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Esterification of Maleic Anhydride with Butanol over Tin Tetrachloride Supported on Silica Aerogels Catalyst

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Abstract: Dibutyl maleate (DBM) and dibutyl fumarate (DBF) are important intermediates extensively used in industrial application. The current paper reports a study on the efficacy of tin tetrachloride supported on silica aerogels catalyst (Sn/Si) in the esterification of maleic anhydride (MA) with butanol (BO) at reflux in which DBM and DBF are synthesized directly. The catalyst was characterized by X-ray powder diffraction (XRD), Infrared (FTIR) spectra, UV-vis diffuse reflectance spectra (DRUV-vis), N_2 sorption and element analysis. The optimal reaction conditions were confirmed as follows: calcination temperature of silica aerogels was 500 ℃, reaction time was 6 h, mol ratio of reactants was 1∶2∶0.0028 (MA∶BO∶Sn/Si). The conversion of MA was up to 86.1%, and the selectivity to DBM and DBF were 68.3% and 1.84% respectively, which almost same as the homogeneous catalyst system. And the Sn/Si catalyst kept a reasonable activity after 6 times reused cycles. The lost of Cl and the reaction of MA, BO, DBM, DBF with the catalyst surface could result in the decrease of the catalytic activity.

Key words: Esterification; Maleic anhydride; Butanol; Silica aerogels; Tin tetrachloride
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Maleic anhydride (MA), manufactured by the oxidation of butane or benzene, is the third-largest anhydride material and applied to produce succinic anhydride, γ-butyrolactone, 1,4-butandiol, tetrahydrofuran. The most application is to produce esters, such as the corresponding esters via the esterification of MA with methanol, ethanol, glycerol and butanol (BO) can be obtained. And the esterification of MA with BO to yield DBM and DBF is an important industrial reaction, as DBM and DBF both are valuable intermediates for the production of paints, adhesives, copolymers and films. Homogeneous acid catalysts such as concentrated sulfuric acid, hydrogen iodide, paratoluenesulfonic acid and aminosulfonic acid, etc., are used for such reaction[1-3]. But concentrated acid is corrosive and environment contaminated. Tin tetrachloride ($SnCl_4$) is a well lewis acid with low equipment corrosion and high product yield, which is highly rationalized to be used as catalyst in the esterification of MA with BO.

During last decades, many groups have undertaken in studying the supported $SnCl_4$ catalysts. Such as Pallavi Shah and co-workers have synthesized SBA-15 incorporated with tin chloride which was prepared by incipient-wetness impregnation method and tested in trans-esterification reaction[4]. Prashant S. Niphadkar and co-workers have synthesized Tin-silicalite-1 (Sn-MFI)[5]. And Farook Adam et al. have prepared rice husk ash supported stannous chloride[6] etc. Besides, the other catalyst carriers include clays, zeolites, carbons are generally used either[1,7-10]. Recently, silica aerogels (Si-aerogels) as catalyst support is a hot subject due to their special properties such as high specific surface areas, low bulk densities and good thermal stability[11] etc. Unlike ordered mesoporous materials, the pore structure of silica aerogel is random, interconnected, 3D network that can prevent the migration of catalyst particles which make it an attractive candidate as a

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catalyst support[12].

In this work, $SnCl_4$ supported on Si-aerogels was synthesized and applied to the esterification of MA with BO for the first time. The optimal conditions had been screened by experimenting with the effects of factors on the reaction, under which the 68.3% DBM and 1.84% DBF selectivity were obtained, reasonable activity were kept after 6 times reused cycles and the reason of activity decrease was discussed. X-ray powder diffraction (XRD), Infrared (FTIR) spectra, DRUV-vis, N_2 sorption and element analysis were used to characterize the catalyst.

1 Experimental

1.1 Chemicals

$SnCl_4$, MA, sulfolane and 1, 2, 3, 4-tetrahydronaphthalene were A. R. grade, obtained from Sinopharm Group Chemical Reagent Co., Ltd; Si-aerogels were prepared according to the step reported previously[13]; BO and toluene were A. R. grade and obtained from Beijing Chemical Works, both were dehydrated by refluxing with sodium wire before used.

