Preparation and Application of Magnetic Nano-Solid Acid Catalyst Fe$_3$O$_4$-PDA-SO$_3$H

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Abstract: A magnetic nano-solid acid catalyst Fe$_3$O$_4$-PDA-SO$_3$H was synthetized through an efficient method, as an eco-friendly and more efficient catalyst. The obtained catalyst has uniform core-shell structure, appropriate particle size, and high acid density. Fe$_3$O$_4$-PDA-SO$_3$H was applied to catalyze the esterification of levulinic acid (LA) with alcohols of different chain length to produce the levulinate esters. The catalytic effect was optimized from the aspects of catalyst dosage, reaction temperature, and acid-alcohol molar ratio. Furthermore, the response surface optimization method was used to obtain the optimal conditions. Verified under these conditions, the experimental results showed that the conversion rate of LA can reach 95.87%, which was much higher than common cationic exchange resin Amberlyst 36 and Amberlyst 46. Furthermore, the recovery and reuse of the Fe$_3$O$_4$-PDA-SO$_3$H was demonstrated six times without obvious loss in the activity.

Keywords: magnetic nano-catalyst; levulinic acid; esterification

1. Introduction

In the past few years, the attention on biomass and its derivatives [1] has increased remarkably. The consumption of fossil fuels [2] and the influence of greenhouse effect continually drive the vigorous development of biomass fuels [3,4]. The requirement of renewable resources [5] has promoted innovation in energy production. Levulinate esters can be used as fuel additives to improve fuel stability and reduce emission of C and N oxides. In addition, alkyl levulinate can also be used as flavors, plasticizers, and solvents, and applied to different fields [6]. Alkyl acetate, such as methyl ester, ethyl ester, n-butyl ester, and octyl acetylpropionate are very attractive candidate compounds, which are widely used in the seasoning and spice industry and can also be used as new miscible diesel biofuels and bio-lubricators [7]. Adding alkyl acetate to diesel fuel can make the fuel have higher lubricity, a more stable flash point, lower sulfur content, and improve viscosity. Among all kinds of advanced biofuels, Levulinate esters are considered to be the best formula for gasoline and diesel as well as the component of biomass oil [8,9].

The methods of preparing levulinate esters from biomass resources can be summarized as follows: Biomass alcoholysis, furfuryl alcoholysis [10], and direct esterification of levulinic acid and alcohol. The transformation of lignocellulosic biomass can yield a number of valuable products that can be used by the chemical industry as platform chemicals [9]. By using biomass chemical conversion technology, lignocellulose can be liquefied to produce fuel and high value-added chemical products. Cellulose and hemicellulose can be hydrolyzed by acid catalysis [11] to produce ethanol, furfural, levulinic acid, and other chemical products. Furfuryl alcoholysis has many disadvantages, such as long reaction...
route, a large amount of energy needed to remove water in the reaction system, and low yield of levulinate. Levulinate esters were synthesized by an esterification reaction of levulinic acid (LA) with different alcohols \([12,13]\) under acid catalyst. LA is an important platform compound and obtained from biomass easily \([14]\). The levulinic acid is readily obtained from biomass, its esterification with alcohols to produce levulinic acid is a very attractive green process \([15]\).

The preparation of levulinate esters utilized homogeneous acid \([16,17]\), such as sulfuric acid, as a catalyst in recent years \([18]\), and the acid catalyst has a high catalytic activity, but is followed by some disadvantages \([19]\), for instance recovery difficulty, increase in cost, equipment corrosion, and environmental pollution \([20]\). Therefore, the emergence of heterogenous acid catalyst solved these problems. Filoklis et al. \([7]\) founded the use of carbon-based heterogeneous sulfonic catalysts for syntheses ethyl levulinate. Al-containing MCM-41 were used by Chermahini et al. \([21]\) for preparation of n-butyl levulinate and selected the optimum conditions including temperature, molar ratio and reaction time. The magnetic nano-catalysts used in the esterification reaction can be separated from the product by applying a magnetic field \([22]\). These catalysts can be recycled and reused; and do not require treatment at the acid or water separation stage. Therefore, it can reduce costs and be environmentally friendly.

