Hybrid catalysis as the next challenge in biorefineries: concept and examples

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Abstract: Hybrid catalysis, a direct combination of biocatalysis and chemocatalysis could yield innovative solutions in the field of biorefineries by straightforwardly merging the advantages of both technologies, rather than sequentially carrying them out. Further, sugars could become a major carbon resource for the catalytic production of fuels and chemicals. In this context, we propose two new conceptual pathways involving hybrid catalysis to overcome limitations resulting from the enzymatic glucose isomerase thermodynamic equilibrium between glucose and fructose, which is a key step when subsequently targeting HMF as a product. These concepts are based on a complexation/transport strategy and a hybrid isomerization, respectively.

Keywords: Hybrid Catalysis, Biorefineries, 5-hydroxymethylfurfural, glucose, fructose, sorbitol, cofactor.

1. Introduction

A new generation of smart catalysts must be developed for biomass upgrading in biorefineries.[1,2] In a conventional approach, biotechnologies and chemocatalysis are sequentially processed. However, recently, successful one-pot transformations have been realized, simultaneously taking advantage of both technologies, under the concept of the so-called 'hybrid catalysis'.[3,4]

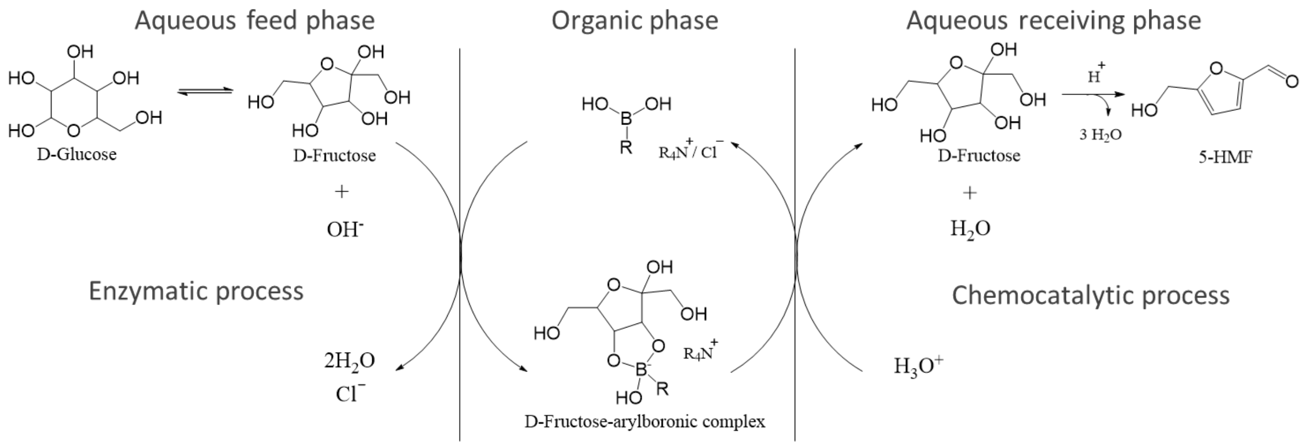

Figure 1. Hybrid catalysis process applied to the transformation of glucose to 5-HMF.

For example, 5-hydroxymethylfurfural (HMF) is a platform molecule derived from glucose through fructose as a key intermediate. To overcome the thermodynamic enzymatic equilibrium between glucose and fructose, which limits efficiency, we propose two strategies based on hybrid catalysis:[5] *(1)* Simultaneous implementation of glucose isomerase and of fructose to HMF dehydration chemocatalyst in a multiphasic way involving fructose complexation and transport[6] (Figure 1) and *(2)* a route through sorbitol avoiding enzymatic isomerization, readily obtained by glucose hydrogenation in which sorbitol is further enzymatically converted to fructose with an *in situ* cofactor regeneration using an organometallic complex[7] (Figure 2).

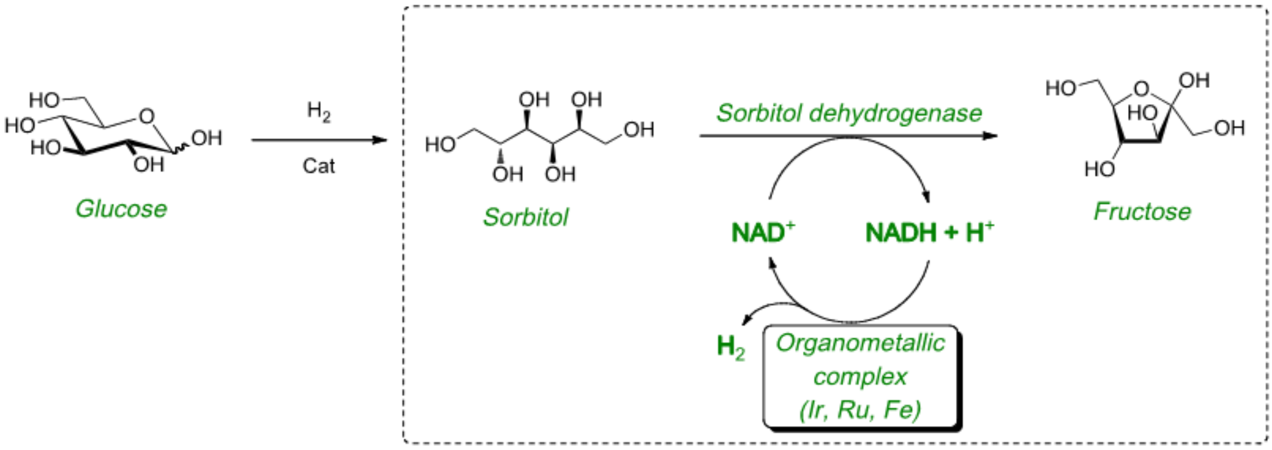

Figure 2. Principle of cofactor regeneration by an organometallic complex in the enzymatic reaction of conversion of sorbitol to fructose.

2. Results and perspectives

One-pot processes that combine bio- and chemocatalysis provide attractive routes to convert biosourced substrates to valuable products. Herein are presented two concepts for efficient HMF production from glucose involving hybrid catalysis with different methodological approaches. Both combinations are relatively simple to achieve and the first results validate the proof of concepts in both cases: *(1)* The limitations resulting from the enzymatic glucose isomerase thermodynamic equilibrium between glucose and fructose has been actually overcome with a glucose conversion of 70%, while it is limited to 46%, without fructose transport; *(2)* Concerning the valorisation *via* sorbitol, we demonstrated the chemical compatibility between sorbitol dehydrogenase and an organometallic complex used for the cofactor regeneration and *ca.* 2 cofactor regenerations by the chemocatalyst can be observed. However, the pH zones of the enzyme and the organometallic complex seems to be conflicting to enable reaching high yields. A modification of one of both catalysts could extend the pH zone toward the zone of the other catalyst.

Moreover, our approaches can be applied to other reactions of interest in the context of biomass valorization, and even, in other fields of chemistry and biotechnology. One-pot bio- and chemo-catalytic processes have an important role to play in future technologies, especially with a large potential for converting biomass to value-added chemical products, using a minimal number of steps in a selective and productive fashion, thus playing an important role in building a more sustainable chemical industry.

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