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Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Article

Study on the pinene isomerization catalyzed by TiM

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ARTICLE INFO

Article history:

Received 3 November 2017

Received in revised form 17 January 2018

Accepted 20 February 2018

Available online 2 March 2018

Keywords:

 α -Pinene isomerization

Camphene

Composite metatitanic acid

ABSTRACT

The isomerization reaction of pinene is one of the most important chemical reactions in the deep processing of pinene. The purpose of this study is to improve the performance of the metatitanic acid by composite. The composite metatitanic acid catalyst TiM was prepared by adding Mn elements in the preparation process. The catalytic performance of TiM was evaluated. Comparison of TiM and metatitanic acid catalyst (Ti-FGP), the reaction rate of TiM catalyst was faster, and after the reaction, the yield of camphene and tricyclene increased about 1%. The catalysts were characterized by an SEM, FT-IR and laser particle size analyzer. The results show that the pinene isomerization reaction requires the synergistic action of the Brønsted acid and Lewis acid. Brønsted acid has great influence on the activity of catalyst, and Lewis acid has a great influence on the selectivity of the catalyst. The structure and morphology of the catalyst have a certain effect on the selectivity of pinene isomerization reaction.

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1. Introduction

Pinene is the primary constituent of turpentine. Pinene is a bicyclic monoterpene chemical compound. There are two structural isomers of pinene found in natural essential oils: α -pinene and β -pinene. As the pinene is chemical active, it is easy to lead the chemical reaction of the isomerization, hydrogenation, oxidation, esterification and saponification, hydration and other chemical reactions.

Pinene isomerization is one of the most important chemical reactions in the deep processing of pinene, and the product of isomerization is camphene, tricyclene, p-cymene, terpinolene, terpinenes, limonene and other substances. Among them, camphene is an important industrial material, widely used in perfume synthesis, drug synthesis and other fields. The main purpose of the pinene isomerization research is to improve the product yield of camphene.

Pinene isomerization has been reported for a long time [1]. The progress of pinene isomerization is carried out under the action of acid catalyst. There are many reports on the acid catalyst, including clay [2], bentonite [3], montmorillonite [4], kaolinite [5], vermiculite [6], aluminosilicate [7], titanium oxide [8], heteropoly acid [9,10], ferrierite type zeolite [11–14], clinoptilolite [15,16], sulfated ZrO₂ [17–20], ion exchange

resin [21,22], mesoporous acid catalyst [23–26], nano-solid acid catalysis [27], MOF catalyst [28] and so on.

The catalyst is the most important factor in the pinene isomerization reaction. The present research on the conversion and selectivity of pinene isomerization has been greatly improved. Almost all catalysts used in industrial materials are metatitanic acid. The conversion is above 99%, and the selectivity of camphene in the factories are different. At the FGP (Fujian Green Pine Co., Ltd.), the selectivity of camphene is about 68%, the reaction temperature is 120 °C, and the reaction time is about 16–20 h.

How to further increase the yield of camphene is the main content of the research on the pinene isomerization reaction. The solutions include computer aided calculation [29,30] and traditional empirical method. The pinene isomerization reaction mechanism is complex, and the traditional empirical method is more effective for it is based on experiment. The pinene isomerization conversion has been reported to almost reach over 99%, but the selectivity of camphene is highest under the action of metatitanic acid catalyst. Therefore, it is the most convenient method to screen the catalyst by improving the metatitanic acid. At present, there are various composite metatitanic acid catalysts which were obtained by adding metal oxides such as ZrO₂. But the effect is not obvious, and some composite metatitanic acid catalysts are costly. In this paper, the composite metatitanic acid catalyst was prepared by adding Mn elements in the preparation process. The activity and selectivity of the catalyst were investigated by experimental tests, and the surface, acidity and particle size of the composite catalyst were characterized.