Metal nanoparticle \(\text{Fe}_3\text{O}_4\) has attracted more attention because of its super paramagnetic application in solid acid catalyst support. In modern research, modified surface coatings can protect carrier materials from corrosion by strong oxidizer, acid, or alkali chemicals. The interaction between the carrier and the surface coating material depends largely on the properties of the surface material and the functional groups of the material. Polydopamine (PDA) exhibits similar characteristics to mussel secreted proteins, which contain sufficient catechin and amine groups and spontaneously form thin, surgically adhered polydopamine coatings on the surfaces of various materials. More importantly, due to a large number of active catechol and amine groups, PDA can be used as reductants and binders, so that various composite materials have good functional characteristics. With \(\text{Fe}_3\text{O}_4\) as the magnetic center, its outer layer is covered with PDA, which not only protects \(\text{Fe}_3\text{O}_4\), but also can more effectively connect its surface functional groups with other functionalized functional groups. Polydopamine-coated \(\text{Fe}_3\text{O}_4\) nanoparticles have been exploited for use in numerous advanced applications, including the separation and enrichment of proteins in proteomic analysis, the detection of pollutants by matrix assisted laser desorption/ionization time-of-flight mass spectrometry, and magnetic solid-phase extraction adsorbent for the determination of trace polycyclic aromatic hydrocarbons in environmental samples \([23]\). Through a sulfonylation reaction, a sulfonate group can be successfully loaded outside the carrier to make it a magnetic nano-solid acid catalyst, which can be applied to the synthesis of important compounds.

Hemmati et al. prepared \(\text{Fe}_3\text{O}_4@\text{PDA-SO}_3\text{H}\) nanosolid acid catalysts for acetylation of alcohols, phenols, amines, and thiols, introducing a novel and efficient acidic magnetic nanocomposite with excellent reusability. The magnetic \(\text{Fe}_3\text{O}_4\) nanoparticles were prepared by the chemical coprecipitation method \([23]\). Elhampour et al. described the first-time preparation and characterization of the H-\(\text{Fe}_3\text{O}_4@\text{DA-SO}_3\text{H}\) magnetic nanoparticle as a superior heterogeneous acid for synthesis of dihydropyridine and dioxodecahydroacridine derivatives \([24]\).

In this present work, magnetic \(\text{Fe}_3\text{O}_4\) nanoparticles were synthesized by means of hydrothermal method. The objective is to prepare \(\text{Fe}_3\text{O}_4@\text{PDA-SO}_3\text{H}\) nano-solid acid catalyst with size uniform and shape regular features. \(\text{Fe}_3\text{O}_4@\text{PDA-SO}_3\text{H}\) was applied to for esterification of levulinic acid with different alcohols. The catalyst was evaluated by the esterification of levulinic with ethanol, n-butanol, and n-caprylic alcohol. The optimal reaction conditions \([25]\) for LA esterification, for example, the reaction temperature and the mole ratio were determined by the maximized conversion of levulinic acid.
2. Materials and Methods

2.1. Materials

Polyethylene glycol (99%), alcohol (99%), n-caprylic alcohol (99.885%), anhydrous sodium acetate, and ferric chloride were obtained from Guangfu Chemical Research Institute (Tianjin, China). Chlorosulfonic acid was purchased from juding chemical reagent Co. Ltd (Shanghai, China). N-butanol was purchased from Aladdin Biochemical Technology Co. Ltd (Shanghai, China). Trihydroxymethyl aminomethane, dopamine hydrochloride, dichloromethane, sodium chloride, and sodium hydroxide were purchased from Damao Reagent Factory (Tianjin, China). All chemicals were pro analytical grade and were used without further purification.

