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Highly efficient and recyclable catalysts $SnCl_2$–$xH_3PW_{12}O_{40}$/AC with Brønsted and Lewis acid sites for terephthalic acid esterification

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ABSTRACT

The esterification of terephthalic acid with monohydric alcohol is an important reaction that has been widely applied in plasticizer industry. However, high pressure, harmful solvent or prolonging the reaction time are always needed to achieve high conversion of terephthalic acid, which increase the production cost. In this work, a series of $SnCl_2$–$xH_3PW_{12}O_{40}$/AC (x = 10, 15, 20, and 30 wt%) catalysts containing both Brønsted and Lewis acidic sites were prepared and used for preparation of terephthalates without any solvent under atmospheric pressure. Compared with the other works in previous reports, the catalysts in this study demonstrated that the high catalytic activity and strong stability in the process of esterification, which could be attributed to the high total surface acidity and the unique *Keggin* structure of catalysts, respectively. Among them, the catalyst $SnCl_2$-$15H_3PW_{12}O_{40}$/AC possesses the highest acid content and exhibits a high conversion of terephthalic acid (99% in 2.5–3 h). The remarkable activity and stability of the catalyst $SnCl_2$–$15H_3PW_{12}O_{40}$/AC hold a great potential application in plasticizer industry.

1. Introduction

Plasticizer is a class of material that can be integrated into plastics, cement, rubber, concrete and wallboard to improve their processability, flexibility and durability. The global production of plasticizers is around five million tons per year [1]. Among various plasticizers, phthalate diesters account for more than 80% due to their good performances and low cost [2]. However, phthalate can easily migrate to the surface of the plasticized polymers, causing environment and health concerns [3–5]. Terephthalates such as dioctyl terephthalate (DOTP) are potential alternative plasticizers to replace di(2-ethylhexyl)phthalate (DEHP) due to its outstanding mechanical properties and much lower toxicity than DEHP [6,7]. Nevertheless, compared with DEHP, DOTP exhibits a lower plasticizing efficiency, and the addition of more DOTP is required to meet processing requirement, thereby increasing the cost of materials and energy consumption. Therefore, it is necessary to design and synthesize new terephthalate with higher plasticizing efficiency, lower toxicity and excellent mechanical properties. Introduction of flexible ether linkages into the plasticizer structure is a useful approach to increase plasticization [8].

To date, some drawbacks still exist in industrial production of terephthalates. Even if homogeneous catalysts including titanate [9], sulfuric acid [10] and stannous salt [11] are used, long reaction time or high pressure is still needed to achieve high conversion of terephthalic acid. Moreover, neutralizing the acidic catalysts results in wastewater. Recently, a series of ionic liquids containing stannous or sulfonic acid groups were introduced as heterogeneous catalysts and demonstrated good catalytic activity in preparation of terephthalates [12–15]. However, the preparations of these ionic liquid catalysts are complicated.

Phosphotungstic acid (PTA) is a solid Brønsted acid that has shown outstanding catalytic performance in some reactions [16,17]. However, its poor thermal stability and dissolution in polar media restrict their applications in heterogeneous acid-catalyzed reactions. Modification of PTA by cations, such as Cs^+ and Ag^+, can reduce the aforementioned weaknesses and tune PTA into the catalysts with both Brønsted and Lewis acid sites [18,19]. The inexpensive stannous chloride is a promising candidate for modifying PTA due to its high Lewis acidity and less corrosion [20,21].

In this work, Brønsted acidic phosphotungstic acid and Lewis acidic stannous chloride were both loaded onto activated carbon by facile impregnation to form novel catalysts $SnCl_2$–$xH_3PW_{12}O_{40}$/AC, (x = 10, 15, 20, and 30 wt%) and they were investigated in the

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esterification of terephthalic acid. For comparison, stannous chloride, PTA, active carbon supported stannous chloride ($SnCl_2$/AC) and PTA ($30H_3PW_{12}O_{40}$/AC) were also employed for the synthesis of terephthalate. In addition, the relationship between structure-acidity and composition of $SnCl_2$–$xH_3PW_{12}O_{40}$/AC was investigated. To the best of our knowledge, catalyzing esterification of terephthalic acid using the heterogeneous catalysts combining $SnCl_2$ and PTA has not been investigated. The findings may inspire peer researchers and engineers to design multifunctional and highly efficient catalysts in a facile and cost-effective way.

2. Experimental

2.1. Catalyst preparation

2.1.1. Phosphotungstic acid supported on activated carbon (x$H_3PW_{12}O_{40}$/AC)

Industrial activated carbon (AC) made from coconut shells was obtained from the Jiangsu Zhuhai Activated Carbon Co., Ltd. (China) and was washed until the pH value reached 7 by distilled water. The $xH_3PW_{12}O_{40}$/AC precursors ($x = 10$, 15, 20 and 30 wt% on the basis of AC weight) were prepared by the incipient wetness impregnation method described in detail elsewhere [22]. Briefly, a known amount of $H_3PW_{12}O_{40}$ was impregnated onto 40.0 g of AC and the resulting was dried overnight at 80 °C. The exact amount of $H_3PW_{12}O_{40}$ loaded onto AC was determined by ICP-OES (Table 1). It should be mentioned that the actual content of $H_3PW_{12}O_{40}$ on AC was not exactly equal to the intended loading level, but for convenience the precursors were still labeled as $xH_3PW_{12}O_{40}$ ($x = 10$, 15, 20 and 30 wt%).

