

A new solid acid SO_4^2 -/TiO₂ catalyst modified with tin to synthesize (1,6-hexanediol diacrylate)

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ABSTRACT

A new solid acid catalyst, SO_4^{2-}/TiO_2 modified with tin, was prepared using a sol-gel method and its physicochemical properties were revealed by nitrogen adsorption-desorption, X-ray powder diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, infrared spectroscopy of adsorbed pyridine, temperature-programmed desorption of ammonia and thermal gravimetric analysis. The structure, acidity and thermal stability of the SO_4^{2-}/TiO_2 -SnO₂ catalyst were studied. Incorporating tin enlarged the specific surface area and decreased crystallite size of the SO_4^{2-}/TiO_2 catalyst. The total acid sites of the modified catalyst increased and Brönsted acid strength remarkably increased with increasing tin content. The decomposition temperature of sulfate radical in the modified catalyst was 100 °C greater and its mass loss was more than twice that of the SO_4^{2-}/TiO_2 catalyst. The SO_4^{2-}/TiO_2 -SnO₂ catalyst was designed to synthesize 1,6-hexanediol diacrylate by esterification of 1,6-hexanediol with crylic acid. The yield of 1,6-hexanediol diacrylate exceeded 87% under the optimal reaction conditions: crylic acid to 1,6-hexanediol molar ratio = 3.5, catalyst loading = 7%, reaction temperature = 130 °C and reaction time = 3 h. The modified catalyst exhibited excellent reusability and after 10 cycles the conversion of 1,6-hexanediol was above 81%. © 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

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1. Introduction

Acrylate monomers, including universal acrylates and special acrylates [1], are basic reaction monomers of high-molecular weight compounds and raw materials for organic reactions. Special acrylates have been used in numerous areas such as leather tanning, papermaking, spinning, coating, adhesives, ink and especially radiation curing [2,3], despite their small scale production with poor yields from industrial syntheses. Radiation curing materials consist of reactive diluents, photoinitiators, oligomers and additives, and a main component comprised of a polymer of acrylate monomers such as polyester acrylate, epoxy acrylate and urethane acrylate [4,5]. The use of acrylates for radiation curing has caused a large market demand to improve the productivity and yields of acrylate syntheses.

The largest obstacle to industry synthesis of acrylates is the catalysts used. Post-reaction separation of catalysts is difficult and cause corrosion to equipment and environmental pollution [6,7]. The catalysts used are generally not recyclable and require rigorous reaction conditions [8]. Traditional acid catalysts (sulfuric acid and *p*-toluene sulfonic acid [9]) are gradually being replaced by solid acids such as metal salts [10], sulfated metal oxides [11,12] and heteropoly acids [13]. The inductive effect of the S=O group in sulfated metal oxides (SO_{4²⁻/MO_x) is so strong that the Lewis acidic strength of the}

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metal cations increases, and if water is adsorbed on the catalyst, a hydrogen atom is readily ionized to generate a Brönsted acid. These two acid types transform each other and coexist so that SO_{4^2}/MO_x are superacid catalysts [14]. This type of solid acid catalysts has the following advantages: (i) strong acidic strength; (ii) nontoxic, non-corrosive and environmentally benign; (iii) liable to separate from the reaction system allowing catalyst reuse. However, further application of SO₄²⁻/MO_x catalysts is slightly restricted because of their low surface area, poor thermal stability and it is especially difficulty to adjust their acidity [15,16]. A common approach to enhance the catalytic activity of $SO_{4^{2-}}/MO_x$ solid acids is to combine frequently used supports such as TiO2, ZrO2 or Fe2O3 with Si, Al, Mo or Sn and some rare earth metals. Yan et al. [17] prepared SO₄²⁻/ZrO₂ and SO₄²⁻/ZrO₂-Al₂O₃ catalysts by impregnation. Li's group [18] successfully designed a SO42-/Fe2O3-SiO2 catalyst with varied acidic strength and Brönsted acid sites. Zhao et al. [19] obtained a SO₄²⁻/ZrO₂-La₂O₃ catalyst by a surfactant-assisted co-precipitation/hydrothermal crystallization with subsequent impregnation method. Esterification of 1,6-hexanediol with crylic acid using other modified catalysts results in poor 1,6-hexanediol diacrylate yields and the catalysts were not reusable. These catalysts have been discounted for this esterification reaction because of insufficient activity and severe deactivation of the esterification reaction. In this work, we modify SO₄²⁻/TiO₂ catalysts by addition of tin (Sn) and evaluate their use in the synthesis of 1,6-hexanediol diacrylate.