2.2. Preparation of Fe$_3$O$_4$ Nanoparticles

Magnetic Fe$_3$O$_4$ nanoparticles were synthesized by means of hydrothermal method. Firstly, FeCl$_3$·6H$_2$O (1 g) was dispersed in ethylene glycol (30 mL) and stirred for 15 min at room temperature until it becomes yellow pellucid solution. Subsequently, sodium acetate (2.7 g) and polyethylene glycol (2.5 g) were added to the mixture with stirring. After 30 min of mechanical agitation and ultrasonic dispersion at room temperature, the mixture was added in a 50 mL teflon-lined stainless steel autoclave. The autoclave was kept at 200 $^\circ$C for 8 h, after the reaction finished, the mixture was cooled down to room temperature. The black solid products were washed three to four times with 100 mL deionized water and twice with 30 mL ethanol and then product dried at 40 $^\circ$C for 24 h.

2.3. Preparation of Fe$_3$O$_4$-PDA Nanoparticles

Previous step generated black products Fe$_3$O$_4$ nanoparticles were dispersed in 500 mL Tris buffer solution (10 mM, pH 8.5), followed by dopamine hydrochloride (1 g), and then the mixture was mechanically stirred for 24 h at room temperature. After the reaction finished, black solid products were obtained, Fe$_3$O$_4$-PDA-SO$_3$H nanoparticles were isolated with magnet and washed three to four times with 100 mL deionized water and twice with 30 mL ethanol and dried at 40 $^\circ$C to get Fe$_3$O$_4$-PDA nanoparticles.

2.4. Preparation of Fe$_3$O$_4$-PDA-SO$_3$H Nanoparticles

Magnetic nanoparticles solid acid catalyst were prepared by sulfonation of chlorosulfonic acid [26]. Firstly, Fe$_3$O$_4$-PDA nanoparticles were dispersed in anhydrous dichloromethane [23] (20 mL) and composites were ultrasound bath for 20 min. Subsequently, chlorosulfonic acid (0.8 mL) was added dropwise for a period of time at room temperature. After adding was completed, the mixture was stirred for 5 h at room temperature. The resulting magnetic mixture was separated by an external magnet, washed three times with 20 mL anhydrous dichloromethane and twice with 30 mL ethanol and then dried at room temperature to obtain Fe$_3$O$_4$-PDA-SO$_3$H nanoparticles.

2.5. Characterization

Morphology of nanoparticles was researched by scanning electron microscopy (SEM). The samples were ultrasonically dispersed in ethanol poured onto monocrystalline silicon, then SEM images were obtained at an accelerating voltage of 30 KV.

Product particle phase identification and degree of crystallization were tested using powder X-ray diffraction (XRD).

Elements in the product were detected by energy dispersive X-ray spectroscopy (EDX) to infer whether the acid was loaded.

Functional groups and structures of products were used for identification by Fourier transform infrared spectroscopy (FT-IR). The products were mixed with KBr to form a thin sheet and scanned after which the spectra were recorded.
2.6. Determination of Acid Density

The surface acid density of the magnetic nano-solid acid catalyst was detected by NaOH solution titration in Formula (1). Zero point one grams of catalyst was dispersed into 1 M NaCl solution, sonicated for 60 min to make the ion exchange sufficient, then centrifuged it, and took the supernatant to add two drops of phenolphthalein indicator. The NaOH solution of 0.01 mol·L⁻¹ was titrated until the color of the solution remained unchanged for 15 s and recorded the volume consumed of the NaOH solution.

\[
\text{Acid density (mmol·g}^{-1}\text{)} = \frac{\Delta V}{m} \times C
\]

where \(m\) represents solid acid mass (g), \(\Delta V\) represents NaOH solution volume (L), and \(C\) represents NaOH solution concentration (mmol·L⁻¹).

The acid density determination mechanism was showed in Figure 1. The result showed the acid density of the surface of the magnetic nano-solid acid catalyst was 1.238 mmol·g⁻¹.

