



Nano-SO₄²⁻/TiO₂ Catalyzed Eco-Friendly Esterification of Dicarboxylic Acids†

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Nano-SO₄²⁻/TiO₂ was prepared by wet impregnation method. The structure and properties of the prepared nano-SO₄²⁻/TiO₂ catalyst was characterized by XRD, SEM, TEM and BET analysis. The catalytic activities of the catalysts were tested by the esterification of sebacic acid with 2-ethyl hexanol and a series of other dicarboxylic acid. The influence factors on the reaction, such as the catalyst calcination temperature, reaction temperature/time and the molar ratio of acid to alcohol were extensively explored. Nano-SO₄²⁻/TiO₂ prepared exhibited much higher catalytic activity in esterification reactions. By applying the optimized reaction condition, *i.e.* 160 °C, 2 h, 5 wt % nano-SO₄²⁻/TiO₂ with a 1:3 molar ratio of sebacic acid to 2-ethyl hexanol, higher than 99 % isolated of the desired ester could be obtained.

Keywords: Nano-SO₄²⁻/TiO₂, Solid acid catalyst, Esterification, Dicarboxylic acids.

INTRODUCTION

In order to avoid global environmental destruction and resource depletion, the development of energy-saving technologies has attracted extensive attentions. Technologies for reducing friction are one of the effective ways for energy-saving¹. In the field of lubrication, synthetic esters are widely used because of their fine and tunable tribological properties². Normally, synthesis esters are obtained by the esterification of corresponding acids and alcohols with mineral acids or Lewis acids as catalysts in industrial processes. However, the conventional mineral acids or Lewis acids such as H₂SO₄, HF, HNO₃, H₃PO₄, AlCl₃ and BF₃ result in risks in handling, containment and disposal because of their toxicity and corrosiveness³. The development of efficient and environmentally friendly catalyst for the preparation of synthetic esters should be highly desirable.

Recently, solid acids have been extensively studied in synthetic chemistry⁴⁻¹¹. As acid catalysts, they exhibit obvious advantages such as ease of separation from reaction mixture, no corrosion to reactor, free from pollution and easy to be recovered and reused⁹. Among the reported solid acid catalyst, SO₄²⁻/TiO₂ has attracted great attention because of its high specific surface area, ordered pore structure, good catalytic activity and high thermal and mechanical stabilities³. Although the synthesis and applications of SO₄²⁻/TiO₂ have been studied

since the end of last century¹². There are very few works reported on the preparation and use of SO₄²⁻/TiO₂ for the synthesis of dicarboxylic acid esters. Therefore, we have prepared nano-SO₄²⁻/TiO₂ by wet impregnation method and studied its application on the synthesis of dicarboxylic acid esters in our early research¹³. Our previous research showed that the specific surface area of the nano-SO₄²⁻/TiO₂ catalyst is much higher than that of the other two SO₄²⁻/TiO₂ prepared with commercial titania and the prepared nano-SO₄²⁻/TiO₂ shows high activity and effective reusable when used as basic catalysts for the synthesis of dioctyl sebacate.

In this paper, the catalytic activities of the catalysts were tested by the esterification of sebacic acid with 2-ethyl hexanol and a series of other dicarboxylic acid. The influence factors on the reaction, such as the catalyst calcination temperature, reaction temperature/time and the molar ratio of acid to alcohol were extensively explored. Results showed that the nano-SO₄²⁻/TiO₂ prepared exhibited much higher catalytic activity in esterification reactions. By applying the optimized reaction condition, *i.e.*, 160 °C, 2 h, 5 wt % nano-SO₄²⁻/TiO₂ with a 1:3 molar ratio of sebacic acid to 2-ethyl hexanol, higher than 99 % isolated of the desired ester could be obtained.

EXPERIMENTAL

All chemicals used in the experiment were analytical grade and used without further purification.

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General procedure: In a typical preparation, nano-TiO₂ was carried out as follows. At room temperature, 19 mL tetrabutyl titanate (TBOT) was dissolved in 86 mL anhydrous ethanol under stirring in a beaker. Then, 5 mL acetic acid and 1 mL distilled water were added into the reaction mixture, respectively. After it was stirred under room temperature for about 2 h, white TiO₂ formed as suspension. Subsequently, the solution was put into an oven at 100 °C for 10 h and a dried sol-gel nano-TiO₂ was obtained.

Nano-SO₄²⁻/TiO₂ solid acid catalysts were prepared by impregnation method. 12 g dry sol-gel nano-TiO₂ was added into 12 mL H₂SO₄ (1 mol/L) at room temperature. After being stirred for 1 h, the solution was dried at 100 °C for 5 h. Finally, the products were calcined at different temperature (350, 400, 450, 500 and 550 °C) for 3 h to obtain the catalyst, designated as nano-SO₄²⁻/TiO₂.