A series of SO₄^{2–}/TiO₂-x%SnO₂ catalysts were prepared using a sol-gel method and applied to catalyze the esterification reaction of 1,6-hexanediol with crylic acid. The structure of the catalysts was analyzed using the nitrogen adsorption-desorption isotherms, X-ray powder diffraction (XRD) patterns, scanning electron microscope (SEM) images, Fourier transform infrared spectrogram (FT-IR), infrared spectrogram of adsorbed pyridine, temperature-programmed desorption profiles of ammonia (NH₃-TPD) and thermogravimetric (TG) curves. The yield of 1,6-hexanediol diacrylate was used as an evaluation index of catalytic activity to attain the optimal reaction conditions by varying acid to alcohol molar ratio, catalyst amount, reaction temperature and time. Finally, the reusability of the SO₄^{2–}/TiO₂-SnO₂ catalyst was evaluated.

2. Experimental

2.1. Catalyst preparation

TiCl₄ and a mass fraction of SnCl₄·5H₂O were dissolved in deionized water and the pH adjusted to 9 by addition of concentrated ammonia. The reaction mixture was aged for 24 h at a low temperature, the precipitate was separated by filtration and washed repeatedly using deionized water until the filtrate was free of chloride ions. The isolated solid was dried at 110 °C

for 12 h and then ground to obtain the catalyst support TiO_2 -SnO₂. Finally, the support was impregnated by sulfuric acid (1 mol/L) for 1 h and calcined at 500 °C for 4 h.

2.2. Catalyst characterization

The textural properties of samples were measured from nitrogen adsorption-desorption isotherms at -196 °C on a TriStar II 3020V instrument and the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation at a relative pressure of 0.03-0.4. Crystal structural features were determined from XRD patterns acquired on a Rigaku D/max-2400 diffractometer over the range of $2\theta = 10^{\circ} - 80^{\circ}$ at a scan rate of 8°/min using Cu K_{α} radiation ($\lambda = 0.15406$ nm). The microscopic surface features of the catalysts were investigated by SEM on a QUANTA-200 at 1.0 kV. The characteristic functional groups of the samples were detected by FT-IR spectroscopy on a Bruker EQUIN-55 over the range of 400 to 4000 cm⁻¹ with a resolution of 0.2 cm⁻¹. The thermal properties of the samples were recorded by TG curves on an American TA Q500 thermoanalyzer in nitrogen at a heating rate of 10 °C/min to 800 °C. The acidity of samples were determined by FT-IR of adsorbed pyridine on a Nicolet Nexus 476 FT-IR spectrometer. Samples were pretreated at 400 °C for 4 h under vacuum and then cooled to room temperature to saturate adsorbed pyridine. Samples were heated to 150 °C and excess pyridine evacuated for 1 h before acquiring their infrared spectrogram. The concentration of each type of acid sites was calculated according to equation $C = IA\pi R^2/(W\varepsilon)$ [20,21], where C = concentration of Lewis or Brönsted acid sites (μ mol/g), IA = integrated absorbance of the Lewis or Brönsted bands (cm⁻¹), R = radius of catalyst disk (cm), W = mass of catalyst disk (g), and ε = molar extinction coefficient ($\varepsilon_L = 2.22 \text{ cm}/\mu\text{mol}$ and $\varepsilon_B = 1.67$ cm/µmol). The acidity of recycled catalysts was analyzed by NH₃-TPD on a Micromeritics ChemiSorb 2720 auto-adsorption apparatus. Samples were activated at 300 °C for 2 h in a N₂ flow of 40 mL/min. After cooling to 100 °C, ammonia was adsorbed by samples for 0.5 h. Samples were heated up to 700 °C at a rate of 10 °C/min in order to desorb ammonia.

