Study on the Synthesized Rosin Glyceride over LaZSM-5 Zeolite Catalyst Synthesized by the in Situ Method

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ABSTRACT: LaZSM-5 zeolite was synthesized by the in situ method and used as catalysts to catalyze the synthesis of rosin glyceride. As a comparison, ZSM-5 was also synthesized and used as catalysts to catalyze the synthesis of rosin glyceride. The synthesized ZSM-5 and LaZSM-5 zeolite catalysts were characterized and analyzed. The experimental results showed that the in situ synthesis of LaZSM-5 made La into the skeleton of ZSM-5 zeolite and increased the amount of Lewis acid on the LaZSM-5 zeolite. Also, Lewis acid was the key to liquid-phase esterification reaction. Compared with ZSM-5 zeolite, LaZSM-5 zeolite contributed to a higher yield and better stability as a catalyst for the synthesis of rosin glycerides.

INTRODUCTION

Rosin glyceride, commonly known as ester gums, is a light yellow transparent solid, and the lighter the color, the better the quality. It has a relative density of 1.095, a softening point of above 80 °C, an acid value of below 10 mg KOH/g, and a refractive index of 1.545. It dissolves in aromatic and aliphatic hydrocarbon solvents, hydrocarbons, terpenes, esters, ketones, orange oil, and most essential oils (such as petroleum, benzene, ethyl acetate, acetone, etc.). It does not dissolve in water and low molecular weight alcohols.1,2 Generally, rosin glyceride is produced by the reaction of rosin and glycerol. The product is a mixture of diglyceride, triglyceride, and glycidyl diglyceride. Compared with rosin, the acid value of rosin glyceride reduces significantly with excellent anti-oxidation nature, light color, high thermal stability, small brittleness, and stickiness as well as no corrosion effect on metal. Therefore, rosin glyceride is widely used in many areas of industries, such as adhesives, food, electronics, medicine, rubber, ink, cable, and so on.3–6

At present, the synthesis of rosin glyceride has been widely researched both at home and abroad. For example, Zhou et al.1 studied the influencing factors for the synthesis of rosin glyceride with ZnO as a catalyst through changing the ratio of raw materials, the amount of catalyst, the reaction temperature, the reaction time, the stirring speed, and the type of protective gas. The optimum reaction conditions are the molar ratio of rosin to glycerol was 2:1, the mass of the catalyst was 0.2% of the mass of rosin, the reaction temperature was 270 °C, the reaction time was 3 h, the stirring rate was 400 r/min, and the protective gas was CO₂. Chen et al.7 synthesized rosin glyceride with rare earth metal oxide as the catalyst, and the catalyst possessed advantages of less dosage and short reaction time. Hou and co-workers9 synthesized rosin glyceride in the presence of carboxylic acid salt and alkali salt as catalysts with the optimum reaction conditions of m (catalyst):m (rosin) = 1:50, n (rosin):n (glycerin) = 1:0.77, reaction time of 10h, and reaction temperature of 230 °C. The acid value of the product was 9.84 mg KOH/g under the appropriate reaction conditions.

Zeolites are porous crystalline aluminosilicates in which the TO₄ (AlO₄ and SiO₄ etc.) tetrahedra are linked together at the

SO₄²⁻/TiO₂−ZrO₂−Gd₂O₃ as a composite catalyst in the reaction of rosin esterification. Also, the esterification rate could reach 98.2%, the product acid value was 8.87 mg KOH/g, and the softening point was 89 °C. The SO₄²⁻/TiO₂−ZrO₂−Gd₂O₃ catalyst was synthesized with the co-precipitation method and impregnation method in the optimal conditions of the catalyst preparation (calcination temperature of 550 °C, roasting time of 4 h, Gd mass fraction of 1.5%). Lu et al.8 synthesized rosin glyceride with rare earth metal oxide as the catalyst, and the catalyst possessed advantages of less dosage and short reaction time. Hou and co-workers9 synthesized rosin glyceride in the presence of carboxylic acid salt and alkali salt as catalysts with the optimum reaction conditions of m (catalyst):m (rosin) = 1:50, n (rosin):n (glycerin) = 1:0.77, reaction time of 10h, and reaction temperature of 230°C. The acid value of the product was 9.84 mg KOH/g under the appropriate reaction conditions.

From the above reaction results, it can be found that these catalysts are difficult to have both high acid value and esterification rate in the reaction of rosin esterification.
corners to form a three-dimensional network with well-defined pore structures on the order of 1.3–13 Å. The pore size depends on the number of T-atoms, for instance, the pore size is about 0.7, 0.5, and 0.4 nm for 12-ring, 10-ring, and 8-ring pore, respectively. 

It is well accepted that zeolites can be used as a catalyst with high activity and selectivity for many reactions due to its ion exchange performance, uniform pore structure, acid catalytic activity, and good thermal stability and hydrothermal stability. 

Among all the zeolites, ZSM-5 zeolite has become a preferred catalyst for the esterification reaction of rosin and glycerol due to its many advantages, such as noncorrosive to the equipment, high temperature resistance, easy preparation, high activity, and good reusability, etc. In addition, it is easily separated from the product because it could be extracted in the state of a solid grain from the reaction mixture. In our previous work, the hydrothermal synthesis method has been used to synthesize ZSM-5 zeolite, and its catalytic activity in the esterification reaction of rosin and glycerol has been investigated. 

