Pd-Catalysed Decarbonylation Free Approach to Carbonylative Esterification of 5-HMF to Its Aryl Esters Synthesis Using Aryl Halides and Oxalic Acid as C₁ Source

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Abstract: A decarbonylation free, polystyrene-supported, Pd (Pd@PS)-catalysed carbonylative esterification of the hydroxy group of 5-hydroxymethyl furfural (5-HMF) to its corresponding aryl esters has been developed. The use of Pd@PS, oxalic acid as CO source, and aryl halides was first explored for the aryl ester of 5-HMF synthesis. Here, we investigated the vital role of a polystyrene support to avoid the commonly known decarbonylation of 5-HMF. The reaction exhibits vast substrate scope with comparably good yield and catalyst recyclability.

In this context, 5-HMF is an important furan-based platform intermediate obtained by acidic dehydration of carbohydrates for the production of various valuable chemicals.^[1] Among them, aryl esters of 5-HMF are the important class of molecules having several applications such as fungicides, additives and surfactants.^[2] Moreover, the 5-HMF aryl esters are also considered as a potential candidate against sickle cell anaemia. The esters of 5-HMF exhibited threefold of anti-sickling potency than normal 5-HMF (Aes-103).^[3,4] However, the synthetic procedures for the selective esterification of 5-HMF is still unexplored and less-developed due to highly labile --CHO functional group. In most of the reported protocols, 5-HMF has been majorly highlighted for the decarbonylation of -CHO functional group under the influence of various metals such as Pd, Rh, Ru and Ir-catalysed conditions.^[5-13] In 2015, Rauchfuss and co-workers reported the Pd/C-catalysed decarbonylation of 5-HMF to corresponding furfuryl alcohol synthesis in good yield at 120°C in 1,4-dioxane solvent conditions (Scheme 1a).^[14] Furthermore, Kawanami et al. also observed the labile nature of the aldehyde (--CHO) group of 5-HMF under Pd/Al₂O₃ catalyst conditions under compressed CO₂ and got furfuryl alcohol as major product at 145 °C (Scheme 1b).^[15] Similarly, decarbon-

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ylation of 5-HMF also noticed under microwave assisted flow conditions using Pd-Hydrotalcite as catalyst.^[16] In literature, maximum reports have been published on the decarbonylation of 5-HMF and furfural, derived by heterogeneous Pd catalysts. More recently, Wu et al. reported the decarbonylation of aldehyde group from 5-HMF and its in situ participation in carbonylative esterification with aryl iodide, Rh(cod)BF4 as catalyst and DPPP as ligand for furfuryl esters synthesis. In this report, they have also noticed the labile behaviour of -CHO group under milder conditions and used 5-HMF as an in situ CO precursor for esterification reaction.^[17] Therefore, the synthesis of aryl esters of 5-HMF keeping the labile --CHO functional group intact following a highly selective manner approaches under heterogeneous Pd-catalysed conditions using oxalic acid as CO source could be a challenging task in recent era of methodology development. Last one decade, we are dedicatedly involved for polystyrene supported transition metal nanoparticles (NPs) as heterogeneous catalyst development, their characterizations (XPS, XRD, SEM, TEM, HR-TEM, EDS, SAED, etc.) and applications in different challenging area of organic synthesis.^[18] Further, we have also explored oxalic acid as a bench-stable, easy-to-handle C1 surrogate by additive free thermal decomposition and its applications for different carbonylation reactions.^[19] Under this study, first time we have applied Pd@PS catalyst and oxalic acid as CO source for aryl esters of 5-HMF synthesis. In this approach, crucial roles of polystyrene surface (PS) in combination with Pd catalyst and oxalic acid have been investigated to achieve aryl esters of 5-HMF avoiding the decarbonylation of labile --CHO functional group in considerably good yield.

The Pd@PS catalyst was prepared following our earlier reported reduction deposition approach and well characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM), energy dispersive spectroscopy (EDS) and selected area electron diffraction studies (SAED).^[18a,19] In addition to this, the use of oxalic acid as CO source also made the established protocol eco-friendly and operationally simple without the need of any high-pressure sophisticated equipment.

