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Introduction

Pentaerythrityl tetrastearate (PETS) is an important chemical material, which can be used as the raw material for producing compatibilizers, surfactants, rubber additives, and so on. PETS is commonly used as a lubricant and release agent in engineering plastics. It can greatly improve the surface gloss of the products and is beneficial to the demoulding of the products. It can also be used as a dispersant for material products, which can accelerate the dispersion of fillers and pigments.

PETS is mainly produced by the catalytic esterification of pentaerythritol and stearic acid. However, to the best of our knowledge, there are very few studies reported on this work. Therefore, we mainly referred to the literature of other esterification reactions and the catalysts used. Traditionally, esterification is catalyzed by mineral acids. However, these homogeneous acid catalysts are corrosive, and result in significant drawbacks on the process and environmental aspects.^{1–3} To overcome these drawbacks, too many kinds of solid acid catalysts are used in the esterification, because solid acid has the advantages of good



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A mesoporous $SnO-\gamma-Al_2O_3$ nanocomposite was synthesized by a seeding-crystallization method and investigated in catalytic esterification of pentaerythritol and stearic acid to produce pentaerythrityl tetrastearate. $SnO-\gamma-Al_2O_3$ prepared by conventional hydrothermal synthesis was also examined for comparison. The catalysts were studied using XRD, N₂ adsorption, NH₃-TPD, SEM, ²⁷Al MAS NMR, pyridine-FTIR and CHNS analysis. According to the results of characterization, the seeding-crystallization method was helpful in reducing the size of the crystal particles, and improving the crystallinity and dispersity of crystal particles. The surface area, especially the external surface area, pore volume and size were increased, and the total acidity was increased. The strong acid sites were transformed into medium strong acid sites, and the strength of the medium strong and strong acid was weakened. Therefore, the formation of coke was retarded, and the pentaerythritol conversion, the pentaerythrityl tetrastearate selectivity and the catalytic stability were obviously improved.

stability, high catalytic activity, good reaction selectivity, no corrosion to equipment, water resistance, heat resistance and no waste water in the reaction process.^{4–13}

Among them, the metal oxide γ -Al₂O₃ has drawn attention for the esterification due to its excellent catalytic activity and outstanding stability, acting as the active component or the support of catalysts. Liu⁸ *et al.* reported that continuous esterification of oleic acid and ethanol to ethyl oleate under sub/ supercritical conditions over γ -Al₂O₃ catalysts achieved a yield over 98% at 325 °C, 200 bar and 1 min residence time. Yuan¹⁰ *et al.* prepared a SO₄²⁻/TiO₂/ γ -Al₂O₃ solid acid catalyst by an impregnation method during the esterification of *n*-butyl alcohol and lauric acid.

SnO catalysts have also attracted the attention of many research teams. Ma *et al.* used SnO as the catalyst during the esterification of pentaerythritol and heptanoic acid to produce pentaerythritol tetraheptanoate.¹⁴ Qian *et al.*¹⁵ synthesized naphthenic acid esters using SnO catalysts, and Jin *et al.*¹⁶ used SnO as the catalyst to synthesize trimethylolpropane palm kernel acid esters. Wang *et al.* used SnO as the catalyst for the esterification of naphthenic acid and methanol.¹⁷ In these studies, SnO catalysts exhibited superior catalytic esterification properties, however, because SnO is a powder, it is difficult for SnO catalysts to be used directly in a fixed bed, and a long stirring reaction can easily cause the SnO powder to become flocculent and separation is very difficult in a continuous stirred-tank reactor.

Combining the respective advantages of SnO and γ -Al₂O₃ catalysts, the SnO- γ -Al₂O₃ composite may exhibit superior



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catalytic esterification properties. Wang *et al.*¹⁸ prepared a SnO– γ -Al₂O₃ catalyst for the esterification of naphthenic acid and methanol. However, the SnO– γ -Al₂O₃ catalyst was prepared by simply mixing SnO, γ -Al₂O₃, Al(OH)₃ and water, and then baked at 500 °C in a nitrogen atmosphere. The BET surface area and pore volume were small, and the interaction between SnO and γ -Al₂O₃ was weak, which are important factors affecting the performance of the catalyst.