The results showed that compared to the commercial ZSM-5 zeolite, the synthesized ZSM-5 zeolite had a higher specific surface area and mesopore volume, exhibiting higher esterification rate, lower product acid value, and better stability. Meanwhile, it has been reported that the LaZSM-5 zeolite catalyst synthesized by the impregnation method has many advantages as a catalyst for the esterification reaction, such as easy separation, high catalytic activity, multiple catalytic but basically no change in activity. Therefore, LaZSM-5 has a high practical value. However, LaZSM-5 zeolite catalyst was synthesized by the impregnation method, which could only load the metal on the surface of the zeolite not entering the skeleton of zeolite, leading to some negative effect on its catalytic performance to some extent. 

To solve the problems, the in situ synthesis method should be adopted to prepare the LaZSM-5 zeolite catalyst according to several studies in which LaZSM-5 zeolite synthesized by the in situ method has been used as catalysts for the catalytic reaction of hydroxylation of phenol with H2O2, the alkylation of toluene with methanol, the amino cyclization of terminal (α,ω)-diols, and so on. However, a few studies on the catalytic performances of in situ synthesis of LaZSM-5 in the esterification reaction of rosin and glycerol conducted. 

In this paper, ZSM-5 and LaZSM-5 zeolite catalysts were synthesized by the hydrothermal synthesis method and in situ synthesis method, respectively. Also, the physicochemical properties of synthesized samples were characterized by ICP, XRD, XPS, FT-IR, SEM, N2 adsorption–desorption, and so on. The catalytic performances of ZSM-5 and LaZSM-5 zeolite catalysts were studied in the esterification reaction of rosin and glycerol.

## RESULTS AND DISCUSSION

### Characterization of Catalyst. ICP.

Table 1 showed the elemental composition (Al and Si) of ZSM-5 and that of ZSM-5 and LaZSM-5. 

| sample     | starting gel composition/molar composition | product composition |
|------------|------------------------------------------|---------------------|
| ZSM-5      | 1.0SiO2:0.02Al2O3                      | (Si0.903Al0.097)O2  |
| LaZSM-5    | 1.0SiO2:0.02Al2O3:0.54 La              | (Si0.983Al0.017La0.077)O2 |

Table 1. Molar Composition of ZSM-5 and LaZSM-5 Zeolites

The XPS spectrum of La in the LaZSM-5 zeolite catalyst is shown in Figure 2. It can be seen that the La 3d XPS spectrum consisted of four peaks, and the binding energy of the electron were 855.8, 852.0, 838.8, and 835.8 eV. It could be observed that both the spin–orbit split 3d5/2 and 3d3/2 levels showed double-peak structures. The peaks at 835.8 and 852.0 eV were identified as the main peaks, and the peaks at 838.8 and 855.8 eV are ascribed to the shake-up satellite peaks of La 3d5/2 and La 3d3/2. According to the literature, the binding peaks of the ZSM-5 phase (2θ = 7.96, 8.83, 23.18, 23.99, and 24.45°) were observed for the LaZSM-5 sample, which were identical to the pure ZSM-5 material. 

### Table 2. Unit Cell Parameters of ZSM-5 and LaZSM-5 Zeolites

| sample     | a/nm     | b/nm     | c/nm     | V/nm³   |
|------------|----------|----------|----------|---------|
| ZSM-5      | 2.1373   | 2.01193  | 1.4710   | 6.65073 |
| LaZSM-5    | 2.1335   | 2.1133   | 1.4700   | 6.62082 |

Figure 1. XRD diagram of ZSM-5 and LaZSM-5 zeolites.
energy of 835.8eV represented the presence of the La⁰ species, the binding energy of 838.8 and 852eV were assigned to the La³⁺ species, and the binding energy of 855.8eV belonged to the La⁴⁺ species. From the above results, it was indicated that La has been incorporated into the skeleton of ZSM-5 because of the variation of the valence state of La.

**SEM.** SEM results of ZSM-5 and LaZSM-5 samples were presented in Figure 3. From Figure 3, it could be seen that the particle of LaZSM-5 were in order compared with ZSM-5. Also, the particle size was within the range of 1 μm × 2.5 μm to 3 μm × 5 μm. According to the literature, zeolites with high crystallinity show a regular morphology. It is reasonable that LaZSM-5 showed a more regular morphology than that of ZSM-5, since it showed higher crystallinity than that of the ZSM-5 sample (Figure 1).

