



Tunable and selective hydrogenation of HMF to furan diols in flow reactor using Ru/C

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1. Introduction

5-hydroxymethylfurfural (HMF) is a key renewable platform-chemical and precursor of several valuable products [1]. In particular, 2,5-bis(hydroxymethyl)furan (BHMF) and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF) are very important monomers for the synthesis of biopolymers and precursors of other relevant monomers, such as caprolactame and 1,6-hexanediol [2]. BHMF and BHMTHF derive from the hydrogenation of the aldehydic group and also of the furanic ring of HMF, respectively (Figure 1).

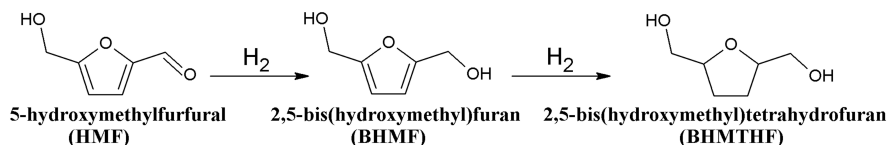


Figure 1. Conversion of HMF to the desired products BHMF and BHMTHF.

The two steps are catalysed by noble metals and Ru/C has already resulted particularly active and selective for the synthesis of each diol performing the reaction in batch in water medium [3]. However, for industrial application the employment of a flow reactor set-up is more suitable because it allows a continuous production and improves the energy efficiency, mixing control and heat transfer. The employment of the flow reactor is fundamental in particular for three phase reactions, as the hydrogenation of HMF. In fact, it allows the increase of the interfacial area between the phases, leading to more efficient heat and mass transfers. Although the advantages of the flow reactor, only recently in the literature it has been used for the HMF hydrogenation to BHMF and BHMTHF. The reaction has been generally carried out in organic solvents, in the presence of *ad hoc* synthesised catalysts, producing only one of the two diols [4]. In this context, the present work proposes, for the first time, the optimization of the selective synthesis of each diol, BHMF and BHMTHF, starting from pure aqueous HMF solution in the flow reactor employing the same commercial catalyst (5 wt% Ru/C), by simply tuning the reaction parameters.

2. Methods

The set-up of flow reactor employed in the HMF hydrogenation was composed of a feeding section, a reactor (ID = 0.7 cm; L = 14.2 cm), a gas-liquid separator and an auto-sampler. In a standard run, the HMF aqueous solution was set in the feed vessel and the proper amount of 5 wt% Ru/C was loaded in the reactor tube. Subsequently, the reactor was closed and the HMF solution was fed through a piston pump. The pressure was increased to the desired value through a back pressure valve and the hydrogen flow started. The reactor was electrically heated to the desired temperature and when the set value was reached the reaction time

started ($t = 0$ h). At different time lapses, liquid sample from the reactor was collected by an auto-sampler and analysed through HPLC (Agilent Technologies 1260 Infinity equipped with a Bio-Rad Aminex HPX-87H column kept at 60 °C, employing 0.005 M H₂SO₄ as mobile phase with a flow rate of 0.55 ml/min). TEM measurements were performed using a CM12 microscope (Philips), operating at 120 keV. N₂ physisorption analyses were carried out with a Micromeritics ASAP 2020 at -196.2 °C, pre-treating the samples under vacuum at 150 °C for 6 h. ICP-OES analyses were performed with an Optima 7000 DV (PerkinElmer) analyser equipped with a CCD array detector.

3. Results and discussion

Preliminary experiments were performed in order to verify the stability of the catalyst, thus the reaction was prolonged up to 50 h as time-on-stream. The catalyst resulted stable up to 14 h and a marked lost of activity was observed lengthening the time-on-stream, thus the steady state was selected between 2 and 14 h. The influence of different reaction parameters, such as reactor space time, temperature, pressure, ratio of H₂ flow/liquid flow and HMF starting concentration was investigated for the synthesis of BHMF and BHMTHF, whose highest yields, respectively of 88.0 and 93.7 mol%, were ascertained under the same reaction conditions and at different reactor space time (Figure 2).

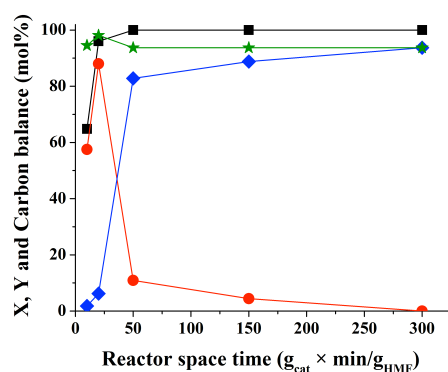


Figure 2. Profile of conversion (X), products yields (Y) and carbon balance versus reactor space time (■ X_{HMF}; ● Y_{BHMF}; ◆ Y_{BHMTHF}; ★ Carbon balance). Reaction conditions: T = 100 °C; P = 50 bar; [HMF] = 0.1 wt%; H₂ flow = 100 ml/min; liquid flow = 1 ml/min.

As previously evidenced, the catalyst lost its activity during the reaction, thus the spent catalyst was characterized by N₂ physisorption, TEM and ICP-OES analyses in order to understand the deactivation. The obtained results showed that the ruthenium particle size and the amount of ruthenium in the spent catalyst were analogous to those in the fresh one, on the contrary the specific surface area decreased from 770 to 136 m²/g. This is in agreement with our previous studies [3], proving that the catalyst deactivation is due to the deposition on its surface of organic matter, such as humins, deriving from HMF degradation.

4. Conclusions

For the first time, the tunable selective hydrogenation of HMF to BHMF and BHMTHF was investigated in a flow reactor under sustainable reaction conditions and in the presence of the same commercial catalyst 5 wt% Ru/C. The highest BHMF and BHMTHF yields, respectively of 88.0 and 93.7 mol%, were obtained under the same reaction conditions adopting different reactor space time. This result is very important in the perspective of industrial application because it enables the selective production of each product on the basis of the market request. At the end, TEM, ICP-OES and N₂ physisorption analyses were performed on the spent catalyst proving that its partial deactivation was mainly ascribable to the humins deposition.

References

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