Preparation of mesoporous titania solid superacid and its catalytic property

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Abstract

Mesoporous titania (TiO_2) was synthesized by hydrothermal method using cetyltrimethyl ammonium bromide (CTAB) as a template and using anhydrous ethanol and tetra-*n*-butyl titanate (TBOT) as raw materials. Mesoporous titania solid superacid and nanosized titania solid superacid catalysts were prepared by wet impregnation method. The structure and property of as-prepared samples were characterized by means of XRD, FT-IR and N_2 physical adsorption. The esterification of salicylic acid with isoamyl alcohol and the condensation of cyclohexanone with ethylene were used as model reactions to test the catalytic activities of the catalysts. On the other hand, the comparison of catalytic activities of the prepared solid superacid catalysts and the conventional liquid acid H_2SO_4 was also carried out under the same experimental conditions. The results show that the catalytic activities of the prepared solid superacid catalysts were higher than that of the conventional liquid acid H_2SO_4, and that the catalytic activity of mesoporous TiO_2 solid superacid is the highest among the three catalysts. Mesoporous TiO_2 solid superacid is a good catalyst for the synthesis of isoamyl salicylate or cyclohexanone ethylene ketal.

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Keywords: Mesoporous titania solid superacid; Nanosized titania solid superacid; Catalytic property; Esterification; Condensation

1. Introduction

Acid catalysis is of fundamental industrial importance, and acid catalysts play an important role in organic synthesis. 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 with acidity stronger than 100% H_2SO_4 ($H_o \leq -12$) 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 its high acid strength, no corrosion for reactor, 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 superacid with nanosized TiO_2 has attracted worldwide attentions because of their wide applications in many organic reactions [4,14–17]. However, solid superacid with nanosized TiO_2 has also some disadvantages such as hard to adjust its acidity and small surface area. Compared with nanosized TiO_2, mesoporous TiO_2 had high specific surface area, ordered pore structure and excellent adsorption property, which are expected to be a new media for heterogeneous reactions. Recently, many efforts were made by researchers in synthesis and application of mesoporous TiO_2. Wang et al. [18] reported that mesoporous TiO_2 synthesized by hydrothermal method exhibited good catalytic activity for degradation of methyl orange. Pavasupree et al. [19] 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.

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In this paper, mesoporous TiO_2 was synthesized by hydrothermal method using cetyltrimethyl ammonium bromide (CTAB) as a template. Mesoporous TiO_2 solid surperacid 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, and the condensation reaction of cyclohexanone and ethylene. In particular, comparison of catalytic activities of the three catalysts (H_2SO_4, nanosized TiO_2 solid superacid and mesoporous TiO_2 solid superacid) was also carried out, and catalytic activity of mesoporous TiO_2 solid superacid is the highest among the three catalysts.

2. Experimental

2.1. Materials

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

2.2. Synthesis of mesoporous titania [18]

The synthesis of mesoporous TiO_2 was carried out 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 using NaOH solution (1 mol/l). The molar ratio of the mixed solution is TBOT:CTAB:H_2O:C_2H_5OH = 1:0.31:4:15.5. 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 to obtain mesoporous TiO_2 sieve, designated as Ti-TMS.

2.3. Preparation of TiO_2 solid superacid catalysts

TiO_2 solid surperacid catalysts were prepared by impregnation with a solution of sulfuric acid (1 mol/l). 12 g of nanosized TiO_2 or mesoporous TiO_2 was 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 samples were heated to 550 °C for 3 h to obtain solid superacid catalysts, designated as SO_4^{2-}/TiO_2 and SO_4^{2-}/Ti-TMS, correspondingly.

2.4. Characterization of catalyst

The XRD patterns of the samples were recorded on a powder X-ray diffraction instrument (Rigaku D/MAX 2500PC) with Cu Kα radiation (λ = 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 Quntachrome 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 4000 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 [20].

2.5. Catalytic activity test

The catalytic properties of the catalysts were tested for the esterification reaction between salicylic acid and isoamyl alcohol and the condensation reaction of cyclohexanone and ethylene.

