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TOPIC(s) : Renewable carbon / Catalytic systems

From waste water to chemical building blocks

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PURPOSE OF THE ABSTRACT

Waste water streams from the agro-food chemistry contain volatile fatty acids (VFAs) which are regarded as waste. The valorization of these VFAs is currently cumbersome because of their low concentration.

An elegant and promising way to concentrate the organic fraction is by using bacteria which can convert the volatile fatty acids into polyhydroxybutyrate (PHB). This PHB can potentially be used as plastic though its properties still need to be optimized. The off-spec PHBs can be used as a source for the production of biobased methylacrylate which is the topic of our investigation. For that the PHB first needs to be converted to methyl crotonate by a transesterification followed by a metathesis using ethylene to make propylene and the desired methyl acrylate (Figure 1).

In this presentation we focus on two issues i.e. 1) the optimization of the first step (PHB to MC) and 2) the development of a heterogeneous catalyst for metathesis e.g., the second step.

First we address a crucial step in this process, the conversion of PHB to methyl crotonate (MC). We will show that PHB can be directly converted into methyl crotonate (MC) at elevated temperatures in methanol without the use of an additional catalyst and below supercritical conditions. Using a temperature profile over the reactor, a system was created with methanol refluxing in the reactor head, creating optimal conditions for the conversion of PHB to MC. At 200 °C, 18 bar and 6 hours, PHB was fully converted with a 70% selectivity towards crotonates. Based on our mechanistic study we propose that the reaction follows a thermolysis pathway to crotonic acid (CA), followed by a catalyst free esterification to form MC. The rate determining step (RDS) is dependent on the reaction pressure and changes at 18 bar. Below 18 bar, esterification of CA to MC is the RDS, while above 18 bar, the thermal conversion of PHB to CA is the RDS [1].

The metathesis step can be performed by homogeneous Grubbs catalysts [2]. However that implies a cumbersome separation of the catalyst after the reaction. Therefore, that step would be preferably carried out by a heterogeneous catalyst. Here we will report on a simple, one step mechanochemical procedure to immobilise ruthenium based metathesis catalysts inside metal organic frameworks (MOFs). Using a solution based "bottle around the ship" method did not result in immobilisation of Hoveyda-Grubbs 2nd generation catalyst (HG2) in MIL-101-NH₂(Al). The successful immobilisation was achieved by grinding MIL-101-NH₂(Al) with Hoveyda-Grubbs 2nd generation or Zhan catalyst. Both MIL-101 based catalysts show metathesis activity. The highest activity in the metathesis of diethyl diallylmalonate was obtained using HG2@MIL-101-NH₂(Al), which showed an initial conversion of 98% and shows activity over 8 consecutive runs. The mechanochemical preparation of the immobilised catalysts modified the structure of the MOF and converted the MIL-101 structure partially to a MIL-53 structure. The Hoveyda-Grubbs entrapped in the MIL-101 part is responsible for the observed

catalytic activity. This is the first report of a mechanochemical immobilisation of an active catalyst in a MOF and given the wide variety of catalysts and known MOF structures available, a new immobilisation technique for homogeneous catalysts is suggested [3]. The activity of this catalyst for the metathesis of methylcrotonate still has to be investigated.

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2. J. Spekrijse, J. Le Nôtre, J. Van Haveren, E.L. Scott, J.P.M. Sanders, *Green Chemistry*, 14, 2012, 2747
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FIGURES

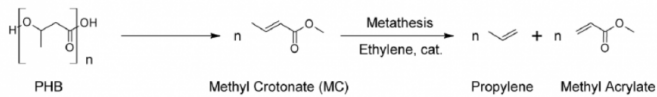


FIGURE 1

Figure 1
Conversion of PHB to propylene and methyl acrylate (MA) via the formation of methyl crotonate (MC).

FIGURE 2

KEYWORDS

volatile fatty acid | metathesis | catalysis | waste water

BIBLIOGRAPHY