2.3. Catalyst performance

The modified SO₄²-/TiO₂-SnO₂ catalysts were applied to the synthesis of 1,6-hexanediol diacrylate by esterification of 1,6-hexanediol with crylic acid (Scheme 1). Reactants were charged to a 100-mL flask equipped with a water separator and magnetic stirring, followed by addition of moderate amount of the catalyst, azeotropic agent and polymerization inhibitor. The reaction system was heated, driving the water produced in the esterification reaction from the mixture. This process inevitably removed some acid because the azeotropic agent also formed weak interactions with organic molecules in the reaction system.

$$HOCH_2-(CH_2)_4-CH_2OH + 2CH_2=CH-COOH \xrightarrow{} CH_2=CH-C-O-(CH_2)_6-O-C-CH=CH_2 + 2H_2O$$

Scheme 1. Synthesis of 1,6-hexanediol diacrylate by esterification of 1,6-hexanediol with crylic acid.

tem. Feeds and products were analyzed by a GC2060 gas chromatograph with an OV-17 capillary column (30 m × 0.53 mm × 1.0 μ m) and a flame ionization detector at 350 °C. The column temperature was initially held at 70 °C for 2 min, then heated to 260 °C at a rate of 10 °C/min, and held at 260 °C for 10 min. A standard curve of 1,6-hexanediol at different concentrations was prepared to allow the content in samples to be measured by an external standard method. The content of 1,6-hexanediol diacrylate in samples was based on the purity test of acrylate monomer with polyfunctional groups using the industrial standard for radiation curing [22]. The conversion of 1,6-hexanediol (*X*) and the yield of 1,6-hexanediol diacrylate (*Y*) were used as proxies for the catalytic activity of the SO₄²-/TiO₂-SnO₂ samples:

 $X = ((m_A)_{\text{feed}} - (m_A)_{\text{product}})/(m_A)_{\text{feed}} \times 100\%$

 $Y = (118 \times (m_{\rm C})_{\rm product})/(226 \times (m_{\rm A})_{\rm feed} - (m_{\rm A})_{\rm product}) \times 100\%$

where m_A is the mass of 1,6-hexanediol, and m_C is the mass of 1,6-hexanediol diacrylate.

Solid catalyst was recovered from the reaction mixture at the end of the reaction and recycled for 10 experiments using optimal reaction conditions in order to examine the reusability of the SO_4^{2-}/TiO_2-SnO_2 . The recovered catalyst was washed with toluene and dried at 100 °C before the next cycle. The amount of reactant was decrease in proportion to the lost catalyst mass.

3. Results and discussion

3.1. Structural analysis of catalysts

3.1.1. Structural parameters

The nitrogen adsorption-desorption isotherms and corresponding pore diameter distribution curves of the tin doped $SO_{4^{2-}}/TiO_{2}$ catalysts are shown in Fig. 1. All of nitrogen adsorption-desorption isotherms are classical type IV according to IUPAC classification and present a H1 hysteresis loop in a p/p_{0} range of 0.4–0.9, which is a common characteristic of mesoporous material (Fig. 1(a)) [23–26]. All of the $SO_{4^{2-}}/TiO_{2-}x\%SnO_{2}$ catalysts exhibited a narrow distribution of small sized pores in the range of 5–15 nm, with the pore diameter mainly distributed around 10 nm (Fig. 1(b)). There was a prominent increase

Table 1

Structural parameters of the SO42-	/TiO ₂ -x%SnO ₂ catalysts
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$A_{\text{BET}}(m^2/g)$	$V_{\rm p}$ (cm ³ /g)	D _{BJH} (nm)	
63	0.094	10.52	
124	0.223	9.98	
126	0.229	9.95	
102	0.193	10.06	
	ABET (m ² /g) 63 124 126 102	A _{BET} (m²/g) V _p (cm³/g) 63 0.094 124 0.223 126 0.229 102 0.193	$A_{\rm BET}$ (m²/g) $V_{\rm p}$ (cm³/g) $D_{\rm B H}$ (nm)630.09410.521240.2239.981260.2299.951020.19310.06

in the quantity of pores from 5 nm to 10 nm in the catalysts doped with tin, especially for (3-6)%SnO₂. This phenomenon is explained by the fact that an appropriate amount of tin weakens the diffusion coefficient of the material surface and indirectly hinders the agglomeration of the crystallites [27]. Pore volume (VP) was approximately obtained from the adsorbed volume of nitrogen at the maximum relative pressure, while specific surface area (A_{BET}) was calculated by the BET equation at lower pressure, and pore diameter (D_{BJH}) was calculated by the Barrett-Joiner-Halenda (BJH) method at medium pressure (Table 1). The specific surface area of the SO₄²⁻/TiO₂-6%Sn catalyst was 126 m²/g, which was twice as large as that of the unmodified catalyst. Both the specific surface area and pore volume increased and then decreased with increasing amounts of tin. The reason for the decrease may be that excessive tin integrated into bulky particles that covered the pores of catalyst, resulting in lower nitrogen adsorbing capacity.