In this work, the SnO– γ -Al₂O₃ composite is prepared by a seeding-crystallization method. This method is beneficial to the preparation of mesoporous SnO– γ -Al₂O₃ nanocomposite, which has the advantages of high surface area, pore volume, crystallinity, dispersity and total acidity. The pentaerythritol conversion, the pentaerythrityl tetrastearate selectivity and the catalytic stability are obviously improved.

Results and discussion

Catalyst characterization

XRD, SEM, NH₃-TPD, Pyridine-FTIR, ²⁷Al MAS NMR and N₂ adsorption-desorption. Fig. 1 displays the XRD patterns of the samples. For the C-1 and C-2 samples, the diffraction planes of (001), (101), (110), (200), (112), (211), (202) and (220) are present, which matches the standard card (JCPDS #06-0395) of the tetragonal tin oxide.¹⁹⁻²³ This proves that the tetragonal tin oxide is successfully prepared by both methods. At the same time, peaks of 38.3, 43.5 and 64.1° are observed in Fig. 1, which is in good agreement with the characteristic peaks of the γ -Al₂O₃ reported in the literature.^{24–27} This proves that γ -Al₂O₃ is also successfully prepared in the C-1 and C-2 samples. Therefore, the main components of the sample C-1 and C-2 are the tin oxide and γ -alumina (SnO- γ -Al₂O₃) complexes. Taking the crystallinity of C-1 (100%) as the standard, the relative crystallinity of C-2 is calculated by comparing the sum of the characteristic peak areas with those of C-1. As shown in Table 1, the relative crystallinity of C-2 is 47.2%, so the crystallinity of C-1 is higher than that of C-2. The seeding-crystallization method may improve the crystallinity of the samples.

SEM images of C-1 and C-2 are shown in Fig. 2. C-1 shows better crystal particle dispersion and more uniform crystal particle size than those of C-2. Moreover, the particle size of C-1 is smaller than that of C-2, and the number of crystals in C-1 is more than that of C-2, and C-1 and C-2 show different crystal morphologies. The reason for this may be that the



Fig. 1 XRD patterns of C-1 and C-2.

seeding-crystallization method is conducive to the formation of a large number of nuclei during the preparation process.

A NH₃-TPD experiment was carried out to characterize the acidic properties of the samples, and the results are shown in Fig. 3 and Table 1. The acid strength is usually determined by the temperature of the ammonia desorption: weak (100–200 °C), medium (200–400 °C) and strong (>400 °C).^{28–32} It is obvious that there are two peaks at 200-300 °C and 500-600 °C on the C-1 and C-2 samples, which reveals the presence of medium and strong acid sites. The amount of strong acid sites on C-1 are less than those on C-2, however, the amount of medium acid sites and the total amount of acid sites on C-1 are more than those of C-2. The temperatures of NH₃-TPD on C-1 are evidently lower than those of C-2, indicating the acid strength of C-1 is weaker than that of C-2. Furthermore, the total amount of acidity on C-1 is more than that of C-2. The key reason may be as follows: The addition of crystal seed provides a rich induction point for the formation of crystal nuclei in the raw material system, leading to an increase in the number of crystal nuclei. However, the amount of raw material in the system is a certain value, unable to provide the raw liquid needed for the crystal nucleus growth, so the crystal particle size becomes smaller. The smaller particles have a larger specific surface area, which exposes more acid sites. Combined with the characterization results of the SEM, the crystal seed method favors the dispersion of the crystal particles, thus affecting the acidity distribution.

Fig. 4 exhibits the pyridine-FTIR spectra of C-1 and C-2. The characteristic vibration bands at 1538 cm⁻¹ and 1445 cm⁻¹ are attributed to Brønsted acid sites and Lewis acid sites, respectively.³³ From the results of Pyridine-FTIR, we can see that there is only Lewis acid sites on C-1 and C-2. The concentrations of Lewis acid sites are shown in Table 1. The amount of Lewis acid sites on C-1 is more than that of C-2, which is the same as the results of NH₃-TPD.

