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CRITICAL REVIEW
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Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: what results? What limitations? What trends?

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Pd-catalyzed *in-situ* domino process for mild and quantitative production of 2,5-dimethylfuran directly from carbohydrates

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An *in-situ* domino process has been developed to be highly efficient for direct and mild conversion of various hexose sugars to the biofuel 2,5-dimethylfuran in almost quantitative yields, without separation of unstable intermediates at 120 ºC in *n*-butanol by using polymethylhydrosiloxane and hydrophobic Pd/C as H-donor and bifunctional catalyst, respectively. Among the cascade reactions, the hydrosilylation process was confirmed by deuterium-labeling and kinetic studies to be favorable for sugar dehydration and exclusively act on deoxygenation of *in situ* formed intermediates including furanic alcohols and aldehydes to DMF via a hydride transfer process that was facilitated by an alcoholic solvent. The catalytic system is more selective than H₂-participated counterpart, and could be scaled up with only 0.04 mol% catalyst loading, giving DMF in a comparable yield of 85%. Moreover, Pd(0) was demonstrated to be the active species for deoxygenation, and the heterogeneous catalyst exhibited good recyclability with little elemental leaching.

Intensification of multistep catalytic processes via mimicking the cascade reaction strategy of living systems is of great potential to enable programmable one-pot synthesis of single and/or multiple products, and avoid the downstream process of unstable/reactive intermediates to substantially reduce the amount of waste and production cost.[1] The sequential use of solid catalysts or bifunctional heterogeneous catalytic materials offers the possibilities to conduct multistep transformations in a single pot, while the unfavorable reaction thermodynamics of different steps and active centers often results in undesired products.[2] Therefore, the development of elegant recyclable catalytic systems to promote the integrated processes in high efficiency is currently encountering enormous challenges.[1b,2a,2d]

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Electronic Supplementary Information (ESI) available: Details of experimental procedures, catalyst preparation and characterization, some catalytic results, and data analyses. See DOI: 10.1039/x0xx00000x

Chemocatalytic conversion of cellulose and hemicellulosic sugars, the most abundant components in lignocellulosic biomass, to platform molecules and biofuels has been considered as one of the promising and renewable alternatives to replace fossil fuel-based products.[3] In connection with this, 5-hydroxymethylfurfural (HMF) and furfural have been identified as key intermediates/starting materials separately for tandem valorization of hexose and pentose sugars to substituted, condensed, oxidized, or hydrogenated compounds.[4] Notably, Ru, Pd, Pt, Ni, and Cu as a hydrogenation metal coupled with a deoxygenation component (e.g., acidic species) in the H₂ atmosphere under relatively harsh reaction conditions have been reported for the conversion of HMF to the potential internal combustion engine fuel 2,5-methylfuran (DMF), which has a comparable energy density (31.5 kJ/mol) to gasoline (35 kJ/mol) but higher research octane number (RON: 119) than gasoline (90-100).[5] In addition, DMF can be used as a biorenewable feedstock for producing *p*-xylene (pX), a commodity precursor of polyethylene terephthalate (PET) with applications in polyester films and fibers.[6] Using fructose instead of HMF as substrate, Dumesic et al. initially explored a two-step catalytic process consisting of HCl and CuRu/C for consecutive reaction steps for dehydration and hydrogenolysis, respectively, accompanied by downstream process in a biphasic reactor for the production of DMF with moderate yields.[7] Recent studies have also illustrated using a combination of Pd or Ru metal with an acid additives can produce DMF with <60 yields from either fructose or glucose via two- or three-step reactions.[8] However, the intermediate separation of intermediates/products seems to be unavoidable in these catalytic systems; otherwise, the monosaccharide dehydration followed by incomplete or full hydrogenation may take place in a single reactor to give 5-hydroxy-2-5-hexanedione (HHD), tetrahydro-2,5-furandimethanol (THFM), and 2,5-dimethyltetrahydrofuran (DTHF), respectively.[9] This apparently demonstrated that the process optimization is indispensable for large scale production of DMF to be cost-effective.[10]

We report here a new and strategic approach to selectively produce DMF unprecedentedly from hexose sugars in *n*-butanol under benign conditions via a single-step process using a simply modified commercial Pd/C catalyst in the presence of liquid H-donor polymethylhydrosiloxane (PMHS). The liquid polymer PMHS with low viscosity is non-toxic, inexpensive, safe, and water/air insensitive,[11] which is a byproduct of the silicone industry and has been applied as an environmental friendly H-donor for the reduction of various organic molecules such as amides, esters, and nitro, carbonyl and hydroxyl compounds over homogeneous metal catalysts.[12] With regard to this, it can be envisioned that acidic and hydrophobic Pd/C is anticipated as a highly efficient and recyclable catalyst for the cascade transformation of hexoses to DMF with PHMS in *n*-butanol.

