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RESEARCH PAPER

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

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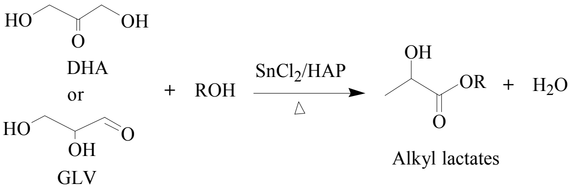
Abstract: We prepared hydroxyapatite-supported tin(II) chloride and tin(IV) chloride Lewis acid catalysts. These catalysts showed catalytic activity for the transformation of trioses in alcohols to yield alkyl lactates. Under optimal conditions, *n*-butyl lactate was obtained in 73.5% yield when dihydroxyacetone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



Scheme 1. Transformation of trioses to alkyl lactates.

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).

1 Experimental

1.1 Preparation of the catalysts

HAP was prepared by the co-precipitation method according

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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 $SnCl_2·2H_2O$. 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, $\lambda = 0.1543$ nm) operating at 40 kV and 40 mA. Diffraction patterns were collected from $2\theta = 5°–90°$.

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.

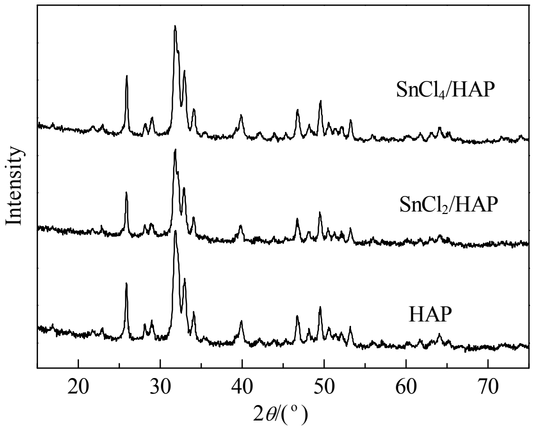

Fig. 1. XRD patterns of HAP, $SnCl_2$/HAP, and $SnCl_4$/HAP.

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-

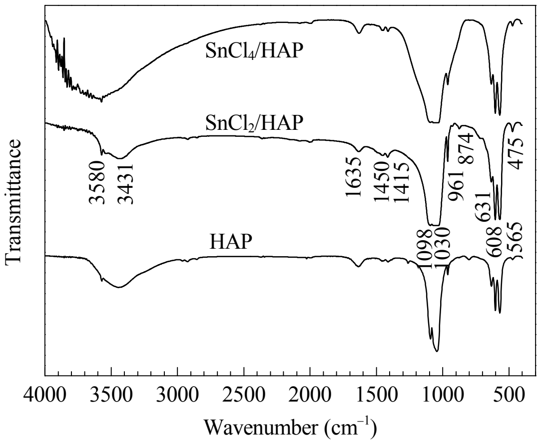

Fig. 2. FT-IR spectra of HAP, $SnCl_2$/HAP, and $SnCl_4$/HAP.

tion of the phosphate group (PO_4^{3-}) and the bending modes of O–P–O were observed at 608, 565, and 475 cm^{-1} [18]. Furthermore, two bands at 1635 and 3431 cm^{-1} indicated that free water was absorbed onto the materials. On the other hand, impurities were also present in the HAP as shown by the bands at 1415 and 1450 cm^{-1}, which were attributed to the asymmetric and symmetric stretching vibration of the carbonate group (CO_3^{2-}). In addition, the band at 874 cm^{-1} indicated that HPO_4^{2-} may also be present in the hydroxyapatite as an impurity.

2.2 Transformation of trioses to *n*-butyl lactate catalyzed by different catalysts

In an earlier study, Hayashi et al. [7] screened a number of Lewis acids for the transformation of trioses in aliphatic alcohols to alkyl lactates. They found that tin chlorides have excellent activities in these reactions. We also carried out a reaction between DHAD and *n*-butanol in the presence of tin chlorides under our reaction conditions (Table 1, entries 1 and 2) and the results were similar to those reported by Hayashi et al. [7]. However, the use of homogenous Lewis acids has some drawbacks such as high environmental toxicity and difficulties in product separation.

To address the issues associated with a homogenous system, we immobilized the Lewis acids onto HAP as it is a good solid material to support Lewis acids. We prepared HAP-supported tin(II) chloride and tin(IV) chloride catalysts and tested their activities for the transformation of DHAD to *n*-butyl lactate. To our surprise, only $SnCl_2$/HAP gave a comparable yield to that obtained with $SnCl_2·2H_2O$ (Table 1, entry 3 vs. entry 1). $SnCl_4$/HAP gave a significantly lower yield (Table 1, entry 4). In addition, when GLA was used as an alternative substrate, a high *n*-butyl lactate yield was obtained in the presence of $SnCl_2$/HAP (Table 1, entry 5). Because the catalysts were composed of the support HAP and the Lewis acids, the reaction was also carried out using HAP instead of $SnCl_2$/HAP. It was clear that HAP had negligible catalytic activity toward the transformation of DHAD (Table 1, entry 6) suggesting that the catalytic center was the Lewis acid metal ions. The tin content in $SnCl_2$/HAP and $SnCl_2$/HAP was determined to be 2.4 wt% and 0.8 wt% by ICP-AES, respectively. The fact that $SnCl_2$/HAP had excellent activity can be attributed to the stronger ability of tin(II) to exchange with calcium(II) in the HAP leading to a stable and active structure. Because tin(IV) is more positive than calcium(II) it is unlikely to remain in the HAP without breaking the charge balance.