**FT-IR.** The FT-IR spectra of ZSM-5 and LaZSM-5 samples showed in Figure 4 were in good agreement with those of ZSM-5 reported in the literature. Also, the peaks of ZSM-5 were assigned as follows: 454 cm⁻¹ was arose from the bending vibration peak of inner tetrahedron TOT; 546 cm⁻¹ was ascribed to the symmetric stretching vibration of outer tetrahedra; 796 and 1060 cm⁻¹ was due to the deformation vibration of a four-membered ring and the deformation vibration of a six-membered ring, respectively. The 1221 cm⁻¹ corresponded to the antisymmetric stretching vibration of inner tetrahedra. The IR spectrum of LaZSM-5 did not bring about significant changes in the structural region of the zeolite pore, indicating that the interactions between the cations and the framework were generally weak. Nevertheless, some small differences in the spectra may be observed, mainly in band symmetry or the displacement theory. The bands at 1099 and 1221 cm⁻¹ showed a shift to 1088 and 1215 cm⁻¹, respectively. This result might occur because of the fact that the covalent radius of the La atom (0.169 nm) was longer than Al (0.118 nm) and Si (0.111 nm) so that the incorporation of La into the framework of ZSM-5 zeolite could cause a decrease in the force constant of TOT lattice vibration. Mal et al. observed analogous phenomena during preparation of the Sn-ZSM-5 zeolite.

**N₂ Adsorption–Desorption Characterization.** Table 3 presented the pore structure parameters of ZSM-5 and LaZSM-5 samples. The N₂ adsorption–desorption isotherms of ZSM-5 and LaZSM-5 samples are shown in Figure 5. The typical N₂ adsorption–desorption isotherms of as-synthesized

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**Figure 2.** XPS spectrum of La.

**Figure 3.** SEM image of (a) ZSM-5 and (b) LaZSM-5 zeolites.

**Figure 4.** FT-IR spectra of ZSM-5 and LaZSM-5 zeolites.
ZSM-5 and LaZSM-5 samples were of the type IV isotherm according to the IUPAC classification. High adsorption of N\textsubscript{2} occurred in the low relative pressure range and obvious hystereses were detected, suggesting the existence of micropores and the secondary mesopores in ZSM-5 and LaZSM-5 samples. A hysteresis between adsorption and desorption branches was observed at medium relative pressure (0.4–1.0) for all the samples, which demonstrated the presence of a large number of secondary mesopores. Figure 5 showed that the secondary mesopores size distributions decreased in the order of ZSM-5 > LaZSM-5. Figure 6 showed pore size distribution of ZSM-5 and LaZSM-5 samples, which was consistent with the characterization results in Figure 5.

The results presented above indicated that the addition of La atoms into the skeleton of ZSM-5 did not affect the surface area of zeolite. However, the pore volume of the LaZSM-5 sample was less than that of ZSM-5, which is possibly due to the fact that a part of La entered into the pore channels of the sample, occupying some pore volume.

\textit{NH}_{3}-\textit{TPD}. The acidic properties are usually evaluated by \textit{NH}_{3}-\textit{TPD}, and the profiles can be differentiated both in the integral area of the profiles and in the shift of peak temperature. The former corresponds to the amount of acid sites, and the latter indicates the strength of the acid sites. The \textit{NH}_{3}-\textit{TPD} results of ZSM-5 and LaZSM-5 samples are presented in Figure 7. The two ammonia desorption peaks at \(\sim280\) and \(490\) \(^\circ\text{C}\) in Figure 7, correspond to a medium strong acid site and a strong acid site, respectively. Figure 7 also showed that the strength of the acid sites of LaZSM-5 has not changed significantly, although the amount of acid sites of LaZSM-5 changed obviously and was higher than that of ZSM-5 when La was added into the skeleton of ZSM-5. Also, the acidity values of ZSM-5 and LaZSM-5 samples are shown in Table 4, indicating that the total acidity of LaZSM-5 was higher than that of ZSM-5. According to the literature reported by He et al., the formation of acid sites of the silica–alumina catalyst heavily depended on the oxygen ligand number of skeleton metal species. More oxygen ligands of skeleton La species in LaZSM-5 could be formed because La has been incorporated into the skeleton of ZSM-5. Therefore, the total acidity of LaZSM-5 was higher than that of ZSM-5.

\textit{Py-IR}. The surface acidity of two samples was determined by the in situ Py-IR technique, and the results are shown in Figure 8 and Table 5. Usually, the bands at approximately 1450 and 1621 \text{cm}^{-1} are assigned to Lewis acid sites, while the bands at around 1540 and 1639 \text{cm}^{-1} are assigned to Brønsted acid sites. In addition, the band at around 1490 \text{cm}^{-1} can be associated with pyridine adsorbed on both Lewis and Brønsted acid sites. Figure 8 and Table 5 showed that both Lewis acid sites and Brønsted acid sites decreased in the order of LaZSM-5 > ZSM-5. However, the pore volume of the LaZSM-5 sample was less than that of ZSM-5, which is possibly due to the fact that a part of La entered into the pore channels of the sample, occupying some pore volume.

| sample   | \(D_{\text{average}}\) | \text{surface area, m}^{2}/g | pore volume, \text{cm}^{3}/g |
|----------|-------------------------|------------------------------|-----------------------------|
|          |                        | \text{BET} | \text{micropore} | \text{external} | \text{total} | \text{micropore} | \text{mesopore} |
| ZSM-5    | 1.82                    | 402      | 373          | 29          | 0.18      | 0.14      | 0.04 |
|          | 1.80                    | 398      | 370          | 28          | 0.16      | 0.12      | 0.02 |

Figure 5. \text{N}_{2} \text{adsorption–desorption isotherm plot of ZSM-5 and LaZSM-5 zeolites.}

Figure 6. Pore size distribution of desorption of ZSM-5 and LaZSM-5 zeolites.