The catalytic activities of the catalysts were tested by the esterification of sebacic acid with 2-ethyl hexanol and a series of other dicarboxylic acid. The experiment was performed in a three-neck flask equipped with a thermometer, a refluxing condenser and a water separator. The experimental conditions are the following: 15 mL xylene was used as water-carrying agent and the molar ratio of sebacic acid to 2-ethyl hexanol was from 1:3.5 to 1:2 and the weight of catalyst was from 3-8 wt % of the total weight of sebacic acid and 2-ethyl hexanol and the reaction temperature and the reaction time were 90-170 °C and 2-4 h, respectively. After cooling to room temperature, the resulting solution was filtrated and washed with saturated solution carbonate and distilled water for at least 3 times, respectively. Then the solution was dried by anhydrous magnesium sulfate for 24 h. The solution was filtrated and distilled under reduced presser at 160 °C to remove water, 2-ethyl hexanol and xylene from the solution and get the product.

Detection method: X-Ray diffractometer (RigaKu D/max-RB, Japan) using CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$) under 40 kV and 30 mA was used to identify the phase of the catalysts. Specific surface areas were determined through the Brunauer-Emmett-Teller (BET) isothermic method. Pore diameter and pore volume were calculated by the Barret-Joyner-Hallenda (BJH) method. The morphologies and sizes of the products were determined by field emission scanning electron microscopy (FE-SEM, JSM-6701F type) and high-resolution transmission electron microscopy (HR-TEM, Jeol JEM 2010 type, accelerating voltage = 200 kV).

RESULTS AND DISCUSSION

XRD analysis of the catalysts: The XRD pattern of nano-SO₄²⁻/TiO₂ solid acid catalysts in Fig. 1 shows that the diffraction peaks match well with literature patterns (JCPDF Card No. 01-0562), indicating that the phase of nano-SO₄²⁻/TiO₂ is anatase.

BET surface area and pore size of the catalysts: The specific surface areas, pores mean diameter and pores volume of the catalysts calcined at different temperatures are listed in Table-1. It can be seen that with the increase of calcination temperature, the specific surface areas becomes lower, while the pores mean diameter becomes higher.

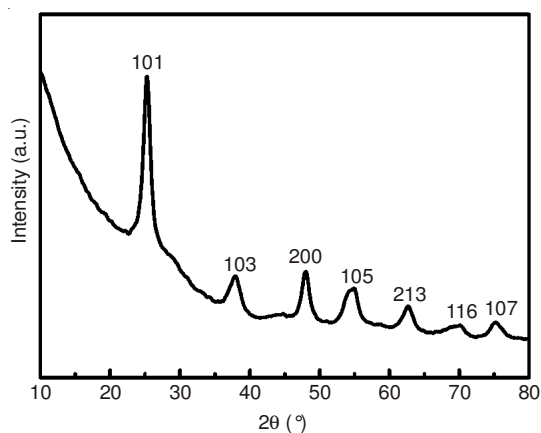


Fig. 1. XRD pattern of nano-SO₄²⁻/TiO₂

TABLE-1
SPECIFIC SURFACE AREA (BET), PORES
MEAN DIAMETER (BJH) AND PORES VOLUME

Catalysts	Specific surface area (m ² /g)	Average pores diameter (nm)	Pores volume (cm ³ /g)
Nano-SO ₄ ²⁻ /TiO ₂ -350 ^a	174.01	3.4	0.16
Nano-SO ₄ ²⁻ /TiO ₂ -400 ^a	157.52	4.3	0.19
Nano-SO ₄ ²⁻ /TiO ₂ -450 ^a	152.39	4.2	0.21
Nano-SO ₄ ²⁻ /TiO ₂ -500 ^a	125.20	5.5	0.21
Nano-SO ₄ ²⁻ /TiO ₂ -550 ^a	72.36	7.5	0.16

^aCalcination temperature.

FE-SEM and HR-TEM analysis of the catalysts: The morphologies and sizes of the catalysts calcined at 450 °C were examined by FE-SEM and HR-TEM. The FE-SEM image of the nano-SO₄²⁻/TiO₂ catalyst shown in Fig. 2a confirms that the product is agglomerate, which is composed of spherical nanoparticles. Fig. 2b shows the HR-TEM image of the nano-SO₄²⁻/TiO₂ catalyst. It can be seen that the size of the spherical nanoparticles is about 6-8 nm.