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2. Experiment

2.1. Catalyst preparation

Hydrated titanium dioxide and manganese sulfate are added to 25% sodium hydroxide solution at a certain proportion. It was filtered and washed 4 times after alkalized at 100 °C for 6 h. Then it was acidulated at pH 5–6 by dilute sulfuric acid for 8 h. It was filtered and washed 3 times after being acidulated. The composite catalyst TiM was obtained after drying at 100 °C.

2.2. Activity measurement

The reaction was carried out at 120 °C in a three necked round bottom flask fitted with a magnetic stirrer ($300 \text{ r} \cdot \text{min}^{-1}$), a thermometer and a reflux condenser. Usually 3.5 g of catalyst and 100 g turpentine (75.82% α -pinene, 15.13% β -pinene, 1.38% camphene) were charged in the flask. The samples were taken during the course of the reaction. They were cooled to RT rapidly and filtered to remove the catalyst. The products were analyzed by flame ionization detector (FID) gas chromatography (Varian CP-3800 with $30 \text{ m} \times 0.25 \mu\text{m} \times 0.3 \mu\text{m}$ SE-54 capillary column). Temperature programming (increase at a rate of $6 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ from 75 °C to 120 °C, hold for 2 min, then increase at a rate of $20 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ until 240 °C, hold for 5 min) was applied for separation at $1 \text{ ml} \cdot \text{min}^{-1}$ N_2 flow.

The conversion of pinene and selectivity to any product are determined by the following equations:

$$\text{Conversion} = \frac{\text{moles of isomerized pinene}}{\text{moles of initial pinene}}$$

$$\text{Selectivity} = \frac{\text{moles of product} - \text{moles of initial product}}{\text{moles of isomerized pinene}}$$

At the end of the reaction, the catalyst can be separated by centrifugation, and then the reusability of the catalyst was tested.

2.3. Characterization of catalysts

The catalysts were characterized by several methods.

The surface of catalysts and EDS were analyzed by a scanning electron microscope (SEM) which were obtained on Hitachi S-4800.

The particle size was analyzed by the laser particle size analyzer BT-9300HT.

Surface acidity was analyzed by the *in situ* pyridine adsorption infrared spectrum, which was recorded on Nicolet nexus FT-IR. The powders were pressed into self-supporting wafers and degassed under vacuum at 120 °C for 1 h prior to contact with the pyridine.

3. Experimental Results

3.1. Reaction study

The isomerization reaction was studied in heterogeneous phase. Turpentine as the reaction material was provided by Fujian Green Pine Co., Ltd. The turpentine contained 75.82% α -pinene, 15.13% β -pinene, and 1.38% camphene. The kinetic curves for TiM catalyst were presented in Fig. 1A. The kinetic curves for Ti-FGP catalyst (provided by Fujian Green Pine Co., Ltd.) were presented in Fig. 1B. From Fig. 1A and B, the pinene concentration (wt%) decreased with the time, and the principal reaction products were the camphene and tricyclene. When the pinene concentration was lower than 1%, it was considered the end of the reaction. Comparison of the TiM and Ti-FGP catalysts, the reaction rate of the TiM catalyst was faster, and after the reaction, the yield of camphene and tricyclene increased about 1%. For the TiM catalyst, after 8 h of the reaction, the conversion of pinene was 98.86%, and the

