CHINESE JOURNAL OF CATALYSIS
Volume 32, Issue 1, 2011
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Chin. J. Catal., 2011, 32: 70–73.

RESEARCH PAPER

Hydroxyapatite Supported Lewis Acid Catalysts for the Transformation of Trioses in Alcohols

ZHANG Zehui[1,2,*], ZHAO (Kent) Zongbao[1,3]

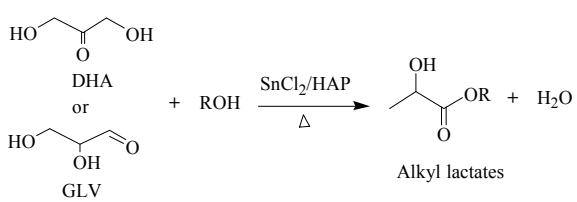
[1]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China
[2]Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[3]Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

Abstract: We prepared hydroxyapatite-supported tin(II) chloride and tin(IV) chloride Lewis acid catalysts. These catalysts showed catalytic activity for the transformation of trioses in alcohols to yield alkyl lactates. Under optimal conditions, *n*-butyl lactate was obtained in 73.5% yield when dihydroxyacetone and *n*-butanol were treated with hydroxyapatite-supported tin(II) chloride.

Key words: triose; hydroxyapatite; alkyl lactate; tin(II) chloride; solid catalyst

Lactic acid is widely used as an acidulant, flavorant, and preservative in the food, pharmaceutical, and textile industries. It is also used to produce biodegradable polylactic acid materials [1,2]. Microbial fermentation is a state-of-the-art technology for lactic acid production in industry [3]. However, the fermentation process presents obvious drawbacks such as the formation of a stoichiometric amount of salt by pH-regulation and the consumption of excess energy to recover lactic acid from the fermentation broth [4]. Lactic acid can also be produced from trioses when catalyzed by Lewis acids in the presence of water [5]. When the reaction is complete in an alcohol solution, dihydroxyacetone (DHA) or glyceraldehyde (GLV) is transformed into alkyl lactates [6,7]. The use of Lewis acids as catalysts usually leads to the discharge of highly toxic byproducts to the environment, contamination of the final product with metal salts and difficulties in separation. Therefore, the use of heterogeneous catalysts has attracted much attention because they are easy to work-up and the quantity of waste is reduced significantly [8,9]. Recently, commercially available zeolites have been used to catalyze the transformation of trioses to produce lactic acid and alkyl lactates in a good yields [10].

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is considered to be a promising support material because of its durable acid-base properties and its high adsorption capacity [11,12]. HAP supported Lewis acids have been used to catalyze many chemical reactions [13,14]. In this work, we report the preparation of the Lewis acids tin(II) chloride and tin(IV) chloride that are impregnated into hydroxyapatite catalysts ($SnCl_2$/HAP and $SnCl_4$/HAP) and preliminary results of the transformation of trioses in alcohols to alkyl lactates promoted by these solid catalysts (Scheme 1).



Scheme 1. Transformation of trioses to alkyl lactates.

1 Experimental

1.1 Preparation of the catalysts

HAP was prepared by the co-precipitation method according

Received 30 June 2010. Accepted 21 September 2010.
***Corresponding author.** Tel: +86-411-84379066; Fax: +86-411-84379211; E-mail: zhangzehui@dicp.ac.cn
Foundation item: Supported by the National High Technology Research and Development Program of China (863 Program, 2007AA05Z403) and the Knowledge Innovation Program of Chinese Academy of Sciences (KGCXZ-YW-336).

DOI: 10.1016/S1872-2067(10)60162-3

to known procedures [15]. $SnCl_2$/HAP was prepared by the impregnation method according to known procedures with some modifications [16]. HAP (2.00 g) was introduced into 100 ml of absolute ethanol containing 4 mmol (0.92 g) of $SnCl_2 \cdot 2H_2O$. The mixture was stirred for 24 h, filtered, and washed several times with ethanol. The recovered solid was dried at 110 °C overnight. Tin(IV) chloride was loaded onto HAP in a similar way to give the solid catalyst $SnCl_4$/HAP.

1.2 Characterization of the catalysts

A Micromeritics NOVA-4000 automated physisorption instrument was used to measure the N_2-adsorption isotherms of the samples at the liquid N_2 temperature (–196 °C). The specific surface area was determined from the linear portion of the BET plot. The pore-size distribution was calculated from the desorption branch of the N_2-adsorption isotherms using the Barrett-Joyner-Halenda (BJH) formula. Before the surface area and pore-size distribution measurements, the samples were degassed in vacuum for 3 h at 350 °C (for HAP) and 110 °C (for $SnCl_2$) to remove physically adsorbed components.

