

A NOVEL PROCESS TO PRODUCE ADIPIC ACID BY CATALYTIC DEHYDROXYLATION OF BIOMASS- DERIVED MUCIC ACID

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Abstract The heterogeneously catalyzed dehydroxylation of mucic acid to produce adipic acid, a highly relevant polymer precursor, was investigated. The use of methanol as solvent is particularly important since it not only acts as reducing agent but also protects the carboxylic acid functionality by esterification. Re/C was found a well-suited catalyst for this reaction and not only showed high activity but was also reusable with suitable reactivation procedure. Under optimized reaction conditions, 98 % of dehydroxylated products could be obtained from mucic acid. Moreover, combining Re/C with a suitable hydrogenation catalyst (e.g. Pd/C) and performing the reaction under H₂ atmosphere steers the reaction towards adipic acid ester. Therefore, it could be shown that adipic acid derivatives are available from biomass-accessible mucic by this novel and renewable approach.

Keywords:
adipic acid,
biomass,
dehydroxylation,
heterogeneous
catalysis,
rhenium

1 Introduction

The production of industrially demanded and value added chemicals from renewable resources such as lignocellulosic biomass is an extensively researched challenge. Adipic acid is a dicarboxylic acid and one of the most important polymer precursors, in particular for the polyamide industry and sustainable processes are sought for its production. A newly developed strategy to produce adipic acid from lignocellulosic biomass is presented here. Lignocellulose-derived sugars, possessing six carbon atoms like adipic acid, are a promising starting point. They can be catalytically oxidized into aldaric acids (e.g. mucic acid). Subsequently, the key reaction step is the selective catalytic dehydroxylation of mucic acid into adipic acid (Fig. 1).

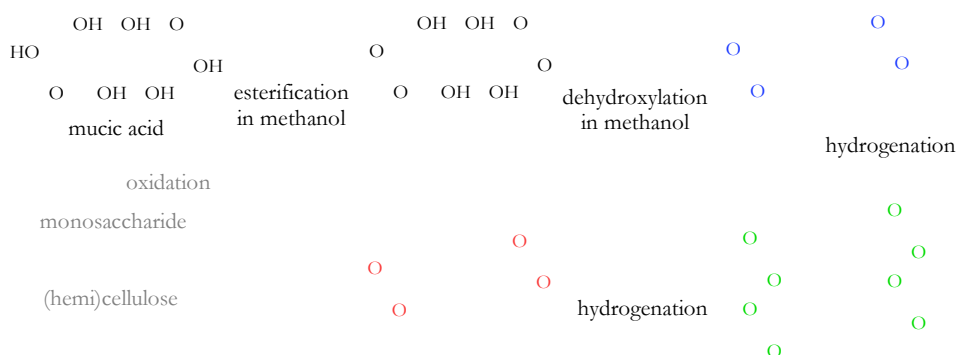


Figure 1: Scheme of the renewable production of adipic acid via selective catalytic dehydroxylation of mucic acid.

Source: own.

Previously, Re-based homogeneous catalysts (e.g. CH_3ReO_3 , HReO_4 or KReO_4) and alcohol solvents have successfully been used for this reaction (Shiramizu & Toste, 2012, 2013; Li *et al.*, 2014; Larson *et al.*, 2017). Following the characteristic deoxydehydration route, pairs of vicinal hydroxyl groups are removed and a double bond is formed. Further hydrogenation then yields adipic acid.

To enable catalyst recycling, the use of solid catalyst is advantageous. Examples of heterogeneously catalyzed processes have been reported for similar reactants (Denning *et al.*, 2013; Ota *et al.*, 2015, 2016; Sandbrink *et al.*, 2016; Tazawa *et al.*, 2016; Nakagawa *et al.*, 2018; Sharkey *et al.*, 2018; Xi *et al.*, 2018). Only very recently, this was shown to be possible also for the case of adipic acid (Hočevár *et al.*, 2021), which

is presented here. The initial study, which also led to a patent application (Hočevár *et al.*, 2019), was soon confirmed by additional studies (Deng *et al.*, 2021; Jang *et al.*, 2021).

Here, we present insights into how the Re-catalyzed dehydroxylation of mucic acid is influenced by various process parameters, including the type of Re catalyst, the role of the solvent, the influence of the presence of H₂ gas and/or hydrogenation co-catalysts as well as the effect of reaction temperature.

2 Materials and Methods

Throughout the study, commercial catalysts were used: Re/C, Re/SiO₂ and Re/Al₂O₃ (each 5 wt.-% Re loading, powders; Riogen, USA) as well as Pd/C (5 wt.-% Pd loading, powder; Sigma Aldrich, USA). Prior to catalytic experiments, the catalyst(s) were reduced in a flow of H₂ (200 mL min⁻¹) at 400 °C for 3 h.

