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COMMUNICATION

Combination of Pd/C and Amberlyst-15 in a single reactor for the acid/hydrogenating catalytic conversion of carbohydrates to 5-hydroxy-2,5-hexanedione

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Here we show that combination of Pd/C and Amberlyst-15 in a single reactor allowed fructose and inulin to be converted to 5-hydroxy-2-5-hexanedione, a valuable chemical platform, in a one pot process.

Production of chemical platforms from biomass has become a top priority in academia and industry not only to create diversity but also to access chemicals with similar or improved properties as compared to fossil-derived chemicals.[1] In this context, diketone derivatives appear as an interesting class of chemical platforms from which valuable derivatives such as polyols, amines, tetrahydrofuran, lactones, among others could be produced.

Diketone derivatives can be produced from biomass for instance by the catalytic oxidation of glycerol[2] (and more generally renewable polyols) or the catalytic conversion of hexoses to levulinic acid.[3] Although of great interest, these routes have shortcomings hampering their industrial development. For instance, oxidation of polyols suffers from a lack of selectivity while the production of levulinic acid requires formic acid, formed as a co-product, to be chemically valorized.

During the last decade, numerous works have focused on the catalytic hydrogenation/hydrogenolysis of furanic derivatives to dimethylfurane or tetrahydrofurane derivatives.[4] To date, only a little attention has been paid to the catalytic conversion of 5-hydroxymethylfurfural (HMF), a chemical derived from hexoses, to hexanedione derivatives. Among them, formation 2,5-hexanedione (HDX) from HMF was reported as a feasible way but one should notice that yields of HDX often remained low (< 10%).[5] Interestingly, in 1991, V. Schiavo et al. reported for the first time that HMF can be converted to 5-hydroxy-2,5-hexanedione (HHD) by hydrogenation over a Pt/C solid catalyst in an aqueous solution of oxalic acid (pH = 2).[6] Later on, van Bekkum also pointed out the formation of HHD when performing the catalytic hydrogenation of HMF in an aqueous solution of HCl.[7] Although these studies have opened an access to a novel functionality from HMF, these are the only two reports in the literature dealing with this reaction. Even more surprising, to the best of our knowledge, no one attempted the

direct conversion of carbohydrate to HHD despite novel and valuable polyols, amino-alcohols or functionalized tetrahydrofurane derivatives could be easily obtained from this diketone derivative, all these chemicals having a strong potential of markets in the field of surfactants, polymers and solvents. The reason for this lack of documentation on HHD (and more generally on diketone derivatives) stems from the huge difficulty to control the selectivity of this reaction from HMF or carbohydrates. The production of HHD from carbohydrates requires the presence of acid and hydrogenating sites on the same catalyst or reactor. A close control of the rate of each elementary step is necessary otherwise many side-products can be formed.
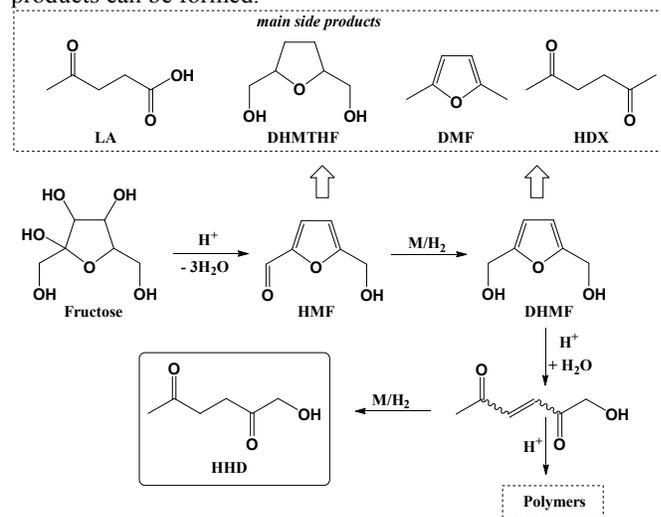
Scheme 1 Conversion of fructose to HHD in a dual acid/hydrogenation catalytic pathway