Figure 7. \text{NH}_{3}-\text{TPD} of ZSM-5 and LaZSM-5 zeolites.

Figure 8. Py-IR spectra of ZSM-5 and LaZSM-5 zeolites.
ZSM-5, which indicated that both Lewis acid sites and Brønsted acid sites increased when La was added into the skeleton of ZSM-5.

Catalytic Performances of the Synthesis of Rosin Glyceride. The catalytic performances of ZSM-5 and LaZSM-5 samples at different reaction times are listed in Tables 6 and 7. As shown in Tables 6 and 7, the acid value and the esterification rate of LaZSM-5 were high compared with ZSM-5. According to the research of Zhang et al.,\(^5\) ZSM-5 was a solid acid, and its surface acidity was the key to catalyzing liquid-phase esterification reaction. The esterification reaction can take place both in the Brønsted acid center and in the Lewis acid center. However, the Lewis acid center was the key to the esterification reaction. Also, the side reaction products ether and olefin are mainly formed in the Brønsted acid center. From the characterization of the catalyst, it was proved that La was introduced into the zeolite framework by in situ synthesis. So, LaZSM-5 contained more Lewis acid centers than ZSM-5 (Table 5). In addition, La has a larger ionic radius than Al, and the introduction of La could be helpful for overcoming the large steric hindrance in resin acids due to the carbonyl group located on the tertiary carbon atom, thereby facilitating the attack of reactions molecules. Therefore, LaZSM-5 has a higher catalytic activity for esterification reaction than ZSM-5.

### CONCLUSIONS

The catalytic performances of ZSM-5 and LaZSM-5 zeolite catalysts were studied in the esterification reaction of rosin and glycerol. Also, the physicochemical properties of ZSM-5 and LaZSM-5 zeolite catalysts were characterized by ICP, XRD, XPS, FT-IR, SEM, N\(_2\) adsorption–desorption, and so on. The ICP, XRD, XPS, and FT-IR characterization results showed that La has been incorporated into the skeleton of ZSM-5 in the synthesis of LaZSM-5. The experimental results showed that the acid value and the esterification rate of LaZSM-5 were high compared with ZSM-5. The amount of Lewis acid sites played an important role in high catalytic performances during the synthesis of rosin glyceride.

### EXPERIMENTAL SECTION

**Catalyst Preparation.** ZSM-5 was synthesized by hydrothermally crystallizing a sol—gel mixture with a composition of 0.2 template:1.0\(\text{SiO}_2\):0.02\(\text{Al}_2\text{O}_3\):0.09\(\text{Na}_2\text{O}\):35\(\text{H}_2\text{O}\). Also, LaZSM-5 was synthesized by an in situ synthesis method from a gel molar composition of 0.2 template:1.0\(\text{SiO}_2\):0.02\(\text{Al}_2\text{O}_3\):0.09\(\text{Na}_2\text{O}\):0.54\(\text{La}_2\text{O}_3\):35\(\text{H}_2\text{O}\). Tetraethyl orthosilicate (TEOS) (40 wt % \(\text{SiO}_2\)) and sodium aluminate (80 wt % \(\text{Al}_2\text{O}_3\)) were used as the source of \(\text{Si}\) and \(\text{Al}\). Tetrapropylammonium hydroxide (TPAOH) was used as the template. Sodium hydroxide (NaOH) and lanthanum nitrate (La\(\text{NO}_3\)) were used as the source of \(\text{Na}_2\text{O}\) and La, respectively. Typically, 16.27 ml TPAOH were added to 63 ml of \(\text{H}_2\text{O}\), the resulting mixture was vigorously stirred for 30 min. Then, 23.07 ml of TEOS, 0.45 g of sodium aluminate, 0.54 g of sodium hydroxide, and 0.12 g of lanthanum nitrate were added, and a final 3 h of stirring time was allowed. The gel mixture was transferred into a stainless steel autoclave, heated in an oven at 200 °C for 24 h. The product thus obtained was

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**Table 4. Acidity Values of ZSM-5 and LaZSM-5 Zeolites**

| sample   | medium strong acid sites | strong acid sites |
|----------|--------------------------|------------------|
| ZSM-5    | 280                      | 0.10             |
| LaZSM-5  | 280                      | 0.13             |

**Table 5. Brønsted Acid Sites and Lewis Acid Sites of ZSM-5 and LaZSM-5 Zeolites**

| sample   | Brønsted acid sites | Lewis acid sites | total acid sites |
|----------|---------------------|------------------|-----------------|
| ZSM-5    | 10.13               | 5.46             | 15.59           |
| LaZSM-5  | 11.26               | 6.04             | 17.30           |

