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# Synthesis of isoamyl salicylate using a novel mesoporous titania superacid as a catalyst

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**Abstract**−Mesoporous titania was prepared by hydrothermal method and mesoporous titania solid superacid catalyst was prepared by wet impregnation method. The structure and property of the as-prepared catalysts were characterized by means of XRD, FT-IR and $N_2$ physical adsorption. Isoamyl salicylate was synthesized by using concentrated sulfuric acid and solid superacid as catalyst, respectively. The effects of the molar ratio of raw material, the amount of catalyst, reaction time and reaction temperature on the yield of the product were systematically investigated. The results show that mesoporous titania solid superacid is a good catalyst for synthesizing isoamyl salicylate. The optimum conditions of isoamyl salicylate synthesized by using mesoporous titania solid superacid are the following: the molar ratio of salicylic acid to isoamyl alcohol is 1 : 4, the quantity of catalyst is 1.6 g, the reaction time is 5 h, the reaction temperature is 130 °C and the yield can reach 94.6%.

Key words: Solid Superacid, Catalysis, Isoamyl Salicylate, Synthesis, Yield

## INTRODUCTION

Acid catalysis is of fundamental industrial importance, and acid catalysts play a vital role in the economic development of the chemical industry. Many organic reactions, for example, alkylation, saturated hydrocarbon isomerization, esterification, cracking, condensation and so on are accomplished by acid catalysts. However, conventional liquid acids such as $H_2SO_4$, HF, HCl and $H_3PO_4$ used in organic synthesis generate great risks in handing, containment and disposal due to their toxic and corrosive nature. On the other hand, increasing waste disposal costs are adding to the environmental costs and the societal costs of an increasingly hostile public toward chemical waste [1]. In addition, the problems of corrosion and pollution of the desired product strongly limit their industrial applications. In consideration of environmental and economic reasons, many researchers have made great efforts to replace conventional acid catalysts with newer solid superacid catalysts. For the past few decades, many kinds of solid superacid catalysts have been found, and they have been used widely in many areas [2-9]. This is principally attributed to the obvious advantages of solid superacid catalysts, such as their high acid strength, no corrosion for reactors, ease of handing, less expensive, and easy to recover and reuse [1,10-13] as compared with traditional liquid acids. Among these prepared solid superacids, solid superacids with nanosized $TiO_2$ have attracted worldwide attention because of their wide applications in many organic reactions [4,14-18]. However, solid superacid with nanosized $TiO_2$ also has some disadvantages, such as to the difficulty in adjusting its acidity and small surface area. Compared with nanosized $TiO_2$, mesoporous $TiO_2$ has high specific surface area, ordered pore structure and excellent adsorption property, which is expected to be a new media for heterogeneous reactions. Recently, many efforts have been made by researchers in synthesis and application of mesoporous $TiO_2$. Wang et al. [19] reported that mesoporous $TiO_2$ synthesized by hydrothermal method exhibited good catalytic activity for degradation of methyl orange. Pavasupree et al. [20] synthesized mesoporous anatase $TiO_2$ nanopowders by hydrothermal method and the as-synthesized mesoporous anatase $TiO_2$ nanopowders showed high activity as compared with nanosized $TiO_2$ (P25) on the oxidation photo-reaction of I to $I_2$ in excess I conditions. Hence, mesoporous $TiO_2$ solid superacid will exhibit excellent catalytic activity in some organic reactions because of its high surface area and unique pore structure.

Isoamyl salicylate is a colorless liquid that is widely applied in the fields of food, cosmetic and essence because its smell is similar to that of clover or some orchids. In addition, isoamyl salicylate also is the most important one of spices having applied value. At present, isoamyl salicylate is synthesized by using concentrated sulfated acid as catalyst of the esterification reaction in the spice industry. However, conventional liquid acid $H_2SO_4$ used in esterification generates great risks such as difficulty of handing, high waste generation and environmental problems and so on. Recently, in order to solve these problems, many kinds of solid superacids were used in esterification reactions as catalysts and they have exhibited excellent catalytic activities [8,21].