2.5.1. Esterification of salicylic acid and isoamyl alcohol

Under an air atmosphere, a three-necked flask equipped with a magnetic stirrer, a thermometer, a refluxing condenser tube and a Dean-stark tape were charged with 1.6 g of solid superacid catalyst (or 1.5 ml of concentrated sulfuric acid), the molar ratio of salicylic acid (0.2 mol) to isoamyl alcohol is 1:4 and the reaction time is 3, 4 and 5 h, respectively. The mixture was allowed to reflux at 130 °C until no water globules in Dean-stark tape appeared and cooled to room temperature. The resulting solution was washed successively with saturated sodium carbonate and distilled water until a neutral solution 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. Under reduced pressure, the fraction in the range of 150–153 °C was collected as product.

2.5.2. Condensation of cyclohexanone and ethylene

The reaction was performed at atmospheric pressure and a three-necked flask equipped with a magnetic stirrer, a thermometer, a refluxing condenser tube and a Dean-stark tape were charged with 1.0 g of solid superacid catalyst (or 0.3 ml of concentrated sulfuric acid). The molar ratio of cyclohexanone (20.66 ml) to ethylene is 1:1.5. 20 ml of cyclohexane was used as water-carrying agent. The reaction time is fixed at 2 h. The mixture was allowed to reflux at 100–120 °C until no water globules in Dean-stark tape appeared and cooled to room temperature. The resulting solution was washed successively with distilled water until a neutral solution 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. Under reduced pres-
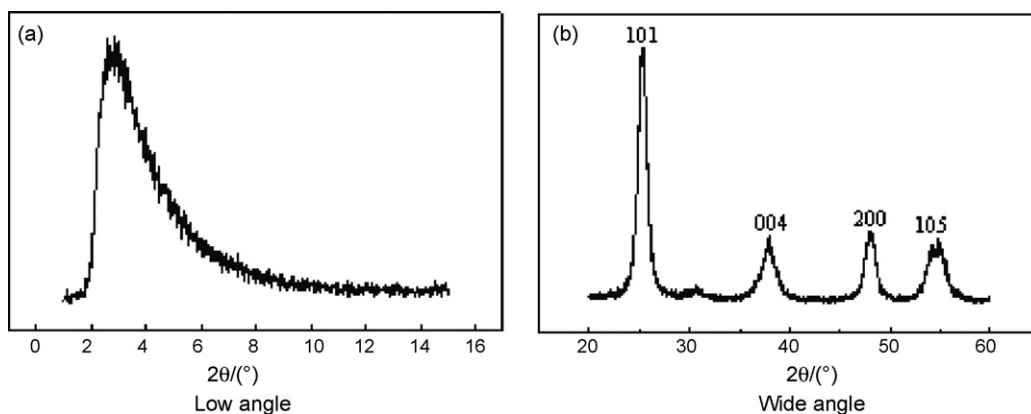
Fig. 1. XRD patterns of the Ti-TMS sample.

sure, the fraction in the range of 170–180 °C was collected as product.

The above obtained products were characterized by IR, and the yield of the product was calculated according to the quantity of the final product and the quantity of the initial salicylic acid (or cyclohexanone). The catalysts were recovered by filtration, washed with distilled water, dried and reused.

3. Results and discussion

3.1. XRD analysis of mesoporous TiO$_2$

Fig. 1 shows the XRD patterns of the Ti-TMS sample; $d_{(1\,0\,0)} = 3.40$ nm calculated by formula $2d_{(1\,0\,0)}\sin\theta = n\lambda$ and the unit cell parameters $a_0 = 3.92$ nm calculated by formula $a_0 = 2d_{(1\,0\,0)}/\sqrt{3}$. As shown in Fig. 1(a), a single narrow diffraction peak can be observed in the 2θ range from 3° to 5°, it is well known that diffraction peak at low angle XRD pattern characterizes a mesostructured material [21,22], showing that TiO$_2$ with mesoporous structure was successfully synthesized. On the other hand, from Fig. 1(b), wide angle XRD pattern of the Ti-TMS sample exhibits the characteristic peaks of anatase phase at $2\theta = 25$°, 38°, 48° and 54°, proving that anatase phase TiO$_2$ in the mesoporous walls is dominant.

