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(Article begins on next page)

Pt-WO₃ oxydehydrates fructose to furans in the gas phase

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Abstract

Bio feedstocks are destined to replace fossil fuels for specialty chemicals but current biorefineries mainly ferment hexose—the most abundant feedstock to ethanol. The maximum theoretical carbon atom efficiency of this process is 67% but the market price of biofuels is several-fold lower than biochemicals and monomers. We report for the first time a gas phase catalytic process that dehydrates fructose to 5-hydroxymethyl furfural (HMF). A two-fluid nozzle atomizes aqueous solutions of fructose into a fluidized bed operating at 350 °C. The solution forms an aerosol (droplet size of 30 µm), which contacts the hot Pt-WO₃/TiO₂ catalyst and reacts to HMF rather than caramelizing. The maximum yield reached 21% and it increased slightly with temperature, and decreased with increasing catalyst, liquid feed flow rate, and fructose feed concentration. At the optimal condition, selectivity continued to increase with time even after 3h reaction. Selectivity to 2,5-diformyl furan reached 42% at 250 °C with HMF as a feedstock.

Keywords: fluidized bed, oxydehydration, frucotse, platinum, atomization, 5-hydroxymethyl furfural

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1 1. Introduction

The elevated oxygen/carbon ratio of carbohydrates versus petroleum con-2 stitutes an advantage to produce specialty chemicals and monomers. Sugar fermentation to bio-ethanol dominates the market at a maximum theoretical carbon atom yield of 67 % [1]. However, specialty chemicals command prices several-fold higher than that of bioethanol at fuel value. Fructose dehydrates to 6 5-hydroxymethyl furfural (HMF), a green intermediate, with a greater selectivity than glucose due to the similar spatial conformation and the faster enolisation 8 reaction [2]. Hydrogen reacts with HMF to dimethyl furan and dimethyl tetrahy-9 drofuran (Figure 1)—a biofuel [3, 4]— while the hydrogenolytic ring opening 10 produces adipic acid—a monomer for nylon-6,6 [5]. Oxygen reacts with HMF 11 to 2,5-diformyl furan [6, 7, 8] and further to 2,5-furandicarboxlylic acid (FDCA) 12 [9, 10]. FDCA is the furanic substitute of terephthalic acid, which is a promising 13 substitute for polyethylene terephthalate. Avantium developed the YXY tech-14 nology that converts HMF to an ether with methanol/ethanol followed by an 15 oxidation step to FDCA [11, 12]. Acidic catalysts, ionic liquids, and supercritical 16 water dehydrate fructose and glucose to HMF [13, 14, 15, 16, 17, 18, 19]. Or-17 ganic solvents are necessary to extract the product otherwise HMF hydrolyzes to 18 levulinic acid and formic acid, or polymerizes to insoluble compounds-humins 19 [20, 21, 22] (Figure 1). 20

Sn-Beta zeolite in tetrahydrofuran and water convert carbohydrates at 70 %
selectivity [23]. Other organic solvents include alkylphenol [24], dimethylsulfoxide (DMSO) and methylisobutylketone [25, 26] and ethyl acetate [27]. These
processes require contact times that range from minutes to hours because of the
poor mass and heat transfer characteristics of multiphase (liquid) reactors.

Metal-based catalysts [9, 10, 28, 29, 30, 31] or enzymatic processes [32, 33, 34]
oxidize HMF to FDCA. Tandem processes in a single vessel reduces complexity

like the multiphase reactor with methyl-isobutyl ketone and 2-butanol as organic 28 phase [35]; the aqueous solution dehydrates fructose to HMF, while the organic 29 phase extracts it and further oxidizes to FDCA [36]. Pt/C oxydehydrates fruc-30 tose to FDCA in γ -valero lactone and H₂O [37]. Combination of ionic liquids 31 and not-noble metals avoid the organic phase and allows the one pot reaction 32 [38]. Fluidized bed reactors operate at higher temperature with superior mass 33 transfer and, consequently, reaction rates orders of magnitude higher. FBRs 34 pyrolyze biomass into energy and chemicals [39]. Glass beads in an FBR cracks 35 aqueous solutions of sugar sparged into the bed [40, 41] Fast pyrolysis of cellulose 36 in FBRs approach 62% yields of levoglucosan, 3.5% of HMF and 1% of furfural 37 [42]. Immobilized anaerobic sludge produces biohydrogen and bioethanol [43]. 38 A magnetically stirred fluidized bed reactor ferments glucose to ethanol within 39 95% of the theoretical yield [44]. Two anaerobic fluidized bed reactors at 55 °C 40 product H_2 and ethanol molar fractions of 59% for a xylose-glucose mixture 41 [45].42