![Figure 1. Acid density determination mechanism.](image)

2.7. Typical Experimental Procedure for Esterification Between LA with Different Alcohols

\(\text{Fe}_3\text{O}_4\text{-PDA-SO}_3\text{H}\) nanoparticles were applied for the esterification of levulinic acid with ethanol [8,19], n-butanol [1,4,27], and n-octanol [28,29]. The influence of reaction conditions on the conversion rate of levulinic acid, including the amount of catalyst, reaction temperature, and acid/alcohol molar ratio, was optimized. All esterification reactions [25] were implemented in a 100 mL round bottom flask connected to a condenser, which was placed in oil bath with magnetic stirring heating. Esterification activity of magnetic nanoparticles solid acid catalyst was measured by the concentration of free levulinic acid after the reaction. The consumption of levulinic acid was calculated by the amount of sodium hydroxide consumed by acid–base titration. Formula (2) is the calculation formula of conversion rate of levulinic acid.

\[
\text{Conversion of LA} = \frac{CV_0 - CV_n}{CV_0} \times 100\% 
\]

where \(CV_0\) represents the initial acid content of the esterification reaction and \(CV_n\) represents the acid content after the reaction \(n\) hours.

At the same time, the catalytic performance of Amberlyst 36 and Amberlyst 46 with the same acid content was compared with that of solid catalyst \(\text{Fe}_3\text{O}_4\text{-PDA-SO}_3\text{H}\).

2.8. Response Surface Optimization

The experiment of optimizing the esterification reaction conditions of the response surface is mainly achieved by esterification of levulinic acid and n-butanol. Take the appropriate amount of levulinic acid and n-butanol in 100 mL round bottom flask, add the corresponding amount of solid acid catalyst, esterification reaction at a certain temperature.

Optimum design of the reaction condition response surface for the solid acid catalytic acetyl propionylation reaction, was mainly done by setting the experiment of four main factors: Reaction temperature, substrate molar ratio, catalyst dosage, and stirring rate. The experimental influencing
factors and levels are shown in Table 1. In the response surface design software design expert 8.0.5, the molar ratio factor was more uniformly selected 1:9, 1:10, 1:12, and 1:13, so the software designed 30 groups of experiments.

Table 1. Experimental factors and levels of orthogonal experiment.

| Experimental Factors | Low  | High |
|----------------------|------|------|
| Temperature of reaction (°C) | 80   | 100  |
| mole ratio           | 1:7  | 1:15 |
| Amount of catalyst (wt%) | 10   | 25   |
| Speed of revolution (r/min) | 320  | 466  |

3. Results and Discussion

3.1. Effect of Sulfonation of Chlorosulfonic Acid

3.1.1. Effect of Chlorosulfonic Acid on Magnetic Nanosolid Acid Catalyst

To investigate the effect of solid acid catalyst preparation conditions on the acid density of solid acid, a single factor optimization experiment was carried out. In the process of loading sulfonic groups, considering the presence of free amino groups on the surface of the support, if the amount of chlorosulfonic acid is less, the acid density of the prepared solid acid catalyst is lower. If the amount of chlorosulfonic acid is too much, when the acid density is saturated, too many sulfonic acid groups will no longer be chemically linked to the amino group on the carrier, resulting in the overuse of chlorosulfonic acid. So, it is necessary to carry out the single factor optimization experiment of the amount of chlorosulfonic acid. The experimental results are shown in Figure 2.

The results showed that the density of solid acid sites increases with the increase of chlorosulfonic acid dosage. When the dosage of chlorosulfonic acid was 0.6 mL, the increase of acid density was 1.204 mmol/g, and that of solid acid was 1.238 mmol/g when the dosage of chlorosulfonic acid was 0.8 mL. With the increase of the content of chlorosulfonic acid, the density of acid level did not increase significantly. Therefore, the single factor analysis showed that the optimal dosage of chlorosulfonic acid was 0.8 mL.