For this purpose, in the present work, mesoporous $TiO_2$ was synthesized by hydrothermal method and using cetyltrimethyl ammonium bromide (CTAB) as a template. Mesoporous $TiO_2$ solid superacid catalyst was prepared by impregnation with a solution of sulfuric acid (1 mol/L), and catalytic activity of the catalyst was investigated by the esterification reaction of salicylic acid and isoamyl alcohol. The reaction condition of the esterification reaction of salicylic acid and isoamyl alcohol was also investigated by using the as-prepared solid superacid as catalyst. In particular, the catalytic activities of the three catalysts ($H_2SO_4$, nanosized $TiO_2$ solid superacid and mesoporous $TiO_2$ solid superacid) were compared, and the catalytic activity of mesoporous $TiO_2$ solid superacid was the highest among the three catalysts.

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## EXPERIMENTAL

### 1. Materials

Chemicals used in the present work, such as cetyltrimethyl ammonium bromide (CTAB), tetra-*n*-butyl titanate (TBOT), anhydrous ethanol, salicylic acid, isoamyl alcohol, magnesium sulfate and concentrated sulfuric acid ($H_2SO_4$), all analytical reagent grade, were purchased from Shanghai Chemical Reagent Corporation, P. R. China. Nanosized $TiO_2$ (P25) used in the study was made by Degussa Corporation, Germany.

### 2. Synthesis of Mesoporous Titania [19]

The mesoporous $TiO_2$ was synthesized by hydrothermal method. First, cetyltrimethyl ammonium bromide (CTAB, 3.98 g) was dissolved in anhydrous ethanol (16 g), and then tetra-*n*-butyl titanate (TBOT, 11.93 g) was added into the solution at room temperature under stirring for 1 h, and a homogeneous transparent solution was obtained. After that, a given amount of alcohol-water (1 : 0.325 w/w) solution was added to the above-mentioned solution. The resultant solution was stirred for 3 h, and the pH of the solution was adjusted to 11 by using NaOH solution (1 mol/L). The molar ratio of the mixed solution was n (TBOT) : n (CTAB) : n ($H_2O$) : n ($C_2H_5OH$)=1.0 : 0.31 : 4.0 : 15.5. The resulting solution was transferred into a Teflon-lined autoclave and aged at 100 °C for 12 h. The precipitate was filtered, washed with distilled water, and dried at 100 °C for 12 h. The dried sample was calcined at 350 °C for 10 h, obtained mesoporous $TiO_2$ sieve, designated as Ti-TMS.

### 3. Preparation of $TiO_2$ Solid Superacid Catalysts

$TiO_2$ solid superacid catalysts were prepared by impregnation with a solution of sulfuric acid (1 mol/L). 12 g of nanosized $TiO_2$ (P25) and mesoporous $TiO_2$ was, respectively, added into 90 ml sulfuric acid (1 mol/L) at room temperature. After stirring for 18 h, the resulting suspension was filtered, washed with deionized water, and dried at 110 °C for 3 h, to obtain a dried sample. The dried sample was heated to 550 °C for 3 h, and the solid superacid catalyst was prepared, designated as $SO_4^{2-}/TiO_2$ and $SO_4^{2-}$/Ti-TMS, correspondingly.

### 4. Characterization

The XRD patterns of samples were recorded on a powder X-ray diffraction instrument (Rigaku D/MAX 2500PC) with Cu K$\alpha$ radiation ($\lambda$=0.15418 nm). The measurement conditions of XRD are: 40 kV, 50 mA, the scanning range is 1-10° and the scanning speed 1°/min. Specific surface area and pore size were measured by using a NOVA2000e analytical system made by Quantachrome Corporation (USA). Fourier transform infrared (FT-IR) spectra of samples were recorded on a Nexus FT-IR470 spectrometer made by Nicolet Corporation (USA) with KBr pellet technique. The effective range was from 400 to 4,000 $cm^{-1}$. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method. Pore size distribution and pore volume were calculated by Barrett-Joyner-Halenda (BJH) method [22].