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One-step production of DMF from fructose was preliminarily examined over various metals (3.4-4.2 wt%, determined by ICP) supported on activated carbon in *n*-butanol comprising PMHS and chlorobenzene (PhCl) that can liberate HCl *in situ*,[13] and the obtained results are shown in Table 1. 2 mol% Pd/C could catalyze fructose to DMF with a good yield of 74% after having reacted at 120 ºC for 1.5 h (entry 1), exhibited higher activity than Co/C, Ni/C, Ru/C, and Pt/C (entries 2-5). A fair yield of DMF (46-60%) was obtained with other Pd-based mixed metals with various supports under identical reaction conditions (Table S1). Despite the degree of metal dispersion (Figure S1), catalytic performance in both activation of PhCl to release HCl and ionic hydrogenation could partially be responsible for the difference in fructose conversion and DMF yield. The major intermediates/byproducts were found to be HMF, 5-methylfurfural (MFF) and 5-methylfurfuryl alcohol (MFA) and overhydrogenated compounds 2,5-hexanedione (HD) and 2,5-dimethyltetrahydrofuran (DTHF) (Figure S2), and the plausible catalytic pathways are provided in Scheme S1. Gratifyingly, Pd/C modified by trimethylchlorosilane (TMS) exhibited quite superior hydrophobicity to the pristine one (Figures 1 & S3), which could facilitate the contact of Pd species with hydrophobic PhCl and PMHS, thus affording an excellent DMF yield of 91% (entry 6). Even at lower temperatures 100 and 80 ºC, comparable DMF yields (62 -85%) were obtained over Pd/C-TMS by slightly extending the reaction time (Table S2). When switching the solvent to other normal and secondary alcohols, a fair to very good yield of DMF (64-82%) was obtained (Table S3, entries 1-4, 6 & 7) but no or a very poor yield of DMF (0-10%) with aprotic solvents (Table S3, entries 8-10), which implied the promotional effect of alcohols rather than H-donor. To get

insight in this perspective, the kinetic isotope effect of methanol (i.e., CH_3OH, CH_3OD and CD_3OD) on the synthesis of DMF from HMF at 60 ºC was studied (Table S4). The distinct discrepancy of reaction constant for normal and deuterated methanol ($k_H = 0.025$ s^{-1} > $k_D = 0.009$ s^{-1}) and no difference between CH_3OD and CD_3OD, indicated the cleavage of O-H bond of methanol is crucial for PHMS-participated hydrogenation, wherein the liberation of hydride (H^-) from PHMS was most likely to be promoted by the protonic alcohols via nucleophilic addition of the alkoxide moiety to the silicon of PHMS. Moreover, the inferior activity of secondary alcohol compared to primary counterpart (Table S3, entries 3-6) could be ascribed to its relatively higher steric hindrance when reacting with PHMS, which further confirms the significant role of alkoxide moiety in the release of H^- from PHMS to promote the hydrogenation process.
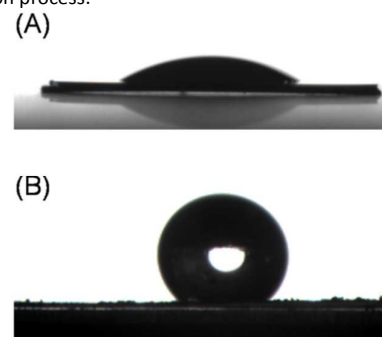