![Figure 2. Effect of the amount of chlorosulfonic acid on acid density.](image)

3.1.2. Effect of Sulfonation Time on Solid Acid Density

Sulfonation time determines the contact time between chlorosulfonic acid and carrier. Polydopamine adheres to the surface of Fe\textsubscript{3}O\textsubscript{4}, and the amino and sulfonic groups on the surface of polydopamine are linked by chemical bonds. It takes some time for chlorosulfonic acid to bind to the amino groups on the support, so the longer sulfonic group becomes more fully contacted...
with the carrier material. However, the contact time is too long can cause a waste of time. Through the optimization test results analysis, sulfonation time of five hours to obtain the highest density of carbon-based solid acid as shown in Figure 3.

3.2. Catalyst Characterization

3.2.1. SEM Characterization

Figure 4 gave the representative images of Fe$_3$O$_4$, Fe$_3$O$_4$-PDA–SO$_3$H solid catalyst. Figure 4a showed that Fe$_3$O$_4$ nanoparticles had a more spherical morphology and relatively uniform. Figure 4b showed that the catalyst was spherical with an average diameter of about 100 nm. In addition, a continuous polymer layer could be observed on the surface of Fe$_3$O$_4$-PDA–SO$_3$H catalyst compared with Fe$_3$O$_4$.

3.2.2. XRD Characterization

The crystallinity of Fe$_3$O$_4$-PDA–SO$_3$H was studied by XRD. As shown in Figure 5, the pattern of XRD founded that the sample characteristic diffraction peaks at 2θ of 30.2°, 35.7°, 43.3°, 53.8°, 57.2°, and 63.4°, are related to (220), (311), (400), (422), (511), and (440) planes of solid acid catalyst. The diffraction peaks correspond to the structure of Fe$_3$O$_4$ [17]. The result confirmed Fe$_3$O$_4$ nano-particles were synthesized successfully, and the loaded of the sulfonic acid group did not affect the structure of the Fe$_3$O$_4$. 

![Figure 3. Effect of sulfonation time on acid density.](image)

![Figure 4. SEM of the (a) Fe$_3$O$_4$ magnetic nanoparticles and (b) Fe$_3$O$_4$-PDA–SO$_3$H solid catalyst.](image)

![Figure 5.](image)
3.2.3. EDX Characterization

Energy dispersive X-ray spectroscopy was used to examine the surface elemental composition of the product. As shown in Figure 6, C, N, O, S, and Fe were observed. The strong peak in Figure 6 was Si element because of the presence of monocrystalline silicon. The presence of C, N, O, and S indicates that polydopamine was attached to Fe$_3$O$_4$, and sulfonic acid group were loaded to Fe$_3$O$_4$-PDA.

3.2.4. FT-IR Characterization

FT-IR was conducted to investigate the functional group $[^9]$ composition of the nanoparticles. As shown in the Figure 7, the feature peak at 588 cm$^{-1}$ relates to the Fe-O functional group $[^{17}]$ vibration, proving the presence of Fe$_3$O$_4$. The peaks at 3410, 2930, and 1465 cm$^{-1}$ can be assigned to O-H stretching, C-H stretching, and C=C stretching corresponding to the presence of functional groups -OH of phenol and -C=C-NH- in the Fe$_3$O$_4$-PDA $[^{23}]$. The absorption peak at 1512 cm$^{-1}$ corresponded the vibration of benzene ring skeleton indicating that the polydopamine was successfully loaded. The peak at 1000 cm$^{-1}$–1250 cm$^{-1}$ represented the vibration of -SO$_3$H groups, inferring that chlorosulfonic acid was properly combined onto Fe$_3$O$_4$-PDA.
3.3. Optimum Reaction Conditions for Fe₃O₄-PDA-SO₃H Magnetic Nano-Solid Acid

3.3.1. Effect of Catalyst Dosage on Esterification Reaction

Before optimizing the other conditions of the esterification reaction, the optimal amount of catalyst should be determined first. According to the report in the literature, the reaction temperature is 120 °C, the reaction time is 4 h. Select the m_catalyst: m_acid was 5%, 10%, 15%, 20%, 25%, and 30%, respectively. The measured conversion of levulinic acid was 60.35%, 75.64%, 85.10%, 89.34%, 88.32%, and 87.82%, respectively, as shown in the Figure 8.

