# The influence of Re-based catalyst and reaction conditions on the kinetics of galactaric acid conversion into adipic acid (esters)

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***Highlights***

- Correlating β-O-4 bond cleavage for efficient lignin depolymerization.
- Higher temperature increases monomer yield and suppresses cross-linking reactions.
- Structural complexity challenges complete prediction of lignin behavior.
- Insights from the lignin model compound support efficient lignin depolymerization.

## 1. Introduction

In this conference contribution, we will report on our developed sustainable catalytic system where adipic acid is produced from bio-based aldaric acids. Adipic acid is the most important dicarboxylic acid with over $7 billion market. Currently it is being produced at low conversions from fossil sources (crude-oil based cyclohexane) using corrosive nitric acid and emitting $NO_x$. A sustainable production route from biobased lignocellulosic biomass has previously been proposed, but as of yet has only been achieved with homogenous catalysts and with low yields.

In our work we demonstrate for the first time a selective (93%) dehydroxylation of aldaric acids over a heterogeneous catalyst and without using gaseous $H_2$ or corrosive HBr reactants. The main findings are that it is possible to use a heterogeneous catalyst for selective dehydroxylation of aldaric acids, facilitating continuous operation (fixed-bed reactor), separation of the product and regeneration of the catalyst.

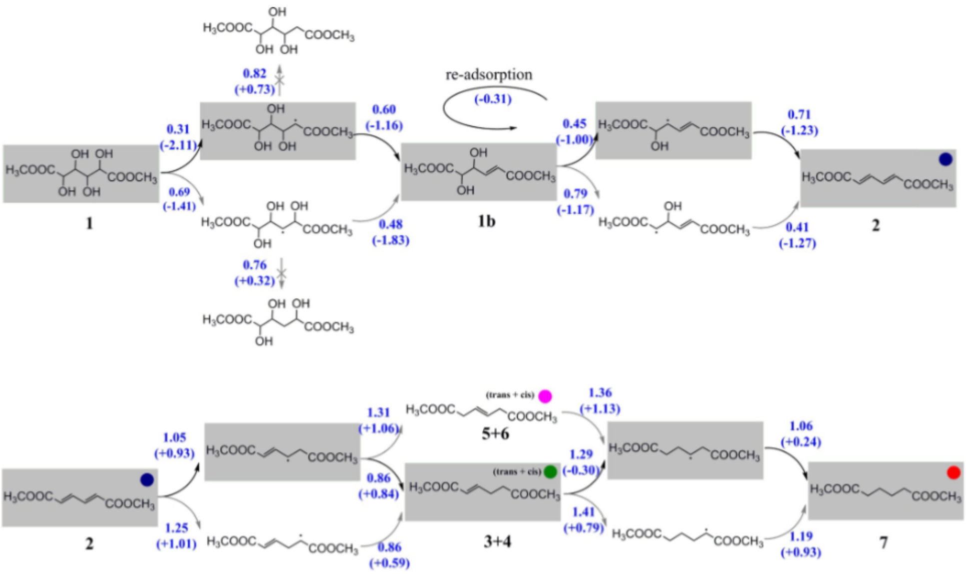


**Figure** 1 Mechanism of dehydroxylation of mucic or glucaric acid and hydrogenation over Re/C. [2]

Re is the only viable catalytically-active metal and is only effective on neutral carbon support (among more than 20 other combinations tested). We demonstrated that no $H_2$ is required for dehydroxylation and subsequent hydrogenation, while any short-chain alcohol can serve as H-donor solvent. For the first time no corrosive solvents are required, in contrast to the process patented by Rennovia.[1] High yields and high selectivity of dehydroxylation products was obtained even at 120 °C. Detailed characterization and extensive DFT studies revealed how metallic Re sequentially removes OH groups and preferentially uses methanol as a hydrogen source. [2]

## 2. Methods

Catalytic tests performed in stirred, heated autoclave reactors using mucic acid in methanol and solid catalysts (Re/C, Pd/C at 5 wt.-% metal loading, or bimetallic catalysts made via incipient wetness impregnation). All catalysts were pre-reduced under $H_2$ at 400°C. Tests were conducted at 120-175°C under N2 or H2, with 72 hour reactions and liquid samples analyzed by GC-MS.

## 3. Results and discussion

The selective dehydroxylation of mucic acid in yields > 90 % is possible at temperatures as low as 120 °C and without $H_2$ gas over monometallic Re/C (Figure 1-left). Methanol is both the reducing agent and protects the carboxyl functionality by esterification.

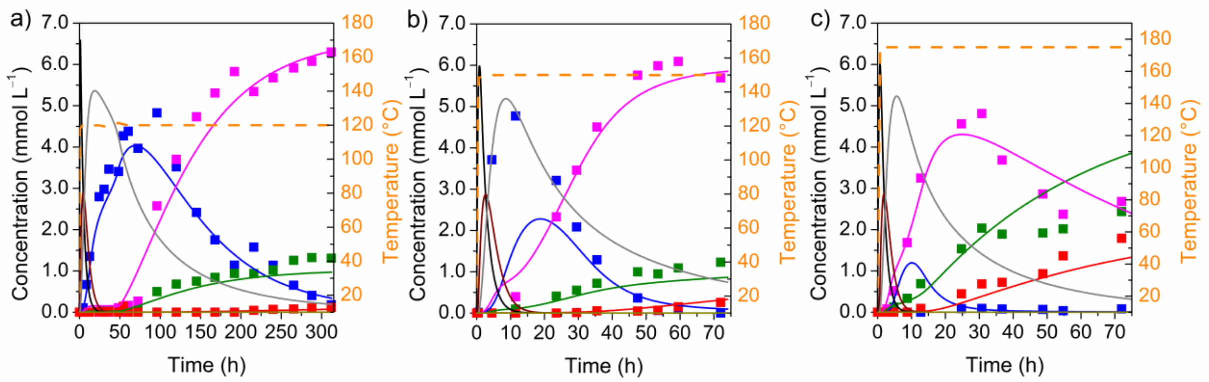


**Figure 2.** Concentration profiles of intermediate and products during dehydroxylation of mucic acid in methanol over a Re/C catalyst a) in nitrogen at 120 °C, b) 150 °C nad c) 175 °C. Color legend as in Figure 1.

## 4. Conclusions

Deoxydehydration and hydrogenation of mucic acid derived from biomass can selectively produce adipates using rhenium-based catalysts. The reaction can be slow with the main product being dimethyl muconate. $H_2$ addition and increased temperature improve hydrogenation, while adding a hydrogenation catalyst like Pd/C can increase selectivity for dimethyl adipate up to 58%. Bimetallic catalysts of Re with noble metals (Pt and Pd) enhance activity and alter product distribution, with Pd/Re/C yielding 35% dimethyl adipate (Figure 1-right). Optimizing Pd loading and reaction time can achieve yields of up to 90%. Ni modification on the other hand is not suitable. To conclude, $H_2$-free production of dimethyl adipate with yields over 90% can be achieved through control of catalyst choice and reaction conditions.


## Acknowledgments

This work was funded by the Slovenian Research Agency (ARRS) under core funding P2-0152 and project number J1-3020. Furthermore, funding from the Young Researchers Program from ARRS is acknowledged.


## References


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## Keywords

Re/C, kinetic modeling, dehydroxylation, adipic acid.