Table 1
Specific surface area of samples

Samples	Surface area (m^2 g^{-1})
P25	50.01
SO$_4{}^{2-}$/TiO$_2$	43.24
Ti-TMS	150.90
SO$_4{}^{2-}$/Ti-TMS	124.53

3.2. 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 a typical type IV isotherms with hysteresis loop caused by capillary condensation in mesopores, further showing that Ti-TMS sample has typical mesostructure [23]. As shown in Fig. 2(b), the Ti-TMS sample has an average pore size of ca. 4.09 nm, and the narrow pore size distribution exhibits the mesoporous range, showing that the as synthesized Ti-TMS sample has the 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 sulfu-
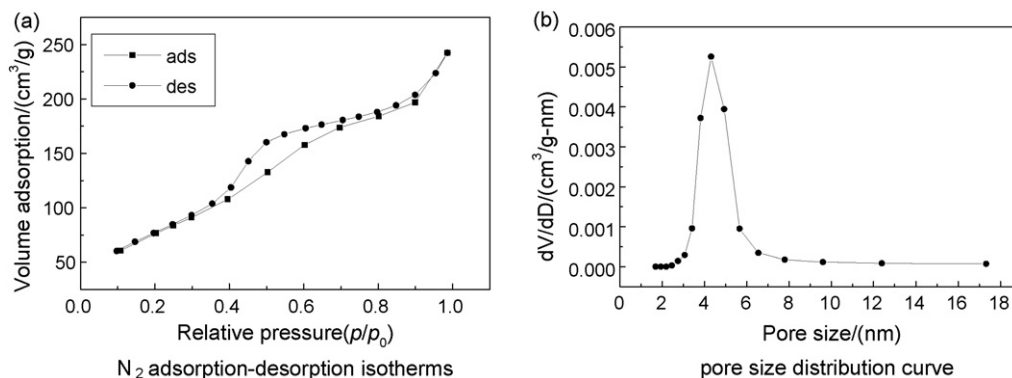
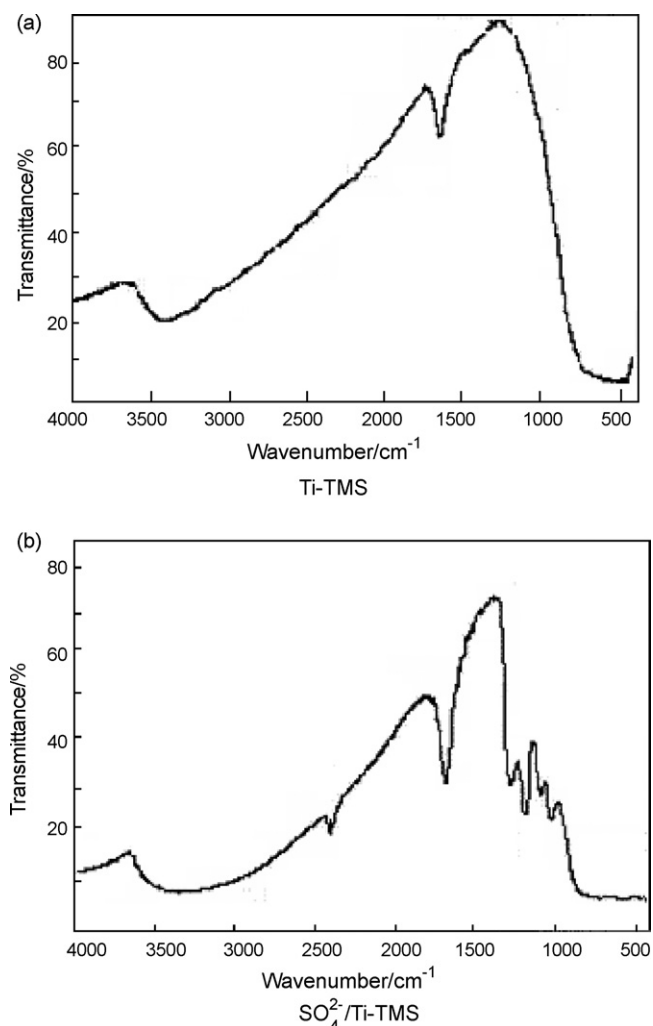Fig. 2. N$_2$ adsorption–desorption isotherms and pore size distribution curve of the Ti-TMS sample.

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

ric acid, the specific surface area of the SO_4^{2-}/Ti-TMS is still higher than that of P25 and SO_4^{2-}/TiO$_2$.