![Conversion of LA (%)](image)

**Figure 8.** Effect of catalyst amount on conversion of levulinic acid operated at reaction temperature: 120 °C, reaction time: 4 h. m_catalyst: m_acid: 5%, 10%, 15%, 20%, 25%, and 30%.

As shown in Figure 8, when the amount of catalyst increased from 5% to 20%, the yield of LA increased significantly. It can be explained by the fact that the reactants are exposed to more active sites due to the large increase of acid in the reaction system, so the reaction rate is accelerated and more target products are formed at the same time. However, as the amount of catalyst continued to increase, the yield of LA decreased, possibly because the presence of too many catalysts reduced the contact between reactant molecules in a state where the active center was essentially saturated. So, 20% of the amount of acid as the reaction condition was chosen.

3.3.2. Effect of Reaction Temperature

In order to optimize the reaction conditions of esterification, Fe₃O₄-PDA-SO₃H catalytic activity was evaluated in the esterification of LA with ethanol, n-butanol, and n-caprylic alcohol, respectively. The reaction system mainly includes 5 mmol of levulinic acid and 10 mL of alcohols. The catalyst mass...
is 0.116 g, which is 20% of the mass of levulinic acid. As shown in Figure 9a, after 5 h of reaction at 100 °C, the conversion of LA in the presence of the Fe₃O₄-PDA-SO₃H was 89.80%. When catalyst was used on LA with n-butanol esterification, conversion of LA was 95.55% at 90 °C in Figure 9b. As can be seen in Figure 9c, after 4 h at 110 °C, LA reacted with n-caprylic alcohol and conversion of LA was 95.65%. The optimum reaction temperatures of levulinic acid and ethanol, n-butanol, and n-octanol were 100 °C, 90 °C, and 110 °C, respectively.

With the increase of reaction temperature, the viscosity of the reactants in the reaction system decreased, the mass transfer rate and reaction rate increase, promoting the equilibrium being to the right, so the reaction equilibrium time is shorter. However, when the temperature is higher than the optimal reaction temperature, the amount of n-butanol steamed into the condenser increases. The acid: Alcohol ratio in the system decreased, the esterification was incomplete, and the acid residue in the system increased. When calculating the conversion rate, the amount of residual acid in the reaction system is detected by titration. So, the activity drops at the higher temperature when n-butanol is used as the solvent. At the same time, the higher reaction temperature can not only promote the intermolecular movement, but also the evaporation of water in the esterification reaction can accelerate the reaction to the positive direction. However, the excessive high temperature causes the evaporation rate of alcohols to be significantly higher than that of water, thus reducing the contact between the molecules and preventing the reaction from taking place.

![Figure 9. Effect of reaction time on the esterification of levulinic acid with (a) ethanol operated at reaction temperature: 70–110 °C, reaction time: 11 h, and catalyst mass: 0.116 g, (b) n-butanol operated at reaction temperature: 70–100 °C, reaction time: 10 h, and catalyst mass: 0.116 g, and (c) n-caprylic operated at reaction temperature: 100–120 °C, reaction time: 6 h, and catalyst mass: 0.116 g.](image)

3.3.3. Effect of Acid: Alcohol Mole Ratio

The effect of acid: Alcohol mole ratio on the esterification of LA at 5 mmol of levulinic acid, 10 mL of n-butanol, 0.116 g of catalyst, temperature (90 °C), and reaction time (5 h). As shown in Figure 10, under the same reaction conditions, the molar ratio of different acid to alcohol has a greater effect on the esterification. With 50.57%, 55.52%, 79.17%, 89.74%, 91.18%, 96.88%, and 95.00% of LA conversion observed for acid: Alcohol ratio 1:3,1:5,1:7,1:9,1:10,1:11,1:12, respectively. The experimental results showed that the conversion rate of LA can be improved by increasing the molar ratio of acid to alcohol.
to a certain extent. When the content of n-butanol in the reaction system exceeded the optimal amount, the conversion rate of LA did not increase and almost stabilized. Mole ratio 1:11 of LA to n-butanol was the optimum molar ratio.