We demonstrated the versatility of atomizing liquids into catalytic fluidized 43 beds: VPO partially oxidizes xylose to C2-C4 carboxylic acids [46]; WO₃/TiO₂ 44 dehydrates glycerol to acrolein [47]; decarbonylates fructose to furfural [48]; and, 45 Keggin-type catalyst oxydehydrates 2-methyl, 1-3-propanediol to methacrylic 46 acid [49]. Here we investigated fructose dehydration to HMF in a μ -fluidized 47 bed reactor. A nozzle atomized the aqueous liquid feed directly into the cat-48 alytic bed. We screened temperature, O₂ concentration, catalyst loading, Pt 49 content on the catalyst, liquid flow rate, feed fructose mass concentration with 50 a Plackett-Burman experimental design. The experimental plan was based on 51 three levels of temperature and O₂:fructose molar ratio and two levels for cata-52 lyst loading. 53



Figure 1: Fructose dehydrates to HMF. Organic solvents suppress the polymerization to humins and the rehydration to levulinic acid and formic acid. Decarbonylation leads to furfural, while the hydrogenation produces 5MF. HMF oxidation gives DFF and further FDCA, the furanic substitute of terephthalic acid.

54 2. Experimental section

A furnace heated a 15 mm ID by 400 mm high quartz tube. Three thermo-55 couples measured the temperature along the length at 20 mm below the bed, 56 $5 \,\mathrm{mm}$ — inside the bed, 90 mm above the distributor, and a fourth monitored 57 the temperature in the exit line. The reactor operated at 1.4 bar while the 58 ΔP between the inlet and outlet—0.001 bar during the reaction. A quartz frit, 59 with a porosity of 150 µm to 200 µm, ensured the gas was distributed uniformly 60 across the reactor diameter (Figure 2). A stream of O₂ in Ar fluidized the cat-61 alytic bed and burned the coke formed during the reaction. A nozzle atomized 62 the aqueous fructose solution into the Pt-WO₃/TiO₂ catalytic bed. An HPLC 63 pump metered the liquid solution feedrate while $50 \,\mathrm{mL}\,\mathrm{min}^{-1}$ of argon atomized 64 it to produce an effervescent spray (Figure 3c) with droplets less than 30 µm 65 to minimize catalyst agglomeration and blocking the nozzle. A ceramic tube 66 enveloped the injector to reduce the heat transfer and ensure that the solvent 67



Figure 2: A nozzle atomizes the fructose solution directly into the catalytic bed. A $DMSO/H_2O$ quench traps the products and an HPLC analyzes the trend. An online MS monitored non-condensable gases.

evaporated in the bed rather than the injector; A stream of $50 \,\mathrm{mL}\,\mathrm{min}^{-1}$ of argon 68 flushed the annular space between the injector and ceramic tube. The exit line 69 (uninsulated) fed into a quench in an ice bath The quench fluid contained 25 g 70 dimethyl sulfoxide to improve furanic solubility and $25 \text{ g H}_2\text{O}$. An on-line mass 71 spectrometer (MS) with a multiple ion detector monitored non-condensable gas 72 concentrations—CO, CO₂, O₂, Ar, CH₄, while an HPLC quantified the liquid 73 samples collected each 15 min during the first hour and then each 30 min until 74 the end of the experiment (Figure 2). Glycerol was the internal standard for 75 the HPLC analysis. At the end of each experiment we cleaned the exit line with 76 5 mL of water and analyzed this sample. 77

⁷⁸ Product selectivity, S_i , is based on a molar balance around each component ⁷⁹ i, n_i^{out} :



Figure 3: 1/16" (1.59 mm) stainless steel pipe filed at the top to obtain an orifice of 45 µm. The IR camera shows that the atomization and the evaporation at the orifice decreased the temperature at the tip, forming a full cone with an angle of 80°.

$$S_i = \frac{\sum_j n_{i,j}^{\text{out}} / \vartheta_{i,j}}{n_{\text{fr}}^{\text{in}} - n_{\text{fr}}^{\text{out}}} \cdot 100 \tag{1}$$

where $n_{\rm fr}^{\rm in}$ and $n_{\rm fr}^{\rm out}$ are the moles of fructose entering and exiting the system and ϑ_i is the stoichiometric coefficient for the carbon component of each reaction j. The median droplet size diameter, d_{50} , exiting the nozzle of an internal mixing air-assist atomizer is [50]:

$$d_{50} = 20 \ u_{\rm L}^{0.5} \ m_L^{0.1} \ d_L^{0.1} \ \sigma^{0.2} \ \rho_g^{-0.3} \ \Delta U^{-1.0} \ \left[1 + \frac{m_{\rm L}}{m_{\rm g}} \right]^{0.5} \tag{2}$$

where $u_{\rm L}$ is the superficial velocity, $m_{\rm L}$ and $m_{\rm g}$ the mass flow of the liquid and the gas, $d_{\rm L}$ the orifice dimension, σ is the surface tension and the ΔU the relative velocity between the liquid and the gas.

