Catalysis Communications 56 (2014) 179–183

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

New heterogeneous Pb oxide catalysts for lactide production from an azeotropic mixture of ethyl lactate and water

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ARTICLE INFO

Article history:
Received 17 June 2014
Received in revised form 8 July 2014
Accepted 17 July 2014
Available online 24 July 2014

Keywords:
Biorefinery
Polylactic acid
Ethyl lactate
Lactide
Heterogeneous catalyst
PbO

ABSTRACT

The heterogeneous PbO, PbO_2 and Pb_3O_4 gave the comparable oligomer yield, oligomer Mw, lactide yield and L-lactide selectivity from ethyl L-lactate with the conventional homogeneous $Sn(Oct)_2$. PbO was also active for ethyl L-lactate containing water as an impurity in distillation process, while $Sn(Oct)_2$ was not active in that condition. No leaching of PbO catalyst was observed during the reaction as well as the recovery process. The recovered catalyst showed no notable loss of activity. By combining this PbO-based catalyst technology with the advanced precipitation process for producing L-ethyl lactate from ammonium L-lactate, L-lactide could be selectively produced in high yield.

1. Introduction

Owing to the rapid depletion of fossil fuel resources in addition to the problems associated with the disposal of plastics, considerable attention is currently being paid to the production of biomass-based materials and biodegradable polymers. Polylactic acid (PLA) is a representative biomass-based polymer, which is expected to be a promising alternative to the petroleum-based polyester terephthalate for the preparation of fibers, coatings, and other plastic materials [1–3].

PLA with a molecular weight (Mw) greater than 100,000 g/mol is produced commercially by the ring-opening polymerization of lactide, a six-membered dimeric cyclic ester of lactic acid [4]. Lactide synthesis is preferentially effected by the prepolymer route, in which lactic acid is first polymerized to an oligomer (Mw < 2000), followed by depolymerization by the backbiting mechanism, over Sn-based catalysts [5–7]. Glucose fermentation is a typical method for lactic acid preparation, but lactic acid formed in this process contains several impurities such as residual sugar, colorings, and other organic acids, which can hinder the final lactide yield and optical purity [8]. The most efficient and economically viable method to obtain polymer-grade lactic acid is the esterification of impure lactic acid with alcohol to produce alkyl lactate, which is then separated easily by distillation [9,10]. Therefore, the direct synthesis of lactide from the distilled alkyl lactate would be more cost-effective than that from impure lactic acid (Fig. 1).

Recently, we attempted the direct synthesis of lactide from alkyl lactate without conversion to lactic acid. Among the various catalysts assessed, $Sn(Oct)_2$ was found to be the most effective for both the oligomerization and deoligomerization reactions [11]. A series of Al, Ti, Zn and Zr compounds were also evaluated as intramolecular transesterification catalysts for producing lactide from lactic acid oligomer [12]. Among them, Zn and Zr-based compounds showed the comparable lactide yield and optical selectivity with $Sn(Oct)_2$. $SnCl_4$ was also studied for production of lactide from butyl lactate [13]. However, most studies have been focused on the homogeneous catalysts that can activate lactic acid or alkyl lactate.

To overcome the aforementioned limitations, we have investigated new heterogeneous catalytic systems for producing lactide from ethyl lactate. To the best of our knowledge, this kind of catalysis has not been reported yet. We also produced lactide using this catalyst from the ethyl lactate distillate containing water as an impurity, which solution was derived from the fermentation broth of ammonium lactate. So, we believe that the present study would be helpful for reducing the cost of the lactide production process as well as for understanding the catalysis in the oligomerization of ethyl lactate.

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http://dx.doi.org/10.1016/j.catcom.2014.07.026
1566-7367/

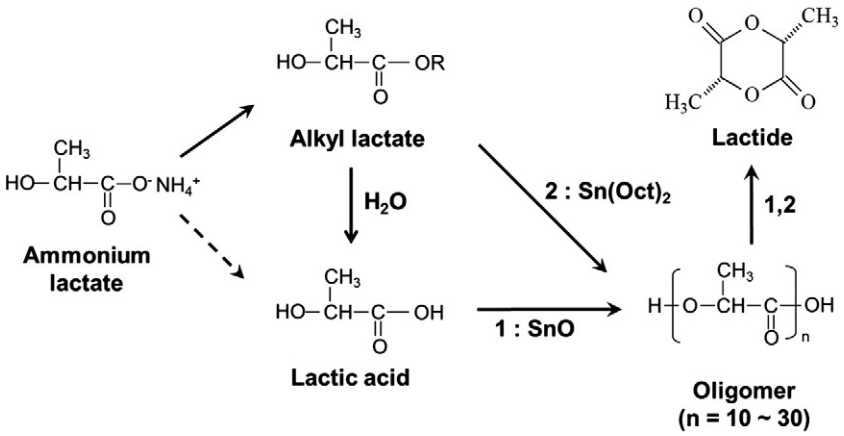

Fig. 1. Reaction pathways for lactide production from ammonium lactate. 1. Indirect oligomerization from alkyl lactate via lactic acid using SnO (conventional process); 2. Direct oligomerization of alkyl lactate using $Sn(Oct)_2$.