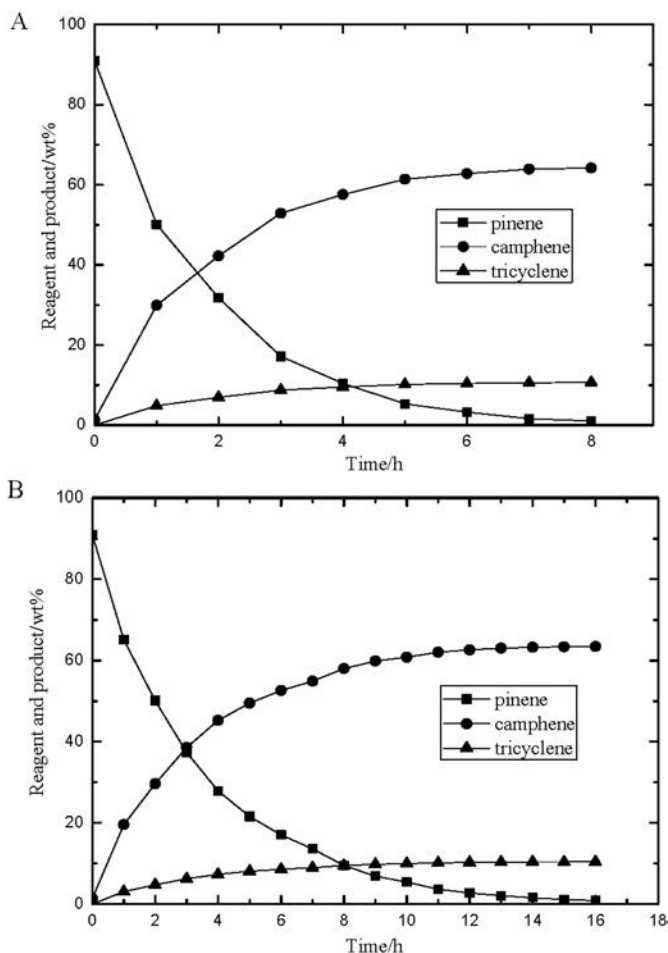


Fig. 1. The kinetic curves for catalyst TiM and Ti-FGP.

selectivity to camphene and tricyclene was 69.86% and 11.93%. For the Ti-FGP catalyst, after 16 h of the reaction, the conversion of pinene was 99.09%, and the selectivity to camphene and tricyclene was 68.86% and 11.53%.

The reusability of the catalyst TiM was shown in Fig. 2A, B and C. It can be seen from these figures that the activity of the TiM catalyst decreased as it was reused, but the selectivity remained unchanged.

3.2. Characterization

The SEM images of TiM and Ti-FGP were shown in Fig. 3A and B, and the size and morphology were different between the TiM catalyst and Ti-FGP catalyst. The average size of the TiM catalyst was bigger than the Ti-FGP catalyst.

The EDS spectra of TiM and Ti-FGP were shown in Fig. 4A and B. The metal element of the catalyst TiM was titanium and manganese, and the content of manganese was 7.38%, while the metal element of the catalyst Ti-FGP was only Ti.

In order to further analyze the particle size distribution of catalyst, the TiM catalyst and Ti-FGP catalyst were analyzed by the laser particle size analyzer BT-9300HT. The results were shown in Fig. 5. The surface diameter of the TiM catalyst (Fig. 5A) was $1.512 \mu\text{m}$, and the specific surface area was $1279 \text{ m}^2 \cdot \text{kg}^{-1}$. The surface diameter of the Ti-FGP catalyst (Fig. 5B) was $1.346 \mu\text{m}$, and the specific surface area was $1437 \text{ m}^2 \cdot \text{kg}^{-1}$.