1.2 Preparation of catalyst

The synthesis procedure of supported $SnCl_4$ catalyst, using schlenk technique, is presented as follows: Si-aerogels (calcined at different temperatures of 300, 400 and 500 ℃, respectively) and toluene were mixed together in a round-bottomed flask with 30 min of stirring, followed by addition of $SnCl_4$ dropwise. Then refluxed at 120 ℃ for 40 h under N_2 atmosphere, subsequently cooled the mixture to room temperature, removed toluene under vacuum. Then, a black solid powder was obtained. After washing with toluene and drying at 90 ℃ for 24 h under vacuum, the $SnCl_4$ supported on Si-aerogels catalyst (Sn/Si) was prepared.

1.3 Catalytic test

The esterification was carried out under N_2 atmosphere in a reflux unit equipped with a Dean-Stark apparatus. MA, BO (molar ratio 1∶2), toluene (water entrainer, 25 mL for each 0.1 mol MA) and catalyst were loaded and kept stirring at 120 ℃ for several hours. The process factors included calcination temperature of Si-aerogels, reaction time, and catalyst amount were studied.

After reaction, cooling the reaction mixture, centrifuging it, then the samples were analyzed by GC-7900 equipped with a Hewlett-Packard 101 capillary column (25 m × 0.2 mm × 0.2 μm film thickness) and a flame ionization detector (FID). The flow rate of nitrogen carrier gas was 25 mL/min (21.3 psig head pressure), the injector and detector temperatures were 250 ℃ and 200 ℃, respectively. Column temperature was 190 ℃ for the analysis of products, then down to 100 ℃ for the analysis of reactants, using sulfolane and 1,2,3,4-tetrahydronaphthalene as internal standards. Normalization method was used to take the quantitative analysis.

1.4 Characterization of catalyst

The Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance X-ray diffractometer with a target of Cu Kα operated at 40 kV and 40 mA with a scanning speed of 6 min and a scanning angle (2θ) range of 10° ~ 80°. Infrared spectra were acquired using a Bruker TENSOR 27 FT-IR spectrometer in the range of 400 ~ 4 000 cm^{-1}. The UV-vis diffuse reflectance spectra of selected samples were obtained using a Cary WinUV 300 spectrometer. The Brunauer-Emmett-Teller (BET) surface areas and the pore properties of support and catalyst were measured by nitrogen physisorption on a ASAP 2020 instrument at -196 ℃. The mass fraction of Sn was determined by the method of Chinese Standard (GB/T 12689.10-2004) and the mass fraction of Cl was determined by turbidimetric method reported in [19].

2 Results and discussion

2.1 Esterification of MA

The mechanism of esterification of MA is well known[14], involves two steps. In the first step, monoester was produced soon, and the rate decreased with the reaction going on; in the second step, motivated by adding catalyst, the formed monoester further reacts with alcohol to yield diester.

In this work, the products contained DBM and DBF, in addition, a by-product (Table 1) produced simultaneously (it is an oligomer may be produced from the polymerization of products during esterification due to the high temperature and long reaction time) during the catalysis process.

2. 1. 1 Effect of support calcination temperature and screening of reaction time　Since the calcination of Si-aerogels has an influence on its texture, such as pore sizes, surface silanol amount etc, which eventually affect the activity of immobilized catalyst in esterification, the Si-aerogels calcinated at 300 ℃, 400 ℃, 500 ℃ were studied. The obtained catalysts were labled as Sn/Si (300), Sn/Si (400), Sn/Si (500).

As shown in Fig. 1, the reaction reached its sufficient yield of DBM over the time of 6 ~ 8 h, considering the by-product content became higher in longer reaction time. Thus, 6 h was selected in the following works.

The effect of support calcination temperature on the catalytic reaction were shown in Table 1, it is observed that the largest content of by-product were produced over catalyst Sn/Si (300) during reaction period around 6h and the DBF yields remained the same over three catalysts. The highest DBM yield of 58.8% were obtained over catalyst Sn / Si (500) among the three catalysts. Thus, it is indicated that the optimum calcination temperature of support was 500 ℃. This result therefore illustrates the proper calcination temperature would keep a proper surface silanol amount to be used in reaction with $SnCl_4$ and also result in a proper surface hydrophobicity and texture structure that is benefit to expel water from the pore, thus permitting the reaction to shift towards the product side.