Table 1 Transformation of trioses to *n*-butyl lactate catalyzed by Lewis acids and HAP supported Lewis acids

Entry	Substrate	Catalyst	Time (h)	Yield (%)	TOF (h^{-1})
1	DHAD	$SnCl_2·2H_2O$	6	77.3	1.29
2	DHAD	$SnCl_4·5H_2O$	6	88.4	1.47
3	DHAD	$SnCl_2$/HAP	6	73.5	8.41
4	DHAD	$SnCl_4$/HAP	6	20.4	7.00
5	GLA	$SnCl_2$/HAP	6	62.8	7.19
6	DHAD	HAP	12	2.5	—
7	DHAD	$SnCl_2$/HAP (recycled)	10	35.2	2.42

Reaction conditions: 100 mg DHAD, 10 mol% Lewis acid or 80 mg solid catalyst, 8 ml *n*-butanol, 110 ºC.
TOF = *n*(butyl lactate)/(*n*(Sn)·*t*).

One of the main advantages of heterogeneous catalysts over homogeneous catalysts is that the former catalysts can be recovered and reused. Thus, $SnCl_2$/HAP was recovered by filtration, washing with *n*-butanol, and drying overnight at 110 ºC. The recovered catalysts gave a far lower *n*-butyl lactate yield even at a reaction time of 10 h (Table 1, entry 7). The reasons for catalyst deactivation were complex [19]. We speculate that the water and other byproducts that form in the reaction are absorbed onto $SnCl_2$/HAP and result in the deactivation of the catalyst.

2.3 DHAD transformation to lactates catalyzed by $SnCl_2$/HAP under different conditions

Temperature has a profound effect on the reaction rate and yield. We investigated the effect of different temperatures (30, 50, 80, and 110 ºC) on the transformation of DHAD to *n*-butyl lactate (Table 2, entries 1–4). It was obvious that higher temperatures favored the formation of *n*-butyl lactate. When the reaction temperature was 30 ºC, *n*-butyl lactate was obtained in 6.1% yield even after 24 h and a large amount of DHAD remained (data not shown). With an increase in temperature, the yields of *n*-butyl lactate also increased even at shorter reaction times. The maximum yield of 73.5% was obtained at 110 ºC over 6 h.

The effect of catalyst dosage was also investigated (Table 2, entries 4–6). When the catalyst dosage was increased from 20 mg to 80 mg, the yield of *n*-butyl lactate increased remarkably from 14.3% to 73.5%. The higher yield with an increase in catalyst loading is due to the larger amount of available catalytic sites.

Table 2 Transformation of trioses to alkyl lactates catalyzed by $SnCl_2$/HAP under different conditions

Entry	Alkyl alcohol	Catalyst amount (mg)	*t*/ºC	Time (h)	Yield (%)	TOF (h^{-1})
1	*n*-butanol	80	30	24	6.1	0.17
2	*n*-butanol	80	50	12	23.3	1.33
3	*n*-butanol	80	80	12	50.1	2.87
4	*n*-butanol	80	110	6	73.5	8.41
5	*n*-butanol	40	110	8	54.9	4.71
6	*n*-butanol	20	110	8	14.3	1.23
7	methanol	80	70	12	11.3	0.65
8	ethanol	80	80	8	21.8	1.87
9	*i*-propanol	80	85	8	48.8	4.19

Reaction conditions: 100 mg DHAD, 8 ml alcohol. TOF = *n*(alkyl lactate)/(*n*(Sn)·*t*).

Finally, the reactions between DHAD and other alcohols were also studied to explore the scope of this method (Table 2, entries 7–9). Because the reflux temperatures of methanol, ethanol, and *i*-propanol are below 110 ºC at ambient pressure the experiments with these alcohols were carried out at their reflux temperatures. Unlike the homogeneous systems with tin chlorides [7] the alcohols had a substantial influence on the $SnCl_2$/HAP catalyzed transformation of DHAD to alkyl lactates. Higher yields of alkyl lactates were obtained using alcohols with more carbons. One important reason was that the catalytic tin(II) center in the heterogeneous state was less active than that in the homogeneous state. On the other hand, a lower reaction temperature should also contribute to lower yields for those alcohols with less carbon atoms. Similar trends were also observed for the influence of temperature on *n*-butyl lactate formation (vide ante). Moreover, the steric effect should also be considered. The larger steric structures of *i*-propanol and *n*-butanol inhibit the formation of the by-product pyruvaldehyde dibutylacetal by the addition of a second alcohol to the reaction intermediate.

3 Conclusions

In conclusion, a green catalytic system was developed for the transformation of trioses to alkyl lactates and the catalyst was HAP-supported tin(II) chloride. The reaction of DHAD with *n*-butanol upon catalysis with $SnCl_2$/HAP afforded a high product yield of 73.5% over 6 h, which is comparable to that obtained with $SnCl_2$. This novel catalytic system is easy to work-up and the quantity of waste is reduced significantly. The method described herein may be valuable to facilitate the cost-efficient transformation of biomass into lactic-based materials and chemical products.

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