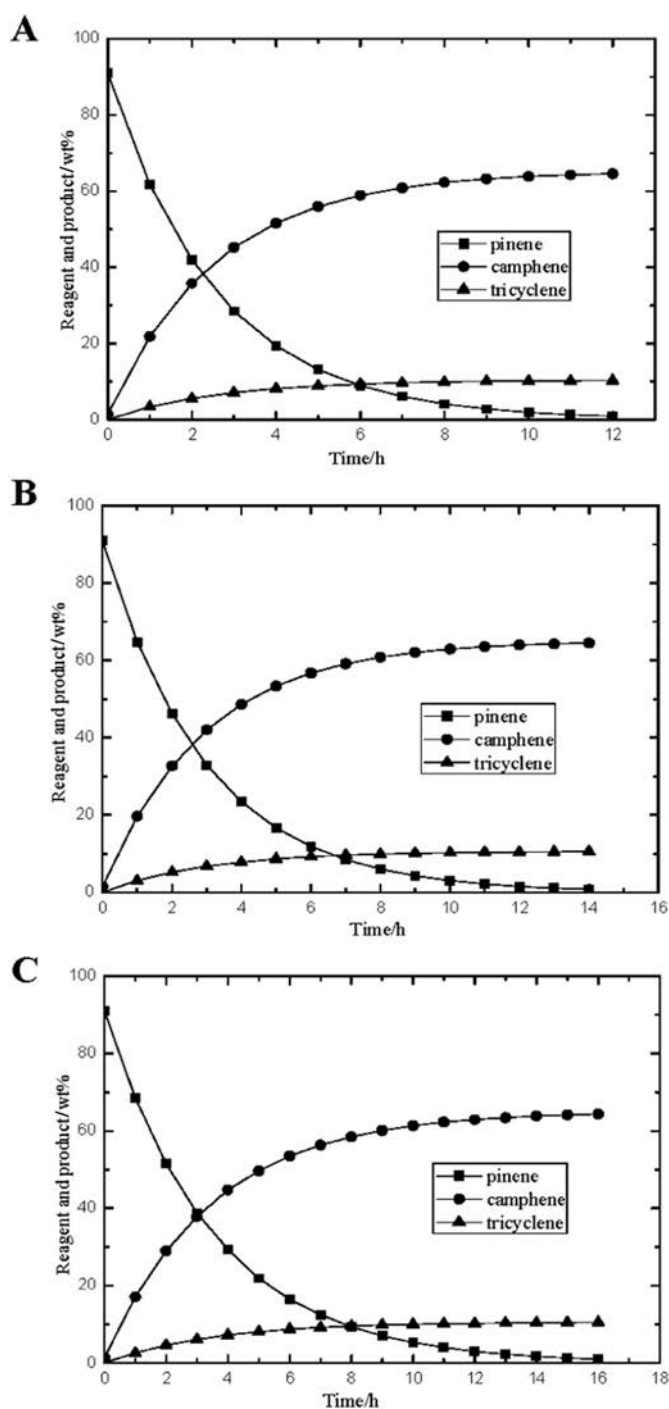


Fig. 2. The kinetic curves for reused catalyst TiM. (A) The first reuse of TiM; (B) the second reuse of TiM; (C) the third reuse of TiM.

The FT-IR spectra of the TiM and Ti-FGP catalysts were shown in Fig. 6. The characteristic bands of pyridine covalently bonded to Lewis acid sites were 1445 cm^{-1} and 1486 cm^{-1} . The absorption characteristic spectrum of Brønsted acid is relatively weak. Fig. 6 also showed that the catalytic reaction was mainly catalyzed by Lewis acid. The catalysts TiM and Ti-FGP had the same acid type.

4. Discussion

Pinene isomerization reaction is carried out by the action of acid. The view of Comelli *et al.* [18] is that only Lewis acid sites