3.1.2. Crystalline structure

The crystal structure of the SO₄²⁻/TiO₂-*x*%SnO₂ catalysts was analyzed by XRD (Fig. 2). The prominent anatase crystal peak of titanium oxide was observed in the SO₄²⁻/TiO₂ samples at around $2\theta = 25.3^{\circ}$, which is assigned to the crystallographic plane (1 0 1). A series of weak peaks at around $2\theta = 37.8^{\circ}$, 48.0°, 53.9°, 62.7° are assigned to the (0 0 4), (2 0 0), (1 0 5) and (2 0 4) planes, respectively. The characteristic peaks of rutile titanium oxide are absent, indicating that the catalyst effectively inhibits the phase transformation of titanium oxide is not observed in the XRD patterns of SO₄²⁻/TiO₂-SnO₂ until the loading value of tin increases to 9%. For this sample, there is a new peak at $2\theta = 27.2^{\circ}$ which is assigned to the prismatic crystal of tin oxide. The XRD results reveal that tin oxide was



Fig. 1. (a) N₂ adsorption-desorption isotherms and (b) pore diameter distribution curves of SO_4^2 -/TiO₂-x%SnO₂. (1) x = 0; (2) x = 3; (3) x = 6; (4) x = 9.



Fig. 2. XRD patterns of the SO_4^2 -/TiO₂-x%SnO₂ catalysts. (1) x = 0; (2) x = 3; (3) x = 6; (4) x = 9.

Table 2

Crystallite size of the SO_4^2 -/TiO₂-x%SnO₂ catalysts.

Catalyst	Crystallite size (nm)
SO ₄ ^{2–} /TiO ₂	13.6
SO4 ²⁻ /TiO2-3%SnO2	12.2
SO4 ²⁻ /TiO2-6%SnO2	11.5
SO42-/TiO2-9%SnO2	10.3

excellently dispersed on the surface or within the channels of the catalysts [30], indicating a large surface area for the tin doped catalysts. The size of the crystal structure of each catalysts was calculated by Scherrer's formula (Table 2). Crystallite size decreased with increasing tin, which is explained by the same principle as that used to explain the increases in pore quantity.

3.1.3. Microscopic features

The SEM images of SO₄^{2–}/TiO₂ and SO₄^{2–}/TiO₂-6%SnO₂ catalysts show that tin makes a difference to the shape and appearance of catalyst (Fig. 3). As expected, the appearance of the SO₄^{2–}/TiO₂ catalyst looks like tabulate, while the appearance of the SO₄^{2–}/TiO₂-SnO₂ catalyst looks like faveolate. The SO₄^{2–}/TiO₂-SnO₂ catalyst has better dispersity and polyporous structure, which is in accordance with the results of the nitrogen adsorption-desorption and XRD analyses.

3.2. Acidity analysis of catalysts

3.2.1. Fourier transform-infrared spectra

The change of chemical bonds in the SO₄²⁻/TiO₂-x%SnO₂



Fig. 3. SEM images of (a) SO_{4^2} -/TiO₂ and (b) SO_{4^2} -/TiO₂-6%SnO₂ catalysts.



Fig. 4. FT-IR spectra of the SO_4^2 -/Ti O_2 -x%Sn O_2 catalysts. (1) x = 0; (2) x = 3; (3) x = 6; (4) x = 9.

catalysts was detected by FT-IR spectrometry (Fig. 4). Sulfate groups can combine with metallic oxide into inorganic chelating bidentate, bridge bidentate and covalent structures [31]. The common band at 1627 cm⁻¹ is assigned to the bending mode of water molecules associated with sulfate groups [17,32]. The bands at 1049, 1139 and 1240 cm⁻¹ are v_3 vibrations of bidentate sulfate groups in a C2v symmetry, corresponding to the asymmetric stretching vibration of S-O, the symmetric stretching vibration of S=O, and the asymmetric stretching vibration of S=O, respectively [21,33-35]. The band at 1406 cm⁻¹ is attributed to the asymmetric stretching vibration of S=O in a covalent sulfate structure and belongs to the split band of v_3 vibrations, which is triggered by the interaction between a sulfate group and metallic oxide in a severely dehydrated condition [34,36]. A new sulfate group band appears at 995 cm⁻¹ for the catalysts with added tin and is considered to be a v_1 symmetric stretching vibration of S–O in a $C_{2\nu}$ symmetry, suggesting the addition of tin decreased the symmetry of bidentate sulfate groups [21,34]. The bidentate sulfate group bands are slightly blue-shifted with increasing tin content. This phenomenon reveals that more and more bidentate sulfate groups connect with metallic elements by chelating instead of *via* a bridge structure because the frequency of v_3 splits in chelate structures are higher than those from bridged structures [36]. The intensity of bands that correspond to the asymmetric stretching frequency of S=O, which is directly related to the acidic sites [18], increases with tin loading, and the catalyst modified by 6% Sn exhibits the maximal acidity.