2. Experimental

2.1. Materials

SnO (99%, Aldrich), MgO (98%, Aldrich), Al_2O_3 (98%, Aldrich), $Sn(Oct)_2$ (97%, Alfa Aesar), PbO (99.9%, Aldrich), PbO_2 (99.9%, J.T. Baker) and $Pb(NO_3)_2$ (99.9%, Aldrich) were used as the catalysts, without further treatment. Lactic acid (89%, Aldrich) and ethyl lactate (99%, Alfa Aesar) and L-lactide (99.9%, Purac) were used as feedstocks, without further treatment. Triethylene glycol dimethyl ether (99.9%, Alfa Aesar) was used as a standard compound for the quantitative analysis of each component in the gas chromatography analysis.

2.2. Methods

2.2.1. Oligomer synthesis

A mixture of 50 g of ethyl lactate and 0.5 g of catalyst was oligomerized in a 250 ml three-necked round bottom flask equipped with a magnetic stirrer, a temperature controller, and a distillation condenser. The reaction was carried out at 160 °C and 720 Torr for 7 h under nitrogen atmosphere (20 ml/min). During the reaction, ethanol was removed continuously from the reactor. After this time, the pressure was decreased to 10 Torr, following which the reaction continued for 2 h so that the unreacted ethyl lactate and ethanol could be distilled off completely from the produced oligomer.

2.2.2. Lactide synthesis from oligomer

The oligomer synthesized from ethyl lactate was transferred to a three-necked 50 ml round bottom flask. The flask was equipped with a magnetic stirrer, a temperature controller, and a distillation column at 100 °C, which was connected to a collector in an ice bath. The reaction was carried out under nitrogen atmosphere at 180 °C and 10 Torr for 5 h.

2.3. Analysis

Concentrations of ethanol, ethyl lactate, and lactide were analyzed using a gas chromatograph (DONAM DS6200) equipped with flame ionization detector (FID) and a Cyclosil B column (30 m × 0.320 mm). The column temperature was increased from 70 °C to 250 °C, with a ramping rate of 15 °C/min. The injector and FID temperatures were maintained at 270 °C and 280 °C, respectively. For quantification of the meso- and L-lactide from the GC chromatogram, the calibration factor of L-lactide was used, because L-lactide is commercially available. The molecular weight of the produced oligomer was analyzed using a gel permeation chromatograph equipped with a refractive index detector (RID-10A, Shimadzu) and Styragel HR1 column (7.8 × 300 mm, Waters) using tetrahydrofuran (THF) as the mobile phase with a flow rate of 1 ml/min. Polystyrenes of known molecular weights, i.e., 580, 780, 1200, 1650, 2340, 3950, 6180, and 10,200 (Shodex® standard, SL-105), were used as calibration standards for producing a universal calibration curve ($K = 1.67 \times 10^{-4}$, $a = 0.692$ in the $[\eta] = KM^a$ Mark–Houwink equation).

3. Results and discussion

We first compared the catalytic activity of various heterogeneous catalysts with that of homogeneous $Sn(Oct)_2$ in the oligomerization of pure ethyl L-lactate without any water impurity (Table 1). In our previous study, we found that the lactide yield and optical purity over $Sn(Oct)_2$ were highly dependent on the oligomer Mw, which was controlled by the reaction temperature and time [11]. Thus, the oligomerization condition was selected for obtaining the oligomer Mw of around 1350, which resulted in the highest lactide yield. When $Sn(Oct)_2$ was used as the oligomerization catalyst for the ethyl L-lactate feed, an oligomer with Mw of 1380 was obtained in 84% yield, while no oligomer was formed when using SnO as the catalyst. Both the basic MgO and the acidic Al_2O_3 gave a negligible oligomer yield after 13 h of reaction time. All the Pb-based oxides tested gave oligomer yields higher than 80% and an oligomer Mw of around 1350, similar to the results obtained with $Sn(Oct)_2$. The loss in the oligomer yield was due to vaporization of

Table 1
Screening of various catalysts for L-lactide synthesis from commercial ethyl L-lactate via the prepolymer route.

Catalyst	Oligomer yield[a] (%)	Oligomer Mw (g/mol)	Lactide yield[b] (%)	L-Lactide sel[c] (%)
SnO	0	–	–	–
MgO	0	–	–	–
Al_2O_3	0	–	–	–
$Sn(Oct)_2$	84	1380	82	98
PbO	85	1360	77	97
PbO[d]	83	1361	76	95
PbO_2	81	1350	73	89
Pb_3O_4	85	1370	78	97
$Pb(NO_3)_2$	83	1340	76	95

[a] Oligomer yield (%) = [oligomer obtained (g) / theoretical amount of oligomer (30.5 g)] × 100.
[b] Lactide yield (%) = [oligomer disappeared (g) / oligomer charged (3 g)] × 100.
[c] L-Lactide sel. (%) = [L-lactide (g) / crude lactide (g)] × 100.
[d] The recovered PbO.