Fig. 5 illustrates the ²⁷Al MAS NMR spectra of C-1 and C-2. There are two peaks at ~60 ppm and ~0 ppm in the 27 Al MAS NMR spectra for both C-1 and C-2, which are attributed to tetrahedral and octahedral Al3+ ions, respectively.27,34 In both of the 27Al MAS NMR spectra, the peak of the tetrahedral Al species are obviously weaker than the peak of the octahedral Al species. The relative intensity of the ²⁷Al MAS NMR spectrum is obtained by the deconvolution method. It is obvious that the relative intensity of octahedral Al follows the order of C-1 (85.7%) > C-2 (79.2%), which is consistent with the variation of relative crystallinity in Table 1. Furthermore, the relative intensity of tetrahedral Al of C-1 (14.3%) is weaker than that of C-2 (20.8%). The relative intensity differences of these aluminum species with different configurations may have very important effects on the acid properties of the samples. The peaks of the ²⁷Al MAS NMR spectrum of C-1 shift slightly to higher frequencies than those of C-2, which may be due to the stronger interaction between tin oxide and alumina in the C-1 sample prepared by the seeding-crystallization method.

The nitrogen adsorption-desorption isotherms and corresponding pore size distributions of the C-1 and C-2 samples are shown in Fig. 6(a and b), and the related textural data are shown in Table 1. The isotherms of the samples show typical type IV features

	Surface area $[m^2 g^{-1}]$		Pore	Pore	Acidity [mmol NH ₃ g _{cat} ⁻¹]			Lewis acid- ity (umol	Relative crystallinity	Particle
Catalyst	$S_{\rm BET}$	S _{ext}	$[\mathrm{cm}^3 \mathrm{g}^{-1}]$	[nm]	Total	Medium	Strong	g_{cat}^{-1}	(%)	(nm)
C-1 C-2	613.8 485.7	223.1 138.2	1.1 0.4	4.8 4.4	512 495	289 208	223 287	153.15 138.37	100 47.2	32 86



Table 1 Physicochemical properties and acidities of C-1 and C-2 catalysts

Fig. 2 SEM images of C-1 and C-2.



Fig. 3 NH₃-TPD curves of C-1 and C-2.



Fig. 4 Pyridine-FTIR spectra of C-1 and C-2.

and have a combination of H2 and H4-type hysteresis loops,³⁵ which are typical characteristics of mesoporous materials.^{36–38} The pore size and volume of C-1 are obviously higher than those of C-2. According to the results of SEM, the particle size of C-1 is remarkably smaller than that of C-2, therefore, the surface area, especially the external surface area of C-1 is higher than that of C-2, which may offer highly effective active sites for the bulk reactant of pentaerythritol in our work.

Catalytic activity

The catalytic esterification performance comparison between C-1 and C-2 is shown in Fig. 7. We can see that the



Fig. 5 ²⁷Al MAS NMR spectra of C-1 and C-2.



Fig. 6 (a) N_2 adsorption isotherms and (b) pore size distributions of C-1 and C-2.

pentaerythritol conversion on C-1 is higher than that of C-2. After seven reaction cycles (21 h), the pentaerythritol conversion decreased from 99.8% to 97.0% on C-1, however, the pentaerythritol conversion decreased from 96.5% to 90.5% on C-2. The stability of C-1 is obviously higher than that of C-2. The reason for this may be that the total amount of acidity on C-1 is more than that on C-2, which is good for improving the pentaerythritol conversion. In Table 1, the surface area, pore volume and size of the C-1 catalyst are larger than those of C-2.



Fig. 7 Pentaerythritol conversion and PETS selectivity on C-1 and C-2.

