ISGC 2022

N°659 / OC
TOPIC(s) : Biomass conversion / Polymers or composites

Aquivion® PFSA-based spray-freeze dried composite catalysts for the one-pot domino reaction from furfural to gamma-valerolactone

AUTHORS

Alessandro ALLEGRI / DEPARTMENT OF INDUSTRIAL CHEMISTRY - UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO 4, BOLOGNA
Claudio OLDANI / SOLVAY SPECIALY POLYMERS SPA, VIALE LOMBARDIA 20, BOLLATE
Alice S. CATTANEO / SOLVAY SPECIALY POLYMERS SPA, VIALE LOMBARDIA 20, BOLLATE
Andrea BRIGLIADORI / ISTEC-CNR, VIA GRANAROLO 64, FAENZA
Ilaria ZANONI / ISTEC-CNR, VIA GRANAROLO 64, FAENZA
Giuseppe FORNASARI / DEPARTMENT OF INDUSTRIAL CHEMISTRY - UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO 4, BOLOGNA
Stefania ALBONETTI / DEPARTMENT OF INDUSTRIAL CHEMISTRY - UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO 4, BOLOGNA

PURPOSE OF THE ABSTRACT

In the collective effort to reduce the global reliance on fossil feedstock, one of the main challenges is to find sustainable ways to produce platform molecules and fuels from renewable sources. In this context, lignocellulosic biomass has been identified as a promising carbon source thanks to its variety, widespread availability, and low price. Among the various molecules that can be obtained from this renewable feedstock, furfural (FU) has been regarded as one of the most promising, thanks to the wide range of possible reactions it can undergo and the plethora of possible applications of its derivatives.[1] Among these, the selective hydrogenation to furfuryl alcohol (FAL) is the most industrially relevant due to its application in the polymer industry. Subsequent hydrolysis of furfuryl alcohol can be an alternative pathway to produce levulinic acid and its esters from biomasses. Levulinic acid/levulinate esters are versatile platform molecules for the synthesis of various chemicals, among which one of the most relevant is gamma-valerolactone (GVL).[2]

In order to develop a sustainable process for the one-pot production of gamma-valerolactone from biomass-derived furfural, two types of catalytic functionalities are required. The first one is aLewis acidity strong enough to promote the Catalytic Transfer Hydrogenation (CTH) of furfural and levulinic acid/levulinate esters, in order to avoid the dangerous and environmentally impactful process of hydrogenation.[1],[2] The second kind of functionality required is a Brønsted acidity capable of promoting the hydrolysis of furfuryl alcohol and its ethers to levulinic acid and levulinate esters.

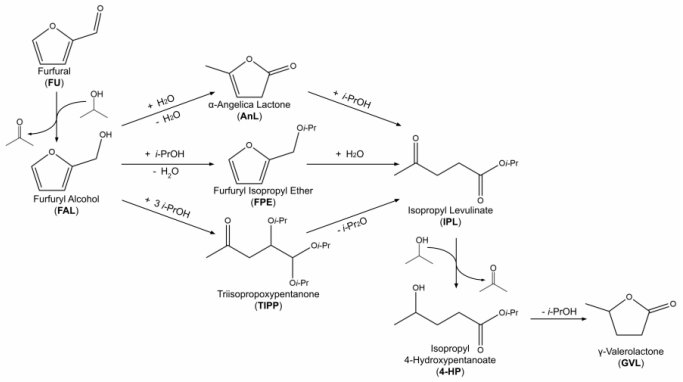
The kind of strong Brønsted acidity necessary to carry out the reaction can be found in Aquivion® PFSA, the most recent commercially available fluorinated acid polymer. This polymer roused interest in the scientific community thanks to their unique and interesting properties such as superacidity and high thermal and chemical resistance.[3] Despite these promising characteristics, however, the direct application of Aquivion® PFSA as a catalyst is generally limited by its high cost and low accessibility of the acid sites.

An innovative approach to offset the limitations intrinsic to the use of Aquivion® PFSA as an acid catalyst is the spray-freeze drying, a low temperature technique capable of producing composite materials with high surface area and good dispersion of the contained phases.[4]

In this study, a range of innovative Aquivion® PFSA-based spray-freeze dried composite organic-inorganic materials were prepared, varying both the oxidic phase therein contained and the amount of polymer, then studying the effect of the calcination temperature on the catalytic performances. The oxides tested were commercial silica, (Ludox HS-40) commercial titania, (Degussa P25) and tetragonal zirconia synthesized via

precipitation at controlled pH. The 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 (IPL) and
gamma-valerolactone. (Figure 1)
All the samples displayed significant, albeit different, activity in the studied reaction. 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, as well as the influence of the reaction conditions, including the water content, on the outcome. In particular, the zirconia-based composite was proven to be the most effective of the series in carrying out the domino reaction, achieving a 20% selectivity toward GVL after 2h at 180°C when starting from furfural, and a 30% GVL selectivity in the same conditions when starting from furfuryl alcohol. (Figure 2)

FIGURES



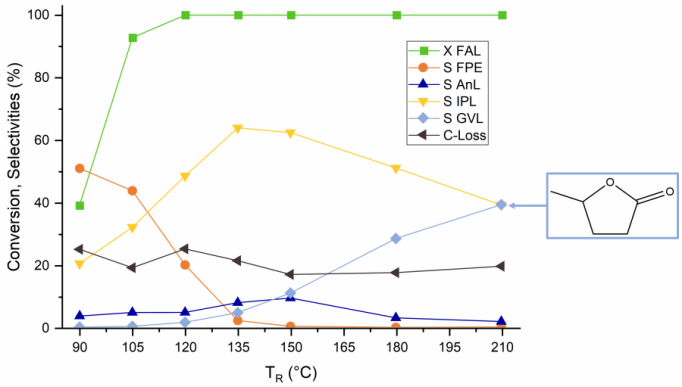


FIGURE 1
Reaction pathway

FIGURE 2
Effect of reaction temperature

Effect of reaction temperature on the catalytic performances of Aq/ZrO2 30wt%.
Reaction conditions: 2h, FAL/H+=100.

KEYWORDS
Aquivion | Composite materials | Spray-freeze drying | Furfural

BIBLIOGRAPHY

[1] Grazia, L., Green Chem. 2017, 19, 4412-4422.
[2] Vásquez, P. B., ACS Sustain. Chem. Eng. 2019, 7, 8317–8330.
[3] Andreoli, S., Appl. Catal. Gen. 2020, 597, 117544-117552.
[4] Lolli, A., Catal. Today 2019, 334, 193–202.