3.3. 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 nanosized TiO$_2$ are similar to that of the Ti-TMS. As shown in Fig. 3(a), before treatment, the bands at 3300–3500 cm^{-1} were assigned to O–H stretching vibration of the adsorbed water; the band at 1600 cm^{-1} is from the vibration of adsorbed water molecules. The bands between 1000 and 400 cm^{-1} are aroused by the stretching vibrations of Ti–O. After treatment with sulfuric acid, the bands at 3300–3500 cm^{-1} of O–H stretching vibration of the adsorbed water are also observed from Fig. 3(b); the band at 1600 cm^{-1} is from the vibration of adsorbed water molecules. Additionally, the characteristic bands at 1000–1500 cm^{-1} are aroused by combining of SO_4^{2-}.

3.4. Esterification of salicylic acid and isoamyl alcohol

3.4.1. Effect of different catalysts on the yield of isoamyl salicylate

The results of esterification reaction of salicylic acid and isoamyl alcohol using SO_4^{2-}/Ti-TMS, SO_4^{2-}/TiO$_2$ and H$_2$SO$_4$ as catalysts were summarized in Table 2. As shown in Table 2, the catalytic activity of the as-prepared SO_4^{2-}/Ti-TMS is the highest among three catalysts after reaction for 3, 4 and 5 h, respectively, and the yield of isoamyl salicylate reaches 94.6% after reaction for 5 h. From Table 2, we found that the order of catalytic activities of the catalysts in the esterification reaction between salicylic acid and isoamyl alcohol was: SO_4^{2-}/Ti-TMS > SO_4^{2-}/TiO$_2$ > H$_2$SO$_4$. 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 higher 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 to the adsorption and desorption of reactants and products [24–26].

3.4.2. Reusability of solid superacid catalyst

The reusability of the prepared solid superacid catalyst was also investigated using the esterification reaction of salicylic acid with isoamyl alcohol (Table 3). From Table 3, solid superacid catalyst can be continuously run for six times at 130 °C without obvious decrease in catalytic activity. Additionally, as shown in Table 3, 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%. It is reasonable to

Table 2
Effect of different catalysts on the yield of isoamyl salicylate

Catalysts	Mole ratio of salicylic acid (0.2 mol) to isoamyl alcohol	Reaction temperature (°C)	Reaction time (h)	Yields (%)
H$_2$SO$_4$	1:4	130	3	30.2
	1:4	130	4	68.8
	1:4	130	5	93.1
SO_4^{2-}/TiO$_2$	1:4	130	3	33.1
	1:4	130	4	71.6
	1:4	130	5	93.3
SO_4^{2-}/Ti-TMS	1:4	130	3	41.9
	1:4	130	4	80.5
	1:4	130	5	94.6

Table 3
Reusability of solid superacid catalyst

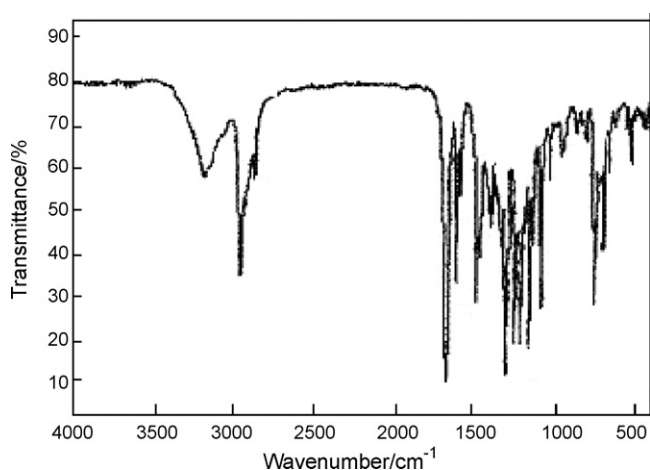| Catalysts	Mole ratio of salicylic acid (0.2 mol) to isoamyl alcohol	Reaction temperature (°C)	Reaction time (h)	Reaction times	Yields (%)
SO_4^{2-}/TiO$_2$	1:4	130	5	1	93.3
	1:4	130	5	2	93.0
	1:4	130	5	3	92.8
	1:4	130	5	4	92.4
	1:4	130	5	5	92.1
	1:4	130	5	6	87.4
SO_4^{2-}/Ti-TMS	1:4	130	5	1	94.6
	1:4	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

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

conclude that the catalytic activity and stability of mesoporous TiO$_2$ solid superacid are higher than that of nanosized TiO$_2$ solid superacid, which is probably attributed to the large specific surface area of the mesoporous TiO$_2$ superacid catalyst.