**Table 6. Acid Value and Esterification Rate of the Product over Synthesized ZSM-5 Zeolite at Different Reaction Times**

| reaction time/h | acid value/(mgKOH/g) | esterification rate/% |
|-----------------|----------------------|-----------------------|
| 1               | 69.72                | 58.99                 |
| 2               | 38.58                | 77.31                 |
| 4               | 20.90                | 87.71                 |
| 6               | 13.05                | 92.32                 |
| 8               | 11.08                | 93.48                 |
| 10              | 10.66                | 93.73                 |

**Table 7. Acid Value and Esterification Rate of the Product over Synthesized LaZSM-5 Zeolite at Different Reaction Times**

| reaction time/h | acid value/(mgKOH/g) | esterification rate/% |
|-----------------|----------------------|-----------------------|
| 1               | 72.67                | 65.25                 |
| 2               | 50.63                | 82.22                 |
| 4               | 22.62                | 90.69                 |
| 6               | 19.12                | 93.75                 |
| 8               | 16.83                | 95.10                 |
| 10              | 15.15                | 98.09                 |
washed, then dried at 120 °C for 12 h, and finally calcined in air at 550 °C for 6 h to remove the template completely.

**Catalyst Characterization.** The elemental compositions of the samples were determined by inductively coupled plasma optical (ICP) emission spectroscopy (Perkin-Elmer ICP OPTIMA-3000).

X-ray powder diffraction (XRD) analysis was performed on a RigakuD/maxB X-ray diffractometer. Diffraction patterns were recorded with Cu Kα radiation at 40 kV and 100 mA in the scan range between 5 and 50° to identify the phase structure of the sample.

Scanning electron microscopy (SEM) was performed with LEO-435VP scanning electron microscopy operated at 20 kV and 50 PA.

XPS spectra were measured by using a Kratos XSAM800 fitted with an Al Kα source (1486.6 eV) with two ultrahigh vacuum (UHV) chambers. The binding energy was referenced to the C 1s peak (284.8 eV) to account for charging effects. The areas of the peaks were computed after fitting of the experimental spectra to Gaussian/Lorentzian curves and removal of the background (Shirley function).

The textural properties of the samples were derived from N2 adsorption—desorption measurement on Micromeritics Tristar 3000. In each case, the sample was outgassed under vacuum at 300 °C for 3 h before N2 adsorption. The specific surface area was calculated according to the BET method, and the volume of porous was obtained by t-plot analysis of the adsorption isotherm.

Fourier transform infrared (FT-IR) spectroscopy spectra of the samples were obtained using a Nicolet 380 FT-IR spectrometer.

The acidity was examined by temperature programmed desorption of ammonia (NH3-TPD) techniques, which was carried out in a flow system with a thermal conductivity detector. All samples were preheated from room temperature to 500 °C in an argon flow and kept at 500 °C for 1 h, which was followed by NH3 saturation in a flowing NH3/Ar stream at 40 °C for 5 min. Evacuation at 40 °C for 40 min was carried out to remove physically adsorbed NH3, then the catalyst was heated to 600 °C at a linear heating rate of 10 °C/min, and the detector signal of NH3 was recorded.

IR spectra of adsorbed pyridine (Py-IR) were recorded using a Nicolet-510P apparatus. Prior to the pyridine adsorption, the calcined samples were pressed into thin wafers and evacuated in situ under vacuum at 300 °C for 2 h, then cooled to room temperature, and successive pyridine was dosed until saturated adsorption on the samples was achieved. Finally, the system was evacuated at different temperatures and pyridine adsorbed IR spectra were recorded.

**Catalyst Evaluation.** The experiments were performed in a 250 mL four vial flask; a thermometer, electric stirrer, rubber stopper, and a water separator were connected to a spherical condenser tube. The mass ratio of rosin to glycerin was 1:5.1, and ZSM-5 and LaZSM-5 zeolites catalysts were 0.1 g, respectively.

Rosin was added in the flask first, gradually heated to be melted. Then, the electric stirrer was turned on, and the temperature was further increased to 260 °C. After that, appropriate amount of the glycerin and zeolite catalyst were added in the flask. The sample was taken at 1, 2, 4, 6, 8, and 10 h after the start of the reaction for subsequent product analysis. After the reaction is completed, water separator and condensation tube were removed, then electric heating and stirrer were stopped, and the remaining materials were produced.

(1) **Reagent.** Neutral benzene-ethanol solution: benzene and absolute ethanol (Analytical Pure) were mixed by 2:1 (volume ratio). Phenolphthalein was used as an indicator (two drops per 100 mL) and titrated with 0.05 mol/L potassium hydroxide ethanol standard solution till reddish for 30 s.

 Phenolphthalein indicator (1%): phenolphthalein (1.0 g) was dissolved in anhydrous ethanol (Analytical Pure), which was diluted to 100mL with absolute ethanol (Analytical Pure).

Potassium hydroxide ethanol standard solution (0.05 mol/L): analytical pure potassium hydroxide (2.8 g) was dissolved with a small amount of water without carbon dioxide, and anhydrous ethanol was added and shook well.

(2) **Determination method.** About 2 g (accurate to 0.001 g) of the sample with the surface removed and crushed into powder was dissolved in a 250 mL conical flask with 50 mL of neutral benzene-ethanol solution (If necessary, heat it slightly to dissolve the sample and allow it to cool). Four or 5 drops of phenolphthalein indicator were added, then titrated with 0.05 mol/L potassium hydroxide ethanol standard solution till reddish for 30 s.

