9      | 32.383             | CLA            | \(C_{18}H_{32}O_2\) | 54.346                |

4 Conclusion

The characteristics of the homemade nanonickel catalyst were observed by XRD, SEM, and TEM characterization methods. Under SEM and TEM, it was found that the homemade nanonickel catalyst showed a small amount of agglomeration, the particles were spherical, and the particle size was between 20 and 75 nm. The X-ray diffraction spectrum shows that the homemade nanonickel powder has a low degree of oxidation. The nanonickel catalyst has obvious diffraction peaks at 44.31°, 51.782° and 76.295°, which is the highest characteristic of nickel metal. Its position is similar to that of the X-ray diffraction spectrum. Matching the standard data of the standard card confirms that the synthesized product is pure nickel powder and does not contain other impurities. The process parameters
of the conjugate isomerization reaction of the nanonickel catalyst in sunflower oil were further optimized, and the ultrasonic power, ultrasonic catalytic temperature, ultrasonic catalytic time and other indicators were tested. The catalytic activity reached 48.24%, and the conjugation reaction of sunflower oil was determined.

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