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Continuous flow oxidation of HMF to FDCA by resin-supported platinum catalysts in neat water

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The oxidation reaction of 5-hydroxymethylfurfural to the bioplastics monomer 2,5-furandicarboxylic acid over heterogenous resin-supported Pt catalysts was investigated in detail, under continuous flow, base-free conditions and in neat water. The product was continuously obtained in 99% yield by running the reaction at 120 °C, 303 s residence time, 1.2 mL min⁻¹ O₂ flow rate and 7.7 bar O₂ pressure. The product was isolated with a high space-time-yield of 46.0 g L⁻¹ h⁻¹ without purifications or acid / base treatments.

2,5-Furandicarboxylic acid (FDCA) is one of the "top" platform chemicals produced from biomass.^[1] FDCA is a monomer either to replace terephthalic acid in PET or to fabricate novel bio-plastic materials, e.g. PEF (polyethylene 2,5-furandicarboxylate).^[2,3] The annual market volume of FDCA is estimated at 200 ktons in 2020.^[4] FDCA can be produced from 5-hydroxymethylfurfural (HMF), which is in turn obtained by threefold dehydration of hexoses, via the 2,5-diformylfuran (DFF), 5-formylfuran-2-carboxylic acid (FFCA) oxidation reaction sequence (Scheme 1).^[5] Several heterogeneous metal catalysts, including the industrial one,^[6,7] have been reported for this process using organic solvents, however with significant drawbacks in terms of toxicity, recalcitrance to full oxidation to FDCA, flammability, formation of by-products, waste and VOCs.^[8,9] Adoption of water solvent is, therefore, an attractive option. In this case, current limitations are related to: use of batch setups and expensive gold catalysts, poor FDCA solubility, need of excess of metal catalyst or strong base additives (e.g. NaOH, K₂CO₃), harsh reaction conditions, corrosion and catalyst deactivation.^[10,11] The development of cleaner and more environmentally acceptable methods for FDCA production is therefore of utmost importance.^[12,13]

Herein, we report the synthesis and characterisation of a heterogeneous, resin-supported Pt catalyst and its use in the one-pot oxidation of HMF to FDCA in neat water, under continuous flow conditions. Choice of resin support was motivated by the commercial availability at low costs, the appropriate swelling in water, the easy and tunable metal

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incorporation, the effective recovery and reuse, and the low back pressure evolution when packed in flow-through reactor systems.^[14,15] Compared to batch operations, running catalysis under continuous flow conditions adds sustainability and intensification to the process, because of the significant benefits in terms of increased safety and productivity, simpler downstream processing, automation, improved heat transfer and process control, smaller hold-up volumes, reduced gas pressures.^[16,17] Continuous refresh of catalyst may also limit active site inhibition due to products adsorption.^[18]



Scheme 1. Pathways for the catalytic oxidation of HMF to FDCA.

Thus, a two step ion-exchange metallation / reduction procedure using an appropriate amount of [Pt(NH₃)₄](NO₃)₂ precursor in water, the sulfonated DOWEX 50WX2-100 strong cation-exchange resin (216 ± 2 µm bead size, geltype, H^+ form, 4.8 meq g⁻¹ exchange capacity) and an excess of sodium borohydride as metal reducing agent, afforded immobilised Pt nanoparticles of 4.1 ± 1.2 nm diameter, gathered in larger aggregates of ca. 14 nm (Figure 1, left).^[19]. ICP-OES analysis showed the bulk Pt content in the final Pt@Dowex-Na catalyst to be 15.6 % wt. EDS measurements showed an uneven distribution of Pt within the catalyst beads, that can be attributed both to high Pt loading and to the effect of borohydride reduction (Figure 1, right).^[20,21] The mean Pd content provided by EDS analysis was in agreement with that obtained from ICP, within the limits of the experiments. Use of an excess of NaBH₄ ensured a quantitative replacement of protons with Na⁺ ions onto the resin, hence removing any Brønsted acid activity of the solid support, that may lead to undesired side-reactions.^[22,23] XPS measurements were carried out to characterise the oxidation state of the supported Pt particles. The XPS spectrum of Pt@Dowex-Na in the Pt 4f region, in which the usual asymmetric doublet of Pt is observed, is reported in Figure 2. The peaks were deconvoluted in one component only, whose binding energies are in agreement with those previously reported for metallic Pt (Pt⁰4f_{7/2} 71.1 ± 0.1 eV, spin-orbit coupling 4.0 eV).^[24,25] No peaks attributable to other oxidation states were detected.