2.1.2. Stannous chloride supported on x$H_3PW_{12}O_{40}$/AC

$SnCl_2$–$xH_3PW_{12}O_{40}$/AC ($x = 10$, 15, 20 and 30 wt%) was synthesized by wet impregnation. Typically, 6.0 g $SnCl_2 \bullet 2H_2O$ and 34.0 g ethanol were charged into a 250 mL flask to form a clear solution and then 10.0 g $xH_3PW_{12}O_{40}$/AC was added to the solution with constant stirring at 60 °C for 5 h. After filtered and washed with ethanol for 3–5 times, the solid product was dried under vacuum overnight at 60 °C. The amount of $SnCl_2$ loaded onto $xH_3PW_{12}O_{40}$/AC was also determined by ICP-OES (Table 1). The solid was finally calcined at 300 °C in the nitrogen atmosphere for 3 h to obtain $SnCl_2$–$xH_3PW_{12}O_{40}$/AC. The preparing method of catalyst $SnCl_2$/AC was similar to $SnCl_2$–$xH_3PW_{12}O_{40}$/AC, except for the support.

2.2. General procedure for the synthesis of terephthalate

Scheme 1 shows the structures of the terephthalates prepared in this work. Esterification of alkoxy alcohol with terephthalic acid was carried out in a 500 mL round bottom flask equipped with a reflux condenser, a water segregator and vigorous stirring apparatus. In a typical run, 60.0 g terephthalic acid (0.36 mol), alkoxy alcohol (0.94 mol), 3.0 g catalyst (5 wt% on terephthalic acid) and 21.0 g *n*–butyl ether as azeotropic dehydrating agent (35 wt% on terephthalic acid) were introduced into the reactor. The reaction mixture was stirred and heated at 190−220 °C for 2.5 h.

After esterification, the catalyst was filtered from the reaction mixture and directly used for the next reaction. Conversion of terephthalic acid was determined by KOH titration according to the literature [23] and the selectivity was calculated based on the results determined by GC-MS (TRACE DSQ, Thermo) and GC with FID detector (GC-9800, Shanghai Kechuang Chromatography Co., Ltd., China). The excess alcohol and unreacted terephthalic acid were removed by distillation and neutralization, respectively. After decoloration with active carbon, yellowish liquid was obtained. S1 shows the results of NMR and MS characterizations of terephthalate.

2.3. Catalyst characterization

The porosities and BET specific areas of catalysts were determined by nitrogen adsorption-desorption isotherm measurements (Micromeritic, ASAP 2020).

FTIR absorption spectra were obtained using a Vertex 80 V (Bruker) FT-IR spectrophotometer. The samples were scanned from 4000 to 400 cm^{-1} using KBr pellets for 64 times

Crystalline states of catalysts $SnCl_2$–$xH_3PW_{12}O_{40}$/AC were determined by XRD (Rigaku, Ultima IV) using Cu–Ka radiation operated at 40 kV and 40 mA. The patterns were recorded from 5° to 50° at a scanning rate of 4°/min.

The morphology of the catalysts was characterized by scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) unit (JEOL, JSM-7600F).

The X-ray photoemission spectroscopy (XPS) analyses were performed on an AXIS Ultra^{DLD} (UK) with Al Kα (X-ray) lamp-house. All the binding energies were corrected by referencing of C1s peak at 284.8 eV.

The chemical compositions of $SnCl_2$–$xH_3PW_{12}O_{40}$/AC catalysts were determined using inductively coupled plasma optical emission spectrometer (ICP-OES) analysis (Perkin Elmer, Optima 5300DV).

The contents of Brønsted and Lewis acid sites on the catalyst were determined by Infrared spectra of adsorbed pyridine (Py-IR) on a Nicolet Nexus 670 FT-IR spectrometer with self-supported wafers. The samples were degassed in vacuum at 250 °C for 3 h and subsequently exposed to the pyridine vapor after cooling down to 25 °C. The amount of Brønsted acid and Lewis acid sites were calculated based on the integral area of the adsorption bands at nearly 1540 cm^{-1} at 1450 cm^{-1}, respectively [19,24].

Thermogravimetric analysis (TGA) was carried out on TGA/DSC1/1100SF instrument (Mettler Toledo). The samples were scanned from room temperature to 600 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

Table 1
BET surface analysis of $SnCl_2$–$xH_3PW_{12}O_{40}$.

Catalyst	$H_3PW_{12}O_{40}$ (wt%)[a]	$SnCl_2$ (wt%)[a]	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	Average pore size (nm)
AC	–	–	1171	1.08	3.7
$SnCl_2$/AC	–	27.5	765	0.75	3.9
$SnCl_2$–$10H_3PW_{12}O_{40}$/AC	9.3	25.9	593	0.61	4.1
$SnCl_2$–$15H_3PW_{12}O_{40}$/AC	14.1	25.6	514	0.53	4.2
$SnCl_2$–$20H_3PW_{12}O_{40}$/AC	17.9	23.9	493	0.51	4.2
$SnCl_2$–$30H_3PW_{12}O_{40}$/AC	26.4	22.8	472	0.49	4.2

[a] Determined by ICP-OES.

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