The accepted mechanism for this reaction is rather complex and involves (1) an acid-catalyzed dehydration of hexoses to HMF followed by (2) hydrogenation of HMF to 2,5-dihydroxymethylfurane (DHMF), (3) acid-catalyzed ring-opening of DHMF to unsaturated diketone derivatives (highly

instable compound) and finally (4) hydrogenation of the C=C bond yielding HHD (Scheme 1).[6,7]

Here, we wish to show that combination of Pd/C and Amberlyst-15 (acid catalyst) in the same reactor allowed HHD to be produced with good yields not only from HMF but also directly from fructose and inulin. In particular, we show that high selectivity of this reaction is associated with a compromise between the pressure of hydrogen and the amount of Pd/C and Amberlyst-15.

Prior to optimization of catalytic conditions from carbohydrates, experiments were first conducted from HMF. In this context, we concentrated our efforts on the hydrogenation of HMF to dihydroxymethylfurane (DHMF) which is the first key intermediate in the production of HHD.[6,8] Pd over charcoal (Pd/C) was selected in our investigations because it is a water-tolerant solid catalyst widely used at an industrial level. Tolerance to water is a crucial aspect considering that molecules of water will be involved to perform the subsequent hydrolysis (acid-catalyzed ring opening) of DHMF. Results are presented in Table 1.

Under mild conditions (80°C) and in neat tetrahydrofurane (THF), HMF was converted to DHMF with 71% yield after 48h of reaction in the presence of 5 wt% of Pd/C and under 50 bar of H_2 (Table 1, entry 1). The only detected secondary product was the 2,5-dihydroxymethyltetrahydrofurane (DHMTHF) resulting from the total hydrogenation of HMF. When the temperature was raised to 120°C, a mixture of DHMTHF (34%) and DHMF (48%) was obtained suggesting that temperatures higher than 80°C are not favorable for the selectivity of the reaction (Table 1, entry 2). Considering that water will be further involved in the reaction mechanism (hydrolysis of DHMF), water was progressively added to the reaction medium to check its influence on the hydrogenation step of HMF. In the presence of 10 wt% of water, DHMF was produced nearly as an exclusive product up to 60% conversion (Table 1, entry 3). No appreciable effect of water (10 wt%) was however noticed on the reaction rate. The formation of undesirable side products (not identified) was observed only when the water content reached 20 wt% (Table 1, entry 4). Hence, 10 wt% was considered as a limit for the water-tolerance of the hydrogenation step. The pressure of hydrogen obviously plays an important role on the reaction rate. An increase of the H_2 pressure from 50 to 80 and 100 bar improved the reaction rate and the yield of DHMF was increased from 57% to 66% and 82%, respectively (Table 1, entries 3, 5, 6). This result may be

ascribed to a better solubility of H_2 in the THF/H_2O phase when the pressure was increased.[9]