(3) **Results and Calculation.** The calculation formula of acid value X1 (mg KOH/mL) = V × M × S.11/W where V is the volume of potassium hydroxide ethanol standard solution consumed during titration, mL; M is the concentration of potassium hydroxide ethanol standard solution, mol/L; W is the weight of the sample, g; and S.11 = 1 mL is the equivalent amount of 1mol/L potassium hydroxide, mg.

Note that the acid value refers to the amount of potassium hydroxide required to neutralize 1 g of product. It can measure the extent of the esterification reaction and the catalytic activity of the catalyst. The smaller the acid value, the more complete the reaction.

Calculation formula of esterification rate esterification rate/% = [(the actual mass of water from esterification/the theoretical mass of water from esterification] × 100% = [(original acid value − product acid value)/original acid value] × 100%

The acid value and the esterification rate are accurate to two decimal places, respectively.

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REFERENCES

(1) Zhou, L. C.; Wang, X. L.; Chen, X. P.; Wei, X. J.; Zhu, Y. J.; Wang, W. L. Study on Esterification of Disproportionated Rosin and Glycerol with ZnO Catalyst. Chem. Word 2007, 9, 557–560.
(2) Wei, X. J.; Chen, X. P.; Liu, Z. J.; Wu, X. Q.; Wen, Y. D. Application of Green Solvent DMC in Determining the Acid Value of Hydrogenated Rosin Glyceride. Sci. Technol. Food Ind. 2009, 30, 296–298.
(3) Jia, Q. M.; Wang, Y. M.; Shan, S. Y. Preparation of Magnetic Nanometer Solid Superacid and Synthesis of Rosin Glyceride. Chem. Ind. For. Prod. 2004, 24, 65–68.
(4) Dehertog, W. J. H.; Fromen, G. F. A Catalytic Route for Aromatics Formation from LPG. Appl. Catal. A: Gen. 1999, 189, 63–75.
(5) Shi, H. C.; Guo, X. Y.; Mao, Z. Q.; Zhang, B.; Jia, J. L.; Wu, J. B.; Ma, G. Z. Preparation and Properties of the Polyurethane Resin Modified by Rosin Glycerin Ester. Polym. Bull. 2012, 9, 71–76.
(6) Zeng, J. C.; Lin, F. S.; Chen, Z. Z. Optimum Craftwork Condition Byproduct Zinc Oxide Catalyst Compose Copolyphonic Tlyceride. J. Shaoyang Univ. 2007, 4, 80–83.
(7) Chen, L. F. Preparation of $\text{SO}_3\cdot\text{TiO}_2\cdot\text{ZrO}_2\cdot\text{GeO}_3$ Solid Superacid and Its Catalytic Activities in Esterification of Ester Gum. Chem. Word 2013, 3, 69–72.
(8) Lu, Y. D.; Liu, Y. R.; Chen, W. C.; Wu, Z. H. Synthesis of Polymerized Rosin Glycerol Ester with Rare Earth Metal Oxides as a Catalyst. Chem. Ind. Times 2005, 19, 20–22.
(9) Hou, P. L.; Liu, S. W.; Yu, S. T. Synthesis of Light-Colored Glycerol Ester of Rosin. Sci. Technol. Chem. Ind. 2018, 26, 7–10.
(10) Yu, L.; Zeng, C.; Wang, C.; Zhang, L. In situ impregnation–gelation–hydrothermal crystallization synthesis of hollow fiber zeolite NaA membrane. Microporous Mesoporous Mater. 2017, 244, 278–283.
(11) Jiang, H.; Guan, B.; Lin, H.; Huang, Z. Cu/SSZ-13 Zeolites Prepared by in Situ Hydrothermal Synthesis Method as NH3-SCR Catalysts: Influence of the Si/Al Ratio on the Activity and Hydrothermal Properties. Fuel 2019, 255, 115875–115604.
(12) Mori, H.; Yamazaki, T.; Ozawa, S.; Ogino, Y. Liquid Phase Reaction of Acetaldehyde over Various ZSM-5 Zeolites. Bull. Chem. Soc. Jpn. 1993, 66, 2498–2504.