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Figure 1. Pt@Dowex-Na: size distribution of Pt particles from TEM analysis (left) and line EDS transversal line maps of an equatorial section of catalyst bead from EDS analysis (right). Top: C (K α 1), bottom: Pt (L α 1).



Figure 2. High-resolution XPS spectrum of Pt@Dowex-Na in the Pt 4f region.

Preliminary batch experiments were run in order to check the viability of the Pt catalyst in the oxidation of HMF in neat water without added bases. The reaction temperature was set at 120 °C, as literature reference value, using a 62 HMF / bulk Pt molar ratio and O₂ as clean oxidant (see Supporting Information for details). Under these conditions, the catalyst showed to be effective in the O_2 pressure range 5-20 bar, with an increasing FDCA yield up to 98% upon increasing the reaction time, at the expenses of the intermediate oxidation products DFF and FFCA, according to the slow kinetic of the stepwise oxidation reaction.^[26] A slight dependence of conversion, hence of selectivity, form the oxygen pressure was observed. Representative data are reported in Table 1. Clear reaction solutions were obtained in any case, that were analysed when warm by HPLC and GC-MS showing no other products other than DFF, FFCA and FDCA. Traces of products consistent with dimers were detected by ESI spectroscopy.^[27] No platinum leaching above the ICP-OES detection limit was observed. The solid catalyst could be recovered by decantation and reused without significant efficiency loss. No meaningful change of the Pt particles size was detected by TEM analysis of the recovered catalyst. Under the same reaction conditions, a lower Pt loading (2.5% wt) led to unrecoverable catalysts and to a yellowish suspension, likely due to polymer degradation in an oxidising environment at high temperature.^[28,29] Stabilisation of cationexchange resins toward oxidation by metallation was previously reported elsewhere.^[30] Use of supported ruthenium or organic solvents (DMSO, methanol, propylene

 γ -valerolactone (GVL)) carbonate, ethanol, invariably in much lower conversions and resulted nealiaible selectivities to FDCA, as well as in extensive formation of solvent oxidation or degradation products (e.g. dimethyl sulfone, dimethyl sulfide, methyl formate, formaldehyde dimethylacetal, 1,2-propanediol, hydroxyacetone, levulinic acid).[31] Use of air instead of oxygen as oxidant led to lower selectivity to FDCA under comparable reaction conditions (Table S4) due to the formation of DFF, FFCA and unidentified by-products, therefore it was not investigated in further details.

Table 1. Oxidation reaction of HMF over Pt@Dowex-Na catalyst under batch conditions. ^[a]							
Entry	$O_2^{\ [b]}$	Time ^[c]	Conversion		Yield [%]		
	[bar]	[h]	[%]	DFF	FFCA	FDCA	
1	10	4	86	24	48	14	
2	20	4	92	14	43	35	
3	20	22	100	0	1	98	
[a] Reaction conditions: HMF 0.025 M in water 20 mL, temperature 120 °C.							

Pt@Dowex-Na 10 mg (15.6% wt Pt). Data from HPLC analysis. [b] Oxygen pressure. [c] Reaction time.