Catalytic experiments were conducted in stirred and heated autoclave reactors (Amar Equipment Pvt. Ltd., India). The reactor was loaded with mucic acid (97 %, Sigma Aldrich, USA), methanol and the catalyst(s), pressurized with nitrogen or hydrogen, heated up to the desired reaction temperature and kept for typically 72 hours. Different commercially available catalysts (Re/C, Re/SiO₂, Re/Al₂O₃) were tested. While there was always a solid Re catalyst present (typically Re/C), in some experiments Pd/C was added as a co-catalyst. Moreover, the reaction conditions were varied, namely the reaction temperature in the range of 120-175 °C and the composition of the gas phase (nitrogen or hydrogen) prior to the catalytic experiments.

The final reaction mixtures were filtered and analyzed by gas chromatography-mass spectrometry (GC-MS). A GCMS-QP 2010 Ultra (Shimadzu, Japan) was used equipped with a nonpolar column (Zebtron™ ZB-5MSi, 60 m, diameter 0.25 mm, film thickness 0.25 μm). Compounds were identified by mass spectrometry and quantified based on external calibrations using the FID signal.

3 Results and Discussion

3.1 Dehydroxylation over Re/C

First, mucic acid dehydroxylation was investigated over a commercially available Re/C catalyst under inert N₂ atmosphere. These results are shown in Fig. 2 (left columns). Since there is no H₂ or other additional reducing agents are, methanol serves as the reducing agent. Moreover, methanol readily forms esters with mucic acid under reaction conditions. Consequently, all detected products are dimethyl esters of the respective dicarboxylic acids.

The dehydroxylation reaction already proceeds at 120 °C, where ca. 93 % of dehydroxylated products were found after 72 hours reaction over Re/C. The main product is the twice-unsaturated analogue of dimethyl adipate (62 %), which is the direct product of full deoxydehydration of mucic acid dimethyl ester, i.e. where all four vicinal hydroxyl groups are removed. Moreover, a considerable amount of this intermediate product was partially hydrogenated to a group of isomers with one double bond (28 % yield) and some even fully hydrogenated to dimethyl adipate.

Increasing temperature to 175 °C lead to a slight increase in product yield (98 % of dehydroxylated products in total). More importantly, a shift in selectivity is apparent and only traces of the primary, twice-unsaturated product were found in the product mixture. While mostly partially hydrogenated products were formed, there was also a substantial amount of dimethyl adipate (31 %). It was confirmed by gas chromatography that in both cases under initially inert atmosphere the hydrogenation activity is related to H₂ formation by methanol decomposition.

When the initial gas phase composition in the reactor was changed from inert N₂ to H₂, hydrogenation activity is similarly enhanced (Fig. 2, right column). While under N₂ atmosphere at 120 °C only around 30 % yield of hydrogenated products was formed over Re/C, under H₂ pressure of initially 10 bar all detected products were either partially (58 % yield) or fully hydrogenated (25 %). These experiments prove that under suitable reaction conditions the combined dehydroxylation and subsequent hydrogenation of mucic acid to adipic acid derivatives is feasible. Moreover, product selectivity can be steered to a certain degree by the choice of the reaction conditions.

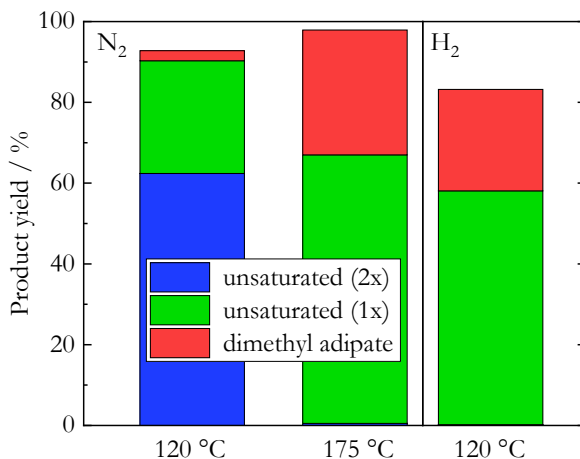


Figure 2: Product yields after 72 h from mucic acid dehydroxylation in methanol over Re/C under different reaction conditions.

Source: own.

3.2 Influence of catalyst support material

Besides Re/C, two other commercially available Re-based catalysts were studied regarding their activity in mucic acid dehydroxylation (Fig. 3). It should be noted that, unlike for the previously discussed results, the catalysts were used as-obtained without reduction before the catalytic experiments. This explains the considerably lower hydrogenation activity over Re/C at 120 °C. Comparing Re/C with Re/SiO₂ and Re/Al₂O₃ it is apparent that the latter two are by a factor of ca. 10 less active in catalyzing the dehydroxylation of mucic acid. Moreover, Re/Al₂O₃ was found to rather catalyze undesired decarboxylation and hydrodeoxygenation reactions resulting in the formation of short-chain as well as cyclization products. Overall, Re/C is exceptionally suited as a catalyst for the dehydroxylation reaction.