Next, Amberlyst-15 (-SO_3H = 4.70 mmol/g) was co-added to the Pd/C to promote the direct conversion of HMF to HHD through *in situ* hydrogenation/hydrolysis of HMF. Amberlyst-15 is a widely used solid acid catalyst in industry and was preferred here for this reason. Note that water was not added in the reaction vessel since wet Amberlyst-15 was used. The water content of the reaction media (THF, HMF, Pd/C and A15) was determined by Karl Fischer analysis and reached 3.8 wt% which is in the range of the water-tolerance defined above for the hydrogenation step of HMF to DHMF. Results are summarized in Table 2. Heating HMF at 80°C in THF containing 6.5 wt% of Pd/C and 11 wt% of Amberlyst-15 led to the production of HHD with 65% yield (Table 2, entry 2). Note that without Pd/C, no formation of HHD was evidenced further supporting the necessity to combine both solid catalysts in the reactor (Table 2, entry 1). Under these conditions, a pressure of hydrogen of 50 bar was found to be optimum. An increase or a decrease of the pressure of hydrogen had indeed a dramatic effect on the yield of HHD. For instance at 30 bar of hydrogen, HHD was produced with only 20% yield (Table 2, entry 3) while the carbon mass balance was decreased to only 44% due to dominant acid-catalyzed reactions (mainly stemming from the acid-catalyzed polymerization/condensation of the intermediate unsaturated diketone derivative). Similarly, at 80 bar of hydrogen, catalytic reduction of HMF to DHMF (25% yield) and DHMTHF (15% yield) was favored and the yield of HHD was decreased to 43% (Table 2, entry 4). Hence a pressure of hydrogen of 50 bar was selected in our experiments. For the same reason, a change of the Pd/C loading obviously dramatically impacted the selectivity to HHD. A decrease of the Pd/C loading from 6.5 wt% to 4 wt% favored the acid-catalyzed reactions and lowered both the yield of HHD to 58% and the carbon mass balance from 84% to 64% (Table 2, entry 5). Reversely, an increase of the Pd/C loading from 6.5 wt% to 13 wt% favored hydrogenation reactions and, in this case, a messy mixture of compounds was produced (Table 2, entry 6). Among them, HHD (7 % yield), DHMTHF (10% yield), dimethylfurane (15% yield) and HXD (6% yield) were detected. Note that at such high loading of Pd/C, the yield of HHD can be improved to 30% only by reducing the pressure of hydrogen from 50 bar to 30 bar (Table 2, entry 7). A similar trend was of course also observed with the loading of

Table 1 Catalytic conversion of HMF to DHMF in the presence of a Pd/C solid catalyst
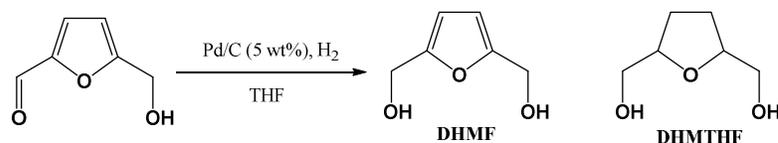
Entry	P_{H_2} (bar)	Solv.	Temp. (°C)	Time (h)	Conv. (%)	DHMF yield (%)	DHMTHF yield (%)	Carbon mass balance (%)[a]
1	50	THF	80	48	98	71	15	86
2	50	THF	120	20	100	48	34	82
3	50	THF/H_2O (9/1)	80	20	60	57	2	99
4	50	THF/H_2O (8/2)	80	20	50	20	0	70
5	80	THF/H_2O (9/1)	80	20	75	66	4	95
6	100	THF/H_2O (9/1)	80	20	97	82	8	93

[a] the carbon mass balance was measured based on detected/identified products. Other were mostly unidentified polymeric black materials.

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Table 2 Catalytic conversion of HMF to HHD in the presence of Pd/C and Amberlyst-15 solid catalysts
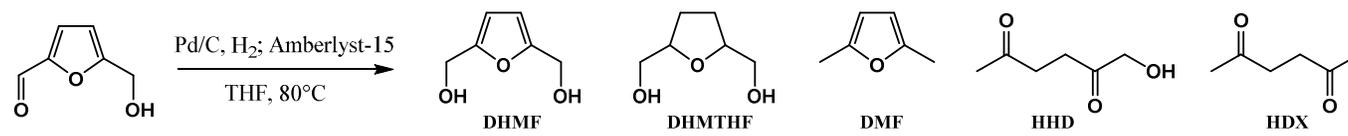
Entry	Pd/C (wt%)[a]	Amberlyst-15 (wt%)[a]	P_{H2} (bar)	Time (h)	Conv. (%)	HHD yield (%)	DHMF yield (%)	DHMTHF yield (%)	DMF yield (%)	HDX yield (%)	Carbon mass balance (%)[b]
1	0	11	50	15	6	-	-	-	-	-	-
2	6.5	11	50	15	100	65	0	2	7	10	84
3	6.5	11	30	15	100	20	0	0	10	14	44
4	6.5	11	80	15	95	43	25	15	0	3	86
5	4.0	11	50	15	90	58	0	0	0	6	64
6	13.0	11	50	15	100	7	0	10	15	6	38
7	13.0	11	30	15	100	30	0	10	9	21	70
8	6.5	5.5	50	15	65	18	32	6	0	0	91
9	6.5	20	50	10	100	67	0	0	1	7	75
10	5.5	20	50	15	100	77	0	0	0	6	83

[a] based on the amount of HMF, [b] the carbon mass balance was measured based on detected/identified products. Other were mostly unidentified polymeric black materials.