87 2.1. Materials

All the reagents are analytical grade without further purification. We acquired D-fructose(99%) from Alfa Aesar. We purchased 5-hydroxymethyl furfural (99%), furfural (99%), 5-hydroxymethyl-2-furancarboxylic acid, 5-formyl-2-furoic acid, 2,5-furandicarboxylic acid (97%), 2,5-furandicarboxaldehyde (97%), 5-methyl-2-furaldehyde ($\geq 98\%$), and tetraammineplatinum(II) nitrate ($\geq 99.9\%$) and ammonium (para)tungstate hydrate (>99.99%) from Sigma Aldrich. Air Liquide Canada supplied the gases: argon (>99.7%), 10.0% O₂ balance Ar, and a mixture of CO (1.04%), CO₂ (1.01%), CH₄ (1.03%) balance Ar. Huntsman Corporation supplied the titanium dioxide (Hombikat 110100).

97 2.2. Catalyst preparation

We sieved the support powder from 90 µm to 150 µm in diameter. The crys-98 talline phase of the titania was pure anatase. A successive wetness impregnation 99 method deposited first WO_3 and then Pt on the TiO_2 support. Initially we de-100 termined the total pore volume by dropwise addition of water. Ammonium 101 paratungstate dissolved in a volume of water equivalent to the pore volume of 102 the support. A rotary evaporator operating at 100 rpm for 3 h mixed the active 103 phase and support. The catalyst then dried at 70 °C and 300 mbar for 2 h. The 104 powder then calcined in a furnace at 120 °C for 4 h to completely remove traces 105 of water. The furnace then ramped temperature at $2.5\,^\circ\mathrm{C\,min^{-1}}$ to $600\,^\circ\mathrm{C}$ in 106 air. The powder remained in the furnace at this temperature for 4 h. 107

108 2.3. Analytical instrumentation

A Philips X'PERT diffractometer generated XRD spectra with a monochro-109 matic Cu-k α beam, $\lambda = 0.15406 \,\mathrm{nm}$, at 50 kV and 40 mA. It scanned the 110 gonio axis from 20° to 85°, at a rate of $0.01 \,{}^{\circ} {\rm s}^{-1}$. The crystalline phases were 111 identified with the ICDD database and the Rietveld refinement (X'PERT high-112 score) gave a semi-quantitative characterization for the phases' weight compo-113 sition. The Scherrer approximation defined the average cubic crystallite size: 114 $D = 0.94 \lambda / \beta \text{Cos}\theta$, where λ is the mentioned instrument wavelength, β is the 115 full-width at half-maximum peak height (FWHM, rad), and θ is the Bragg angle 116 for the most intense peak (half of the 2θ position). 117

The FE-SEM-JEOL JSM-7600F scanning electron microscope (SEM) acquired the catalyst images between 5 kV to 30 kV, using secondary and backscattered electrons detectors (secondary electron image —SEI, low secondary electron image —LEI and backscatter image —LABe). The energy dispersive X-ray detector (EDX) mapped the surface of the catalyst and qualitatively quantified the composition and the different phase regions.

A laser diffractometer (Horiba, LA-950) evaluated the particle size distribution (PSD) based on the Mie Theory:

$$D_{4,3} = \frac{\sum d_i^4 \cdot N_i}{\sum d_i^3 \cdot N_i} \tag{3}$$

with N_i as number of particles with diameter d_i . The particle refractive index was 2.75 + 0.00i (R and Chi parameter below 0.05).

A Quantachrome Autosorb-1 N₂ physisorption instrument recorded the ad-128 sorption and desorption isotherms at 77 K. A degasser, operating under vacuum 129 at 300 °C for 6 h, removed the gas adsorbed on the surface [51]. The Brunauer-130 Emmett-Teller (BET) theory regress the specific surface area at P/P_0 0.05 to 131 0.3. The instrument estimated the mesopore size distribution over the desorp-132 tion branch $(P/P_0 0.15-0.995)$, based on the Barrett-Joyner-Hallender (BJH) 133 theory. The total pore volume is evaluated at the maximum filling pressure 134 $(P/P_0 \ 0.995)$, considering all pores with a diameter smaller than 300 nm. 135

A LECO CS744 CHN analyzer measured carbon build up on the catalyst surface after each experiment. An internal balance measured the sample weight loss, when heated above 1000 °C in air. A further CO trap converted the remaining carbon monoxide to CO₂.