![Graph](image)

**Figure 10.** Effect of Acid: Alcohol Mole Ratio on the esterification of levulinic acid with n-butanol operated at reaction temperature: 90 °C, reaction time: 5 h, catalyst mass: 0.116 g, and acid: Alcohol ratio: 1:3, 1:5, 1:7, 1:9, 1:10, 1:11, and 1:12.

3.4. Optimization of Esterification Conditions of Solid Acid Catalyst Fe₃O₄-PDA-SO₃H

After the response surface software was designed, the solid acid catalyst was used to catalyze the esterification of levulinic acid with n-butanol according to the experimental scheme. Based on the response surface optimization method, the effects of two interaction parameters on the response value R1, the conversion rate of levulinic acid was shown in Figure 11, were plotted using Design Expert software.

The existence of the convex surfaces above indicated that there is an optimal value, i.e., the maximum conversion of levulinic acid, which can be obtained by optimizing the reaction conditions of the response surface. The optimum reaction conditions were that the reaction temperature was 90.55 °C, the molar ratio of acid to alcohol was 1:12.94, the optimum amount of catalyst was 23.99% of the mass of levulinic acid in the reaction system, and the stirring rate was 401 r/min. Verified under these conditions, the experimental results showed that the conversion rate of acetic acid is 95.87% and the predicted value is 97.12%, which is close to the experimental results. The main reasons for not reaching the predicted value may be the error caused by the titration result which takes the average value three times when the experimental result is detected, and the corresponding error in the course of the experiment.

![Graph](image)

**Figure 11.** Cont.
Figure 11. Cont.
Figure 11. Effect of esterification conditions on the conversion of levulinic acid. Setting conditions: (a) reaction temperature: 80–100 °C, acid: alcohol ratio: 1:7–1:15; (b) reaction temperature: 80–100 °C, m_{catalyst}: m_{acid}: 10%–25%; (c) reaction temperature: 80–100 °C, speed of revolution (r/min): 320–466; (d) acid: alcohol ratio: 1:7–1:15, m_{catalyst}: m_{acid}: 10%–25%; (e) acid: alcohol ratio: 1:7–1:15, speed of revolution (r/min): 320–466; (f) speed of revolution (r/min): 320–466, m_{catalyst}: m_{acid}: 10%–25%.

3.5. Recyclability of Catalyst

The reusability and recovery of the catalyst are important issues for the catalytic reactions. The results of repeated use of magnetic nanometer solid acid catalyst Fe₃O₄-PDA-SO₃H for the esterification of levulinic acid and n-butanol are shown in Figure 12. After the reaction time was 5 h at 90 °C, the conversion rate of levulinic acid could reach 95.55%. After an esterification reaction, the solid acid catalyst was separated from the product by magnetic separation. It was washed with ethanol then, dried at 40 °C. The experimental results showed that the catalyst can still catalyze reaction effectively after being used for six times.

Figure 12. Reusability of the nano-catalyst operated at reaction temperature: 90 °C reaction time: 5 h, and catalyst mass: 0.116 g.