Figure 1. Water contact angle of (A) Pd/C: 28º and (B) Pd/C-TMS: 134º

Table 1. Direct conversion of fructose to DMF with different catalysts

| Entry	Catalyst	Fructose conv.(%)	Product yield (%)						DMF selec.(%)	TOF $(h^{-1})^b$	Carbon balance (%)
			HMF	MFF	MFA	HD	DTHF	DMF			
1	Pd/C	88	4	<1	2	1	3	74	84	29	97
2	Co/C	16	11	0	0	0	0	0	--	5	95
3	Ni/C	24	15	<1	0	0	0	0	--	8	92
4	Ru/C	37	9	1	<1	2	<1	13	27	12	90
5	Pt/C	71	7	<1	15	2	1	36	51	23	91
6	Pd/C-TMS	97	2	<1	<1	<1	1	91	94	32	99
7^c	Pd/C-TMS	99	1	2	<1	3	4	75	76	25	87
8^d	Pd/C-TMS	52	<1	1	2	<1	<1	43	83	13	97
9^c	Metal free	81	62	0	0	0	0	0	--	--	81
10^d	Pd/C-SO₃H	93	6	3	1	3	2	72	77	23	94
11^d	Pd/C-SO₃H-TMS	96	<1	1	<1	2	2	88	92	24	98
12^e	Pd/C-SO₃H-TMS	84	24	5	1	<1	<1	35	42	21	83
13^f	Pd/C-SO₃H-TMS	98	<1	<1	<1	2	3	85	87	408	95

[a] Reaction conditions: 5 wt% fructose, 2 mol% metal, 2.5 mmol PMHS (9 equiv. H^-), 1.5 mL *n*-butanol, 3 μL PhCl (10 mol%) as acidic additive, 120 ºC and 1.5 h. [b] TOF (turnover frequency) = (mole of converted fructose) / (mole of metal × time). [c] Equivalent HCl instead of PhCl was added; 2 h. [d] No acidic additive; 2 h. [e] 1 atm of O_2 filled in a balloon. [f] 15 mmol fructose, 0.04 mol% Pd/C-SO₃H-TMS, 9 equiv. PMHS, 75 mL *n*-butanol, 10 mol% Amberlyst-15, 120 ºC and 6 h.

The addition of equivalent HCl instead of PhCl gave a yield of 76% DMF, with TOF decreasing from 32 to 25 h^{-1} (Table 1, entries 6-7), inferring that HCl released *in situ* influenced on the yield of DMF to some degree. Interestingly, an unexpected DMF yield of 43% was obtained with Pd/C-TMS where no acid additive added (entry 8), wherein HMF was probably generated *in situ* via autocatalysis mediated with the byproduct formic acid.[14] However, only HMF was formed in the presence of HCl (entry 9) at fructose conversion of 81% was much lower than what obtained (99%) over Pd/C-TMS-HCl system (entry 7), evidently demonstrating the cooperative effect on the yield of DMF and shifting the chemical equilibrium toward fructose dehydration. Further kinetic studies on producing DMF from fructose and HMF revealed that the rate-determining step could be the dehydration of fructose (Table S5). As acid additive played a significant role on the yield of DMF, the combination of Pd/C-TMS with solid acids (e.g., beta zeolite, Amberlyst-15, Dowex, and Nafion) were performed and found DMF yields in the range of 59-79% (Table S6), apparently showing a positive role of Brønsted acidity on fructose dehydration.

Intrigued by above findings, a single bifunctional catalysts Pd/C-SO₃H and Pd/C-SO₃H-TMS were prepared by simple methods (see Supporting Information), characterized and found to have decreased surface areas and pore volumes, but increased average pore diameters with good dispersion of metals (Table S7, Figures S1, S4-S7). As compared with Pd/C-SO₃H, the hydrophobic Pd/C-SO₃H-TMS showed an improved DMF yield with few hydrogenated intermediates (Table 1, entries 10 & 11). Although Pd/C-SO₃H-TMS afforded comparable DMF yield to the catalytic system consisting of Pd/C-TMS and PhCl (Table 1, entries 6 & 11; Table S8), a relatively lower reaction rate (TOF: 24 h^{-1} *vs* 32 h^{-1}; *k*: 0.021 s^{-1} *vs* 0.052 s^{-1}) were observed, due to more coverage of Pd(0) and Pd(II) species by post-grafted components substantiated by XPS analyses (Figure S8). However, mineral acid HCl and benzene released from PhCl posed a major burden in large-scale production. From an environmental and economic point of view, the use of a single bi-functional catalyst Pd/C-SO₃H-TMS for the direct synthesis of DMF from carbohydrates thus became more attractive. To examine the existence of H^-, 1 atm of O_2 was filled with a balloon during reaction. Remarkably, the yield of DMF descended to 35% with an increase in HMF yield (24%;

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Table 1, entry 12) and the water content raised by about 160%, suggesting that O_2 could compete with furyl aldehydes and alcohols to capture the hydrides (H⁻) being reduced to H_2O,[15] other than hydrogenated furanics.