A Varian ProStar 325 HPLC, equipped with a UV detector at 260 nm, quantified species concentration of the liquid samples. A MetaCarb 87H column, kept at 60 °C, separated the compounds. The pump flowed a 0.05 N aqueous H₂SO₄ solution at $0.35 \,\mathrm{mL\,min^{-1}}$. Each analysis lasted 70 min to ensure the products separation.

¹⁴⁵ 3. Results and discussion

146 3.1. Catalyst characterization

147 3.1.1. Fluidization and particle size distribution

Geldart classified particles into 4 categories based on the catalyst diameter 148 and the differential of the particle density and the gas density [52]. Geldart 149 group A powders are best suited for catalytic fluidized beds with diameters 150 (d_{50}) on the order of 70 µm. Based on the Horiba LA-950, the average spher-151 ical particle diameter of fresh catalyst increased from 85 µm to 95 µm (Figure 152 4). Coke covered the surface (SEM-EDX) and increased the average particle 153 diameter by $10 \,\mu\text{m}$. The bulk density was $770 \,\text{kg}\,\text{m}^{-3}$, so that we classify it as 154 a group A powder. 155

The minimum fluidization velocity, $u_{\rm mf}$, with 3 g of catalyst in the reactor 156 was $8 \,\mathrm{mm \, s^{-1}}$. Catalyst attrition resistance is a major concern for fluidized 157 beds particularly with high velocity jets where particles collide and fragments or 158 cleaves surface asperities. To prevent this phenomena we opted for the catalyst 159 synthesis by incipient wetness impregnation, which minimizes surface defects 160 and thus asperities. We tested the attrition rate in an air jet mill according to 161 the ASTM 5757 [53]. The high velocity simulates the mechanical stress coming 162 from the nozzle and the distributor. A filtered vessel collected the elutriated fines 163 after 24 h. The catalyst attrits at $5.4 \,\mathrm{mg}\,\mathrm{h}^{-1}$, which is well within commercial 164 practice [54]. 165

166 3.1.2. XRD

We analyzed the calcined catalyst before reaction with a mass fraction of 5 % WO_3 on TiO₂ and 0.5 % Pt or 1.5 % Pt. We characterized the catalyst at the end



Figure 4: Catalyst particle size distribution in logarithmic scale. Coke deposits broadened the peak and increased the average.

Table 1: Variation of the catalyst physical characteristics after the reaction

Fresh	Used
85	95
51.4(1)	71(2)
0.165	0.064
8	
770	
5.4	5.4
	$Fresh \\ 85 \\ 51.4(1) \\ 0.165 \\ 8 \\ 770 \\ 5.4$

of experiment t12 (1.5 % Pt), which had the most coke. XRD analysis detected 169 two crystalline phases: anatase for the titania (ref: 96-900-9087) and platinum 170 (ref: 96-101-1114) while EDX confirmed the presence of W since it was below the 171 XRD detection limit [48]. The titania support maintained a tetragonal structure 172 during calcination and reaction. The platinum presented a cubic structure, with 173 a submicron crystallinity, which increased with Pt loading and decreased due to 174 the coke deposition during the reaction. SEM confirmed the results, providing 175 images of crystals with several hundred nanometers size and a round-prismatic 176 shape. Each crystal contained several crystallites, growing in different directions 177

Table 2: *D* crystallite size (standard deviation among Pt signals); Riet.Pt Rietveld refinement of the Pt phase, the complementary fraction was anatase TiO₂; BET surface area by nitrogen physisorption, results are within $\pm 3 \%$ (n = 3, 95 % confidence interval, CI); ϕ pore volume (CI $\pm 8 \times 10^{-5} \text{ mL g}^{-1}$); $\Delta_{dS(d)} dS(d)$ characteristic pore median (ads. BJH for mesopore and QSDFT for micro); V - t micropore area.