3.4.3. Composition analysis of isoamyl salicylate

The as synthesized isoamyl salicylate is a liquid with fragrant and sweet smell, and its refractive index $n_D^{20} = 1.5040$ (the refractive index of the standard isoamyl salicylate $n_D^{20} = 1.505$). Fig. 4 displays FT-IR spectrum of the isoamyl salicylate synthesized using SO_4^{2-}/Ti-TMS as a catalyst. As shown in Fig. 4, the band at 3184 cm^{-1} was assigned to the adsorption peak of hydroxyl of hydroxybenzene; the adsorption peaks at 2959 and 2872 cm^{-1} correspond to the flex vibration of C–H; the band at 1670 cm^{-1} is from the characteristic adsorption peak of C=O

of ester; the bands at 1614 and 1466 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 using SO_4^{2-}/Ti-TMS as a catalyst.

3.5. Condensation of cyclohexanone and ethylene

3.5.1. Effect of different catalysts on the yield of cyclohexanone ethylene ketal

The results of condensation reaction of cyclohexanone and ethylene using SO_4^{2-}/Ti-TMS, SO_4^{2-}/TiO$_2$ and H$_2$SO$_4$ as catalysts, respectively, were summarized in Table 4. From Table 4, we can conclude that the catalytic activity of SO_4^{2-}/TiO$_2$ is higher than that of the conventional acid catalyst (H$_2$SO$_4$), and the catalytic activity of SO_4^{2-}/Ti-TMS is the highest for the condensation reaction of cyclohexanone and ethylene, and the yield of cyclohexanone ethylene ketal can reach 82.1%. Hence, we can conclude that the prepared mesoporous TiO$_2$ solid superacid is a good catalyst for synthesis of cyclohexanone ethylene ketal.

3.5.2. Composition analysis of cyclohexanone ethylene ketal

The as synthesized cyclohexanone ethylene ketal is a colorless transparent liquid with fragrant smell, and its refractive index $n_D^{20} = 1.4579$ (the refractive index of the standard cyclohexanone ethylene $n_D^{20} = 1.4583$). Fig. 5 displays FT-IR spectrum of the cyclohexanone ethylene ketal synthesized using SO_4^{2-}/Ti-TMS as a catalyst. The adsorption peaks at 2942, 2863, 1462 and 763 cm^{-1} correspond to the flex vibration of C–H; the bands at 1163 and 1109 cm^{-1} were aroused by the characteristic adsorption peak of C–O–C. According to the FT-IR analysis, we can conclude that the synthesized product is cyclohexanone ethylene ketal.

Table 4
Effect of different catalysts on the yield of cyclohexanone ethylene ketal

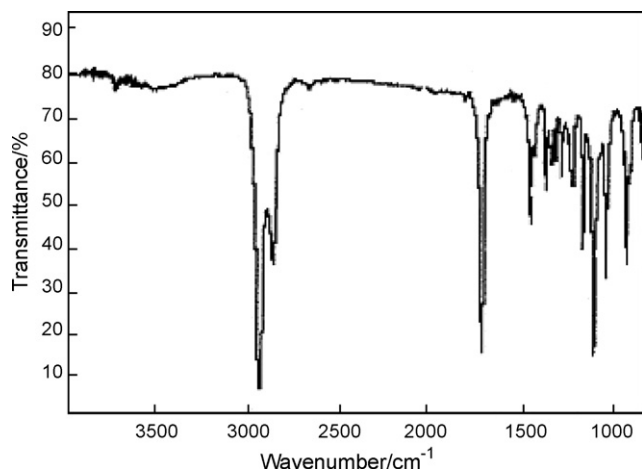| Catalysts	Mole ratio of cyclohexanone (20.66 ml) to ethylene	Reaction temperature (°C)	Reaction time (h)	Yields (%)
H$_2$SO$_4$	1:1.5	100–120	2	54.7
SO_4^{2-}/TiO$_2$	1:1.5	100–120	2	66.1
SO_4^{2-}/Ti-TMS	1:1.5	100–120	2	82.1

Fig. 5. FT-IR spectrum of the cyclohexanone ethylene ketal synthesized using SO_4^{2-}/Ti-TMS as a catalyst.

4. Conclusions

In this paper, 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 highest catalytic activity among the three catalysts for synthesis of isoamyl salicylate and cyclohexanone ethylene ketal, and that 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 and isoamyl alcohol and the condensation reaction of cyclohexanone and ethylene.

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