3.2.2. Infrared spectra of pyridine

The IR spectra of pyridine adsorbed on metal oxides is used to determine the nature of acid sites. Of the four ring vibrations (ν_{CCN}) modes (8a, 8b, 19a, and 19b), the 8a and 19b vibration modes are the most sensitive to interactions of the pyridine molecules nitrogen lone pair electrons [37]. Brönsted acid sites are detected by reaction with pyridine, and pyridinium ion bands appear at about 1637 cm⁻¹ (ν_{Ba}) and 1541 cm⁻¹ (ν_{19b}); whereas pyridine molecules coordinate with Lewis acid sites and these are detected at around 1622 cm⁻¹ (ν_{Ba}) and 1454 cm⁻¹ (ν_{19b}) [20,38–41]. Both Brönsted and Lewis acid site coex-



Fig. 5. IR spectra of pyridine adsorbed on the SO_{4^2} //TiO₂-*x*%SnO₂ catalysts. (1) *x* = 0; (2) *x* = 3; (3) *x* = 6; (4) *x* = 9.

Table 3 The amount of acid sites in the $SO_{4^2}/TiO_{2^2}x\%SnO_2$ catalysts.

Catalwat	Amount of acid sites (µmol/g)			
Catalyst	Brönsted acid	Lewis acid	Total acid	
SO ₄ ²⁻ /TiO ₂	18	41	59	
SO42-/TiO2-3%SnO2	65	43	108	
SO42-/TiO2-6%SnO2	122	45	167	
SO42-/TiO2-9%SnO2	96	46	142	

ist in the series of SO₄^{2–}/TiO₂-*x*%SnO₂ catalysts (Fig. 5). The band at 1489 cm⁻¹ is ascribed to corporate vibrations of a coordinated pyridine molecule and a pyridinium ion. The intensity of the band at 1541 cm⁻¹ obviously increases with the amount of tin in the catalysts and Brönsted acid sites range from 18 µmol/g to a maximum of 122 µmol/g (Table 3), while Lewis acid sites remain relatively stable at around 40 µmol/g. The number of total acid sites for the catalyst with 6%SnO₂ was 167 µmol/g, indicating that modifying the catalyst SO₄^{2–}/TiO₂ with tin increased the number of acid sites.

3.3. Thermal analysis of catalysts

TG curves analyzing the thermal properties of the SO₄²⁻/TiO₂ and SO₄²⁻/TiO₂-6%SnO₂ catalysts are displayed in Fig. 6. The weightlessness of catalysts mainly occurred at two various temperature sections. The first weightlessness is caused by the desorption of surface water below 200 °C [42]. The second weightlessness occurs above 500 °C and could be a result of the loss of a sulfur source on the surface of the catalyst, which is caused by the collapse of porous channels at high temperature [31]. The decomposition temperature of sulfate radicals is 630 °C in the SO42-/TiO2-SnO2 catalyst, approximately 100 °C higher than the SO₄^{2–}/TiO₂ catalyst, suggesting that the bond between the sulfate radical and titanium oxide is more thermally stability in the catalyst with moderate tin doping. The mass of sulfate radical lost in the SO42-/TiO2-SnO2 catalyst (11.0%) is more than twice that of the SO_4^{2-}/TiO_2 catalyst, which shows that the addition of tin contributes to the sulfate radical site in place of hydroxide radical sites and produces more acid sites.



Fig. 6. TG profiles of $SO_4{}^{2-}/TiO_2$ (1) and $SO_4{}^{2-}/TiO_2{-}6\% SnO_2$ (2) catalysts.