In order to develop an efficient and facile approach for aryl esters of 5-HMF synthesis, we started our optimisation studies choosing 5-HMF and 4-iodoanisole as standard reactants. Further, various reaction parameters such as base, solvent, CO surrogate, catalyst and their equivalency as well as effect of temperature and time were scrutinized carefully to access the anticipated product with maximum yield. The initial screening



Previous work:

a) Rauchfuss, 2015 (Pd/C-catalysed decarbonylation of 5-HMF)^[14]

b) Kawanami, 2018 (accelerated decarbonylation of 5-HMF under compressed CO_2)^[15]

c) Kostal, 2019 (decarbonylation of biomass derived aldehyde)^[16]

d) Wu et al. 2020 (carbonylation of 5-HMF as both CO precursor and coupling partner)^[17]



Scheme 1. Synthesis of 5-HMF aryl esters by metal-catalysed carbonylative esterification.

of different organic as well as inorganic bases showed that the reaction didn't proceed in the presence of organic bases whereas the maximum yield of the desired product (5-formylfuran-2-yl)methyl 4-methoxybenzoate (**3a**) was procured with Na₂CO₃ as base (Table 1, entry 5). Further, various polar and nonpolar solvents were also screened and among them, DMF was found to be the most suited solvent for the desired product formation (Table 1, entries 6–9).

Subsequently, we further tested a diverse range of homogeneous and heterogeneous Pd catalysts like Pd(OAc)₂, Pd(PPh₃)₄, Pd(OAc)₂·dppb and Pd/C (5 wt%) for the desired transformation (Table S1, entries 1-5). Overall, Pd@PS was found to be the best catalyst for the desired product formation owing to its effective CO gas holding capacity. This result, an increase in the CO gas concentration over the polystyrene surface which further enhanced the possibility of interaction with catalyst on the surface^[18,19] and also minimised the decarbonylation tendency of --CHO group, could be the factor responsible for the desired product synthesis. Moreover, the employment of different C₁ surrogates such as *N*-formylsaccharin and formic acid in place of oxalic acid also gave the desired product 3a with 43 and 9% yields respectively (Table 1, entries 10 and 11). This clearly indicates the superiority of oxalic acid over other C₁ surrogates as it decomposes easily to give CO, as mentioned in our previous reports.^[18c] Moreover, no product formation was observed in the absence of either Pd@PS or oxalic acid (Table S1, entries 6 and 7). The reactions were performed at different temperatures; among these, 125 °C was found to be the optimum temperature for fruitful conversion to the desired product (Table 1, entry 12). Finally, after careful examination of various reaction parameters, we found the standard reaction conditions as: 4-iodoanisole (1.0 equiv.), 5-HMF (1.2 equiv.), Pd@PS (3 mol% Pd), Na₂CO₃ (1.2 equiv.) and oxalic acid (6.0 equiv.) in DMF solvent at 125 °C for 20 h, gave the highest yield of the product **3a** in 67% (Table 1, entry 5). Therefore, the hydrophobic mesoporous inner core of PS could be playing a crucial role to stabilized the aldehyde functional group of 5-HMF, avoiding the tendency of decarbonylation reaction and enhance the scope of aryl ester of 5-HMF synthesis. In another hydrophobic core^[19] which further increase CO concentration and restrict the decarbonylation of –CHO group of 5-HMF through shifting the equilibrium of the reaction in backward direction.

To check the substrate scope of the reaction, the optimised process was further investigated for different substituted aryl halides for aryl esters of 5-HMF synthesis (Table 2). Initially, iodobenzene was employed under the optimised conditions and the reaction ended with the desired product, (5-formylfuran-2-yl)methyl benzoate 3b in 51% yield (Table 2). Similarly, the electron rich p- and m-CH₃ substituted aryl iodides also underwent the expected conversion under set protocol and afforded the corresponding aryl esters of 5-HMF 3c and 3d in 61 and 57% yields respectively along with the corresponding aryl acid as minor by-product (Table 2). Further, highly electronic rich 1-(tert-butyl)-4-iodobenzene was also found to be suitable for the same carbonylative esterification reaction with 5-HMF to produce the desired corresponding benzoate ester 3e in 63% yield (Table 2). To check the effect of steric factor, different 2-alkyl substituted aryl halides such as 2-ethyl