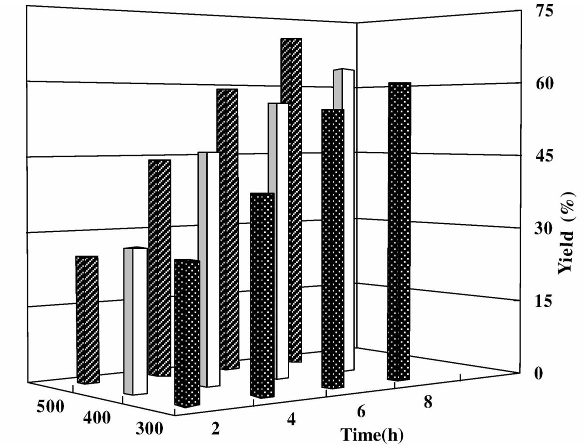

Fig. 1 Yield of DBM at different reaction times (300-Sn/Si (300), 400-Sn/Si (400), 500-Sn/Si (500))

Table 1 Effect of support calcination temperature on the esterification at the time of 6 h

Catalyst	Conversion (%)	Selectivity of DBM (yield) (%)	Selectivity of DBF (yield) (%)	Selectivity of by-product (yield) (%)
Sn/Si (300)	97.8	55.5 (54.3)	1.85 (1.81)	42.6 (41.7)
Sn/Si (400)	82.7	67.2 (55.8)	2.11 (1.75)	30.6 (25.3)
Sn/Si (500)	86.1	68.3 (58.8)	1.84 (1.58)	29.8 (25.7)

Reaction conditions: 4.903 g MA, 7.4 g BO, 12.5 mL toluene, 0.5 g catalyst, 120 ℃

2. 1. 2 Effect of catalyst amount　The results of esterification with different catalyst amount taking Sn/Si (500) as catalyst were shown in Table 2. The figure revealed that the conversion increased with the gradual increase of catalyst amount. It may be explained by the fact that when more catalyst amount supplied to the reaction system, more active sites are available. However, the optimum yield was achieved with 0. 5 g catalyst. It indicates that in presence of an appreciable amount of catalyst, products formation is more up to a certain extent and after which the effect is insignificant, which is possibly due to establishment of equilibrium. Besides, although the little higher selectivity of DBM and low content by-product were observed with adding 0. 3 g catalyst, the lower conversion and yield made it unsuitable. From a practical view, using 0. 5 g catalyst (mol ratio of reactants was 1∶2∶0.0028(MA∶BO∶Sn/Si)) may be a more favorable choice to ensure obtaining the satisfactory catalysis results.

2. 1. 3 Recyclability studies　The catalyst recycled activity was shown in Table 3. After six times cycles, the catalyst activity decreased 30% but was also twice as much as the blank system.

Table 2 Effect of catalyst amount on the esterification

Catalyst amount (g)	Conversion (%)	Selectivity of DBM (yield) (%)	Selectivity of DBF (yield) (%)	Selectivity of by-product (yield) (%)
0	27.3	99.1 (27.1)[a]	0 (0)	0 (0)
0.3	57.8	69.6 (40.3)	1.73 (1.00)	28.6 (16.6)
0.5	86.1	68.3 (58.8)	1.84 (1.58)	29.8 (25.7)
0.7	91.2	58.2 (53.1)	1.63 (1.49)	40.1 (36.6)
0.9	92.6	56.7 (52.6)	1.51 (1.40)	41.7 (38.7)

Reaction conditions: catalyst Sn/Si (500), 4.903 g MA, 7.4 g BO, 12.5 mL toluene, 120 ℃, 6 h

a: The 0.88% selectivity in blank system is belong to monoester, the data is not given in the table

Table 3 Recycled activity studies

Cycle times	Conversion (%)	Selectivity of DBM (yield) (%)	Selectivity of DBF (yield) (%)	Selectivity of by-product (yield) (%)
Ⅰ	86.1	68.3 (58.8)	1.84(1.58)	29.8(25.7)
Ⅱ	74.9	76.4 (57.3)	1.93(1.45)	21.5(16.1)
Ⅲ	68.5	83.0 (56.9)	2.01(1.38)	14.9(10.2)
Ⅳ	61.1	90.0 (55.1)	2.06 (1.26)	7.85(4.80)
Ⅴ	55.9	90.9 (50.8)	2.13(1.19)	6.96(3.90)
Ⅵ	50.2	91.6 (46.0)	2.25 (1.13)	6.15(3.09)
Blank system	27.3	99.1 (27.1)[a]	0 (0)	0 (0)

Reaction conditions: 4.903 g MA, 7.4 g BO, 12.5 mL toluene, 0.5 g catalyst Sn/Si (500), 120 ℃, 6 h

2.2 Characteristic results

2.2.1 Characteristic of Sn/Si (500) and Si-aerogels calcined at 500 ℃ (labled as Si (500)) Element analysis confirms the Sn/Si (500) catalyst contained Sn 6% and Cl 4%. The mol ratio of Sn∶Cl is about 1∶2, implies half of Cl is released during the immobilization steps owing to the reaction of SnCl$_4$ with surface silanol groups.