3.6. Comparison with other Typical Solid Acids

The reactant conversion rate of esterification can be used to evaluate the catalytic properties. The solid acid catalyst, Amberlyst 36 and Amberlyst 46 as typical catalysts were selected for the esterification of LA with different alcohols. The acid density of the three catalysts is shown in Table 2. For the same acid density, the mass of the three catalysts of Fe₃O₄-PDA-SO₃H, Amberlyst 36 and Amberlyst 46 were 0.116 g, 0.0266 g and 0.0463 g, respectively. As shown in Figure 13a, esterification reaction of LA with ethanol in the presence of Fe₃O₄-PDA-SO₃H, Amberlyst 36 and Amberlyst 46, the conversion of LA was 89.80%, 10.59% and 52.50%, respectively. Similarly, as can be seen in Figure 13b,
esterification reaction of LA with n-butanol, conversion of LA was 95.55%, 13.14% and 35.56%, respectively. In Figure 13c, esterification reaction of LA with n-caprylic alcohol, conversion of LA was 95.65%, 39.53% and 71.28%, respectively. Obviously, the solid acid catalytic effect is FeO₄-PDA-SO₃H > Amberlyst 46 > Amberlyst 36 at same reaction conditions and commensurable acid content.

**Table 2.** Comparison of the effects of different catalysts on levulinic acid esterification.

| Type of Catalyst         | Acid Density (mmol/g) | LA Conversion with Ethanol (%) | LA Conversion with n-Butanol (%) | LA Conversion with n-Octanol (%) |
|--------------------------|-----------------------|--------------------------------|---------------------------------|---------------------------------|
| FeO₄-PDA-SO₃H            | 1.238                 | 89.8                           | 95.55                           | 95.65                           |
| Amberlyst 36             | 5.4                   | 10.59                          | 13.14                           | 39.53                           |
| Amberlyst 46             | 3.1                   | 52.5                           | 35.56                           | 71.28                           |

**Figure 13.** Different catalysts for the esterification of levulinic acid with (a) ethanol operated at reaction temperature: 90 °C, reaction time: 5 h, and catalyst mass: 0.116 g, (b) n-butanol operated at reaction temperature: 90 °C, reaction time: 5 h, and catalyst mass: 0.0463 g, and (c) n-octanol operated at reaction temperature: 90 °C, reaction time: 5 h, and catalyst mass: 0.0463 g.

From SEM image can be seen that the solid acid catalyst FeO₄-PDA-SO₃H particle size was about 100 nm, which were smaller than the cation exchange resins that about 0.5 mm, so that the sulfonic acid group can be sufficiently contacted with the reaction system, the reaction can be sufficiently carried out under the same time and reaction conditions, thereby increasing the conversion of levulinic acid. The surface of the solid acid is supported with groups such as -SO₃H, phenolic hydroxy, which formed a strong affinity between the hydrophilic portion of the substrate in the reaction system and the neutral hydroxyl in the catalyst FeO₄-PDA-SO₃H. Therefore, during the esterification reaction, the substrate includes alcohols, especially ethanol was a strong hydrophilic molecule, which easily forms an affinity with the -OH group of the solid acid, and the catalyst is more easily contacted with the reactant system, thereby improving reaction speed.

**4. Conclusions**

In summary, this study showed that a homogeneous sized heterogeneous catalyst with clearer morphology, highly activity, and environmental friendliness was prepared for esterification of levulinic acid with ethanol, n-butanol, and n-octanol. The results obtained are listed below:
(1) FT-IR and EDX demonstrated successful loading of polydopamine and sulfonic groups. SEM and XRD showed that the catalyst showed a complete and uniform core-shell structure, and the loading of chlorosulfonic acid would not affect the crystal form of Fe$_3$O$_4$.

(2) The optimum reaction conditions for catalytic reaction of Fe$_3$O$_4$-PDA-SO$_3$H were obtained by single factor and response surface optimization. The optimum experimental reaction conditions were the reaction temperature is 90.55 °C, the molar ratio of acid to alcohol is 1:12.94, optimal amount of catalyst is 23.99% of the mass of acetylpropionic acid and the stirring rate is 401 r/min. The conversion of acetylpropionic acid was 95.87% under this condition.

(3) The results of LA with different alcohol esterification can be proved that this solid acid catalyst has highly efficient and good reusability. Compared with the common cation exchange resin Amberlyst 36 and Amberlyst 46, the results showed that the effect was better under the same reaction conditions.

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