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Table 1. Optimisation of reaction condition for carbonylative esterification of 5-HMF. $^{\rm [a]}$							
OCH 1a	+ HO 2a 3 + C ₁ source	H catalyst base, solvent 125 °C, 20 h H ₃ CC	Ja O O O O	0 H + H₃CO	о ОН 3*		
	Catalyst (mol %)	CO source	Base (equiv.)	Solvent	Yield [%] ^[b]		
1	Pd@PS (3)	(COOH) ₂	N(CH ₂ CH ₃) ₃ (1.2)	DMF	10		
2	Pd@PS (3)	(COOH) ₂	^t BuOK (1.2)	DMF	Nd		
3	Pd@PS (3)	(COOH) ₂	Cs ₂ CO ₃ (1.2)	DMF	51		
4	Pd@PS (3)	(COOH) ₂	K ₂ CO ₃ (1.2)	DMF	57		
5	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (1.2)	DMF	67		
6	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (1.2)	PEG- 400	Traces		
7	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (1.2)	DMSO	35		
8	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (1.2)	<i>p-</i> xylene	20		
9	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (1.2)	DMA	52		
10	Pd@PS (3)	N-formylsac- charin	Na ₂ CO ₃ (1.2)	DMF	43		
11	Pd@PS (3)	Formic acid	Na ₂ CO ₃ (1.2)	DMF	09		
12 ^[c]	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (1.2)	DMF	38 (67) ^[d]		
13	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (0.5)	DMF	48		
14	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (1.5)	DMF	65		
15 ^[e]	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (1.2)	DMF	43		
16 ^[f]	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (1.2)	DMF	38 (66) ^[g]		
17 ^[h]	Pd@PS (3)	(COOH) ₂	Na ₂ CO ₃ (1.2)	DMF	29 (67) ^[i]		
[a] Reaction conditions: DLV system (double-layer vial) inner vial: 4-							

[a] Reaction conditions: DLV system (double-layer vial) inner vial: 4iodoanisole (1.0 equiv.), 5-HMF (1.2 equiv.), Pd@PS (0.03 equiv.), Na₂CO₃ (1.2 equiv.), DMF (1.5 mL); outer vial: oxalic acid (6.0 equiv.), DMF (0.5 mL), 125°C, 20 h. [b] Isolated yields. [c] T=115°C. [d] T=135°C. [e] Reaction time 10 h. [f] Reaction using 2 mol% Pd@PS. [g] 4 mol%. Reaction involving [h] 3.0 equiv. and [i] 6.0 equiv. of oxalic acid. * The yield was 20% under best optimised reaction condition.

and 2,3,5,6-tetra methyl iodobenzenes were also performed for the carbonylative esterification reactions of 5-HMF under the optimised conditions and interestingly ended with the corresponding esterification products 3f and 3g in considerably good yields. Similarly, electro-deficient o- and m-OCH₃ substituted aryl halides were also subjected under the set reaction conditions and no significant effect was noticed on the product yields (3h, 3i, yields 51-67%) (Table 2). To check the chemoselectivity, different dihalo-aryl compounds (--Cl, --F, --CF₃ and -I) were selected for the same esterification reactions but the reaction was found to be highly specific only for iodo compound and other-halogens remained unchanged under the optimised conditions (Table 2, entries 3j-n). Similarly, methyl 4iodobenzoate ester also participated in the carbonylative esterification reaction with 5-HMF and gave the di-ester product, (5-formylfuran-2-yl)methyl methyl terephthalate (3o) in 53% yield and no noticeable by product was observed. Diaryl substituted halides also participated for the same reaction and ended with desired esterification product of 5-HMF (3p, 3q) in satisfactory yields (Table 2). Further to check the viability of the developed methodology for heterocyclic compound, 2-iodothiophene was also performed under the same reaction conditions and furnished the corresponding esterification



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[a] Reaction conditions: inner vial: aryl iodide (1.0 equiv.), 5-HMF (1.2 equiv.), Pd@PS (0.03 equiv.), Na₂CO₃ (1.2 equiv.), DMF (1.5 mL); outer vial: oxalic acid (6.0 equiv.), DMF (0.5 mL), 125 °C, 20 h; All yields are isolated yields. *The corresponding thiophenecarboxylic acid was obtained up to 30%.

product of 5-HMF (**3**r) in 45% yield along with thiophenecarboxylic acid as undesired by-product in 30% yield, which might be attributed the high reactivity of thiophene intermediates.

Further, due to our curiosity as well as to enhance the applicability of the developed methodology, various benzyl alcohols were also screened along with aryl iodide under the standard reaction conditions and procured the desired benzyl esters in considerably good yields (65-78%; Table S2). Further, to understand the role of polystyrene resin (PS) to restrict 5-HMF decarbonylation, we performed a set of experiments. Initially, to study the rate of decarbonylation of 5-HMF, Pd@PS was compared with commercially available $\mathsf{Pd}/\mathsf{Al}_2\mathsf{O}_3$ and Pd/C catalysts (Figure 1). We have attempted these reactions with 5.0 mol% of the palladium catalyst known in literature for decarboxylation reaction^[14] of 5-HMF under DMF solvent at 125°C for 15 h. When the reaction was performed under Pd@PS-catalysed conditions, only 9% decarbonylative product of furfuryl alcohol (FA) was noticed (Figure 1). Whereas, in the case of Pd/Al_2O_3 and Pd/C catalysts, the decarbonylative product (FA) was formed dramatically up to 63% yields. This clearly indicated the crucial role of the polystyrene surface (PS) in this reaction to limit the decarbonylation step. The plausible reaction mechanism was mentioned in Scheme 2.