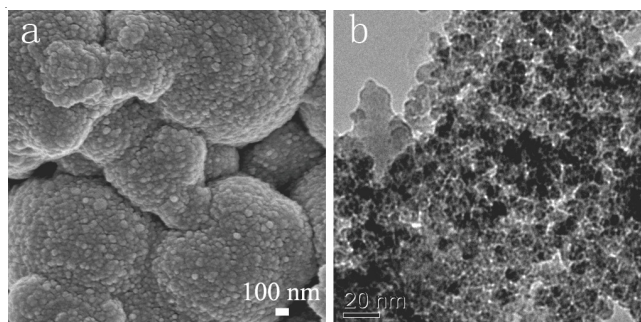


Fig. 2. FE-SEM and TEM micrographs of nano-SO₄²⁻/TiO₂

Synthesis of diethyl sebacate

Influence of the calcination temperature of nano-SO₄²⁻/TiO₂ catalysts on the conversion of sebacic acid: Fig. 3 presents the influence of the different calcination temperature of nano-SO₄²⁻/TiO₂ catalysts on the conversion of the sebacic acid. It can be observed that the catalytic activity of the prepared nano-SO₄²⁻/TiO₂ calcined at 450 °C is the highest and the conversion reached to 99.1%. The suitable calcination temperature was 450 °C.

Reaction condition optimization: Fig. 4a presents the influence of the reaction temperature on the reaction. The

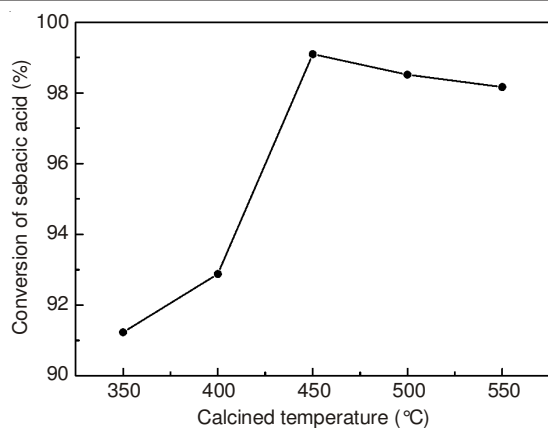


Fig. 3. Influence of different calcination temperatures of nano-SO₄²⁻/TiO₂ catalysts on the reaction. Reaction conditions: T = 160 °C; catalyst amount = 5 wt %; reaction time = 2 h; 2-ethyl hexanol/sebacic acid = 3:1

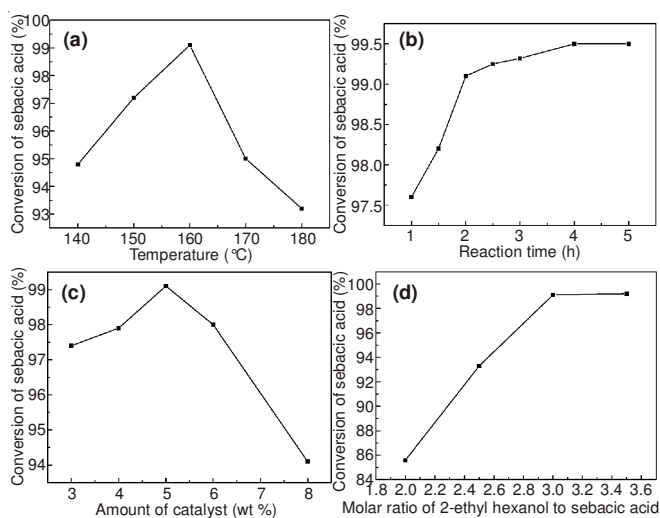


Fig. 4. Influence of factors on the reaction: (a) temperature, (b) time, (c) amount of the catalyst and (d) molar ratio of 2-ethyl hexanol to sebacic acid. Reaction conditions: (a) catalyst amount = 5 wt %; reaction time = 2 h; 2-ethyl hexanol/sebacic acid = 3:1; (b) T = 160 °C; catalyst amount = 5 wt %; 2-ethyl hexanol/sebacic acid = 3:1; (c) T = 160 °C; reaction time = 2 h; 2-ethyl hexanol/sebacic acid = 3:1; (d) T = 160 °C; catalyst amount = 5 wt %; reaction time = 2 h

results indicate that elevating the temperature ranging from 140 to 160 °C, the conversion of sebacic acid increased from 94.8 to 99.1 %. However, when the temperature exceeded 160 °C, the conversion of sebacic acid significantly decreased. Fig. 4b shows the influence of the reaction time on the reaction. It is clearly observed that the conversion of sebacic acid increased to > 99 % with the reaction time prolonged from 1 to 5 h. If the reaction time exceeded 2 h, the conversion of sebacic acid increased slowly. Fig. 4c shows the influence of the amount of catalyst on the reaction. It is clear that the conversion of sebacic acid increased with adding the amount of catalyst and it reached the maximum (> 99 %) when the amount of catalyst was 5 wt %. Surprisingly, when the amount of catalyst further increased, *i.e.*, 6-8 wt %, the conversion of sebacic acid decreased to 94 %. It was similar with the former report¹³. Up to now, the reason for the lower conversion of sebacic acid when the catalyst is more 5 wt % is still not clear. Fig. 4d presents the influence of the molar ratio of 2-ethyl