The amount of Pd/C-SO$_3$H-TMS was found to greatly influence the yield of DMF from fructose, and the results were summarized in Table S9. A higher Pd/C-SO$_3$H-TMS dosage of 4 mol% was susceptible to the formation of DTHF (5%) and HD (4%), thus slightly diminishing DMF yield to 83%. Encouragingly, Pd/C-SO$_3$H-TMS with a relatively lower dosage of 0.4-1.2 mol% exhibited a superior activity in terms of DMF selectivity (up to 98%) and yield (90-93%) at 120 ºC after 3-5.5 h. Increasing the amount of fructose from 0.3 to 15 mmol with decreased catalyst loading of 0.04 mol% resulted in a good DMF yield of 85% after 6 h. Enhancing the PMHS dosage (12-21 equiv.; Table S9) in the reaction mixture displayed no significant effect on DMF yield, while less PMHS gave rise to byproducts such as HMF ethers and *n*-butyl levulinate that might have hampered the proceeding of the deoxygenation process.
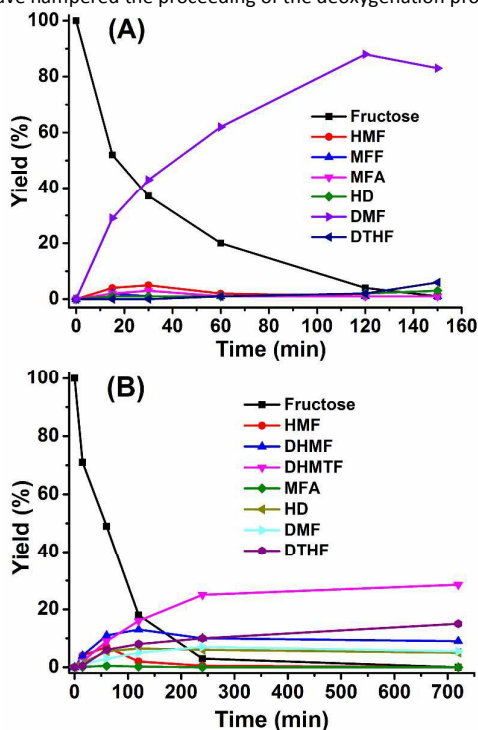

Figure 2. Comparison of producing DMF from fructose over Pd/C-SO$_3$H-TMS at 120 ºC in *n*-butanol using PMHS (A) and H_2 (B) as H-donor

As H_2 has been prevailingly employed as the most atom-efficient H-donor for different reduction reactions, it is necessary to compare the performance of the current catalytic system under identical reaction conditions. Figure 2 shows that DMF was obtained with an excellent selectivity (92%) and yield (88%) with Pd/C-SO$_3$H-TMS after 2 h. Conversely, the product distribution was quite complex in the atmosphere of H_2 and only 7% yield of DMF was obtained after a relatively longer reaction time of 4 h. By prolonging to 12 h, the major products were found to be 2,5-dihydroxymethyltetrahydrofuran (DHMTF), DTHF, and 2,5-dihydroxymethylfuran (DHMF), but the maximum yield was still lower than 30%. Although a two-step process involving the dehydration of fructose to HMF catalyzed by Amberlyst-15 and subsequent hydrogenolysis over Ru-Sn/ZnO under 1 MPa H_2 has been reported to be efficient for producing DMF (up to 92% yield) from fructose[16], an integrated process by combining both catalysts in a single pot gave less than 15% yield of DMF under identical conditions. Moreover, 1-3% total yields of sorbitol and mannitol was obtained from the hydrogenation of fructose, but interguingly, hexitols were not

formed in the presence of PMHS. To substantiate this, catalytic hydrosilylation of 1,3-dihydroxyacetone and glyceraldehyde with Pd/C-SO$_3$H-TMS was thus conducted, and the absence of glycerol evidently indicated the insusceptibility of ketose and aldose to be hydrogenated in the PMHS system.

