

# Environmentally Friendly Heterogeneously Catalyzed Production of Lactide: 2nd Generation of PLA Process

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## Abstract:

A 2nd generation polylactic acid (PLA) process was developed in an environmentally friendly procedure by direct heterogeneously catalyzed synthesis of L-lactide (L-LD) from aqueous 90% lactic acid (LA) to avoid the current commercially applied prepolymerisation and depolymerisation as well as the use of hazardous chemicals such as H<sub>2</sub>SO<sub>4</sub> and homogeneous Sn containing catalysts. Various heterogeneous catalysts such as zeolites,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> etc. were tested in a fixed bed reactor in the gas phase. The acidity of the catalysts plays an important role. The L-LD selectivity can be improved by high temperature and reduced pressure achieving up to 99 %.

**Keywords:** PLA, Lactide from aqueous lactic acid, heterogeneous catalysts, gas phase.

## 1. Introduction

The reduction of carbon dioxide emission and the substitution of crude oil e.g. in the polymer production is a great challenge in the 21st century. One of these topics is in the field of biodegradable polymers starting from renewable resources by using the carbon framework of nature. The aliphatic polyester polylactic acid (PLA) has become the most promising biodegradable polymer in recent years. PLA is well known for biomedical applications over years [1] and there is a highly increasing demand for its use as a thermoplastic polymer [1-4]. PLA is a practical alternative to the commonly used plastics based on petrochemicals such as polyterephthalate. Moreover the biocompatibility by its degradation into CO<sub>2</sub> and water, the highly versatile properties and the low toxicity towards humans are even of more advantageous.

In collaboration with the engineering company Uhde Inventa Fischer, Switzerland/Germany [5] a 2nd generation PLA process was developed by direct synthesis of L-lactide (L-LD) from aqueous commercially available 90 % lactic acid (LA) in the presence of a heterogeneous catalyst to avoid the current commercially used intermediate prepolymerisation and depolymerisation steps as well as the application of hazardous chemicals such as H<sub>2</sub>SO<sub>4</sub> and homogeneous Sn containing catalysts as it is illustrated in figure 1.

## 2. Experimental

Experiments were conducted in a continuous plug flow fixed bed reactor under gas phase conditions. In the presence of various heterogeneous catalyst such as zeolites [6],  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, AlPO<sub>4</sub> etc. the influence of pressure, temperature, residence time and water content of the starting material was investigated. The catalysts were characterized by inductively coupled plasma atomic emission spectroscopy (ICP AES), X-ray powder diffraction (XRD), nitrogen adsorption isotherms (BET), temperature programmed desorption of ammonia (NH<sub>3</sub> TPD) and pyridine Fourier transformed infrared spectroscopy (Py FTIR).

## 3. Results and discussion

The cheap amorphous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with its simple structure was chosen for the parameter optimization. It was observed that conversion and selectivity increase in the temperature range 90°C to 270°C. Under subatmospheric pressure of 20 mbar and WHSH = 2,3 h<sup>-1</sup> the conversion rises from 9 % (90 °C) to about 20% (240°C) because of the accelerated kinetic. In addition the selectivity increases from 1.4 % at 90 °C to 98.9 % at 240 °C. The results prove the expected correlation between the catalyst acidity and the LA conversion. Moreover the acidity has an impact on the LD selectivity.

Conversion and selectivity are also strongly influenced by the pressure. As illustrated in figure 2, the selectivity is increased from about 15% at 1000 mbar to about 50% at 0,5 mbar. In contrast the conversion declines from 65% to 25%. The temperature as well as the pressure influence demonstrate that the desorption of the lactide from the catalyst surface must be facilitated to achieve high selectivity.

The aqueous 90% LA consists of different amounts of monomer ( $L_1A$ ) and oligomers such as linear dimer lactoyllactic acid ( $L_2A$ ) which is assumed to be the starting material of LD. Changing the starting material (90% LA) to highly concentrated oligomer rich 97% LA with a minor amount of water leads to a slight selectivity decrease but increased the conversion from 15 to 53.6%.

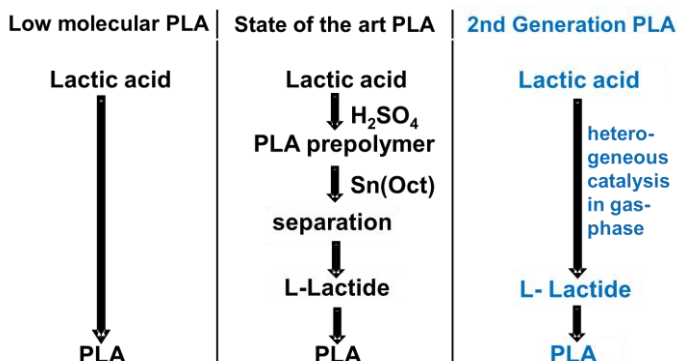


Figure 1. PLA production routes

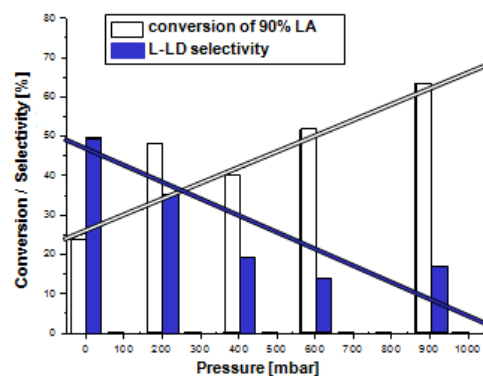


Figure 2. Pressure dependence over  $\gamma\text{-Al}_2\text{O}_3$  at 180°C

The activities of three H ZSM 5 zeolites were strongly connected to their module. The conversion decreases with an increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio due to the less acidic centers from 54,0% (M 25) over 52,3% (M 300) to 33,7% (M 1000). The highest selectivity achieved over these pentasil zeolites was 71,7% using the H-ZSM-5 with a modul of 300. The H ZSM-5 with the lower ratio of 25 has too many acidic sites with strong (500 °C  $\text{NH}_3$  desorption) acidic centers as well as a high number of Brønsted acid sites. These properties lead to low selectivity due to cracking reactions. The formation of acrylic acid, acetone, acetaldehyde, formaldehyde and carbon dioxide could be observed in minor amounts.

Furthermore it was found that

- High acidity and high number of acidic sites yield by-products
- Materials with Lewis acid sites favor the desired reaction
- Materials with Bronsted acid sites favor cracking reactions
- The higher the BET surface, the higher the conversion
- High space time yield due to short residence time in gas phase

#### 4. Conclusions

In this study a new pathway for 2nd generation PLA, a very valuable polymer based on the renewable feedstock lactic acid, was found. Thereby, L-lactide was produced directly from commercially available aqueous LA. By this new procedure the prepolymerisation and depolymerisation steps in presence of the homogeneous catalysts  $\text{H}_2\text{SO}_4$  and Sn compounds could be replaced by a single heterogeneously catalysed step. It is not only a shorter and less investment intensive process procedure but also an environmentally benign route because the disadvantageous of homogenous catalysis can be avoided by the application of a heterogeneous catalyst.

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