hexanol to sebacic acid on the reaction. It was shown in Fig. 4d, the conversion of sebacic acid increased dramatically to > 99 % with increasing the molar ratio of 2-ethyl hexanol to sebacic acid from 2:1 to 3.5:1. The addition of more alcohol doesn't improve the reaction again. The optimized condition for the synthesis of dioctyl sebacate is 5 wt % catalyst, 160 °C, 2 h and the molar ratio of sebacic acid to 2-ethyl hexanol is 1 : 3.

Composition analysis of dioctyl sebacate: Dioctyl sebacate is a colourless liquid. The product was characterized by FT-IR and ¹H NMR. The FT-IR spectrum of the synthesized dioctyl sebacate is listed in Fig. 5. As shown in Fig. 5, the absorption peaks at 2959, 2924 and 2863 cm⁻¹ are aroused to the stretching vibration of C-H. The absorption peak at 1734 cm⁻¹ is the characteristic adsorption peak of C=O of the ester. The band at 1466 cm⁻¹ can be attributed to the vibration of C=C and the band at 1173 cm⁻¹ can be assigned to the extension vibration of C-O-C.

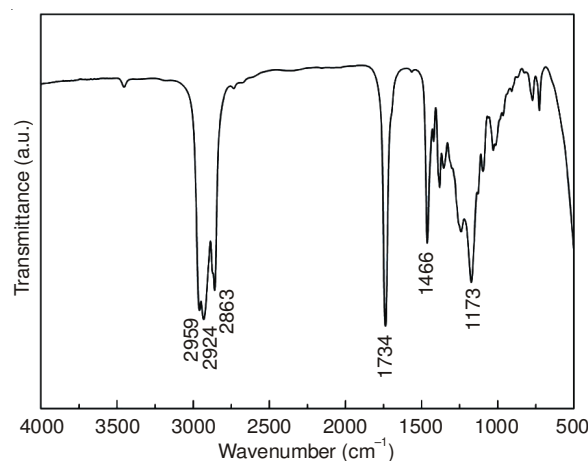


Fig. 5. FT-IR spectrum of dioctyl sebacate

¹H NMR spectral for the synthesized dioctyl sebacate: ¹H NMR (400 MHz, CDCl₃): δ 0.84 (t, 12H, J = 5.6HZ), δ 1.18-1.33 (m, 24H), δ 1.47-1.57 (m, 6H), δ 2.23 (t, 4H, J = 7.6HZ), δ 3.92 (d, 4H, J = 12.8 HZ).

Catalytic activities of the nano-SO₄²⁻/TiO₂ for esterification of other dicarboxylic acid: In order to obtain catalytic activities of the nano-SO₄²⁻/TiO₂, the esterification of a series of other dicarboxylic acid with 2-ethyl hexanol were tested. Table-2 showed that the conversion for most of reactions can reach more than 70 %. It is concluded that the as-synthesized nano-SO₄²⁻/TiO₂ was a good catalyst for many esterifications.

TABLE-2
YIELDS OF OTHER DICARBOXYLIC
ACID ESTERS SYNTHESIS^a

Entry	Alcohol:acid (mol:mol)	Alcohol	Organic acid	Yields (%)
1	3:1	2-Ethyl hexanol	Hexanedioic acid	90
2	3:1	2-Ethyl hexanol	Succinic acid	97
3	3:1	2-Ethyl hexanol	Glutaric acid	95
4	3:1	2-Ethyl hexanol	Azelaic acid	94
5	3:1	2-Ethyl hexanol	Phthalic acid	86
6	3:1	2-Ethyl hexanol	M-Phthalic acid	51
7	1:3	1,6-Dihydroxyhexane	Haxanoic acid	73
8	1:3	1,4-Butanediol	Haxanoic acid	60

^aReaction conditions: T = 160 °C; catalyst amount = 5 wt %; reaction time = 2 h.

Conclusion

We have synthesized nano-SO₄²⁻/TiO₂ by wet impregnation method and was used in the synthesis of dioctyl sebacate and other dicarboxylic acid esters. Under the optimized reaction condition, the conversion of sebacic acid reached to > 99 %. The catalyst could also be easily recovered and reused without severe deactivation.

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