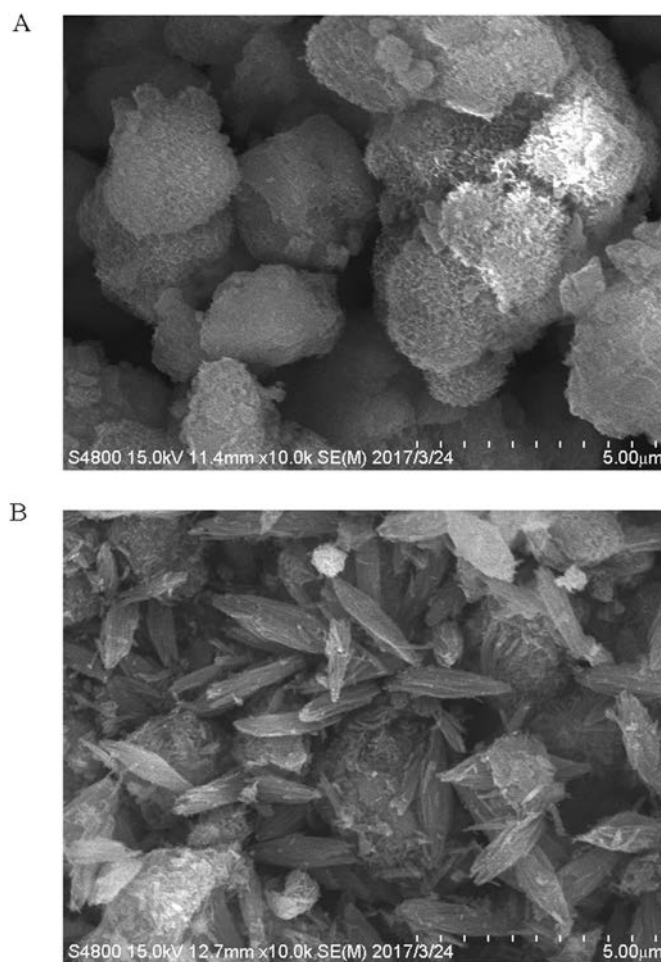


Fig. 3. The SEM image of TiM and Ti-FGP.

are present as there is no activity to the isomerization of pinene, and only Brønsted acid sites are present as there is almost no activity. We also verified that under the catalysis of Brønsted acid (CH_3COOH) only, the conversion rate of pinene isomerization was also extremely low. The pinene isomerization reaction requires the synergistic action of Brønsted acid and Lewis acid. The synergistic action of Brønsted acid and Lewis acid is the most important factor to the rate and selectivity of the pinene isomerization reaction. The infrared spectrum (Fig. 6) shows that the absorption characteristic spectrum of Lewis acid is obvious, and the absorption characteristic spectrum of Brønsted acid is relatively weak. According to the reports and our experimental results, it can be deduced that the Lewis acid has great influence on the selectivity of camphene, and Brønsted acid has auxo-action on the rate of pinene isomerization reaction. If the auxo-action of the Brønsted acid is low, the rate of pinene isomerization reaction is slow. But if the concentration of the Brønsted acid is too high, the reaction is vigorous. And it is difficult to control the reaction temperature for its rise rapidly. It brings out a side reaction increase and the selectivity of camphene is reduced.

The infrared spectra shown in Fig. 6 show that the absorption of Brønsted acid to the TiM catalyst is weak, but it is stronger than that of the Ti-FGP catalyst. Under the action of the TiM catalyst, the isomerization reaction time is about 8 h, and the isomerization reaction time of Ti-FGP is about 16 h. The reaction rate with the Ti-FGP is slower. Most of the reported reaction time of pinene isomerization is 1–4 h, and the selectivity of camphene and tricyclene less than 80%. The reason is most likely that the Brønsted acid concentration of the catalyst is too high.