The XRD powder diffraction patterns of Si (500) and Sn/Si (500) are both exhibit weak amorphous signals of silicon oxide at about $2\theta = 23^\circ$. And there is no characteristic bands of SnCl$_4$ or SnO$_2$ are observed in Sn/Si (500), which indicate that tin species exist in a well dispersed state on the support surface[15,16].

The IR spectra of Si (500) and Sn/Si (500) are shown in Fig. 2. The band observed in the range of 850 ~ 770 cm^{-1} accounts for the symmetric stretching vibrations of the Si-O-Si bonds and the band at 1 090 cm^{-1} is assigned to the asymmetric (Si-O-Si) vibrations. In the hydroxyl region (3 200 ~ 3 600 cm^{-1}), a very broad absorption band centered at 3 426 cm^{-1} is ascribed to the silanol groups occurring with strong hydrogen bonded interactions[15]. It is concerned that the decrease in intensity of silanol groups after the immobilization reaction is due to the active participation of surface silanols in the bond formation with SnCl$_4$. And the band at 960 cm^{-1} is attributed to the presence of υ (Si-OH) vibrations of the Si- aerogels due to terminal Si-O stretching of silanol groups present at " defective sites ". The intensity of this peak is apparently reduced after refluxing with SnCl$_4$. It is suggested that there is interaction between SnCl$_4$ and silanol groups in Si-aerogels[17].

Diffuse reflectance UV-visible spectroscopy of Si

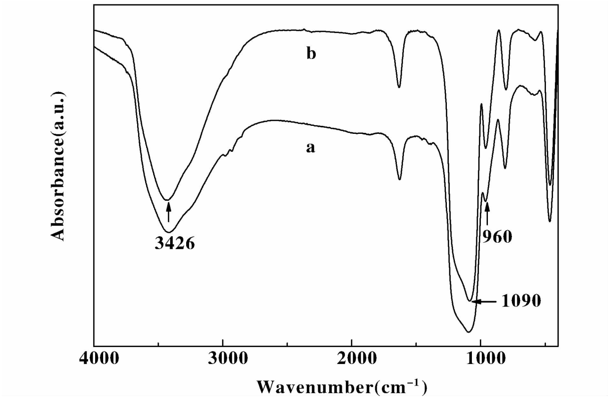

Fig. 2 IR spectra of Si (500) and Sn/Si (500):
a. Sn/Si (500) b. Si (500)

(500) and Sn/Si(500) are indicated there is no band at 280 nm after immobilization, which demonstrate that no polymeric Sn-O-Sn type species formed in Si/Sn (500)[18].

Besides, shown in Table 4, after immobilization of $SnCl_4$, BET surface areas decrease from 822 m^2/g to 638 m^2/g, total pore volumes decrease from 4.19 cm^3/g to 3.89 cm^3/g and the average pore sizes increase from 19.7 nm to 21.9 nm, which due to the filling of pores by tin species.

Table 4 Pore structure of Si (500) and Sn/Si (500)

Sample name	S_{BET} $(m^2/g)^a$	Vp $(cm^3/g)^b$	Dp $(nm)^c$
Si (500)	822	4.19	19.7
Sn/Si (500)	638	3.89	21.9

a. Specific surface area; b. Total pore volume;
c. Average pore diameter

2.2.2 Characteristic of the catalyst after six times reused　The IR spectra of Sn/Si(500) and Sn/Si (500) catalyst after six times reused cycles (Sn/Si (500)-6) are shown in Fig. 3. It is observed that four new bands appeared: 2 961 cm^{-1}, 1 266 cm^{-1}, 806 cm^{-1} and 670 cm^{-1}. The band in the range of 2 961 ~ 2 879 cm^{-1} accounts assigned to the stretching vibrations of saturated C-H bonds and the band at 1 266 cm^{-1} is assigned to the stretching vibrations of C-O bonds, the band at 670 cm^{-1} is assigned to the stretching vibrations of the Sn-O bonds[20]. It is suggested that some reactants (MA and BO) has adsorbed on the catalyst surface and some of them has reacted with the surface to produce species of Si-O-Sn-O-R (R = Bu, MA, DBM or DBF)[21] during the reaction cycles. Besides, the intensity of 806 cm^{-1} band which is belong to the stretching vibrations of the Si-O-Si bonds has increased more after the reaction cycles, indicating Si-aerogel has changed slightly within the reaction cycles.