Having established an effective system for the catalytic oxidation of HMF in water, experiments under continuous flow conditions were performed using a home-made equipment, allowing for concurrent and controlled streams of oxygen and substrate solution through the catalytic reactor (Scheme S1). To this purpose, 60 mg of catalysts were packed into a glass tube (50 mm length, 3 mm internal diameter) and scrutinised under a combination of oxygen (0.8 - 8.0 mL min⁻¹) and solution flow rates (0.05 - 0.20 mL min⁻¹), O₂ pressures and HMF concentrations. Within the above flow ranges, the spontaneous back pressure generated by the packed catalyst was ca. 2 bar, i.e. a pressure drop of ca. 1 bar. As expected for such a flow system,^[32] at a given temperature, conversion and selectivity showed to be ruled by the residence time τ (the amount of time that the substrate spends inside the reactor, depending on the solution flow rate), $^{\left[33,34\right] }$ and by the O_{2} / substrate molar ratio (which depends from the O2 flow rate). Reproducible reaction patterns were observed anyhow. The effect of the two parameters were investigated separately.

Under a fixed τ , an increase of the O₂ / HMF ratio (i.e. an increase of the oxygen flow rate) resulted in an increase of HMF conversion and FDCA yield, at the expenses of FFCA and DFF. As representative example, the reaction mixture composition upon change of the O₂ / HMF ratio in the range 56 - 213, under a fixed 303 s τ value, is reported in Figure 3, left. Selectivity to FDCA therefore increased with increasing HMF conversion. A conversion / selectivity diagram could be drawn as reported in Figure 3, right. In the O₂ flow rates range examined, the O₂ pressure at the reactor inlet did not change significantly, which can be attributed to the scarce flow resistance of the packed catalyst. Analogous results were obtained for different τ values.^[31]

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Figure 3. Continuous flow oxidation of HMF over Pt@Dowex-Na catalyst. Reaction conditions: residence time 303 s (solution flow rate 0.07 mL min⁻¹), HMF 0.025 M in water, temperature 120 °C, Pt@Dowex-Na 60 mg (15.6% wt Pt), O₂ pressure ca. 2 bar. Left: effect of the O₂ / HMF molar ratio change on the reaction mixture composition (O₂ rate 1.5 - 5.4 mL min⁻¹). Right: corresponding conversion / selectivity diagram. Data from HPLC analysis.

Similarly, under a fixed O_2 / HMF ratio, an increase of τ (i.e. a decrease of the solution flow rate) resulted in an increase of HMF conversion and FDCA selectivity. The reaction mixture composition as a function of τ in the range 212-424 s, under a fixed O_2 / HMF ratio of 212, is reported in Figure 4, left, as representative example. Analogous results were obtained for different ratio values.

For conversion values above 100%, the selectivity to FDCA could be further increased by increasing τ or the O₂ / HMF ratio. Representative data are reported in Figure 4, right, under fixed t 424 s. It is therefore clear that the FDCA yield can be maximised by an appropriate combination of these two parameters. A complete performance picture of the catalytic system was obtained on these basis, as shown in Figure 5 (Figure S12). Under an O₂ pressure of ca. 2 bar and a reaction temperature of 120 °C, a FDCA yield up to 97% was obtained within the flow rate ranges examined, upon selection of the proper flow values. Selected data are reported in Table 2 entry 1, wherein productivity (mmol_{FDCA} g_{cat}^{-1} h⁻¹) and space-time-yield (STY, kg_{FDCA} $L_{reactor}^{-1}$ h⁻¹) of FDCA are indicated.



Figure 4. Continuous flow oxidation of HMF over Pt@Dowex-Na catalyst. Reaction conditions: HMF 0.025 M in water, temperature 120 °C, Pt@Dowex-Na 60 mg (15.6% wt Pt), O₂ pressure ca. 2 bar. Left: effect of the residence time change on reaction mixture composition (solution flow rate 0.05 - 0.10 mL min⁻¹, O₂ / HMF molar ratio 212, O₂ flow rate 4.0 - 7.0 mL min⁻¹). Right: selectivity dependence from O₂ / HMF molar ratio for conversions > 100% (fixed residence time 424 s). Data from HPLC analysis.