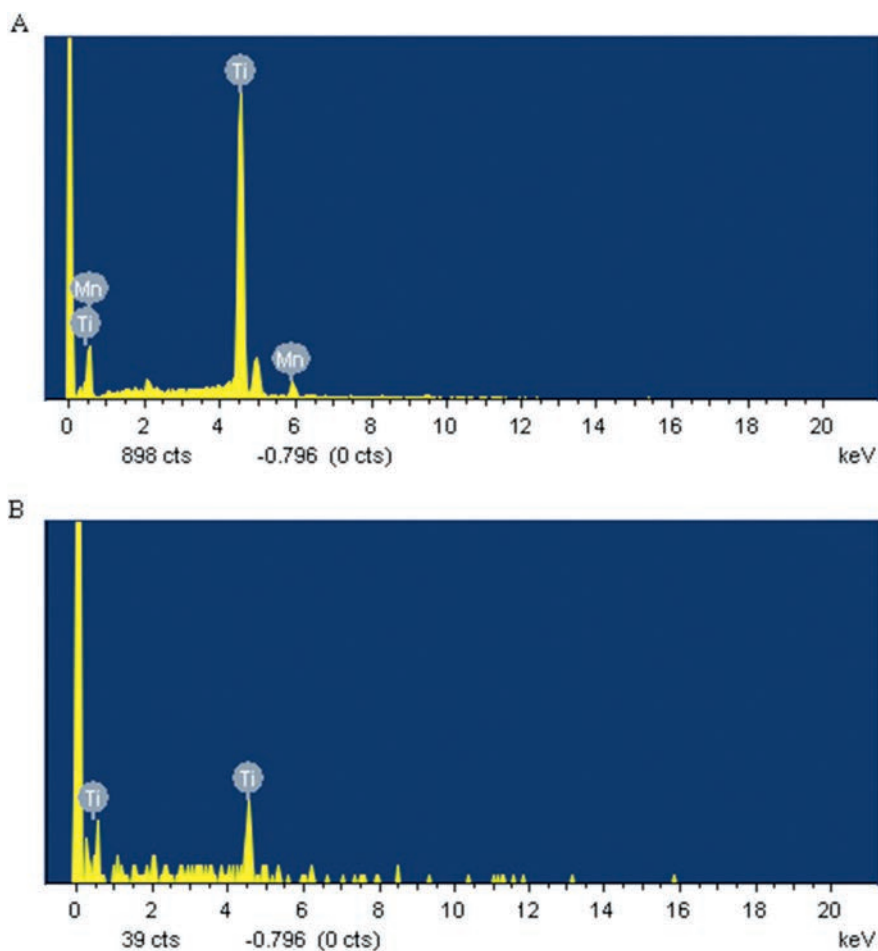


Fig. 4. The EDS spectrum of TiM and Ti-FGP.

Pinene isomerization reaction is carried out in the presence of acid catalyst. Almost all catalysts used in industrial materials are metatitanic acid. Ti-FGP is the metatitanic acid prepared by FGP (Fujian Green Pine Co., Ltd.). The SEM images (see Fig. 3A and B) show the difference of morphology between TiM and Ti-FGP. It can be deduced that the different yields of camphene and tricyclene are due to the differences of catalyst structure and morphology. The main factors affecting the pinene isomerization are the synergistic effect of Brönsted acid and Lewis acid, but the structure and morphology of the catalyst have a certain effect on the selectivity of pinene isomerization reaction.

Generally speaking, the catalyst particles are small, which is beneficial to eliminate the influence of internal diffusion in the reaction and increase the reaction rate. This experiment is a heterogeneous reaction. At the end of the reaction, stirring was stopped. The Ti-FGP catalyst slowly clarified, and the TiM catalyst quickly clarified. It is conducive to the separation and reuse of catalyst. If the catalyst particle is too small, it is difficult to clarify and separate after the complete pinene isomerization reaction.

Under the catalyst of metatitanic acid, the selectivity of camphene for the pinene isomerization reaction is high, and it is not easy to further improve the selectivity. It is necessary to make an intensive study on the microstructure of the catalysts. It is helpful to improve the catalysts and optimize the kinetics, thereby optimize the process of pinene isomerization.

5. Conclusions

Through the composite modification of the metatitanic acid catalyst, the activity and selectivity of the catalyst are improved compared with