### 5. Catalytic Activity Test

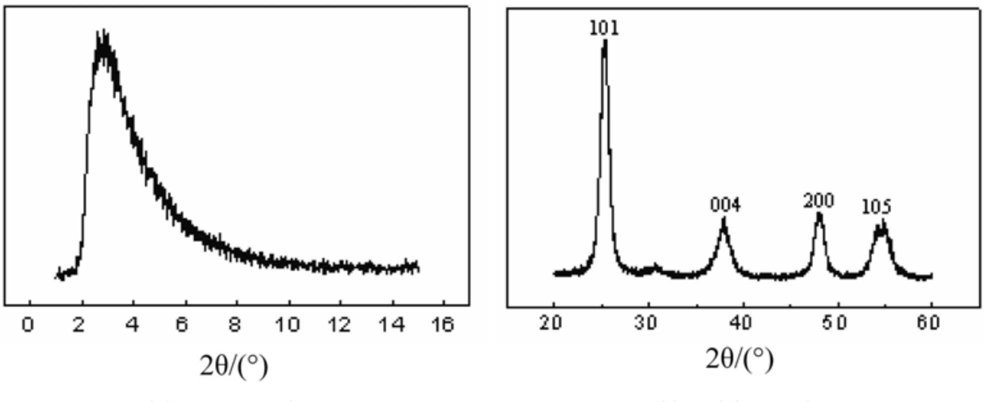
The catalytic properties of catalysts were tested on the esterification reaction between salicylic acid and isoamyl alcohol. Under an air atmosphere, a three-necked flask equipped with a magnetic stirrer, a thermometer and a refluxing condenser tube and a Dean-stark trap was charged with a given amount of salicylic acid, isoamyl alcohol and catalyst. The mixture was allowed to reflux in the range of 120-140 °C until no water globules in Dean-stark trap appeared and cooled to room temperature. The resulting solution was washed successively with saturated sodium carbonate and distilled water until a neutral solution was obtained. The washed solution was displaced into a separating funnel to settle, and then an organic phase was separated. The organic phase was dried by anhydrous magnesium sulfate and distilled water. Under reduced pressure, a fraction in the range of 150-153 °C (2 KPa) was collected and the product was obtained.

## RESULTS AND DISCUSSION

### 1. Characterization of Catalyst

1-1. XRD Analysis of Mesoporous $TiO_2$

Fig. 1 shows XRD patterns of the Ti-TMS sample; $d_{100}$=3.40 nm calculated by formula $2d_{100}\sin\theta=n\lambda$ and the unit cell parameters $a_0$=3.92 nm calculated by formula $2d_{100}/\sqrt{3}$ [23]. As shown in Fig. 1(a), a single narrow Bragg reflection peak can be observed in the $2\theta$ range from 3° to 5°; it is well known that the diffraction peak at low angle XRD pattern characterizes a mesostructured material [24,25], showing that $TiO_2$ with mesoporous structure was successfully synthesized. On the other hand, from Fig. 1(b), a wide angle XRD pattern of the Ti-TMS sample exhibits the characteristic peaks



(a) Low angle (b) Wide angle

**Fig. 1. XRD patterns of the Ti-TMS sample.**

**Table 1. Specific surface area of samples**

| Samples | P25 | $SO_4^{2-}/TiO_2$ | Ti-TMS | $SO_4^{2-}$/Ti-TMS |
|---|---|---|---|---|
| Surface area/$m^2 \cdot g^{-1}$ | 50.0 | 43.2 | 150.9 | 124.5 |

of anatase phase at $2\theta=25°$, 38°, 48° and 54°, further proving that anatase phase $TiO_2$ in the mesoporous walls is dominant.