To perform the recyclability of the Pd@PS catalyst, we carried out an experiment with 4-iodoanisole and 5-HMF under our optimised protocol (see the Supporting Information).

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Figure 1. a) Comparative study of the decarbonylation of HMF in the case of Pd@PS, Pd/Al₂O₃ and Pd/C. b) Rate of decarbonylation of HMF; reaction conditions: HMF (1.0 equiv.), catalyst (5 mol%), Na₂CO₃ (1.2 equiv.), DMF (1.5 mL), 125 °C, 15 h.



Scheme 2. Proposed reaction mechanism.



Figure 2. a) Pd@PS catalyst recyclability experiment. b) Pd@PS hot filtration test.

Surprisingly, the catalyst was found to be highly active and recycled up to three cycles with negligible yield loss, followed by some loss in activity in fourth and fifth cycles (Figure 2a). The reason behind the loss in catalyst activity was noticed due to the enhancement of particle size through aggregation as per our similar earlier experiences.^[18c,d]

Further, to know the heterogeneous nature of the Pd@PS catalyst, we performed hot filtration test with 4-iodoanisole and 5-HMF as standard substrate (see the Supporting Information).

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After, hot filtration no further enhancement in the yield of the desired product **3a** (21%) was observed, thus supporting the heterogeneous behaviour of the Pd catalyst (Pd@PS) in the reaction (Figure 2b).

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In conclusion, we have reported the chemoselective synthesis of aryl esters of 5-HMF through carbonylative esterification while keeping the --CHO group unaffected, with aryl iodides as coupling partner, catalysed by Pd@PS. We developed a robust, easy-to-operate approach and also introduced oxalic acid as a solid, low-cost, bench-stable C1 surrogate for aryl esters of 5-HMF synthesis. The additional features of the developed methodology include catalyst recyclability up to five cycles, avoid direct utilization of harmful CO gas easily from in situ oxalic acid and also DLV (Double Layer Vial) system replace highly sophisticated equipment required for CO gas.. The reaction exhibited good compatibility with a wide range of substrates and gave good-to-moderate yields of corresponding 5-HMF esters. To the best of our knowledge, this work is the first example of carbonylative esterification of 5-HMF for the synthesis of aryl esters of 5-HMF.

Experimental Section

Typical experimental procedure for the synthesis of (5-formylfuran-2-yl)methyl 4-methoxybenzoate (3 a): With a double-layer vial system (DLV), 4-iodoanisole (1.0 equiv., 50 mg), 5-HMF (1.2 equiv., 32.3 mg), Pd@PS (0.03 equiv., 143.3 mg), Na2CO3 (1.2 equiv., 27 mg) and DMF (1.5 mL) was added in 2 mL vial (inner vial) and this vial was placed inside 5 mL reaction vessel (outer vial) which contain oxalic acid dihydrate (6.0 equiv., 115.3 mg) and 0.5 mL of DMF. The 5 mL reaction vessel was tightened with solid PTFE cap and stirred at 125 °C for required time. The progress of reaction was monitored with the help of TLC. After the completion of reaction, the inner vial was taken out and reaction mixture quenched with the help of water, organic layer was extracted with ethyl acetate. The extracted organic layer was dried over sodium sulphate and concentrated over rotary evaporator. The crude mixture was further purified by column chromatography using hexane: ethyl acetate (90:10) as eluent, afforded compound 3a as yellow oil (37.3 mg); yield: 67%.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: aryl iodides · carbonylative esterification · decarbonylation · oxalic acid · polystyrene supported · hydroxymethylfurfural



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COMMUNICATION



✓ Avoid facile decarbonylation of -CHO group Oxalic acid as ecofriendly CO source
 Ligand free

Aldehyde unaffected: Selective carbonylative esterification of 5-HMF was achieved on a polystyrene-supported palladium (Pd@PS) catalyst with aryl halides as coupling partner. Using oxalic acid as a solid and environmen-



0 0 н (18 examples, up to 67% yield) ✓ Wide substrate scope

 Recyclable catalyst ✔ Good to moderate yield

tally benign CO source avoided the need for highly sophisticated equipment to trap CO gas. A series of aryl esters of 5-HMF were synthesized in good-to-moderate yield by overcoming the issue of decarbonylation.

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