3.4. Performance of catalyst in the esterification reaction

3.4.1. Catalytic activity studies

The activity of the SO₄²⁻/TiO₂-*x*%SnO₂ catalyst was assessed by the conversion of 1,6-hexanediol and the yield of 1,6-hexanediol diacrylate. The amount of tin doped in the SO₄²⁻/TiO₂-*x*%SnO₂ influenced catalytic activity (Fig. 7). The reaction conditions used were a crylic acid to 1,6-hexanediol molar ratio = 3.5, catalyst loading = 7%, esterification temperature = 130 °C and time = 3 h. The yield of 1,6-hexanediol diacrylate raised from 59.7% for the unmodified catalyst to 81.6% for the catalyst with 3% SnO₂. Increasing the tin content to 6% increased the consumption of 1,6-hexanediol and the yield of 1,6-hexanediol diacrylate to 95% and 87%, respectively. The catalytic activity of the modified SO₄²⁻/TiO₂-SnO₂ was superior to that of the conventional SO₄²⁻/TiO₂ catalyst.

The effects of crylic acid to 1,6-hexanediol molar ratio, catalyst (SO_{4^2} -/TiO₂-6%SnO₂) loading, reaction temperature and reaction time on the esterification are depicted in Fig. 8. The conversion of 1,6-hexanediol monotonically increases with increasing acid to alcohol molar ratio, while the yield of 1,6-hexanediol diacrylate increased to a maximum value of 84.5% at a molar ratio of 3.5 and decreased suddenly at a higher ratio. This trend is likely because the esterification reaction is reversible and abundant crylic acid can drive the equilibrium



Fig. 7. Effects of tin content on the catalytic activity.



Fig. 8. Reaction condition effects on 1,6-hexanediol conversion (1) and 1,6-hexanediol diacrylate yield (2). (a) Acid/alcohol molar ratio (7%, 3 h, 130 °C); (b) Catalyst amount (3.5, 3 h, 130 °C); (c) Esterification temperature (3.5, 7%, 3 h); (d) Esterification time (3.5, 7%, 130 °C).

towards products. However, excess crylic acid has more of a chance to react with 1,6-hexanediol diacrylate to form side-products, such as homopolymer and copolymer, when the reaction reaches equilibrium, resulting in a decrease of ester yield and raising the cost of product separation. The catalytic effect is not significant when the amount of SO₄²⁻/TiO₂-SnO₂ used in the reaction is small because of a limited quantity of available acid sites (Fig. 8(b)). The conversion of 1,6-hexanediol increases obviously from 71.4% for 1% catalyst to 93.8% for 7% catalyst. Increasing the catalyst amount further did not increase the amount of 1,6-hexanediol converted and the yield of 1,6-hexanediol diacrylate dropped. A large amount of catalyst increases catalytic activity, but the polyporous catalyst has a strong adsorption function for products and a large amount of 1,6-hexanediol diacrylate is adsorbed in the porous channel of the catalyst. Esterification temperature and time also influence the activity of catalyst in the reaction. The conversion of 1,6-hexanediol and the yield of 1,6-hexanediol diacrylate have the same trend with increasing reaction temperature (Fig. 8(c)). Increasing the reaction temperature up to 130 °C improved both conversion and yield to maxima of 95.9% and 87.3%, respectively. The drop of 1,6-hexanediol conversion from 95.9% to 89.2% at higher temperature is likely caused by the exothermal effect of the esterification reaction, with high temperature suppressing reaction progress and shifting the reaction equilibrium towards reactants. Meanwhile, polymerization reactions occur more readily at high temperature, low-



Fig. 9. Reusability of the SO_4^2 -/TiO₂-6%SnO₂ catalyst.

ering product yield. Conversion and yield are also dependent on reaction time, with conversion of 1,6-hexanediol increasing drastically from 54.2% after 1 h to 94% after 3 h (Fig. 8(d)). Reactions longer than 3 h did not convert substantially more 1,6-hexanediol and the yield of the target decreased slightly. This trend is probably caused by the polymerization of 1,6-hexanediol diacrylate and crylic acid after esterification equilibrium has been reached.