1-2. Specific Surface Area and Pore Size of Mesoporous $TiO_2$

The specific surface areas of the four samples (P25, $SO_4^{2-}/TiO_2$, Ti-TMS and $SO_4^{2-}$/Ti-TMS) calculated by Brunauer-Emmett-Teller (BET) method are listed in Table 1. Fig. 2 shows the $N_2$ adsorption-desorption isotherms and pore size distribution curve of the Ti-TMS sample. In agreement with the XRD results, Fig. 2(a) shows typical type IV isotherms with hysteresis loop caused by capillary condensation in mesopores, further showing that the Ti-TMS sample has typical mesostructure [26]. As shown in Fig. 2(b), the Ti-TMS sample has an average pore size range of ca. 4.09 nm, and pore size distribution exhibits the mesoporous range, showing that the as-synthesized Ti-TMS sample has a regular mesoporous framework. Additionally, from Table 1, the specific surface area of the Ti-TMS is the highest among the four samples. After treatment with sulfuric acid, the specific surface area of the $SO_4^{2-}$/Ti-TMS is still higher than that of P25 and $SO_4^{2-}/TiO_2$.

1-3. FT-IR Analysis of the Ti-TMS Sample Before and After Treatment with Sulfuric Acid

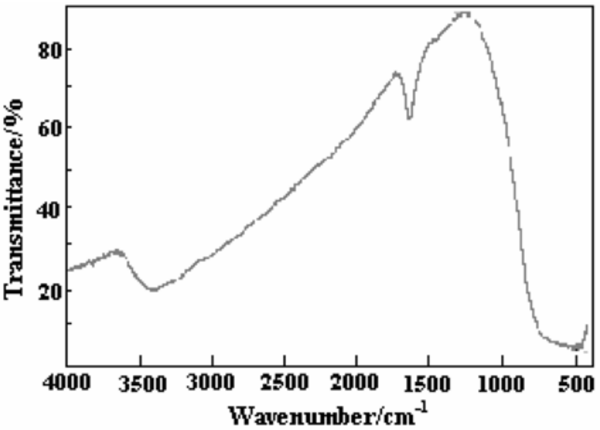
Fig. 3 shows FT-IR spectra of the Ti-TMS sample before and after treatment with sulfuric acid. The FT-IR spectra of the nano-sized $TiO_2$ is similar to that of the Ti-TMS. As shown in Fig. 3(a), before treatment, the bands at 3,300-3,500 $cm^{-1}$ were assigned to O-H stretching vibration of the adsorbed water; the band at 1,600 $cm^{-1}$ is from vibration of the adsorbed water molecules. The bands between 1,000 and 400 $cm^{-1}$ are aroused by stretching vibration of Ti-O. After treatment with sulfuric acid, the bands at 3,300-3,500 $cm^{-1}$ of O-H stretching vibration of the adsorbed water are also observed from Fig. 3(b); the band at 1,600 $cm^{-1}$ is from vibration of the adsorbed water molecules. Additionally, the characteristic bands at 1,000-1,500 $cm^{-1}$ are aroused by combining of $SO_4^{2-}$.

**2. Synthesis of isoamyl salicylate**

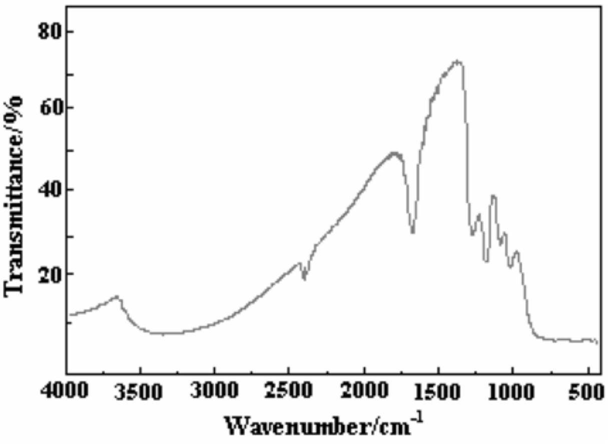
2-1. Effect of Molar Ratio of Salicylic Acid to Isoamyl Alcohol on the Yield of the Product

Table 2 lists the results of the effect of different catalysts and molar ratio of salicylic acid to isoamyl alcohol on the yield of the product. In the reaction process, 0.2 mol of salicylic acid, 1.6 g of solid superacid catalyst (or 1.5 ml of concentrated sulfuric acid) and the different amount of isoamyl alcohol was, respectively, added into the reactor; the reaction time was 5h and the reaction temperature range was 120-140 °C.

