Aquivion® PFSA-based Spray-freeze Dried Composite Catalysts for the One-pot Domino Reaction from Furfural to γ-valerolactone

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Abstract

Among the various molecules that can be obtained from lignocellulosic biomasses, furfural has been regarded as one of the most promising for the substitution of non-renewable carbon feedstock, thanks to the wide range of possible reactions it can undergo and the plethora of possible applications of its derivatives.[1] The aim of this study was to investigate the possibility of the one-pot domino reaction from furfural to γ-valerolactone represented in Figure 1.

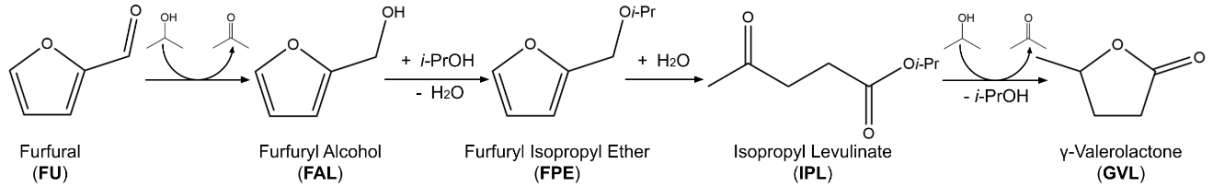

Figure 1. Studied reaction scheme.

In order to develop a sustainable process for the one-pot production of γ-valerolactone (GVL) from biomass-derived furfural (FU), both Lewis and Brønsted acidity are required. Lewis acidity is needed to promote catalytic transfer hydrogenation, while Brønsted acidity are necessary to convert furfuryl alcohol (FAL) to isopropyl levulinate (IPL). [1],[2] The materials utilized to carry out the process are zirconia and Aquivion® PFSA, the most recent commercially available fluorinated acid polymer. [3]

To combine the two phases, spray-freeze drying was employed. [4] Such technique allowed for the preparation of a range of composite materials with a varying polymer content, obtaining a high surface area and a good dispersion of the phases. The prepared materials were characterized by means of SEM, TGA, MAS NMR and porosimetry, then tested as catalysts in the conversion of biomass-derived furfural and furfuryl alcohol to isopropyl levulinate and γ-valerolactone. By examining the produced species in the reaction mixture at different reaction times and temperatures by means of GC-MS, insight was provided into the different produced intermediates and their associated reaction pathways. The optimization of the Lewis/Brønsted acidity ratio led to a further improvement of the reaction outcome, with a GVL yield above 40% after 2h at 180°C, through a four-step one-pot domino reaction. The optimized catalysts were then tested in a continuous-flow fixed-bed reactor, and the influence of reaction parameters on the outcome was once again investigated.

References

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