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Preparation of Nano-SO_4^{2-}/TiO_2 Catalyst and Its Application in Esterification of Sebacic Acid with 2-Ethyl Hexanol[1]

Xianbing Ji[a,b], Yinxia Chen[a,b], Xiaobo Wang[a], and Weimin Liu[a]

[a] *State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000 P.R. China*

[b] *Graduate School of Chinese Academy of Sciences, Beijing, 100039 P.R. China*

e-mail: wangxb@licp.cas.cn; jixb1981@hotmail.com

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Abstract—A pure anatase phase nano-SO_4^{2-}/TiO_2 catalysts were synthesized and their catalytic activities were tested. Nano-SO_4^{2-}/TiO_2 shows high activity and effective re-usable when used as basic catalysts for the synthesis of dioctyl sebacate.

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During the last few decades, SO_4^{2-}/TiO_2 solid acid has attracted great attention because of its high specific surface area, ordered pore structure, high selectivity, good catalytic activity, high thermal and mechanical stabilities. Recently, many researchers have explored the synthesis and applications of SO_4^{2-}/TiO_2 solid acid [1–5]. Several synthesis methods to prepare SO_4^{2-}/TiO_2 have been reported, including sol-gel and hydrothermal methods [6–9]. Jiang et al. reported the preparation of mesoporous SO_4^{2-}/TiO_2 by hydrothermal method. The good activity in esterification of salicylic acid with isoamyl alcohol and the condensation of cyciohexanone with ethylene is due to the higher specific surface area and mesoporous structure [8]. De Almeida et al. [9] reported the preparation of SO_4^{2-}/TiO_2 by sol-gel method and used it as catalyst in transesterification reaction of vegetable oils. The relation of structure and catalytic activity of the prepared materials have been evaluated. However, to the best of our knowledge, there are very few works reported on the preparation and use of SO_4^{2-}/TiO_2 for the synthesis of dicarboxylic acid esters. In this communication, we have investigated the catalytic activities of the nano-SO_4^{2-}/TiO_2 solid acid tested by the esterification of sebacic acid with 2-ethyl hexanol (Scheme 1). On the other hand, the comparison of catalytic activities of the prepared nano-SO_4^{2-}/TiO_2 catalyst and the other two SO_4^{2-}/TiO_2 prepared with commercial titania was also carried out under the same experimental conditions.

TiO_2 was prepared by sol-gel method [10], and then the synthesized TiO_2 was added into H_2SO_4 (1 mol/l) by g/ml. After being stirred for 1 h, the solution was calcined at 450°C for 3 h [11, 12] to obtain the nano-SO_4^{2-}/TiO_2. Nano-SO_4^{2-}/TiO_2-P25 and nano-SO_4^{2-}/TiO_2-P were prepared by the same method using P25 and titania purchased from "Sinopharm Chemical Reagent Co., Ltd" as raw materials, correspondingly.

Fourier transform infrared spectroscopy (FT-IR) spectra analysis of catalysts is listed in Fig. 1. The band at 3424 cm^{-1} is assigned to the O–H stretching vibration of the absorbed water, and the band at 1630 cm^{-1} is the vibration of the absorbed water molecules [13]. Several absorption peaks in the 900–1300 cm^{-1} region are also observed on the spectra for the three catalysts, which are aroused by combining of SO_4^{2-} [6, 14]. The absorption bands at 1226 and 1135 cm^{-1} are the anti-symmetric and symmetric S=O stretching vibrations, respectively, and the bands at 1040 and 983 cm^{-1} indicate the anti-symmetric and symmetric S–O stretching vibrations of the SO_4^{2-} groups, respectively. Therefore, the FT-IR measurements suggest the formation of SO_4^{2-} modified titania.

X-ray diffraction (XRD) and N_2 physical adsorption were performed in order to study the phase of the catalysts and the specific surface area of the catalysts.

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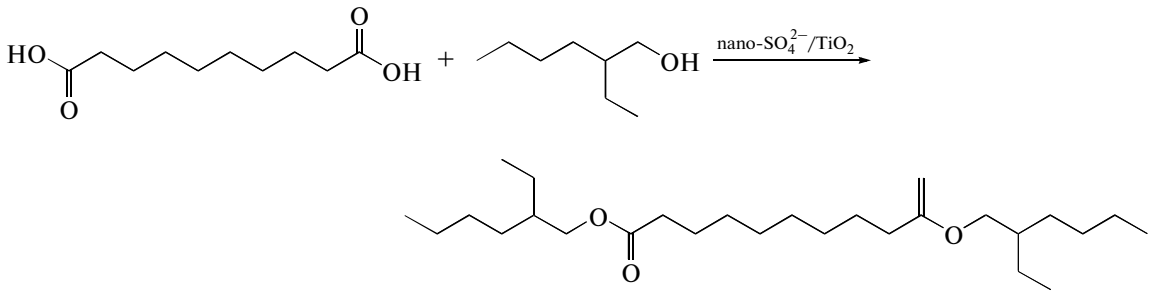

Scheme 1. Esterification of sebacic acid with 2-ethyl hexanol catalyzed by nano-SO_4^{2-}/TiO_2.