To extend the substrate scope, different mono-, di-, and polysaccharides (e.g., fructose, glucose, sucrose, cellobiose, and inulin) were also used for DMF production. Figure 3 summarizes sugar conversions, and the yields of DMF and major byproducts obtained from corresponding sugars at 120 ºC in optimal reation times. A high DMF yield about 72-88% was obtained from sugars containing fructose unit regardless of carbohydrate in a short duration of 2-3 h. In contrast, glucose and cellobiose exhibited a little bit lower reactivity in terms of conversion (~80%) at 120 ºC, and a little longer reaction time of 4-5 h was required for obtaining a moderate yield of DMF around 60%. These results further proved that Pd/C-SO$_3$H-TMS might be lack of enough active sites for glucose-to-fructose isomerization that is a prerequisite of the subsequent dehydration process.[17] However, it is worth mentioning that the efficiencies of this catalytic system in a single-step production of DMF from different sugars were unprecedentedly higher, compared with previously reported two-step processes.[8]
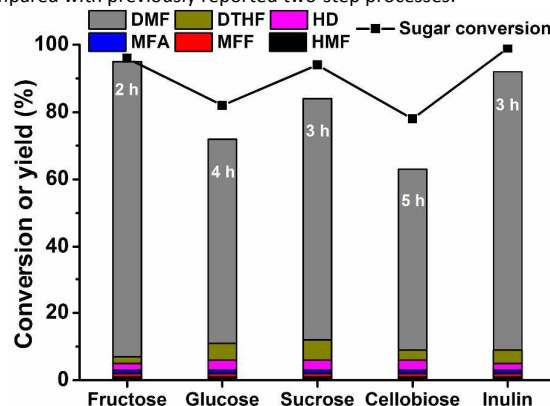

Figure 3. One-step catalytic production of DMF from different sugars (Reaction conditions: 5 wt% sugar, 2 mol% Pd/C-SO$_3$H-TMS, 2.5 mmol PMHS (9 equiv. H⁻), 1.5 mL *n*-butanol, and 120 ºC)

For practical application of this heterogeneous protocol, the recyclability of the Pd/C-SO$_3$H-TMS catalyst under the employed reaction conditions is of fundamental significance. After each cycle, Pd/C-SO$_3$H-TMS was recovered by centrifugation, successively washed with ethanol and *n*-hexane for three times, dried at 90 ºC in N_2 for 6 h, and directly used for the next run. Interestingly, the yields of DMF remained about 88-96% with high selectivities of 91-96% at near quantitative fructose conversion in six consecutive cycles (Figure 4), demonstrating that this catalytic system is highly suitable for reuse. XRD patterns of fresh and recovered Pd/C-SO$_3$H-TMS after six cycles did not show any noticeable changes in the structure (Figure S9). The BET surface area of the reused catalyst after the sixth run was measured and found to be 449 m²/g, which is close to the pristine one (452 m²/g). In addition, the leaching of Pd (<0.3 ppm) and S (<0.5 ppm) was found to be quite low in the reaction mixture, as determined by ICP-OES. XPS analysis further demonstrated that Pd(II) in the surface of fresh Pd/C-SO$_3$H-TMS was mostly reduced to Pd(0) after six runs (Figure S10), which was most likely to be the active centers for deoxygenation, as corroborated by immediate addition of fresh Pd/C-SO$_3$H-TMS into the reaction mixtures at room temperature causing to release H_2 bubbles. In the case of recovered catalyst after the second cycle, fewer bubbles were emerged (see images in Figure S11). The slighly improved efficiency of the reused catalyst together with less formation of H_2, implied that the deoxygenation could be fulfilled through the hydride transfer process, which is in agreement with the result of the O_2-

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competing experiment (Table 1, entry 12). It could further be deduced that the evolution of H_2 from PMHS caused by the reduction of Pd(II) to Pd(0) might be responsible for the formation of the byproducts DTHF and DH (Scheme S1).
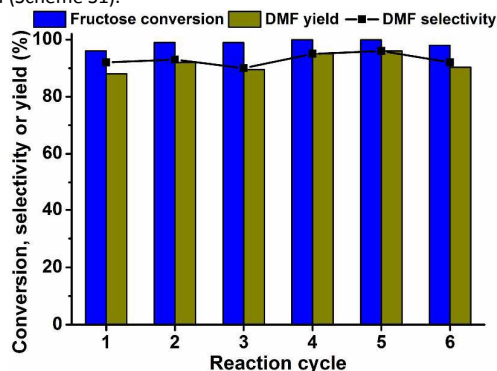
Figure 4. Reuse of Pd/C-SO₃H-TMS for producing DMF directly from fructose (Reaction conditions: 5 wt% fructose, 2 mol% Pd/C-SO₃H-TMS, 2.5 mmol PMHS (9 equiv. H⁻), 1.5 mL *n*-butanol, 120 ºC, and 2 h)