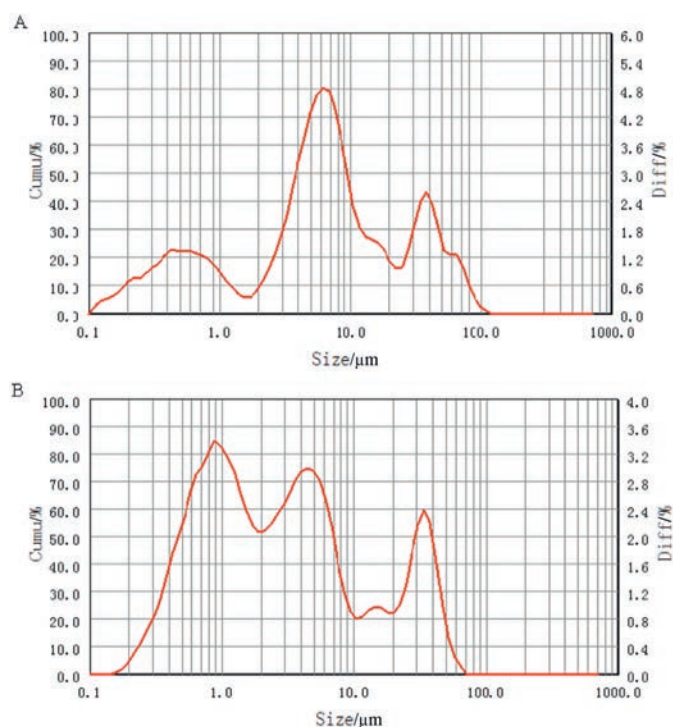


Fig. 5. The particle size distribution of TiM and Ti-FGP.

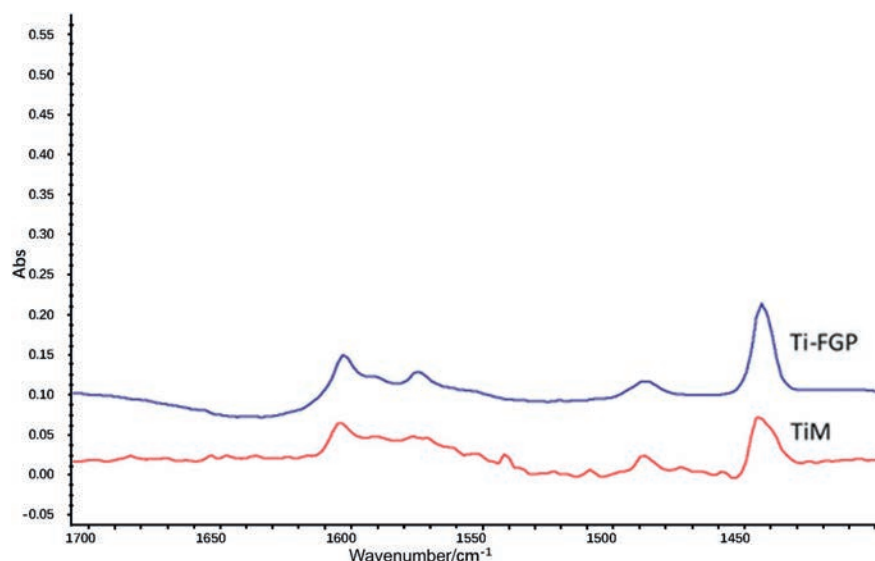


Fig. 6. The FT-IR spectra of TiM and Ti-FGP catalyst.

the industrial metatitanic acid catalyst (Ti-FGP). According to the results of experimental and catalyst characterization, the pinene isomerization reaction requires the synergistic action of the Brønsted acid and Lewis acid. The pinene isomerization reaction is sensitive to acids. Brønsted acid has great influence on the activity of catalyst, and promotes the occurrence of reaction in a certain range. But the excess is disadvantageous to the reaction stability, and it is easy to bring out side reactions. Lewis acid has a great influence on the selectivity of the catalyst. The structure and morphology of the catalyst have a certain effect on the selectivity of pinene isomerization reaction. The improvement of the composite metatitanic acid is a fast and effective method. With the intensive study on the microstructure of catalysts, it is advantageous to the improvement of catalyst and the optimization of pinene isomerization reaction in theory and practice.

Acknowledgments

This work was supported by the Fujian Green Pine Co., Ltd (NO. 2016001).

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