Amberlyst-15. A decrease of the Amberlyst-15 loading from 11 wt% to 5 wt% led to dominant hydrogenation reaction and thus lowered the yield of HHD to 18% (Table 2, entry 8). Interestingly, an increase of the Amberlyst-15 loading from 11 wt% to 20 wt% had however a positive effect on the reaction rate while the yield to HHD (67%) was not affected (Table 2, entry 9). At such loading of Amberlyst-15, a slight decrease of the Pd/C loading from 6.5 wt% to 5.5 wt% allowed HHD to be produced with an even higher yield of 77% (Table 2, entry 10). Note that a further decrease of the Pd/C loading to 4 wt% dropped the yield of HHD to 60%.

Altogether, these results suggested that a high selectivity of HHD in this reaction may require a close control of the amount of acid and reductive catalytic sites. A Pd/C and Amberlyst-15 loadings of 5.5 wt% and 20 wt%, respectively, were found to be optimum at 80°C while the pressure of hydrogen should be preferentially maintained at 50 bar.

HMF is commonly produced through an acid-catalyzed triple dehydration of hexoses.[10] Extraction of HMF from an aqueous catalytic phase is not so trivial because (1) HMF is rather unstable and (2) the partition coefficient of HMF between aqueous and organic phase is not very high, thus requiring multistep extraction. Considering that HMF is only a reaction intermediate, we then attempted the direct conversion of fructose to HHD in a single reactor to circumvent the costly intermediate extraction/purification of HMF. Although of great interest from an economical point of view, this reaction is however scientifically relevant and requires the close control of four different steps in a single reactor.

Inspired by our above described results, a solution of 5 wt% of fructose was heated at 80°C in THF in the presence of Pd/C (6.5 wt%) and Amberlyst-15 (11 wt%). The pressure of hydrogen was decreased to 10 bar since at 50 bar reduction of fructose to hexitol and C-C bond cracking products were observed. Unfortunately, under these conditions, HHD was produced in a trace amount. In addition, formation of HMF was not observed suggesting that fructose was not dehydrated in these particular reaction conditions. Hence, the amount of Amberlyst-15 was increased to 35 wt%. Under these conditions, fructose was converted but the reaction did not achieve a high HHD selectivity and a complex mixture of compounds was obtained. It should be noted that dehydration of fructose and an increase of the amount of Amberlyst-15 from 11 wt% to 35 wt% contribute to increase the water content of the media and thus may also affect here the selectivity of the reaction as suggested in Table 1. Interestingly, addition of 0.3 wt% of dimethylsulfoxide into the THF led to the complete conversion of fructose and the formation of HHD with 23% yield together with HDX (6.5% yield) and HMF (45 % yield) (Table 3, entry 1). An increase of the pressure of hydrogen from 10 to 20 bar allowed HHD to be produced with 35% yield (after 15h of reaction) while the yield of HMF was concomitantly decreased to 12% (Table 3, entry 2). At prolonged reaction time (20h), no HMF was detected anymore in the reaction media and HHD was obtained with a maximum yield of 55% (Table 3, entry 3). It should be noted that similar yield of HHD can be obtained at only 10 bar of hydrogen but, in this case, it was necessary to use 13 wt% of Pd/C, otherwise acid-catalyzed reaction were dominant (Table 3, entry 4).