(13) Kianfar, E.; Hajimirzaee, S.; Mousavian, S.; Mehr, A. S. Zeolite-based Catalysts for Methanol to Gasoline Process: A review. Microchem. J. 2020, 156, 104822–104831.
(14) Kianfar, E.; Salimi, M.; Pirouzfar, V.; Koohestani, B. Synthesis of Modified Catalyst and Stabilization of CuO/NH4-ZSM-5 for Conversion of Methanol to Gasoline. Int. J. Appl. Ceram. Technol. 2018, 15, 734–741.
(15) Kianfara, E. Synthesis and Characterization of AlPO4/ZSM-5 Catalyst for Methanol Conversion to Dimethyl ether. Russ. J. Appl. Chem. 2018, 91, 1711–1720.
(16) Kianfara, E. Ethylene to Propylene Conversion over Ni-W/ ZSM-5 Catalyst. Russ. J. Appl. Chem. 2019, 92, 1094–1101.
(17) Kianfar, E.; Salimi, M.; Pirouzfar, V.; Koohestani, B. Synthesis and Modification of Zeolite ZSM-5 Catalyst with Solutions of Calcium Carbonate (CaCO3) and Sodium Carbonate (Na2CO3) for Methanol to Gasoline Conversion. Int. J. of. Chem. React. Eng. 2018, 16, 1–7.
(18) Kianfar, E. Comparison and Assessment of Zeolite Catalysts Performance Dimethyl Ether and Light Olefins Production Through Methanol: a Review. Rev. Inorg. Chem. 2019, 39, 157–177.
(19) Kianfar, E. Ethylene to Propylene over Zeolite ZSM-5: Improved Catalyst Performance by Treatment with CuO. Russ. J. Appl. Chem. 2019, 92, 933–939.
(20) Kianfar, E. Nanozeolites: Synthesized, Properties, Applications. J. Sol-Gel Sci. Technol. 2019, 91, 415–429.
(21) Kianfar, E.; Azimikia, R.; Faghih, S. M. Simple and Strong Dative Attachment of ε-Diimine Nickel (II) Catalysts on Supports for Ethylene Polymerization with Controlled Morphology. Catal. Lett. 2020, 150, 2322–2330.
(22) Onishchenko, M. I.; Kulikov, A. B.; Maksimov, A. L. Application of Zeolite Y-Based Ni-W Supported and In Situ Prepared Catalysts in the Process of Vacuum Gas Oil Hydrocracking. Pet. Chem. 2017, 57, 1287–1294.
(23) Schwanke, A.; Villarroel-Rocha, J.; Papag, K.; Diaz, U.; Corma, A.; Pergher, S. Dandelion-Like Micromesospheric MCM-22 Zeolite Using BP 2000 as a Hard Template. ACS Omega 2018, 3, 6217–6223.
(24) Selvaraj, T.; Renganathan, R. Influence of Different Zeolite Frameworks on the Geometry of Platinum(II)tetrammine Complex. ACS Omega 2018, 3, 2558–2563.
(25) Vannmolee, W.; Beltramini, J. N.; Atanda, L.; Bartley, J. P.; Laosiripojana, N.; Doherty, W. O. S. Effect of HCOOK/Ethanol on Fe/HUSY, Ni/HUSY, and Ni–Fe/HUSY Catalysts on Lignin Depolymerization to Benzylic Alcohols and Bioaromatics. ACS Omega 2019, 4, 16980–16993.
(26) Zhang, P.; Wang, M.; Sun, B.; Yang, X.; Hou, J. L.; Zhao, L. Y.; Liu, Z. M.; Fei, D. T.; Yan, X. L.; Wang, X. X. Synthesis of Rosin Glyceride Catalyzed by ZSM-5 Zeolite Synthesized Hydrothermally. Nat. Gas Chem. Ind. 2017, 42, 58–61.
(27) Li, J. L.; Xu, X. S.; Li, B.; Fang, X. P. Synthesis of Rosin Glyceride Catalyzed by LaZSM-5 Zeolite. Chemistry 2004, 4, 245–246.
(28) Xu, X. T.; Li, B.; Li, J. L.; Wei, C. Q. Characterization and study on esterification activity of LaZSM-5 zeolite. J. Guangxi Univ. (Nat. Sci. Ed.) 2000, 4, 276–278.
(29) Gao, X. F.; Ding, C. M.; Liu, W. L.; Wang, J. W.; Zhang, K.; Liu, P. Methanol to Gasoline over La/ZHSZ-5 Catalyst Modified by Na2CO3. Adv. Mater. Res. 2014, 953, 1215–1220.
(30) Othman, I.; Mohamed, R. M.; Ibrahim, I. A.; Mohamed, M. M. Synthesis and Modification of ZSM-5 with Manganese and
Lanthanum and Their Effects on Decolorization of Indigo Carmine dye. Appl. Catal. A: Gen. 2006, 299, 95–102.