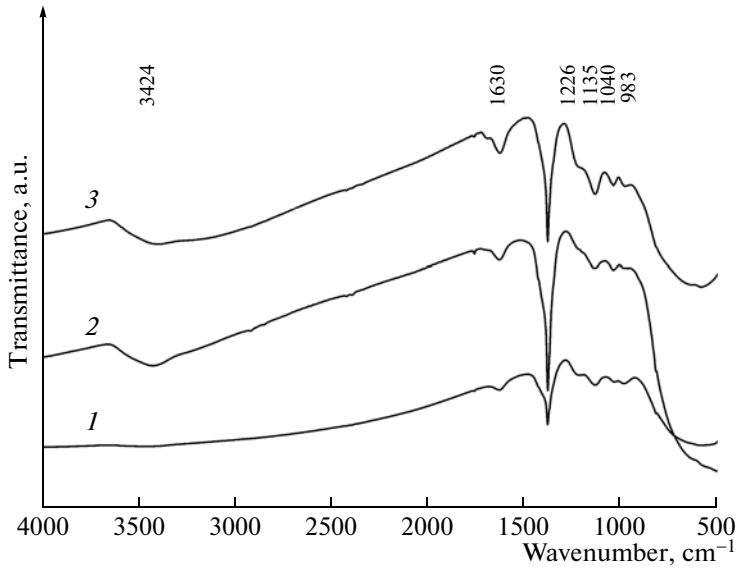

Fig. 1. FT-IR spectra of the catalysts: *1*—nano-SO_4^{2-}/TiO_2-P, *2*—nano-SO_4^{2-}/TiO_2-P25, *3*—nano-SO_4^{2-}/TiO_2.

Figure 2 shows the XRD patterns of the catalysts. As shown in Fig. 2a, the nano-SO_4^{2-}/TiO_2 catalyst exhibits the characteristic peaks of anatase phase at $2\theta = 25°$, 38°, 48°, 54°, 63°, 70°, and 75°. This proves that the nano-SO_4^{2-}/TiO_2 catalyst is pure anatase phase. While the XRD patterns of nano- SO_4^{2-}/TiO_2-P25 and nano-SO_4^{2-}/TiO_2-P catalysts show that the phase of the nano-SO_4^{2-}/TiO_2-P25 and nano-SO_4^{2-}/TiO_2-P catalysts is a mixture of anatase and rutile. The relative fraction of rutile in the crystalline phases of the nano-SO_4^{2-}/TiO_2-P25 and nano-SO_4^{2-}/TiO_2-P is 15.6 and 27.7%, respectively, which was calculated by the Rao equation [15].

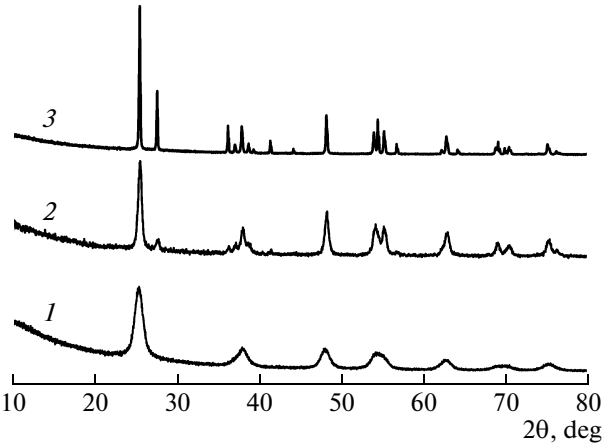

Fig. 2. XRD patterns of the catalysts: *1*—nano-SO_4^{2-}/TiO_2, *2*—nano-SO_4^{2-}/TiO_2-P25, *3*—nano-SO_4^{2-}/TiO_2-P.