WO_3/TiO_2	D nm	Riet. Pt gg^{-1}	$_{m^2g^{-1}}^{\rm BET}$	$V_{ m pore}$ mL g ⁻¹	$\begin{array}{c} \Delta_{\mathrm{d}V(d)} \\ \mathrm{nm} \end{array}$	$\begin{array}{c} V-t\\ \mathrm{m}^2\mathrm{g}^{-1} \end{array}$
0.5% Pt 1.5% Pt Used, t12, 1.5% Pt	$na \\ 52(7) \\ 88(2) \\ 60(10)$	na 0.008 0.03 0.02	$\begin{array}{c} 63.8(0.1)\\ \text{na}\\ 51.4(0.1)\\ 71(2) \end{array}$	0.180 na 0.165 0.064	$9.6(0.1) \\ na \\ 11.0(0.1) \\ 0.7(0.3)$	$\begin{array}{c} 4.3(0.5) \\ \text{na} \\ 1.0(0.5) \\ 50(2) \end{array}$

(Figure 9). At 50 kV, the X-ray penetrated the catalyst down to 35 µm (Pott's 178 equation): this surface analysis overestimated the Pt fraction with respect the 179 TiO_2 support. As coke builds up, the intensity of the Pt signals decrease and 180 broaden (Table 2). During calcination, WO₃ precursor penetrated the titania 181 lattice thereby reducing the tungsten signal. Calcination at 600 °C was low 182 enough to minimize phase segregation and so the WO₃ remained amorphous. 183 A weak, unidentified peak emerged at 31.6° after reaction. Reaction conditions 184 may have crystallized part of the amorphous WO₃ in the mesoporous titania 185 structure however, SEM-EDX could not confirm WO₃ crystals on the surface of 186 the catalyst but N₂ physisorption detected a decrease in pore size after reaction. 187 The small crystallite size (30 nm) and the strong chemical interaction with the 188 surrounding environment (coke and titania) shift the signal. 189

190 *3.1.3.* BET

The TiO₂ support and tungsten salt precursor contribute most to the specific surface area (SSA), pore size distribution and pore volume (PV) of the catalyst after calcination (Figure 6) [48]. Calcined catalyst has a type IV isotherm and an H2 hysteresis loop: mesoporous structure with a narrow distribution of pore necks. A mass fraction of 1.5 % Pt decreased the SSA with respect to calcined WO₃/TiO₂ catalyst. EDX images show Pt on the surface but not in the interior



Figure 5: Stacked spectra recorded with the same conditions and smoothed with an 11 points cubic function, Cu- $k\alpha$ sidebands were removed: coke deposits on the used sample reduced the signal to noise ratio. Four sharp Pt signals (39.6°, 46.0°, 67.4°, 81.2°) and their respective planes [hkl] have been identified. The remaining peaks belong to the titania support (anatase) [55].

so the drop in SSA and PV is due to pore-blocking. Pt obstructed pores smaller 197 than 10 nm, which increased the characteristic pore median (dS(d)) by 1 nm. 198 The "t12" catalyst has a type I-IV isotherm and an open H4 hysteresis: a 199 microporous network developed as coke partially filled the internal mesoporous 200 structure. Despite coke deposits, furanic selectivity improved with time. The 201 SSA increased with respect to calcined catalyst, suggesting a selective coke 202 deposit. This phenomenon decreased the reagent and product degradation, 203 despite the pore size dropping from 11.0 nm to 0.7 nm) and the lower pore volume 204 (Table 2). The BJH surface distribution shrunk in the mesopore region. The 205 quenched solid state functional theory (QSDFT) for SSA deviated less than 5%206 from the BET SSA. 207

208 3.1.4. Field Emission Scanning Electron Microscopy (FE-SEM)/EDX

The tungsten oxide was homogeneously dispersed on the titania support. Pt crystals were poorly dispersed on the surface as SEM images show regions



Figure 6: Nitrogen physisorption isotherms. The used catalyst loses the microporous fraction and the total pore volume decreases as a consequence. Carbon obstructing the mouth of the micropores accounts for the large reduction at $P/P_o > 0.7$.

with bright spots with Pt particles (Figure 7). Furthermore, some particles have much more Pt than others. The Pt submicron crystals were 250 µm on average (Figure 8). After reaction, Pt particles formed agglomerate with several hundred crystals but the powder remained free flowing. Only on the sparger tip circumference did powder agglomerate [46].

An EDX scan at 20 kV of the catalyst surface to a depth of 10 µm confirmed that W covered the surface uniformly. On the contrary, Pt forms submicron crystals rather than forming a monolayer on the surface or in the interior. Titanium-oxygen molar ratios were coherent with the TiO₂ composition. Pt was only in the metallic form since the EDX oxygen image showed dark spots corresponding to the Pt crystals (Figure 10).

We crushed used catalyst and the SEM images of the chunks showed no coke in the interior. As much as $(20 \,\mu\text{m})$ of coke covered some of the particles but most of it was homogeneously distributed on the surface (Figure 10). Clearly, since the carbon coverage was uniform WO₃ rather than Pt initiated the growth of the coke layer. An EDX spectrum on the coke deposit identified a molar



Figure 7: Fresh 1.5% Pt over WO₃/TiO₂ particles. The LABe detector enhanced the signal from heavy elements and the Pt crystals appeared as bright white spots.