From Table 2, the yield of isoamyl salicylate increases with the increase of isoamyl alcohol in reaction process. However, when

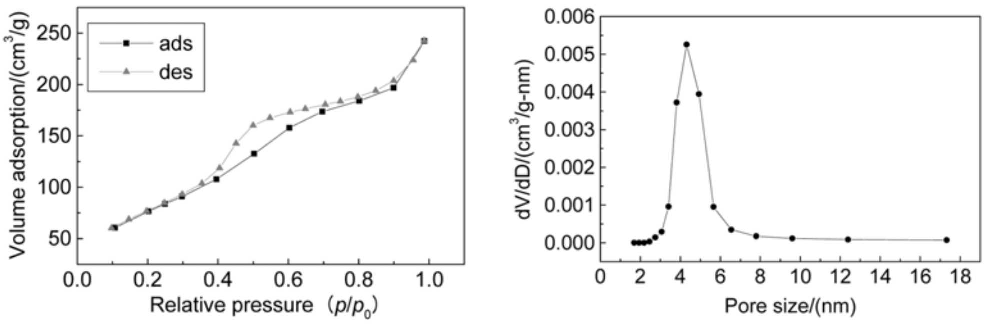


(a) Ti-TMS



(b) $SO_4^{2-}$/Ti-TMS

**Fig. 3. FT-IR spectra of the Ti-TMS sample before and after treatment with sulfuric acid.**



(a) $N_2$ adsorption-desorption isotherm (b) pore size distribution curve

**Fig. 2. $N_2$ adsorption-desorption isotherms and pore size distribution curve of the Ti-TMS sample.**

**Table 2. Effect of molar ratio of salicylic acid to isoamyl alcohol on the yield of the product**

| Molar ratio of salicylic acid to isoamyl alcohol | 1 : 2 | 1 : 3 | 1 : 4 | 1 : 5 | 1 : 6 |
|---|---|---|---|---|---|
| $H_2SO_4$ (yield%) | 68.7 | 73.2 | 93.8 | 93.1 | 92.8 |
| $SO_4^{2-}/TiO_2$ (yield%) | 75.4 | 81.3 | 93.3 | 89.7 | 88.8 |
| $SO_4^{2-}$/Ti-TMS (yield%) | 76.8 | 83.7 | 94.6 | 92.3 | 89.7 |

**Table 3. Effect of different reaction temperature on the yield of the product**

| Reaction temperature/(°C) | 120 | 130 | 140 |
|---|---|---|---|
| $H_2SO_4$ (yield %) | 64.1 | 93.3 | 89.7 |
| $SO_4^{2-}/TiO_2$ (yield %) | 65.6 | 92.8 | 90.8 |
| $SO_4^{2-}$/Ti-TMS (yield %) | 70.2 | 94.8 | 91.8 |

**Table 4. Effect of different reaction time on the yield of the product**

| Reaction time/h | 3 | 4 | 5 | 6 |
|---|---|---|---|---|
| $H_2SO_4$ (yield%) | 35.2 | 69.8 | 93.1 | 93.6 |
| $SO_4^{2-}/TiO_2$ (yield%) | 33.7 | 71.8 | 92.3 | 92.9 |
| $SO_4^{2-}$/Ti-TMS (yield%) | 38.9 | 76.5 | 94.1 | 94.5 |

**Table 5. Effect of amount of catalyst on the yield of the product**

| Amount of solid superacid/g | 0.75 | 1.0 | 1.25 | 1.6 | 1.8 |
|---|---|---|---|---|---|
| $SO_4^{2-}/TiO_2$ (yield%) | 64.3 | 80.3 | 84.2 | 93.3 | 88.8 |
| $SO_4^{2-}$/Ti-TMS (yield%) | 67.2 | 83.7 | 88.5 | 94.6 | 90.7 |

the molar ratio of salicylic acid to isoamyl alcohol is over 1 : 4, the yield of isoamyl salicylate decreases, which is probably attributed to the concentration of salicylic acid decreasing with the increase of isoamyl alcohol used in the reaction process, resulting in the speed of esterification decreases, and thus the yield of the product also decreases. From the data listed in Table 2, we can conclude that the optimum molar ratio of salicylic acid to isoamyl alcohol is 1 : 4.