Figure 5. Contour plot diagram for the continuous flow oxidation reaction of HMF to FDCA over Pt@Dowex-Na catalyst. Reaction conditions: O_2 pressure ca. 2 bar, temperature 120 °C, HMF 0.025 M in water, Pt@Dowex-Na 60 mg (15.6% wt Pt), reactor volume 353 μ L. Oxygen flow rate range 1.1 - 8.0 mL min⁻¹. Solution flow rate range 0.05 - 0.10 mL min⁻¹.

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Table 2. Selected data for the oxidation reaction of HMF over Pt@Dowex-Na catalyst under continuous flow conditions. ^[a]									
Entry	Entry Solution		O ₂		O_2 / $HMF^{[d]}$	Conversion ^[e]	FDCA ^[f]		
	Flow rate [mL min ⁻¹]	τ ^[b] [S]	Flow rate [mL min ⁻¹]	Pressure ^{ic]} [bar]	ratio	[%]	Yield [%]	Productivity [mmol g _{cat} -1 h ⁻¹]	STY [kg L ⁻¹ h ⁻¹]
1	0.05	424	8.0	1.7	450	100	97	1.22	0.032
2	0.07	303	2.9	3.1	213	100	79	1.39	0.037
3	0.07	303	2.9	6.5	443	100	96	1.69	0.045
4	0.07	303	1.2	7.7	213	100	99	1.74	0.046

[a] Reaction conditions: HMF 0.025 M in water, temperature 120 °C, Pt@Dowex-Na 60 mg (15.6% wt Pt), reactor volume 353 μ L. Data from HPLC analysis. [b] Residence time (τ). [c] O₂ pressure at the reactor inlet. [d] Oxygen to HMF molar ratio at the reactor inlet. [e] HMF conversion. Average value over 8 h time-on-stream. Start time: attainment of steady state conditions ca. 0.5 h. [f] Average values over 8 h time-on-stream.

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The effect of the oxygen pressure on the system performance was examined using an in-line backpressure regulator located at the reactor outlet. An increase in the O_2 pressure, while maintaining the same O_2 flow rate, had the obvious effect to increase the O_2 / HMF molar ratio, therefore increasing the FDCA yield (Table 2, entry 3 vs. entry 2).^[31] On the other hand, the O_2 pressure could be increased while keeping a low O_2 / HMF molar ratio (213) by reducing the O_2 flow rate, therefore allowing for a significant oxygen saving (Table 2, entry 4 vs. entry 2). Under these conditions, a FDCA yield up to 99% was obtained under 7.7 bar O_2 , corresponding to a high productivity of 1.74 mmol g_{cat}^{-1} h⁻¹.

A reduction of the reaction temperature from 120 to 90 °C was also explored at given flow parameters, however resulting in a significant lowering of the FDCA yield, hence in an unfavourable FDCA productivity. The yields observed at O₂ / HMF molar ratio 120 and residence time 303 s are reported in graphical format in Figure 6, as representative example. An increase of the reaction temperature to 140 °C did not result in a significant improvement of the reactor efficiency.



Figure 6. Continuous flow oxidation of HMF over Pt@Dowex-Na catalyst at different temperatures. Reaction conditions: O_2 / HMF molar ratio 120, residence time 303 s (solution flow rate 0.07 mL min⁻¹) HMF 0.025 M in water, Pt@Dowex-Na 60 mg (15.6% wt Pt), O_2 pressure ca. 2 bar.