 $_{227}$ composition of 90 % soft carbon type and 10 % oxygen.

228 3.2. Internal-mixing two-fluid nozzle

Operating the fluidized bed was problematic due to frequent interruptions in 229 the fluid flow due to solids build up in the sparger. The large surface to volume 230 ratio of the sparger was a contributing factor as the water would evaporate in the 231 tube and the fructose would then crystalize. We injected Ar at $50 \,\mathrm{mL}\,\mathrm{min}^{-1}$ to 232 reduce the residence time of the solution in the tube and improve the effervescent 233 spray of the liquid. The gas and fluid first mix at the t-junction below the 234 sparger tip. We reduce the internal diameter of the top part of a stainless 235 steel pipe of 1.6 mm OD and 0.127 mm ID (Figure 3a) to create a $45 \,\mu\text{m}\pm5 \,\mu\text{m}$ 236 orifice (Figure 3b), which is a 65% reduction of the internal diameter. The 237 setup produced a full cone spray with an angle of $80^{\circ}\pm5^{\circ}$, measured by infrared 238 camera after heating the nozzle to 400 °C. 239

²⁴⁰ Based on Equation 2, the median droplet size was 5 µm, with a Weber num-²⁴¹ ber of 7. The gas flow was laminar around the particles ($N_{\text{Re}} = 11$) and at the



Figure 8: Fresh 1.5% Pt over WO₃/TiO₂ particles. The metallic platinum crystals appeared as multi-facets prisms. Considering their sizes (submicron), the crystallite size of 88 nm (XRD) and the crystal structure of metallic Pt (cubic), several crystallites compose the crystal.

²⁴² orifice ($N_{\text{Re}} = 750$). Higher Re and We numbers increase the atomization speed ²⁴³ and reduce the droplet diameter. Internal mixing increased the contact between ²⁴⁴ the gas and the liquid producing finer droplets [50].

245 3.3. Screening test and full factorial design

A Plackett-Burman screening design assessed the influence of six factors: temperature (150 °C and 300 °C), O₂:fructose molar ratio (2:1 and 20:1), catalyst mass (2.5 g and 5 g), Pt loading (0.5 % and 1.5 %), feed flow rate (50 μ L min⁻¹ and 100 μ L min⁻¹) and feed fructose mass concentration (2.5 % and 5 %). The design comprised 12 experiments.

All the tests demonstrated total conversion of fructose and produced coke, COx, and various organic compounds. Some of the fructose degraded along the walls and exit line.

The dehydration reaction was independent of oxygen concentration but it helped control coke build-up on the surface. The two levels of mass of catalyst



Figure 9: Used "t12" catalyst's surface. Shiny "metallic-lookalike" coke chunks were dispersed around the spherical catalyst particles after mechanical breakage. Some particles broke as well.

loaded varied the contact time, while two flow rates modified the weight hour
space velocity and the gaseous partial pressure of water.

Catalyst loading accounted for most of the variance in the data: furanic 258 products selectivity was greater with less catalyst. The maximum total product 259 selectivity never exceeded 6 %, due to the extreme conditions of the screening 260 test. CO_2 and CO rose with temperature, reaching 59% and 4% at 300 °C, 261 respectively. Furthermore, higher oxygen concentration produced more CO_2 . 262 HMF, the dehydration product, increased with higher liquid flow rate and lower 263 catalyst loading. Increasing the partial pressure of water increased the cat-264 alytic surface saturation, lowering the degradation kinetics. HMF conversion 265 increased with higher contact time. Furfural, the decarbonylation product of 266 HMF (Figure 1), depended only on catalyst loading—it increased with longer 267 contact time. Maximizing the contact time, determined the fructose and the 268 intermediate degradation to coke and COx. HMF hydrodehydrates to 5MF 269 (Figure 1). Higher temperature and lower catalyst loading increase selectivity. 270



Figure 10: SEM and EDS mapping of the used "t12" catalyst's surface. Carbon (C, red) partially covered the surface and suppressed the underlying elements' signals. Oxygen (O, blue) was predominant were titanium was also present (Ti, yellow), less were carbon was present and absent were platinum was present (Pt, violet). Tungsten (W, green) was homogeneously distributed along with titanium.

Furthermore, lower O_2 concentration reduces the conversion of H_2 to water, increasing the hydrogenation reaction rate. Increasing the Pt favoured hydrogen adsorption, and consequently 5MF.