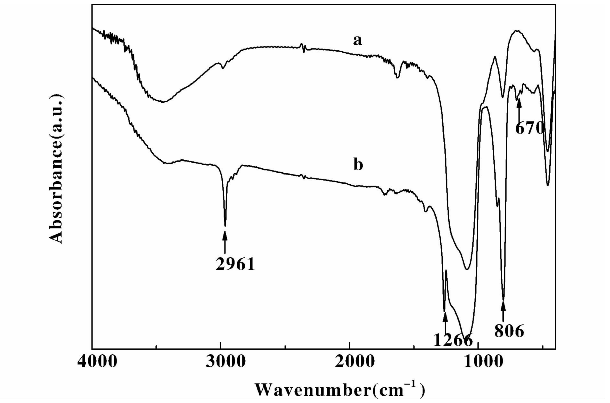

Fig. 3 The IR spectra of Sn/Si(500) and Sn/Si (500)-6
a. Sn/Si(500) b. Sn/Si (500)-6

As shown in Table 5, the BET surface areas and total pore volumes are both decrease, and the average pore sizes is increase after six times reused cycles. The reason may be related to the adsorption and reaction of MA, BO, DBM and DBF with the catalyst surface.

Table 5 Pore structure and element analysis of Sn/Si (500) and Sn/Si (500)-6

Sample name	S_{BET} $(m^2/g)^a$	Vp $(cm^3/g)^b$	Dp $(nm)^c$	Sn: Cl (mol ratio)
Sn/Si (500)	638	3.89	21.9	1:2
Sn/Si (500)-6	100	0.72	23.1	1:0.3

a. Specific surface area; b. Total pore volume;
c. Average pore diameter

The element analysis of Sn/Si(500) and Sn/Si (500)-6 are also shown in Table 5, it is observed that the content of Sn is not change while the Cl content is down from 2 to 0.3 mol ratio after six times reused cycles in the esterification. It is suggested that the most of Cl is lost after the reaction.

In summary, the activity decrease may be due to the losing of Cl and the adsorption and reaction of MA, BO, DBM and DBF with the catalyst surface during the reaction process.

3 Conclusion

Tin tetrachloride supported on silica aerogels catalyst were successfully prepared and applied in the esterification of maleic anhydride with butanol. The characterization confirmed the successfully immobilize tin species via the reaction of surface silanol with tin tetrachloride, and no polymeric Sn-O-Sn type species formed in the catalyst. The optimal conditions for catalytic reaction were: calcination temperature of silicon aerogels was 500 ℃, reaction time was 6 h, mol ratio of reactants was 1∶2∶0.0028 (MA∶BO∶Sn/Si). The Sn/Si catalyst kept a reasonable activity after 6 times reused cycles and the activity decreased due to the losing of Cl and the adsorption and reaction of MA, BO, DBM and DBF with the catalyst surface.

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SiO_2 气凝胶负载无水四氯化锡催化顺酐与正丁醇酯化反应的研究

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摘　要：通过表面反应制备了气凝胶 SiO_2负载无水四氯化锡催化剂并应用于顺酐与正丁醇的酯化反应．结果表明，酯化产物主要为马来酸二丁酯（DBM）与富马酸二丁酯（DBF），其优化条件为：载体 SiO_2气凝胶焙烧温度 500 ℃，物料摩尔比 顺酐∶正丁醇∶催化剂 ＝ 1∶2∶0.0028，反应时间6 h．并且通过 XRD，FTIR，DRUV-vis，N_2物理吸附以及元素分析技术对所合成催化剂进行表征．结果表明：无水四氯化锡成功负载于 SiO_2气凝胶表面，在催化酯化反应当中实现了86.1%的顺酐转化率，此结果接近于国内外所报道的均相体系成果，同时在催化回收利用六次后，其活性虽逐步下降，但仍是空白的2倍．分析测试表明，反应过程中 Cl 的流失量较大、反应物及产物在催化剂表面产生了吸附，这些可能是导致催化活性下降的主要原因．

关键词：酯化反应；顺酐；正丁醇；SiO_2气凝胶；无水四氯化锡