3.4.2. Catalyst reusability studies

The reusability of a catalyst plays a crucial role in evaluating its performance, and we conducted 10 repeat experiments to determinate the stability of the SO₄²⁻/TiO₂-SnO₂ catalyst. The conversion of 1,6-hexanediol was above 93% for the first three cycles because the catalyst removed some of the polar impurities and water by accumulating at the acid sites (Fig. 9). The conversion dramatically decreases from 93.7% to 82.0% for the successive five cycles, which can be attributed to leaching of sulfur sources from the surface of the titanium oxide. The acid strength and the amount of acid sites on the surface of the modified catalyst were determined after the third and eighth reaction cycles by NH₃-TPD (Fig. 10). There are narrow desorption peaks of NH₃ at about 120 °C, corresponding to the weak acids, and broad distributed peaks in the range of 200-450 °C, corresponding to the medium and strong acids [8,17]. The abundance of acid sites is listed in Table 4. The distribution of



Fig. 10. NH₃-TPD profiles of the SO_4^2 -/TiO₂-6%SnO₂ catalyst after the third (1) and eighth (2) cycles.

 Table 4

 The amount of acid sites of recycled SO₄²⁻/TiO₂-6wt.%SnO₂ catalyst.

Dogralad astalizat	The amount of acid sites (µmol/g)			
Recycleu catalyst	Weak acid	Medium strong acid	Total acid	
Third recycled	64	102	166	
Eighth recycled	59	98	157	

acid strength in the catalyst after eight cycles is nearly consistent with that of the catalyst after three recycles. However, of the amount of total acid sites is obviously less (157 μ mol/g) after eight cycles compared with the catalyst after tree cycles (166 μ mol/g) because of losses of sulfur sources. This indirectly indicates that some of the active sites of the modified catalysts are removed by the reaction solvent, resulting in the decreased alcohol conversion by recycled catalyst. Even when the SO₄^{2–}/TiO₂-SnO₂ catalyst was recycled 10 times, a relatively stable conversion of 81% was obtained, suggesting good catalytic activity durability of the tin modified catalysts.

4. Conclusions

Solid acid SO₄²⁻/TiO₂ catalysts modified with tin were successfully prepared by a sol-gel method and evaluated for the esterification reaction of 1,6-hexanediol with crylic acid. The modified catalysts are obviously superior to the SO₄²⁻/TiO₂ catalyst because of larger specific surface area, smaller crystallite size, more numerous acid sites, stable chemical structure, and physicochemical properties. Optimal synthesis condition of 1,6-hexanediol diacrylate were obtained and produced 1,6-hexanediol diacrylate in 87% yield. This catalyst was remarkably stable and was reusable for 10 reaction cycles. The modified SO₄²⁻/TiO₂-SnO₂ catalyst has potential for industrial manufacture. However, the preparation of the catalyst should be considered and its mechanical strength, activity and active life require further research.

References

- Y. S. Omori, Acrylate and Its Polymer, Chemical Industry Press, Beijing, 1985, 90–126.
- [2] G. Y. Tilak, Progr. Org. Coatings, 1985, 13, 333-345.
- [3] Y. J. Hou, Paint Coatings Ind., 2011, 41(3), 75-80.
- [4] J. W. Xu, W. F. Shi, J. Coatings Technol., 2002, 74(928), 67–72.
- [5] Q. M. Zhang, Chem. Enterprise Management, 2014, (26), 35-36.
- [6] J. L. Ropero-Vega, A. Aldana-Pérez, R. Gómez, M. E. Niňo-Gómez, *Appl. Catal. A*, **2010**, 379, 24–29.
- [7] K. X. Zeng, Z. P. Huang, J. Yang, Y. L. Gu, Chin. J. Catal., 2015, 36, 1606–1613.
- [8] Y. Kuwahara, W. Kaburagi, K. Nemoto, T. Fujitani, *Appl. Catal. A*, 2014, 476, 186–196.
- [9] I. Pravst, M. Zupan, S. Stavber, *Tetrahedron*, 2008, 64, 5191–5199.
- [10] X. M. Lu, L. F. Ren, X. L. Zhang, T. T. Qiang, China Surfactant Detergent Cosmetics, 2008, 38, 349–355.
- [11] B. Kumar, Y. S. Negi, *Polymer*, **2015**, 80, 159–170.
- [12] Y. P. Zhao, Liaoning Chem. Ind., 2008, 37, 528–530.
- [13] Y. Wu, Progr. Chem., 1998, 10, 158–171.
- [14] W. Y. Su, Y. L. Chen, X. Z. Fu, K. M. Wei, Chin. J. Catal., 2001, 22, 175–176.
- [15] Y. X. Jiang, X. M. Chen, Y. F. Mo, Z. F. Tong, J. Mol. Catal. A, 2004, 213, 231–234.
- [16] Q. Zhao, S. M. Meng, J. L. Wang, Y. S. Qiao, Z. P. Li, Y. Guo, *Ceramics International*, **2015**, 41, 12186–12191.
- [17] H. P. Yan, Y. Yang, D. M. Tong, X. Xiang, C. W. Hu, *Catal. Commun.*, 2009, 10, 1558–1563.
- [18] H. J. Li, H. L. Song, L. W. Chen, C. G. Xia, Appl. Catal. B, 2015, 165, 466–476.
- [19] Z. K. Zhao, J. F. Ran, Appl. Catal. A, 2015, 503, 77–83.
- [20] C. A. Emeis, J. Catal., 1993, 141, 347–354.
- [21] K. Saravanan, B. Tyagi, R. S. Shukla, H. C. Bajaj, Appl. Catal. B, 2015, 172–173, 108–115.
- [22] Industrial Standard, HB/FG03-2009, Jiangsu, 2009.
- [23] B. B. Dong, B. B. Zhang, H. Y. Wu, X. Chen, K. Zhang, X. C. Zheng, *Mater. Res. Bull.*, **2013**, 48, 2491–2469.
- [24] K. A. Shah, J. K. Parikh, K. C. Maheria, Catal. Today, 2014, 237,



