R

CNPq

XXVII Congresso de Iniciação Científica Unicamp 16 a 18 de outubro de 2019 - Campinas | Brasil

Synthesis of a 5-(Hydroxymethyl)furfural-based resin and its use as heterogeneuos catalyst.

Lucas P. Fernandes*, Renan Galaverna, Gustavo R. Gomes and Julio C. Pastre.

Abstract

The synthesis and characterization of a new 5-(Hydroxymethyl)furfural-based resin was evaluated. The product obtained, a dark brownish solid and insolluble in several organic solvents and water, presents acidic properties (-COOH). The characterization was performed by using FTIR, solid carbon NMR, TGA, DSC analyses and the results showed an amorphous material. Its acidity was explored in an organic reaction under continuous flow conditions.

Key words:

Flow chemistry, Green chemistry, Heterogenous catalysis

Introduction

The use of renewable raw materials, such as biomassderived compounds, to the production of chemicals and materials has gained considerable attention aiming at the substitution of fossil-based compounds.

In this study, a polymeric material was obtained after an unsuccessful attempt to do a Diels-Alder reaction between 2,5-di(hydroxymethyl)furan (DHMF) and maleic anhydride. In view of the acidity presented by the synthesized compound, it was investigated as a heterogeneous catalyst for a known transformation, allowing its comparison to an acid sulphonic acid resin reported in the literature.¹

Results and Discussion

Firstly, the diene (DHMF, **2**) was prepared from 5-HMF and was used in the Diels-Alder reaction with maleic anhydride (**3**).



Scheme 1: DHMF synthesis and Diels-Alder reaction using maleic anhydride as dienophile.

The desired Diels-Alder adduct could not be isolated using several conditions (solvent and temperature screening). At 140 °C, a dark brownish solid was formed after a few seconds of mixing and several analyses were performed in order to characterize this material. **Scheme 2** shows part of the solid state ¹³C NMR spectrum obtained and the carbon assignment.



Scheme 2: Solid state ¹³C NMR for the HMF-based resin.

According to the pattern observed, the mechanism that follows was proposed to explain the structure and the acidity of the synthetized solid.



Scheme 3: Proposed mechanism for the resin formation.

After the structure was elucidated, the ionic change capacity was measured and defined as 1.7 mmol.g⁻¹. Then, this acidic resin was evaluated as a heterogenous catalyst in the dehydration of fructose.

Table 1. Acid catalyzed dehydration of D-Fructose to 5-HMF in continuous flow regime.

	U			
HO	1 mL	HMF-based polymer	6 bar	HO
но" 📜 `ОН 🗩	0.05 and (min	2,5 g		\sim
но он	0,25 mL/min	120 °C		HMF (1)
D-Fructose (4) 0.1M				

Entry ^[a]	T (ºC)	Flow rate (mL.min ⁻¹)	P (bar)	Yield ^[b] (%)
1 [c]	120	0.25	6	62
2	120	0.25	6	50
3	120	0.25	6	40
4 [d]	120	0.25	6	70
5	120	0.25	6	40
6	120	0.25	6	40
7	120	0.25	6	40

^[a] Fructose in DMSO/*i*-PrOH (15% v/v) and only *i*-PrOH as solvent ^[b] Yield was determined by using 1,3,5-trimethoxybenzene as internal standard for ¹H NMR. ^[c] First run after activation using HCl 1M in the 1 mL loop.^[d] First run after a second reactivation using HCl 1M.

Conclusions

The strategy adopted here allowed the characterization of the unexpected polymeric product. Its physicochemical properties were determined and an application for this material was presented. Although it leads to lower yields than those reported in the literature, the resin showed potential application as a heterogeneous catalyst.

Acknowledgement

The authors gratefully acknowledge financial support from FAPESP, CNPq, CAPES and FAEPEX.

¹ R. Galaverna, M. C. Breitkreitz, J. C. Pastre, ACS Sustainable Chem. Eng. **2018**, 6, 4220–4230.