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and the particle size of the C-1 catalyst is smaller than that of C-2, and the length of pores is shorter than that of C-2, which would reduce the constraints to the mass transfer and usually improve the performance by facilitating both the access of the reactants to the active sites and the diffusion of the reaction products. It is generally accepted that the strong acidity can easily lead to organic deep cracking to carbon deposition. From the results of NH₃-TPD, the amount of strong acidity over C-1 is less than that of C-2, therefore, the amount of coke on C-1 (1.8 wt%) is less than that of C-2 (3.1 wt%), and the deactivation of C-1 is slower than that of C-2. The PETS selectivity on C-1 is remarkably higher than that of C-2. Combined with the results of the NH₃-TPD experiment, we speculate that the medium strong acid is beneficial to improve the PETS selectivity. The formation of carbon deposits is an important factor affecting selectivity. As the reaction proceeds, the resulting carbon deposits cover some of the strong acid sites on the catalyst, therefore, the PETS selectivity is improved at the beginning of reaction. The rate of selectivity increase of the C-2 catalyst is obviously higher than that of C-1, and the reason for this may be that the rate of carbon production on C-2 is higher than that of C-1.

Reaction mechanism

According to the results of pyridine-FTIR, the catalytic activity mainly relies on Lewis acid sites during the catalytic esterification of pentaerythritol and stearic acid. According to the literature,³⁹⁻⁴² the reaction pathways of the catalytic esterification of pentaerythritol and stearic acid should still follow the well-established Fischer esterification mechanism. Therefore, we propose the mechanism for the catalytic esterification of pentaerythritol and stearic acid using SnO-y-Al2O3 catalysis to be as follows: the stearic acid is adsorbed on the Lewis acid site of the catalyst through its carbonyl carbon to form an activated complex. Through a step involving the nucleophilic attack of the pentaerythritol and subsequent loss of water, the formation of the PETS finally takes place. On the C-1, the augmented Lewis acid sites could facilitate a nucleophilic attack by pentaerythritol on the adsorbed stearic acid. Therefore, the catalytic activity of C-1 is higher than that of C-2.

Experimental

Materials

In the present synthesis, all reagents were of reagent grade and used without further purification: aluminum isopropoxide [Al(iPrO)₃, Sinopharm Chemical Reagent Co. Ltd], tetrapropyl ammonium hydroxide (TPAOH, 25 wt% in water, Beijing Wokai Biotechnology Co. Ltd), ammonia water (NH₃·H₂O, 25 wt% in water, Beijing Wokai Biotechnology Co. Ltd), ammonium stannate [(NH₄)₄SnO₃, Jiangyan Chemical Reagent Co. Ltd] and deionized water.

Preparation of catalysts

Preparation of crystal seed: Moles of aluminum isopropoxide, ammonia water and ammonium stannate were measured by Al₂O₃, NH₃ and SnO, respectively. The molar ratio of aluminum isopropoxide, TPAOH, ammonia water and deionized water was Al_2O_3 :TPAOH: NH_3 : $H_2O = 1:0.5:10:200$. A calculated amount of aluminum isopropoxide, TPAOH, ammonia water and deionized water were mixed and stirred for 6 h at room temperature. Then the mixture was transferred into a PTFE lined reactor, and was treated under autogenous pressure at 50 °C for five days.

Preparation of $SnO-\gamma-Al_2O_3$: The preparation method for solution A was that a calculated amount of aluminum isopropoxide, TPAOH, ammonia water and deionized water were mixed and stirred for 3 h at 30 °C. The molar ratio was the same as that of the crystal seed. The preparation method of solution B was that a calculated amount of ammonium stannate and deionized water were mixed and stirred for 3 h at 30 °C. The molar ratio of ammonium Stannate and deionized water was $SnO:H_2O = 1:24$. Then, solution B and crystal seed were dripped simultaneously into solution A. The mass ratio of solution A and B was 0.6, and the amount of crystal seed was 10 wt% of the total mass of the A and B solution. The mixture was stirred for 3 h at 60 °C, and the sol-gel was formed, which was transferred into a PTFE lined reactor, and was treated under autogenous pressure at 170 °C for 48 h. After hydrothermal treatment, the sample was separated by filtration, washed with deionized water ten times, dried overnight at 120 °C, and calcined at 550 °C for 3 h in a nitrogen atmosphere. The sample was represented by C-1. In this work, we also prepared the C-2 sample, which was prepared by the same method as that of C-1, except for the addition of the crystal seed.