(31) Jiang, H.; L.; Wang, X. S. Study on Hydrothermal Synthesis and Characterization of LaZSM-5. Acta. Petrolei. Sinica. 1996, 12, 17–23.

(32) Zhang, L.; D.; Gao, J. H.; Hu, J. X.; Li, W. H.; Wang, J. H. Preparation of LaZSM-5 and Catalytic Behavior for Toluene Alkylation with Methanol. Chem. Ind. Eng. Prog. 2008, 27, 446–450.

(33) Bani, V. B.; Srinivas, N.; Kulkarni, S. K.; Raghavan, K. V. Amino Cyclization of Terminal (α,ω)-diols over Modified ZSM-5 Catalysts. J. Mol Catal A: Chem. 2002, 187, 237–246.

(34) Ausavasukhi, A.; Sooknoi, T. Tunable Activity of [Ga] HZSM-5 with H3 Treatment: Ethane Dehydrogenation. Catal. Commun. 2014, 45, 63–68.

(35) Frache, A.; Palella, B.; Cadoni, M.; Pirone, R.; Ciambelli, P.; Pastore, H. O.; Marchese, L. Catalytic DeNO(x) Activity of Cobalt and Copper Ions in Microporous MeAlPO-34 and MeAPSO-34. Catal. Today 2002, 75, 359–365.

(36) Liu, Z.; Tang, L.; Chang, L.; Wang, J.; Bao, W. In Situ Synthesis of Cu-SAPO-34/Cordierite for the Catalytic Removal of NOx from Diesel Vehicles by Cu-H4. Chinese J. Catal. 2011, 32, 546–554.

(37) Wu, J. M.; Li, N.; Wang, B. Y.; Li, Z. Y.; Xiang, S. H. Influence of Some Metal Salts on the Crystallization of Zeolite MCM-22. Acta Sci. Nat. Univ. Nankaiensis 2006, 39, 1–6.

(38) Finund, E. F. Mechanism of the Crystallization of Zeolite X. J. Cryst. Growth 1976, 34, 11–23.

(39) Feng, S. H.; Li, S. G.; Xu, R. R.; Fei, P. S. The Mechanism of Formation and Crystal Growth of Molecular Sieve Zeolite (XII)-The Crystallization Kinetic Model for a Spontaneous Nucleation System of the M-Si-ZSM-5-type Zeolites. Chem. Res. Chin. Univ. 1985, 6, 855–860.

(40) Zhang, P.; Guo, J.; Zhao, P.; Zhu, B.; Huang, W.; Zhang, S. Promoting Effects of Lanthanum on the Catalytic Activity of Au/TiO2 Nanotubes for CO Oxidation. RSC Adv. 2015, 5, 11989–11995.

(41) Siab, W. R.; Lintang, H. O.; Yuliati, L. Role of Lanthanum Species in Improving the Photocatalytic Activity of Titanium Dioxide. Catal. Sci. Technol. 2017, 7, 159–167.

(42) Martinez, R.; Romero, E.; Guimon, C.; Bilbao, R. CO2 Reforming of Methane over Coprecipitated Ni-Al Catalysts Modified with Lanthanum. Appl. Catal. A: Gen. 2004, 274, 139–149.

(43) Rao, R. R.; Srinivas, N.; Kulkarni, S. J.; Subrahmanyan, M.; Raghavan, K. V. A New Route for the Synthesis of 3,5-bis(aminomethyl)-2-pyridine over Modified ZSM-5 Catalysts. Appl. Catal. A: Gen. 1997, 161, 37–42.

(44) Baelo, C., Bennett, J. M., Depmeier, W., Fitch, A. N., Jobic, H., Koningsveld, J. M., McAllister, W. M., Penninger, A. Molecular Sieves Science and Technology: Structures and Structure Determination; Karge, H. G., Weitkamp, J., Eds.; Springer: Netherlands, 1999.

(45) Kokottalo, G. T.; Lawton, S. L.; Olson, D. H.; McAllister, W. M. Structure of synthetic zeolite ZSM-5. Nature 1978, 272, 437–438.

(46) Gackowski, M.; Podobiński, J.; Hunger, M. Evidence for a Strong Polarization of n-hexane in Zeolite H-ZSM-5 by FT-IR and Solid-State NMR Spectroscopy. Microporous Mesoporous Mater. 2019, 273, 67–72.

(47) Poignant, F.; Freyze, J. L.; Daturi, M.; Saussey, J.; Lavallely, J. C. In situ FT-IR Study of the Selective Catalytic Reduction of NO by Propane on Cu-ZSM-5: Evidence of a Reaction Pathway by Oxygen Pulses. Stud. Surf. Sci. Catal. 2000, 130, 1487–1492.

(48) Fu, T.; Zhou, H.; Li, Z. Controllable Synthesis of Ultra-tiny Nano-ZSM-5 Catalyst Based on the Control of Crystal Growth for Methanol to Hydrocarbon Reaction. Fuel Process. Technol. 2021, 211, 106594–106604.

(49) Huang, L.; Zhou, Y. M.; Zhang, Y. W.; Li, Q. N.; Tian, X. M. Propane Dehydrogenation over PtSnNa Catalyst Supported La-ZSM-5 Zeolite. Chin. Pet. Process. PE. 2010, 12, 18–24.

(50) Ramaswamy, A. V.; Mal, N. K.; Ramaswamy, V.; Ganapathy, S. Synthesis of Tin-silicate Molecular Sieves with MFL Structure and Their Catalytic Activity in Oxidation Reactions. Appl. Catal. A: Gen. 1995, 125, 233–245.

(51) Wang, J.; Zhang, R.; Han, L.; Wang, J.; Zhao, L. Seed-Assisted Synthesis and Characterization of Nano and Micron ZSM-5 Molecular Sieves in Template-Free System. J. Solid State Chem. 2020, 290, 121536–121548.

(52) Yang, Y.; Jiang, W.; Jiang, J.; Qiu, Q.; Mao, P.; Wu, M.; Zhang, L. Synthesis of Hierarchical ZSM-5 Zeolites Templated by Sodium Alginate Toward Enhanced Catalytic Activity for Esterification. J. Solid State Chem. 2020, 292, 121686–121692.