29–37.

- [25] L. Li, D. P. Zhang, Y. N. Fan, Chin. J. Inorg. Chem., 2011, 27, 2201–2204.
- [26] T. S. Jiang, J. L. Cheng, W. P. Liu, L. Fu, X. P. Zhou, Q. Zhao, H. B. Yin, J. Solid State Chem., 2014, 218, 71–80.
- [27] H. Yu, Y. H. Zhu, C. Liu, Z. H. Yang, X. H. Lu, X. Feng, Chin. J. Catal., 2009, 30, 265–271.
- [28] Z. Q. Ye, H. R. Chen, X. Z. Cui, J. Zhou, J. L. Shi, *Mater. Lett.*, 2009, 63, 2303–2305.
- [29] D. H. Guan, M. Q. Fan, J. Wang, Y. Zhang, Q. Liu, X. Y. Jing, Mater. Chem. Phys., 2010, 122, 278–283.
- [30] Y. Chen, Y. Cao, Y. Suo, G. P. Zheng, X. X. Guan, X. C. Zheng, J. Taiwan Inst. Chem. Eng., 2015, 51, 186–192.
- [31] Q. Zhang, J. Chang, T. J. Wang, Y. Xu, Chin. J. Catal., 2006, 27, 1033–1038.
- [32] E. Liu, A. J. Locke, R. L. Frost, W. N. Martens, J. Mol. Catal. A, 2012, 353–354, 95–105.
- [33] M. H. Zhang, A. X. Sun, Y. L. Meng, L. T. Wang, H. X. Jiang, G. M. Li,

Microporous Mesoporous Mater., 2015, 204, 210-217.

- [34] H. F. Guo, P. Yan, X. Y. Hao, Z. Z. Wang, *Mater. Chem. Phys.*, 2008, 112, 1065–1068.
- [35] H. M. Wang, J. S. Xu, R. H. Xiao, H. Z. Cheng, J. Mol. Catal. A, 2006, 248, 70–75.
- [36] P. Yan, H. F. Guo, H. Shu, Y. N. Wu, Y. F. Liu, X. L. Cui, *Chem. Res. Appl.*, **2006**, 18, 638–642.
- [37] M. Akcay, Appl. Catal. A, **2005**, 294, 156–160.
- [38] M. Tamura, K. I. Shimizu, A. Satsuma, Appl. Catal. A, 2012, 433–434, 135–145.
- [39] H. Atia, U. Armbruster, A. Martin, Appl. Catal. A, 2011, 393, 331–339.
- [40] M. I. Zaki, M. A. Hasan, F. A. Al-Sagheer, L. Pasupulety, *Colloids Surf. A*, 2001, 190, 261–274.
- [41] T. Barzetti, E. Selli, D. Moscotti, L. Forni, J. Chem. Soc. Faraday Trans., 1996, 92, 1401–1407.
- [42] H. W. Jing, X. M. Wang, Y. Liu, A. Q. Wang, Chin. J. Catal., 2015, 36, 244–251.