ISGC 2022

N°272 / OC

TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Single-Atom Ru in zeolites for producing terephthalates from bio-based muconic acid

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PURPOSE OF THE ABSTRACT

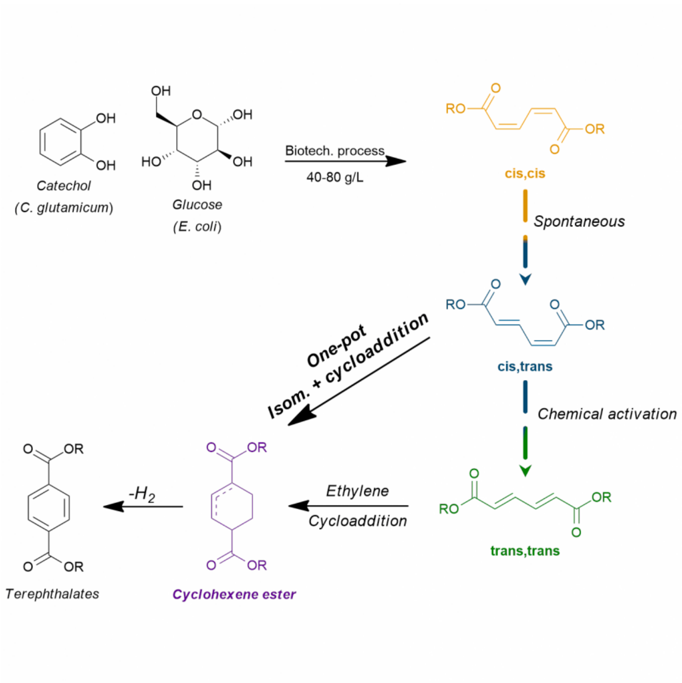
Muconic acid (MA) is a high value-added product that can be present in 3 isomeric forms: cis,cis (cc), cis,trans (ct), and trans,trans (tt). The high growth in its market size (7-10% annually) is mainly due to its potential as a starting material for the synthesis of value-added derivatives such as adipic and terephthalic acids, via hydrogenation (any of the isomers) and Diels-Alder cyclo-addition (only tt isomer), respectively.

Recently, biotechnological routes to produce ccMA and ctMA from biomass-derivatives are developed, showing satisfying yields. However, an additional isomerization step is still required to obtain the value-added trans,trans-isomer, needed for terephthalates production. Existing isomerization processes rely on the use of Pd/C catalyst or sacrificial iodine radicals under UV irradiation.

However, the expensive cost of Pd and the limitations in MA concentration in the iodine system have forced the development of new pathways that can combine high productivity with moderate reaction conditions.

In this context, our work focuses on developing single-atom Ru supported on low-cost zeolite catalysts that can produce tt-mucontaes from the ct-isomer in ethanol as a solvent. Low metal loading (0.2%) and suitable solvents are used to ensure a selective isomerization (>95%) with high turnovers (>2500 mol/mol) and extremely high productivity (around 85 g/L.h). Kinetic and thermodynamic studies were performed to estimate the order and the activation energy (101 kJ/mol) of the isomerization. In addition, deep characterization was performed to prove the single atom distribution of Ru on the zeolite. Mechanistic studies were elaborated using EXAFS, XPS, and FT-IR spectroscopy to reveal the active form of Ru and investigate the pathways leading to the deactivation of the catalyst. From these findings, regeneration attempts were performed to recover the loss in activity observed after several cycles. Finally, one-pot isomerization/Diels-Alder was conducted to produce the terephthalic intermediate (cyclo-hexene diester) at a total conversion of ct-muconates. The one-pot reaction was also found to be applicable with various muconic esters, namely: dimethyl, diethyl, and dibutyl esters leading to the production of different terephthalate esters.

FIGURES



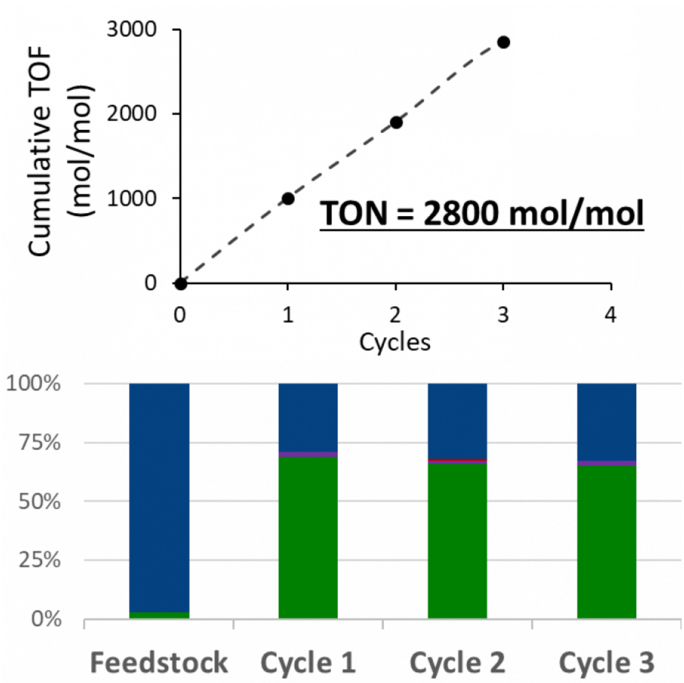


FIGURE 1

Scheme for the production of terephthalates from bio-based muconates

The production of terephthalates intermediates is occurring via the one-pot isomerization/Diels-Alder of bio-based cis,trans muconates.

Orange: cis,cis-muconates

Blue: cis,trans-muconates

Green: trans,trans-muconates

Purple: terephthalates intermediate

FIGURE 2

Cumulative TON of formation of trans,trans-diethylmuconates (ttDEM) through 3 consecutive isomerization cycles.

Blue: cis,trans-diethylmuconates (ctDEM)

Green: trans,trans-diethylmuconates (ttDEM)

KEYWORDS

Single atom Catalysis | Heterogeneous Catalysis | Biomass derivatives | Ruthenium on Zeolites

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