2-2. Effect of Different Reaction Temperature on the Yield of the Product

The results of the effect of different reaction temperature on the yield of esterification are listed in Table 3. For the molar ratio of salicylic acid to isoamyl alcohol of 1 : 4, 1.6 g of solid superacid catalyst (or 1.5 ml of concentrated sulfuric acid) was, respectively, added into the reactor, and at different reaction temperature to experiment.

From Table 3, the speed of esterification was slow at the low reaction temperature, but the speed of esterification became fast with the rise of the reaction temperature, so the yield of esterification increased. When the reaction temperature was about at 130 °C, the yield of esterification was the highest, and the color of isoamyl salicylate was the optimum. In addition, when the reaction temperature was heated to over 140 °C, the color of the resulting solution became black, and the color of isoamyl salicylate became yellow. At the same time, the yield of isoamyl salicylate also decreased, which is probably attributed to the higher reaction temperature resulting in more by-products in the reaction process, and also resulting in decomposition of the main production. From the above discussion, the optimum reaction temperature was at 130 °C.

2-3. Effect of Different Reaction Time on the Yield of the Product

Table 4 lists the results of the effect of different reaction time on the yield of the product. For the molar ratio of salicylic acid to isoamyl alcohol of 1 : 4, 1.6 g of solid superacid catalyst (or 1.5 ml of concentrated sulfuric acid) was, respectively, added into the reactor, and the reaction temperature was 130 °C, at different reaction times (3, 4, 5 and 6 h, respectively ) to experiment.

As shown in Table 4, the yield of the product increases with the prolonging of the reaction time, but the yield of the product slowly increases after the reaction time is prolonged to over 5 h. Additionally, the long reaction time will result in the increases of secondary reaction and energy input; instead, the yield of the product increases. Therefore, the optimum reaction time is 5 h.

2-4. Effect of Amount of Catalyst on the Yield of the Product

The results of the amount of catalyst on the yield of the product are listed in Table 5. For the molar ratio of salicylic acid to isoamyl alcohol of 1 : 4, reaction temperature is 130 °C and reaction time is 5 h. The effect of different amount of solid superacid catalyst ($SO_4^{2-}$/Ti-TMS and $SO_4^{2-}/TiO_2$, respectively) on the yield of the product was investigated. Additionally, the effect of different amount of con-

**Table 6. Reusability of solid superacid catalyst**

| Catalysts | Molar ratio of salicylic acid to isoamyl alcohol | Reaction temperature/(°C) | Reaction time/(h) | Reaction times | Yields (%) |
|---|---|---|---|---|---|
| $SO_4^{2-}/TiO_2$ | 1 : 4 | 130 | 5 | 1 | 93.3 |
| | 1 : 4 | 130 | 5 | 2 | 93.0 |
| | 1 : 4 | 130 | 5 | 3 | 92.8 |
| | 1 : 4 | 130 | 5 | 4 | 92.4 |
| | 1 : 4 | 130 | 5 | 5 | 92.1 |
| | 1 : 4 | 130 | 5 | 6 | 87.4 |
| $SO_4^{2-}$/Ti-TMS | 1 : 4 | 130 | 5 | 1 | 94.6 |
| | 1 : 4 | 130 | 5 | 2 | 94.2 |
| | 1 : 4 | 130 | 5 | 3 | 94.0 |
| | 1 : 4 | 130 | 5 | 4 | 93.7 |
| | 1 : 4 | 130 | 5 | 5 | 92.8 |
| | 1 : 4 | 130 | 5 | 6 | 92.3 |

centrated sulfuric acid on the yield of the product was also investigated. The results show that the optimum quantity of solid superacid catalyst is 1.6 g, and the optimum quantity of concentrated sulfuric acid is 1.5 ml.