Table 3 Direct conversion of carbohydrates to HHD in the dual acid/hydrogenating catalytic system
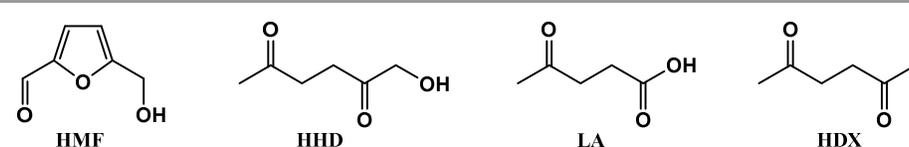
Entry	Carbohydrate	Pd/C (wt%)[a]	P_{H2} (bar)	Time (h)	Conv. (%)	HHD yield (%)	HMF yield (%)	LA yield (%)	HDX yield (%)	Carbon mass balance (%)[b]
1	Fructose	6.5	10	15	95	23	45	5	6.5	79.5
2	Fructose	6.5	20	15	95	35	12	9	7.5	63.5
3	Fructose	6.5	20	20	95	55	0	11	12	82
4	Fructose	13	10	15	95	50	15	2	11	78
5	Inulin	13	35	36	95	27	5	4	17	53

[a] based on the amount of carbohydrate; [b] the carbon mass balance was measured based on detected/identified products. Others were mostly unidentified polymeric black materials.

At the moment we have no rational explanation for the role of DMSO. It should be however noted that when DMSO was used in a larger amount or as a solvent, HHD was not produced anymore. One may suspect that DMSO helps for the dissolution of fructose in THF or modifies the surface of palladium by adsorption.

Then, inulin, a natural biopolymer of fructose, was tested. Results are presented in table 3. We and others have previously showed that inulin can be converted to HMF under acidic conditions.11 To our delight, using the conditions described in Table 3 entry 1, inulin was converted to HHD with 27% yield (entry 5) showing that this system is capable of catalyzing in a single reactor (1) the hydrolysis of inulin to fructose followed by (2) the dehydration of fructose to HMF, (3) the hydrogenation of HMF to DHMF, (4) the rehydration of DHMF and (5) hydrogenation to HHD. Considering that HHD was produced in a one pot process with 27% yield from inulin, the average yield of each elementary steps is 77%, further demonstrating the selectivity of this catalytic reaction. The low carbon mass balance observed in the case of inuline (53%) was mostly due to the side formation of unidentified soluble and insoluble black materials.

Conclusions

In conclusion, we report in this communication that combination of two widely used solid catalysts such as Pd/C and Amberlyst-15 in a single reactor allowed fructose to be converted to HHD with 55 % yield opening a direct route to a chemical platform exhibiting a high potential of market in the field of surfactants, monomers and solvents. In addition, inulin, a natural biopolymer of fructose, was also converted to HHD demonstrating the usefulness of this process. In this dual acid/hydrogenating catalytic pathway, the control of the reaction selectivity is obviously the main key. In particular, the rate of acid and hydrogenation catalytic steps was controlled by adjusting the amount of each catalyst and the pressure of hydrogen. From an ecological point of view, this work also gathers few advantages such as 1) 100% carbon atom economy, 2) the release of only two molecules of water and 3) one-pot process. Although no leaching of catalytic sites was evidenced in the reaction media, it should be noted that an important drop of catalyst activity and selectivity was observed during the second run mostly due to the difficulty to separate insoluble black polymers (side products) from the suspension of Pd/C-Amberlyst-15 solid catalysts. The deposition of palladium species over an acid solid support, the design of a continuous flow process and transposition to other valuable biopolymers is now the topic of current investigations.

Experimental section

Chemicals: all chemicals were purchased to Sigma-Aldrich. Dry Amberlyst-15 was kindly provided by Rohm & Hass. The sulfonic loading of dry Amberlyst-15 is 4.70 mmol/g. Pd/C was purchased to Sigma-Aldrich. It contains 5 wt% of Pd. The Pd/C has a surface area of 832 m^2/g, an average pore sizes of 19.5 Å and the particle sizes are within the range of 1-60 nm.

Analytical methods: Gas chromatography analyses were performed on a Bruker GC-456 equipped with an on column injector (250 °C), an FID detector (325 °C) and an HP-5ms column (30 m × 0.25 mm ×0.25 μm). NMR spectra were recorded on BRUKER ADVANCE DPX 400 spectrometers at 400.13 MHz for ^{1}H and 100.6 MHz for ^{13}C. Data for HHD, DMF, HDX, HMF, LA, DHMF and DHMTHF are already described in the existing literature and were used to ascertain the formation of targeted products.