Catalyst characterization

The crystalline structure was obtained by X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation (k = 0.15406 nm), operated at 40 kV and 30 mA and scanned from 10° to 90°. The relative crystallinity of the samples was calculated by comparing the sum of characteristic peak areas at $2\theta = 10^{\circ} - 90^{\circ}$. To investigate the sample morphologies, scanning electron microscopy (SEM) was carried out on a Quanta 250 instrument. The specific surface area, pore size and pore volume of the samples were obtained by nitrogen adsorption-desorption isotherm using a Micromeritics ASAP 2020 instrument. The specific surface area was calculated by the BET method. The total pore volume was determined by N₂ adsorption at a relative pressure of 0.99, and the pore diameter was obtained from the desorption isotherm by the BJH method. Ammonia temperature-programmed desorption (NH₃-TPD) profiles were obtained by Builder PCA-1200, and the amount of acid sites was calculated by quantifying the desorbed NH₃ from NH₃-TPD. IR spectra of adsorbed pyridine (pyridine-FTIR) were carried on a Shimadzu FTIR-8700 spectrometer, and the amount of acid sites was determined by quantifying the peak area of adsorbed pyridine from pyridine-FTIR. ²⁷Al MAS NMR analysis was performed on an Advance III HD 600 MHz instrument at a spectrometer frequency of 119.2 MHz, using a Bruker 4.0 mm double-resonance MAS detector to acquire 48 kHz MAS spectra, and the chemical shifts were referenced to solid $(NH_4)Al(SO_4)_2$. The carbon content in the used catalyst was analyzed for elemental analysis by using a CHNS analyzer (Vario EL III).

Catalyst evaluation

A 100 mL three-necked flask was placed in a high-temperature oil bath, and the stirrer rod of a motor stirrer was fixed on the middle neck of the three-necked flask. One peripheral neck was sealed with a glass stopper. A condenser was placed in the third neck and its other interface was connected to a vacuum pump connection, and the vacuum degree is 0.02 MPa. One of the purposes of vacuum operations is to remove water, and the other purpose is to prevent SnO from being oxidized to SnO₂.

The molar ratio of pentaerythritol and stearic acid was 1:4.5, and the amount of catalyst was 1.0 wt% of the total mass of pentaerythritol and stearic acid. The esterification reaction was conducted at 100 °C for 3 h during a reaction cycle. After the reaction, heating was terminated and stirring was continued until the system cooled to room temperature. After breaking the vacuum, the reaction mixture was filtered. The filtrate was stood for one hour, and then the upper liquid layer was analyzed by a SP 6890 gas chromatograph equipped with a flame ionization detector and stainless-steel column (10%SE-30 + 102 silanized support, 3 m \times 3 mm). Pentaery-thritol conversion and product selectivity were quantified as follows:

Pentaerythritol conversion (%) = (Moles of pentaerythritol reacted/Moles of pentaerythritol in the feed) × 100

Product selectivity (%) = (Moles of pentaerythritol consumed by the generated PETS/Moles of pentaerythritol reacted) \times 100

Conclusions

In this work, we prepared a mesoporous $\text{SnO}-\gamma-\text{Al}_2\text{O}_3$ nanocomposite by a seeding-crystallization method for the first time and compared the catalytic behavior with the $\text{SnO}-\gamma-\text{Al}_2\text{O}_3$ prepared by conventional hydrothermal synthesis in the catalytic esterification of pentaerythritol and stearic acid to produce pentaerythrityl tetrastearate. The seeding-crystallization method was helpful in reducing the size of the crystal particles and improving the crystallinity. The surface area, especially external surface area, pore volume and size were increased, and the total acidity was increased. The strong acid sites were transformed into the medium strong acid sites. Therefore, the formation of coke was retarded, and the pentaerythritol conversion, pentaerythrityl tetrastearate selectivity and the catalytic stability were obviously improved.

Author contributions

Conceptualization: Y. Z., R. S. and J. D. Methodology and investigation: W. D. and M. C. Data curation: L. W. Interpretation of results: W. D. and W. X. Writing – original draft: W. D. and M. C. Writing – review and editing: W. D., M. C. and J. D. Project administration: R. S. and J. D. Funding acquisition: Y. Z., Y. W., M. C. and J. D. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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