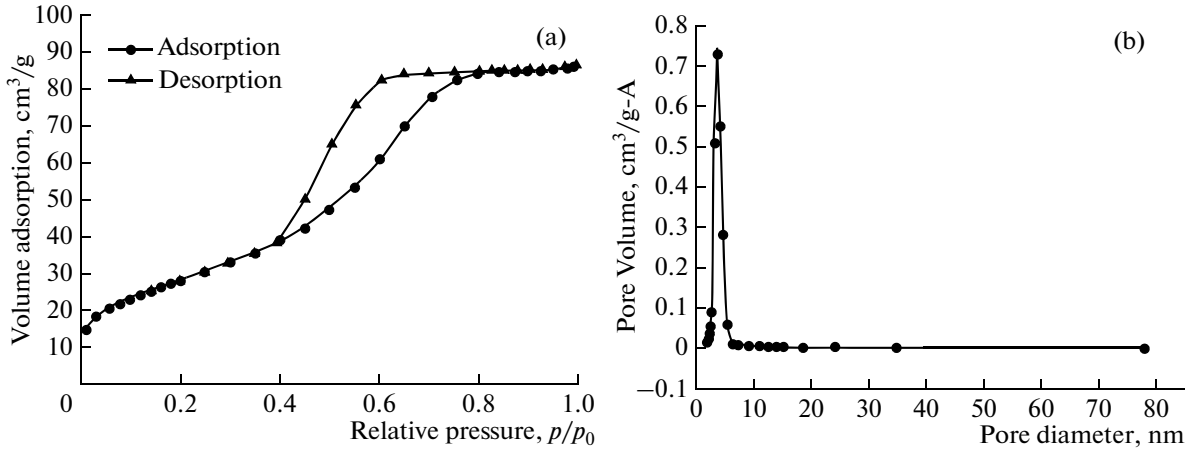

Fig. 3. Nitrogen adsorption–desorption (a) and pore size distribution curve isotherms (b) of the nano-SO_4^{2-}/TiO_2.

The specific surface areas of the catalysts are listed in table. The specific surface area of the nano-SO_4^{2-}/TiO_2 catalyst is much higher than that of nano-SO_4^{2-}/TiO_2-P25 and nano-SO_4^{2-}/TiO_2-P. Figure 3 gives the nitrogen adsorption–desorption isotherms and the pore size distribution curve of the nano-SO_4^{2-}/TiO_2. As shown in Fig. 3a, the nitrogen adsorption isotherms of the nano-SO_4^{2-}/TiO_2 catalyst shows **IV** type isotherms. Pore size distribution obtained from nitrogen adsorption experiments in Fig. 3b indicates the nano-SO_4^{2-}/TiO_2 catalyst has narrow pore size distribution and the average pore size of the catalyst is 4.2 nm.

The catalytic performance of the catalysts was investigated for the esterification of sebacic acid with 2-ethyl hexanol at 95° with a sebacic acid : 2-ethyl hexanol ratio of 1 : 3. Nano-SO_4^{2-}/TiO_2 results in the most active catalyst with a conversion of 87% after 2 h. In comparison the nano-SO_4^{2-}/TiO_2-P25 catalyst reaches a conversion of 50% after the same time, whereas nano-SO_4^{2-}/TiO_2-P shows a much lower conversion just 32%. The different catalytic performance of the three catalysts is probably attributed to the fact that they have different specific surface area (see table). Another reason may be that the rutile phase of titania deteriorates the catalytic activity of the catalysts. The nano-SO_4^{2-}/TiO_2 is pure anatase phase of titania, while the other two catalysts are the mixture of anatase and rutile phases of titania. The higher the catalyst contains rutile phase of titania, the lower the catalyst catalytic performance is.

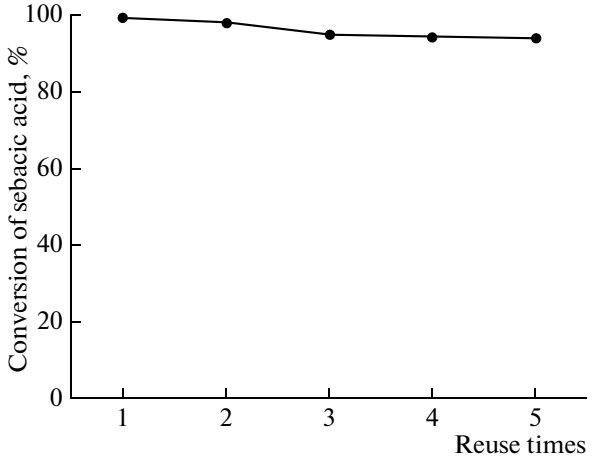

Fig. 4. Stability of the nano-SO_4^{2-}/TiO_2 catalyst.

Recycling tests were carried out in order to study the stability of nano-SO_4^{2-}/TiO_2. In this study, nano-SO_4^{2-}/TiO_2 was used as a test catalyst at a temperature of 160° instead of 95° in order to accelerate the process. After each run, the solid catalyst was separated from the reaction mixture by filtration, washing several times with methanol and drying it at 80° for the next cycle. Figure 4 shows that by regenerating the catalyst after each run, only a slight deactivation was detected. After five cycles, the conversion of the product catalyzed by nano-SO_4^{2-}/TiO_2 still can reach 94%, only 5% decrease of the conversion. This may be due to the leaching of a small amount of the anchored SO_4^{2-} and the inevitable loss of catalyst during the recycling test in the batch reactor. Thus, we can conclude that the nano-SO_4^{2-}/TiO_2 prepared by sol-gel and wet impregnation methods is a suitable catalyst for application in esterifacation of sebacic acid with 2-ethyl

Specific surface area (BET), average pore diameter (BJH) and pore volume

Catalysts	Specific surface area, m^2/g	Average pore diameter, nm	Pore volume, cm^3/g
Nano-SO_4^{2-}/TiO_2	152.4	4.2	0.21
Nano-SO_4^{2-}/TiO_2-P25	44.0	29.2	0.34
Nano-SO_4^{2-}/TiO_2-P	2.0	9.5	0.0044

hexanol. The higher specific surface area and pure anatase phase of titania yield the higher catalytic activity of the catalysts.

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