Selected data for HHD: ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 2.16 (s, 3H, -CH$_3$), 2.59 (t, J = 6.4 Hz, 2H, -CH$_2$), 2.80 (t, J = 6.4 Hz, 2H, -CH$_2$), 3.12 (bs, 1H, -OH), 4.29 (s, 2H, -CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 29.7 (-CH$_3$), 31.7 (-CH$_2$), 36.8 (-CH$_2$), 68.2 (-CH$_2$OH); LC/MS (ESI), m/z = 132.1 uma

Procedure for the hydrogenation of HMF to DHMF and DHMTHF: To a mixture of THF (5 mL, may contain a maximum of 0.5 mL of water), and HMF (150 mg, 1.19 mmol) was added Pd/C (8 mg, 0.0038 mmol, *i.e.* 5 wt% relative to

HMF). The solution was then placed inside the autoclave and flushed with H_2. Next, the reactor was heated at 80 °C under a pressure of H_2 (50-100 bar, see Table 1) for 20 hours. After this period, the reactor was cooled down to room temperature, vented and opened. A syringe filter was used to remove the catalyst from the reaction mixture, and the recovered solution was then analyzed by GC.

Procedure for the hydrogenation of HMF to HHD: To a mixture of THF (5.6 mL), A15 (30 mg) and HMF (150 mg, 1.19 mmole) was added Pd/C (9.7 mg). The solution was placed inside the autoclave and was flushed with H_2. Next, the reactor was heated at 80°C under a pressure of H_2 (preferentially 50 bar) for 10 hours. See Table 2 for the optimal experimental parameters. After this period, the reactor was cooled down to room temperature, vented and opened. A syringe filter was used to remove the catalyst from the reaction mixture, and the recovered solution was then analyzed by GC.

Procedure for the hydrogenation of fructose to HHD: To a mixture of THF (5.6 mL), DMSO (0.01 mL), A15 (87 mg), and fructose (250 mg, 1.39 mmol) was added Pd/C (16.3 mg). The solution was then placed in an autoclave and flushed with H_2. Next, the reactor was heated to 80 °C under a pressure of H_2 of 20 bar. The reaction was stirred under these conditions for 20 hours. After this period, the reactor was cooled down, vented and opened. A syringe filter was used to remove the catalyst from the reaction mixture, and the recovered solution was then analyzed by GC.

Procedure for the hydrogenation of inulin to HHD: the procedure was similar to the one used for fructose except that the amount of Pd/C and the pressure of hydrogen were fixed at 32.6 mg and 35 bar, respectively. The reaction time was also increased from to 36h in the case of inulin.

Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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Graphical abstract

Combination of Pd/C and Amberlyst-15 in a single reactor for the acid/hydrogenating catalytic conversion of carbohydrates to 5-hydroxy-2,5-hexanedione

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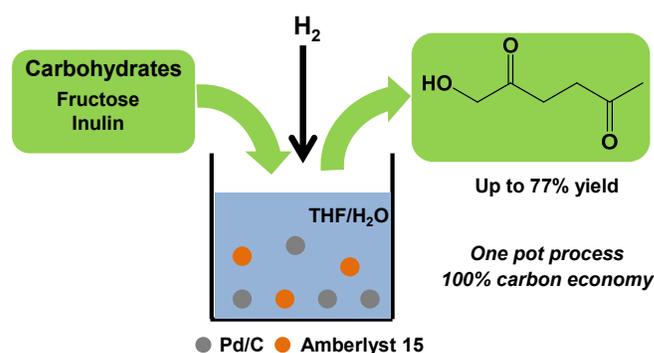
Here we report an effective cooperation between Pd/C and Amberlyst-15 for the catalytic conversion of fructose and inulin to 5-hydroxymethyl-2,5-hexanedione in a one pot process.

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