The catalytic flow system was investigated in the HMF concentration range $6.0 \cdot 10^{-3}$ - $2.5 \cdot 10^{-2}$ M, showing no significant dependence of the performance from the concentration, except for the obvious change of the residence time required to achieve full conversion and FDCA yield. Care must be taken at the higher concentration, since the room temperature solubility of FDCA in water is above the limit, at full substrate conversion, in that case. $\ensuremath{^{[35]}}$ This may lead to significant underestimates of FDCA yield by HLPC analysis of the reaction mixture collected at the reactor outlet, due to FDCA precipitation. In this case, quantification was achieved via HLPC and gravimetric analysis of the reaction mixture, after water removal by lyophilisation and redissolution to appropriate dilution. In order to minimise quantification errors, the outlet line should be kept warm throughout. Neither products other than DFF, FFCA and FDCA, nor significant mass unbalance were detected anyhow by HPLC, GC-MS and NMR (DMSO-*d*₆).

Continuous flow experiment were typically carried out for 8h time-on-stream. The long-term resistance of the catalyst was tested during five days reaction time, provided overnight switching-offs for safety reasons. The catalyst exhibited excellent stability, since it retained 100% of its starting activity and selectivity after 43 hours time-on-stream. In a representative example, an average FDCA yield of 98.0 ± 0.8 % was observed under 5.0 mL min⁻¹ O₂ and 0.10 mL min⁻¹ HMF solution flow rate (Figure 7). FDCA could be isolated in the solid state by water lyophilisation of the solution collected at the reactor outlet without further purifications, and the recovered water could be recycled. No leached Pt was detected by ICP-OES. Under the same flow conditions, use of commercial Pt@C catalyst resulted in much lower conversion and FDCA selectivity (Table S3).



Figure 7. Continuous flow oxidation of HMF to FDCA over Pt@Dowex-Na catalyst: O₂ flow rate 5.0 mL min⁻¹, solution flow rate 0.10 mL min⁻¹, O₂ pressure 2.1 bar, temperature 120 °C. Drop lines represent overnight switch-offs. FDCA yield 98.0 \pm 0.8 %. Data from HPLC analysis.

In conclusion, we have reported a detailed investigation of the base-free, continuous flow oxidation reaction of HMF to FDCA over resin-supported Pt catalysts in neat water. FDCA was obtained in high yield under relatively mild conditions and with high catalyst stability. Within the temperature and flow rate ranges examined, the system afforded FDCA in > 99 % yield under 120 °C, 7.7 bar O₂ (1.2 mL min⁻¹) and 303 s residence time (LHSV 12 h⁻¹).^[36] The product could be isolated in the solid state in 99% purity after simple water withdrawal, without addition of organic solvents or removal of inorganic salts at any time. The resulting space-time-yield productivity was 46.0 g_{FDCA} L⁻¹ h⁻¹.

A number of heterogeneous catalysts have been described in the literature for the batch oxidation of HMF to FDCA in water, without addition of soluble bases or co-solvents (Table 3 and Table S4). However, these often used basic support materials which partly dissolves (e.g. MgO or hydrotalcite), thus resulting in product contamination and in alkaline solutions, and very low substrate / metal molar ratios. The main advantages provided by present Pt@Dowex-Na system are: use of inexpensive, commercially available support, ease of catalyst preparation and recovery, implementation into continuous flow operations, inherent

process safety, no significant carbon loss, high productivity, catalyst stability, no need of remarkable catalvst regeneration, product re-acidification or troublesome downstream purifications. To the best of our knowledge, only two continuous flow systems have been previously reported for the catalytic oxidation of HMF to FDCA (Table S5). The first used 5% Pt@ZrO2 in base-free water, however with low mass balance (50-70 %), moderate FDCA yields (ca. 60 %) and productivity (0.1 mmol_{FDCA} $g_{cat}^{-1} h^{-1}$; 11.0 $g_{FDCA} L^{-1} h^{-1}$), due to the long residence time required (1200 s, LHSV 3 h⁻ 1).^[37,38] The second was based on 5% Pt@C catalyst and GVL:H₂O = 80:20 solvent mixture, to give FDCA in 60 % yield with low productivity (0.04 mmol_{FDCA} $g_{cat}^{-1} h^{-1}$, under 100 °C and 40 bar O₂).^[39] Compared to the reported systems, the positive performance of the Pt@Dowex-Na catalyst can be attributed to the proper combination of Pt loading, support swellability in water, beads size, steric and electrostatic stabilisation of resin-supported metal nanoparticles.^[40,41] When swollen in water, gel-type (low-crosslinked) resins ensure fast diffusion of the solvent throughout the polymeric material, thus allowing a good active-sites accessibility to all soluble reactants, while minimising catalyst blocking and inhibition, because of the low surface area.^[14,42]