Oxygen reacts with HMF to HMFCA and DFF (Figure 1). Oxidation kinet-274 ics of the hydroxyl moiety of HMF is faster than the conversion of the aldehydic 275 functional group. DFF only reached a maximum selectivity of 1%, while HM-276 FCA never exceeded 0.05%. Lower catalyst loading and higher temperature 277 increased the selectivity, which is consistent for a high activation energy for 278 HMF oxidation. Furthermore, as for all the furanic compounds, lower catalyst 279 loading reduced the contact time and the degradation process. A further oxi-280 dation of HMFCA and DFF led to FDCA. The amount of catalyst tested was 281 high, leading to elevated contact time and increasing the degradation. 282

We executed a full factorial design including three levels for temperature (300 °C, 350 °C, and 400 °C) and O₂ content (0.5, 1 and 10 molar ratio with fructose) and two levels of catalyst loading (1.5 g and 3 g). We kept Pt loading (1.5 %) constant, increasing the liquid flow rate (300 μ L min⁻¹) and keeping the fructose mass percentage in the feed at 2 % (Table 3).

The contact time, τ , between the fructose injected and the catalyst varied

$\operatorname{Exp} \#$	Cat	T	O_2/fruct	$S_{\rm CO_2}$	$S_{\rm CO}$	$S_{\rm CH_4}$	S_{Coke}	$S_{\rm HMF}$	$S_{\rm FUR}$	S_{5MF}	$S_{\rm DFF}$
	g	$^{\circ}\mathrm{C}$		%	%	%	%	%	%	%	%
1	3	300	0.5	6	6	9	8	0	5	3	1
2	3	400	1	12	10	5	10	4	5	1	1
3	1.5	300	10	20	4	17	6	6	4	0	1
4	1.5	400	1	2	3	1	12	9	3	0	0
5	3	350	10	4	3	4	55	3	2	1	1
6	3	300	1	3	12	2	43	3	1	0	0
7	1.5	350	10	0	2	0	21	1	1	0	0
8	3	350	0.5	8	5	4	54	0	5	4	3
9	1.5	300	0.5	2	0	1	13	0	1	0	0
10	1.5	300	1	4	2	3	36	5	6	1	1
11	3	350	1	12	6	5	57	1	5	4	3
12	1.5	350	1	7	5	5	49	11	6	1	2
13	1.5	350	0.5	4	3	4	31	12	6	1	1
14	1.5	400	1	7	3	5	48	7	3	1	3
15	3	400	10	47	1	17	43	0	0	0	0
16	3	300	10	41	1	15	66	1	2	0	1
17	3	400	0.5	4	2	2	24	1	9	6	2
18	1.5	400	10	11	8	3	20	0	7	4	2

Table 3: Fructose oxydehydration full factorial design of experiments over 1.5% Pt-WO₃/TiO₂. Factors include catalyst loading (2 levels), temperature (3 levels), and O₂:fructose molar ratio 3 levels). The selectivities are calculated from time 0 min to 180 min. HMF: 5-hydroxymethyl furfural; FUR: furfural; 5MF: 5-methyl furfural; DFF: diformyl furan.

between 0.3 s to 0.4 s and fructose conversion was complete for all experiments 289 (Table 3). The carbon balance was between 57% to 97%. Carbon losses were 290 due to product degradation on the reactor wall or inside the exit line. The 291 catalyst becomes increasingly selective with time and this induction time can 292 exceed 2 h so the reported selectivities are pessimistic since they are calculated 293 based on the 3 h from when the pump started. The mass balance of several tests 294 were less than 50% so we have ignored these tests while assessing the impacts 295 of the various factors. The sum of the selective oxidation products—HMF, 296 furfural, 5-methyly furfural, and DFF—reached 20%. The highest yield of DFF 297 was only 3% but HMF, the first step of the process, reached 12%. According to 298 a power-law regression model, the furanic's concentration increases linearly with 299 temperature but decreases with the square root of mass of catalyst and decreases 300 to a lower power with the oxygen:fructose ratio—feeding more oxygen reduces 301 the productivity (Figure 11). The correlation explains 63% of the variance in 302



Figure 11: Surface chart of HMF selectivity with 1.5 g catalyst loading.

the data but excludes experiments for which the mass balance closure is less than 50 %. The reason relates to the temperature, which was too low to react. The CO₂ selectivity reached 20 % while the maximum CO selectivity and CH₄ selectivity were 12 % and 17 %, respectively. The concentration of CO₂ was highly correlated with CH₄. Excluding experimental data for which the mass balance closed to below 50 %

$$CH_4 = 1.2 \frac{CO_2}{W} \quad R^2 > 0.9$$
 (4)

where W is the mass of catalyst (Figure 12). Data CO_2 selectivity was essentially independent of temperature; it increased with the square-root of the O2:fructose ratio, and increased more than linearly with the mass of catalyst. Considering the complete decomposition to the stoichiometric lowest common denominator, we would expect a strong correlation between S_{CO_2} and S_{CH_4}

$$C_6 H_{12} O_6 \to 3 C H_4 + 3 C O_2 \tag{5}$$



Figure 12: CH_4 parity plot. Data from 1 experiment was excluded because of the poor mass balance (closed circle).