X-ray powder diffraction (XRD) patterns of the prepared samples were measured on a Philips CM-1 powder X-ray diffractometer (Cu K_α, λ = 0.1543 nm) operating at 40 kV and 40 mA. Diffraction patterns were collected from 2θ = 5°–90°.

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker EQUINOX 55 FT-IR spectrometer with a spectral resolution of 4 cm^{-1} in the wave number range of 400–4000 cm^{-1}. The samples and KBr were fully dried before the FT-IR analyses to exclude the influence of water.

The actual tin loading was determined by inductively coupled plasma/atomic emission spectroscopy (ICP/AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

1.3 Catalytic test

In a typical run, a mixture containing 100 mg of dihydroxyacetone dimer (DHAD) and 8 ml of *n*-butanol was preheated at 80 °C for 1 h to depolymerize the dimer into monomeric DHA. To the mixture was added some catalyst and the reaction was heated under specified conditions. At different time intervals, samples were withdrawn and analyzed by gas chromatography using methyl palmitate as an internal standard.

2 Results and discussion

2.1 Characterization results of HAP, $SnCl_2$/HAP, and $SnCl_4$/HAP

The surface area of the prepared HAP sample was estimated to be 50 m^2/g. The total pore volume (V_p) calculated by the BJH method was p/p_0 = 0.98 (V_p = 0.40 cm^3/g). The surface area and pore volume for $SnCl_2$/HAP were determined to be 43 m^2/g and 0.25 cm^3/g, respectively. The values for $SnCl_4$/HAP were almost the same as those for $SnCl_2$/HAP.

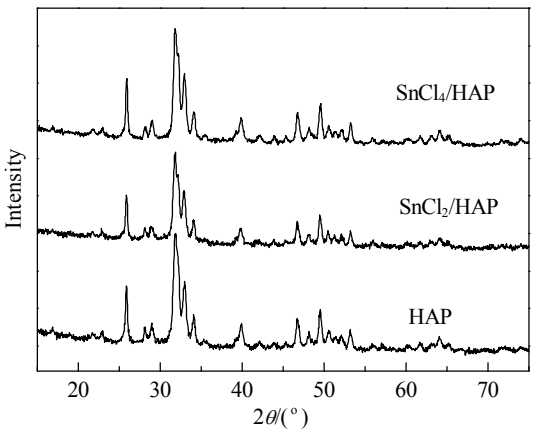


Fig. 1. XRD patterns of HAP, $SnCl_2$/HAP, and $SnCl_4$/HAP.

XRD patterns of HAP, $SnCl_2$/HAP, and $SnCl_4$/HAP are shown in Fig. 1. HAP has a typical hexagonal crystal structure and belongs to the space group $P6_{3/m}$. The lattice parameters of the HAP sample agreed well with the standard data: a = 0.9412 nm and c = 0.6837 nm. The XRD patterns of $SnCl_2$/HAP and $SnCl_4$/HAP were similar to that of HAP and their typical diffraction peaks showed no substantial change in intensity. It should also be noted that no $SnCl_2$ and $SnCl_4$ phases were detected in the $SnCl_x$/HAP sample indicating that $SnCl_2$ and $SnCl_4$ were highly dispersed. These results indicate that the modification of HAP by impregnating with $SnCl_2$ and $SnCl_4$ does not change the crystalline structure of the solid material.

The characterization of HAP, $SnCl_2$/HAP, and $SnCl_4$/HAP was further carried out by FT-IR (Fig. 2). There was no obvious difference between the support and the catalysts. The bands at 3580 and 631 cm^{-1} were assigned to the stretching and bending modes of the OH groups in the hydroxyapatite structure, respectively [17]. The bands at 1098, 1030, and 961 cm^{-1} were attributed to the asymmetric and symmetric stretching vibra-

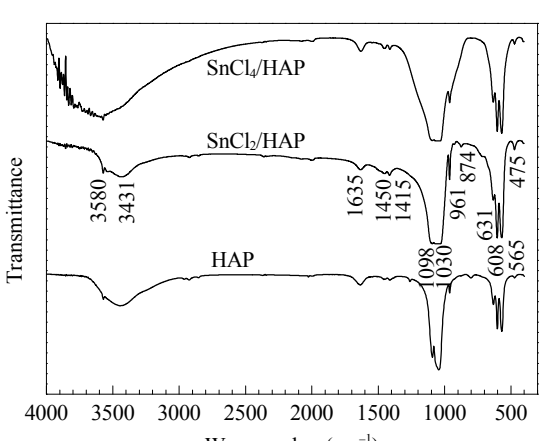


Fig. 2. FT-IR spectra of HAP, $SnCl_2$/HAP, and $SnCl_4$/HAP.