To explicitly elucidate the reaction mechanism of Pd-catalyzed deoxygenation of HMF formed *in situ* from hexoses, ¹H NMR spectrum of fructose-to-DMF conversion in methanol-d₄ under identical conditions was recorded (Figure S12). However, the integral area of methyl protons in DMF was found to be 1.8 times higher than that of H in the furan ring, which should normally be 3-fold, indicating that the deuterium (D) incorporation from CD₃OD occurred via a facile H/D exchange with the surface-generated Pd-H species. This speculation can be substantiated by the presence of three varied m/z values of DMF (i.e., MS, MS+1 and MS+2), as shown in GC-MS spectrum (Figure S13 A). Intriguingly, no H/D exchange was observed (Figure S13 B-C), when chloroform-d₃ was used as solvent although the yield of DMF was relatively low (<10%). Using MFF as starting substrate and diphenylsilane-d₂ as H-donor, the hydrogenation/deoxygenation of MFF in chloroform-d₃ could exclusively give MFA and DMF with 1 and 2 more m/z (Figure S14), respectively, demonstrating that both hydrogenation and deoxygenation processes were proceeded via hydrosilylation by separately offering hydride species to aldehyde and alcoholic groups of furanics. Moreover, a trace of 2,5-diformylfuran from the oxidation of *in situ* formed HMF was observed during reactions (Figure S15), suggesting the possibility in oxidative addition of Pd(0) to hydroxymethyl group.

On the basis of above discussions, the plausible reaction pathways for producing DMF from sugars can be envisaged to proceed via the following steps (Scheme S2): (1) HMF is first generated via acid-catalyzed hydrolysis/dehydration of sugar (Reac. A), wherein Pd does not play a role in the hydrogenation of the sugar to hexitols; (2) Oxidative addition of Pd(0) to the hydroxyl group of HMF takes place (Reac. B), followed by dehydration (Reac. C) and hydride transfer (Reac. D) to give MFF, which can be supported by the absence of DHMF and DHMTF while the formation of carbocation intermediates during the reaction is not ruled out because of etherified products (Figure S16)[18]; (3) Pd(0)-catalyzed hydrosilylation of the aldehyde group of MFF occurs (Reac. E), and then DMF is obtained via repeating Reac. C-D while a small amount of MFA can be formed through reverse Reac. B.

Conclusions

In conclusion, the chemocatalytic production of DMF with almost quantitative yields directly from different hexose sugars could be achieved over a highly recyclable modified Pd/C catalyst under mild conditions. A scale-up procedure catalyzed by 0.04 mol% Pd/C-SO₃H-TMS was also able to produce DMF in a good yield of 85%. Further, kinetic and deuterium-labeling studies demonstrated that the

hydrosilylation reaction, inert for the carbonyl groups of aliphatic compounds while favorable for in situ dehydration of sugars, exclusively acted on the deoxygenation of furanic intermediates to DMF via a hydride transfer process facilitated by an alcoholic solvent. This new and simple catalytic process shows great potential to be performed in a batch mode or a fixed-bed continuous reactor, rendering the possibility of good product quality and high-volume production with a lower unit cost but time and energy savings, which can be used as a reference for developing intensified production systems for complex reactions.

Acknowledgements

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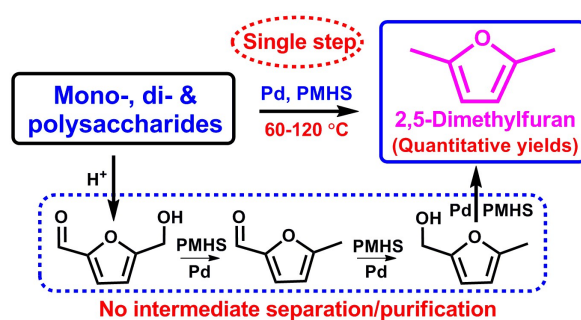
A highly sustainable catalytic system consisting of industrial byproduct polymethylhydrosiloxane (PMHS), hydrophobic Pd and biobutanol has been developed to be efficient for quantitative production of 2,5-dimethylfuran (a promising candidate for biofuel and *p*-xylene) directly from carbohydrate biomass *via* **an *in situ* domino process under mild conditions**.