 $_{
m 314}$ or $S_{
m CO}$ and $S_{
m H_2O}$

$$C_6 H_{12} O_6 \to 6 H_2 O + 6 C O \tag{6}$$

The strong correlation of the former could be related to the decomposition of a 315 C₂ substrate like methylformate. Dimerization of formaldehyde leads to methyl-316 formate and this Tishchenko-like reaction is improbable at the reaction condi-317 tions. Feeding formalin across the reactor at these conditions would confirm 318 this reaction mechanism. We exclude methanation as a reaction pathway and 319 sequential combustion of methane from the oxygen in the fructose as this would 320 produce water. Coke formation is related to the decomposition of the feed or 321 the products on the catalyst and built up in all experiments and agglomerated. 322

323 3.4. HMF to DFF

We investigated the oxidation of HMF to DFF at four temperatures between 250 °C to 400 °C and two catalyst loading, 1.5 g and 5 g, maintaining the O_2 :HMF molar ratio of 2 (Table 4). Higher catalyst loading reacted all the HMF at the expense of DFF selectivity which approached at most 4 %. On the other hand, at low catalyst loading and 350 °C or 400 °C DFF selectivity was 26 % and 16 %, respectively. Conversion dropped to 86 % at 250 °C and DFF selectivity increased to 42 %.

Mass g	$T^{\circ}C$	$\stackrel{\rm Conversion}{\%}$	$S_{\mathrm{CO}_2} \ \%$	$S_{ m CO} \ \%$	$S_{ m FUR} \ \%$	$S_{5\mathrm{MF}} \ \%$	$S_{ m DFF} \ \%$
1.5	350	100	6	6	9	11	26
5	350	100	4	6	0	1	0
1.5	400	100	23	6	4	12	16
5	400	100	11	5	1	2	4
1.5	300	92	3	28	1	11	15
1.5	250	86	15	18	6	18	42

Table 4: Higher contact time increase the degradation kinetic. Decreasing the temperature decreases the conversion but raise the DFF selectivity. The O₂:HMF ratio was 2 for all experiments.

5MF, the main by-product of the reaction, is mainly controlled by temperature and catalyst inventory. In fact, at higher contact time, the selectivity dropped to 2%, while decreasing the temperature from 400 °C to 200 °C, the selectivity increased from 12% to a maximum of 18%. Furfural, the other main by-product, remained almost stable around 6% for all the reactions with lowest amount of catalyst, but ranged was 1% with 5g of catalyst Coke built up on the catalyst, but was insensitive to either temperature or catalyst loading.

CO and CO_2 the selectivity varied considerably with both temperature and catalyst loading. At low temperature and low catalyst loading, CO was higher than CO_2 , but increasing the two variables, the ratio became 1:1 and with a further increase CO_2 selectivity became higher than that of CO. The higher contact time increased the degradation of the molecules and carbon oxide selectivity increased with temperature.

344 4. Conclusions

Gas phase fructose oxydehydration is a new pathway to platform chemicals from organic feedstocks. It avoids organic solvents, decreases reaction time to fractions of a second, and facilitate product separation. Fructose first dehydrates to HMF followed by tandem reactions to furfural, 5-MF, and DFF.

Other undesirable products are CO, CO₂, CH₄, and coke. The CH₄ is linearly 349 correlated with CO_2 while the selectivity to coke was highest among the prod-350 ucts detected. Generally, the mass balance was greater than 50% but for 5 of 351 the 18 experiments in the full factorial design it was less than this. HMF se-352 lectivity from fructose reached 12 % at 350 °C. Other partial oxidation product 353 selectivities were less than 7%. Even shorter contact times are required to im-354 prove selectivity and reduce conversion. Since the catalyst induction time was 355 on the order of 2 h (the catalyst continued to activate), the product selectivities 356 are certainly higher. Coke built up on the catalytic surface, agglomerated the 357 catalyst but also covered the strongest acid sites, enhancing the selectivity to 358 the furanic compounds. Feeding HMF rather than fructose demonstrated that 359 lower temperatures are required to increase the furanic's selectivity. 360

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