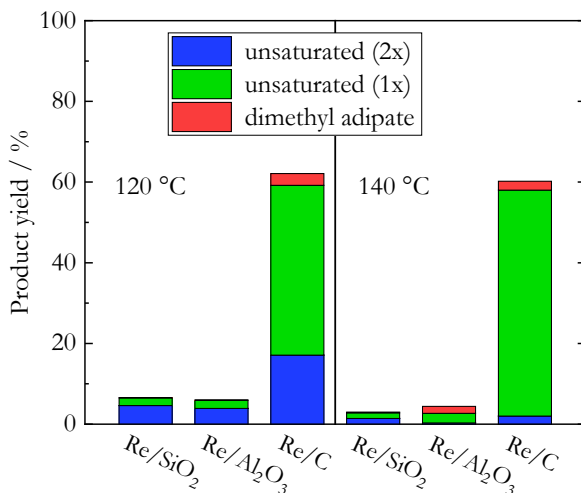


Figure 3: Product yields after 72 h from mucic acid dehydroxylation in methanol over different solid Re catalysts under H₂ atmosphere at different temperatures.

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2.3 Influence of a hydrogenation co-catalyst

The formation of the twice-unsaturated dehydroxylation product proceeds considerably more facile over Re/C than the subsequent hydrogenation reactions, as was shown in section 2.1. Therefore, the addition of a hydrogenation co-catalyst is one option to increase selectivity for hydrogenated products, in particular dimethyl adipate, without resorting to harsher reaction conditions. The results in Fig. 4 clearly show that the presence of additional Pd/C (molar ratios $n_{\text{Pd}} n_{\text{Re}}^{-1} = 1:6$ or $1:4$) shifts product selectivity almost completely towards fully hydrogenated dimethyl adipate. Yields of up to 60 % were obtained with only ca. 3 % of unsaturated products. Therefore, the use of Pd/C as a hydrogenation co-catalyst facilitates hydrogenation and enables the efficient one-pot dehydroxylation and hydrogenation of mucic acid into adipic acid.

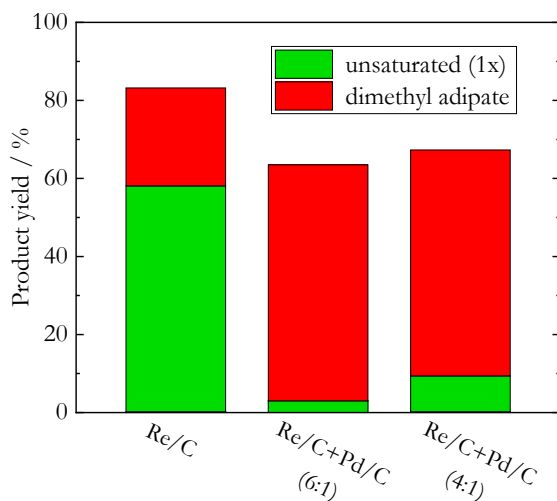


Figure 4: Product yields after 72 h from mucic acid dehydroxylation in methanol over Re/C with or without co-catalyst Pd/C under H₂ atmosphere at 120 °C.

Source: own.

4 Conclusions

The use of solid Re-based catalysts for the dehydroxylation of mucic acid in combination with subsequent hydrogenation to adipic acid was investigated. One important aspect is the use of methanol as a solvent that also protects the carboxylic groups by esterification and can serve as a reducing agent and a H₂ source. Re/C was shown to be a highly efficient catalyst for the heterogeneously catalyzed dehydroxylation reaction, in particular compared to other solid Re catalysts. Moreover, the reaction conditions and the presence or absence of an additional Pd/C hydrogenation catalyst are influential parameters that allow to steer product selectivity of the process. Under N₂ atmosphere, methanol serves as reducing agent and mostly the direct dehydroxylation product, which contains two double bonds, is obtained over Re/C at 120 °C in yields of up to 62 %. Overall, the yield of dehydroxylated product was up to 98 %. This includes also partially hydrogenated as well as fully hydrogenated products, the latter being the target product dimethyl adipate. These subsequent hydrogenation reactions are enhanced by higher reaction temperature, H₂ atmosphere as well as the use of a Pd/C co-catalyst. Adjusting the reaction conditions in this manner allows for selective production of dimethyl adipate from biomass-derived mucic acid. Due to the heterogeneous catalytic nature

of the process, which enables catalyst recycling, as well as the non-toxic and renewable reactants the presented process is a considerable improvement compared to conventional processes for the production of adipic acid.

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