### 3. Reusability of Solid Superacid Catalyst

The reusability of the prepared solid superacid catalyst was also investigated by using the esterification reaction of salicylic acid with isoamyl alcohol (Table 6). From Table 6, solid superacid catalyst can be continuously run for six times at 130 °C without obvious decrease in catalytic activities. Additionally, as shown in Table 6, after the sixth run, the yield of the product catalyzed by $SO_4^{2-}$/Ti-TMS can reach 92.3%, and the yield of the product catalyzed by $SO_4^{2-}/TiO_2$ only reaches 87.4%. Therefore, it is reasonable to conclude that the prepared mesoporous $TiO_2$ solid superacid exhibits good catalytic activity for the esterification reaction of salicylic acid and isoamyl alcohol. This may be due to the fact that the $SO_4^{2-}$/Ti-TMS catalyst has high specific surface area as compared with the $SO_4^{2-}/TiO_2$ catalyst (see Table 1). On the other hand, the high catalytic activity of the $SO_4^{2-}$/Ti-TMS catalyst is probably attributed to the formation of mesoporous structure, which is beneficial for the adsorption and desorption of reactants and products [27-29].

### 4. Composition Analysis of Isoamyl Salicylate

The as-synthesized isoamyl salicylate is a liquid with fragrant and sweet smell, and its refractive index $n_D^{20}=1.5040$, while the refractive index of the standard isoamyl salicylate $n_D^{20}=1.505$. Fig. 4 displays FT-IR spectrum of the isoamyl salicylate synthesized by using $SO_4^{2-}$/Ti-TMS as catalyst. As shown in Fig. 4, the band at 3,184 $cm^{-1}$ was assigned to the adsorption peak of hydroxyl of hydroxybenzene; the adsorption peaks at 2,959 and 2,872 $cm^{-1}$ correspond to the flex vibration of C-H; the band at 1,670 $cm^{-1}$ is from the characteristic adsorption peak of C=O of ester; the bands at 1,614 and 1,466 $cm^{-1}$ were aroused by the adsorption peak of C=C of aromatic ring framework. The FT-IR results indicate that isoamyl salicylate was successfully synthesized by with $SO_4^{2-}$/Ti-TMS as catalyst.

## CONCLUSIONS

Mesoporous $TiO_2$ was synthesized by hydrothermal method and a new type of mesoporous $TiO_2$ solid superacid catalyst was also prepared by impregnation method. Catalytic reaction tests show that mesoporous $TiO_2$ solid superacid catalyst exhibits the best catalytic activity among three catalysts for synthesis of isoamyl salicylate; and the catalytic activity of nanosized $TiO_2$ solid superacid catalyst is higher than that of concentrated sulfuric acid (98%). Mesoporous $TiO_2$ solid superacid is a good catalyst for the esterification reaction of salicylic acid. The optimum condition of isoamyl salicylate synthesized by using mesoporous titania solid superacid : the molar ratio of salicylic acid to isoamyl alcohol is 1 : 4, the quantity of catalyst is 1.6 g, the reaction time is 5 h, the reaction temperature is 130 °C, and the yield can reach 94.6%.

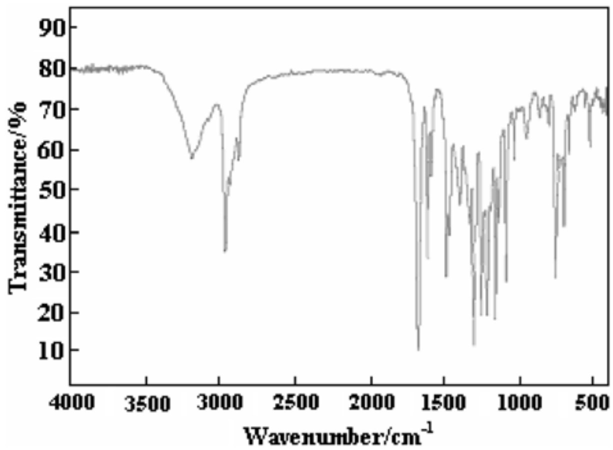


**Fig. 4. FT-IR spectrum of the isoamyl salicylate synthesized using $SO_4^{2-}$/Ti-TMS as catalyst.**

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