The results herein obtained can be useful to develop greener and more sustainable catalytic processes for the production of FDCA from renewable biomass. Particularly, the high reactor volume productivity (two order magnitude higher compared to batch operations) point out to the great potential for process scale-up with significant waste prevention.

Table 3. Representative literature data for the base-free oxidation of HMF to FDCA over heterogeneous catalysts in neat water under batch conditions.								
Catalyst	HMF / M ratio ^[a]	Temp. [°C] ^[b]	Oxidant [bar]	Yield [%] ^[c]	Ref.			
Pt@Dowex-Na	62	120	O ₂ (20)	98	this work			
Ru@CTF ^[g]	40	140	air (20)	41.1	[43]			
Ru@MnCo ₂ O ₄	33.6	120	air (24)	99	[44]			
Pd@Mg-AI-HT [h]	20	100	O ₂ (1)	99.9	[45]			
Pt@ N-doped C	25	110	O ₂ (10)	96	[46]			
Ru@HT ^[h]	20	140	O ₂ (1)	100	[47]			
Pt@C-MgO	46	110	O ₂ (10)	97	[25]			
Pt@PVP	20	80	O ₂ (1)	95	[48]			
Au:Pd@CNT	80	100	O ₂ (5)	94	[49]			
Au@HT ^[h]	40	95	O ₂ (1)	99	[50]			
Pt@CNT 🛛	100	95	O ₂ (5)	98	[51]			
Ru@C	10	120	O ₂ (2)	88	[52]			
Au@TiO ₂ -HT ^[h]	150	90	O ₂ (3.4)	94	[53]			
Fe ^{III} @POP ^[m]	n.a.	100	air (10)	79	[54]			
Ru@ZrO ₂	31	120	O ₂ (10)	96	[55]			

[a] HMF / metal molar ratio. [b] Reaction temperature. [c] FDCA yield. [d] Reaction time. [e] HMF conversion. [f] Space-time-yield. [g] CTF, covalent triazine framework. [h] HT, hydrotalcite. [i] Carbon-coated MgO. [l] CNT, carbon nanotubes. [m] POP, porous organic polymer.

Experimental Section

Catalytic reactions under continuous flow conditions were carried out in O₂ atmosphere using a home-made, metal-free continuous-flow reactor system (Scheme S1). In a typical experiment, 60 mg of Pt@Dowex-Na catalyst were packed into a glass tube (3 mm inner diameter x 50 mm length), that was connected to the continuous flow system via 1/16" PEEK tubing and scrutinised under a combination of concurrent, controlled flows of oxygen and HMF water solution. The temperature of reactor was regulated using a controller accurate ± 0.1 °C. The attainment of steady state conditions (ca. 0.5 h) was taken as the reaction start time. At the outlet of the reactor, the reaction solution was collected and periodically analyzed by HPLC, GC-MS. Aliquots were sampled for Pt leaching determination by ICP-OES. The reaction products were unequivocally identified by comparison of the HPLC retention times, mass and NMR (DMSO-d₆) spectra with those of authentic specimens. Quantitative analyses were carried out via HPLC based on calibration curves of the pure compounds.

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Conflicts of interest

The authors declare no conflict of interest.

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