An MOF immobilized Hoveda-Grubbs metathesis catalyst for the production of methyl acrylate from waste water

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The successful synthesis and characterization of an immobilized Hoveda-Grubbs metathesis catalyst on a MOF support will be discussed. This catalyst is essential to design an effective catalytic process in which volatile fatty acids present in waste water are converted to methyl acrylate, a chemical building block.

1. Waste water as feedstock

Waste water streams from the agro-food chemistry and the paper and pulp industry 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. Alternatively, the PHB 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).

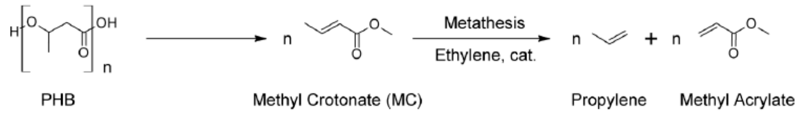

Figure 1: Conversion of PHB to propylene and methyl acrylate (MA) via the formation of methyl crotonate (MC).

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.

2. Results and discussion

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 immobilize ruthenium based metathesis catalysts inside metal organic frameworks (MOFs). Using a solution based 'bottle around the ship' method did not result in immobilization of Hoveyda-Grubbs 2nd generation catalyst (HG2) in MIL-101-NH2(Al). The successful immobilization 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 immobilized 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 immobilization of an active catalyst in a MOF and given the wide variety of catalysts and known MOF structures available, a new immobilization technique for homogeneous catalysts is suggested [3]. The activity of this catalyst for the metathesis of methylcrotonate is currently under investigateion and will be presented at the conference.

3. Conclusions

We report here on the successful preparation of an immobilized Hoveda-Grubbs metathesis catalyst. That catalyst is active for methathesis and thus can (potentially) perform methathesis of methylcrontonate to form methyl acrylate from form metacrylate from methyl crotonate. The methyl crontonate in turn can be made from PHB which can be obtained from waste water. Thus this research contributes to a more sustainable use of feedstocks. We estimated that upto 29 million ton of polyhydroxy alkanoates (PHB being one of them) could be available per year as waste stream from paper and pulp processing. That would then be enough to cover upto 10% of the world's plastic consumption using only carbon from pulp and paper wastewater streams. These streams are large enough to become interesting as a feedstock for bulk chemicals.

References

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