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Valorisation of bio-based furfurals by hybrid catalysis: towards the synthesis of new amine polymers and surfactants.

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PURPOSE OF THE ABSTRACT

The new and highly innovative field of research called "hybrid catalysis", that combines chemo and biocatalysts, has emerged over the last two decades.[1] It is still in its infancy but already reveals numerous advantages compared to traditional processes, particularly in terms of energy savings, atom savings, but also eco-friendliness. Therefore, one of the application fields in which hybrid catalysis seems particularly attractive is that of biomass valorisation. In particular, hybrid catalysis could help achieving the production of numerous new highly valuable building blocks from complex feedstocks. Among them, 5-hydroxymethylfurfural (HMF) is described as one of the most important biobased platform molecules, with various production processes from lignocellulose. Still, its valorisation in the form of furfurylamines has been little studied, and the routes for their synthesis remain generally complex and sustainable. Nevertheless, several of these furfurylamines are very promising molecules for numerous applications, such as 5-aminomethyl-2-furancarboxilic acid (AMFC) which, thanks to its free amine and carboxylic acid moieties, can be used as a precursor of new polyamides or surfactants. Recently, several works have described the synthesis of the latter by biocatalysis, but none of them were able to directly synthesise it from HMF.

Thus, we recently proposed the synthesis of AMFC directly from HMF using a hybrid one-pot/two-step process combining a platinum nanoparticle and a transaminase, both immobilised on silica beads (Fig. 1).[2] This process resulted in a 77% yield of the desired product, with 100% conversion of HMF and only one by-product, FDCA, another high value compound. This first work was recently published, making the cover of the first issue of ChemCatChem in 2021, but an even more efficient one-pot/one-step process is currently being developed using a newly discovered thermostable transaminase and will soon be published as well.

In addition, this first hybrid step has since been complemented by a second step to obtain new amphiphilic molecules from AMFC, to target the production of innovative surfactants. The idea was to be able to graft aliphatic chains onto the amine function through the formation of an amide bond using sustainable catalysts and common alcohols. We therefore developed a second hybrid route, this time combining a gold nanoparticle immobilised on different supports to carry out the oxidation of the aliphatic alcohols into fatty acids, the latter then being coupled to the AMFC with the help of a CoA ligase, also thermostable. Here, 71% and 44% of amide formation could be obtained after 64h with butanol and pentanol as starting material respectively, in a one-pot/two-step process. Noteworthy, the limiting step remains the enzymatic one with 100% of alcohols to acids conversion. In addition to the overcoming of this bottleneck, a fully integrated one-pot/one-step process is also currently being developed.

FIGURES

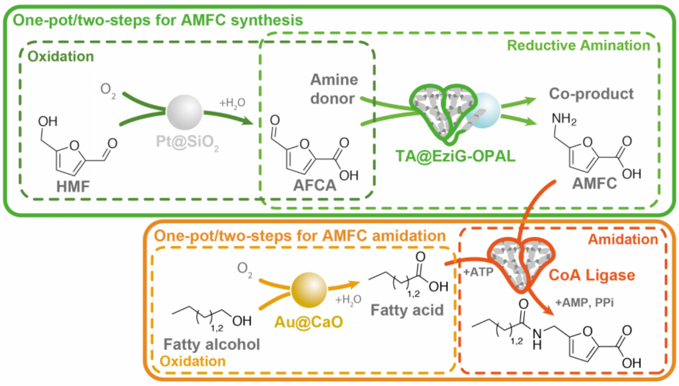

FIGURE 1

Fig. 1

Hybrid catalytic processes for AMFC synthesis and amidation

FIGURE 2

KEYWORDS

hybrid catalysis | biocatalysis | heterogeneous catalysis | biomass

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BIBLIOGRAPHY

[1] E. Heuson and F. Dumeignil, The various levels of integration of chemo- and bio-catalysis towards hybrid catalysis. Catal. Sci. Technol. (2020) 10, 7082-7100.

[2] A. Lancien et al., Hybrid conversion of 5-hydroxymethylfurfural to 5-aminomethyl-2-furancarboxylic acid: toward new bio-sourced polymers. ChemCatChem. (2021) 13, 247–259.