

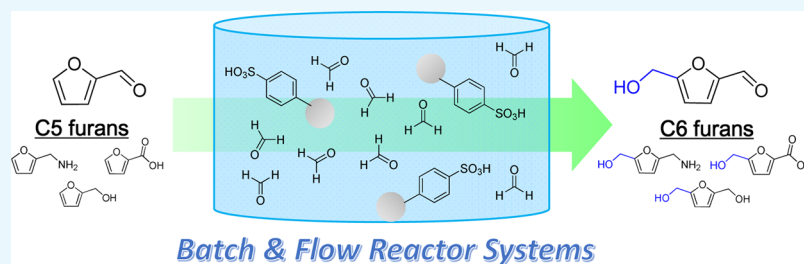
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Description	

Direct Hydroxymethylation of Furaldehydes with Aqueous Formaldehyde over a Reusable Sulfuric Functionalized Resin Catalyst

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Supporting Information



ABSTRACT: Transformation of C5 furaldehydes to the corresponding C6 furaldehydes over a heterogeneous catalyst is a versatile but demanding reaction process. This report describes our discovery that Amberlyst-15, a conventional sulfuric functionalized resin, affords a 43.1% yield for 5-hydroxymethyl-2-furaldehyde (HMF) production with 57.5% selectivity via direct hydroxymethylation of 2-furaldehyde (furfural) with an aqueous formaldehyde reagent. This report is the first to describe an important achievement on the heterogeneous acid catalyst-assisted HMF production from furfural via direct hydroxymethylation in a batch reactor system. The Amberlyst-15 was also reusable and applicable for C5 furaldehyde upgrading of various types: furfuryl alcohol, furfurylamine, and furoic acid toward the corresponding C6 furaldehydes. Results show that a liquid flow system becomes an advanced tool for the continuous production of upgrading furaldehydes through a fixed Amberlyst-15 catalyst bed. Accordingly, the sulfuric functionalized resin-catalyzed direct hydroxymethylation of furaldehydes with aqueous formaldehyde in both batch and flow reactor systems is worthwhile and opens up new avenues for biomass transformations in particles, an important area of inedible biomass utilization.

INTRODUCTION

Highly efficient transformation of biomass resources to chemicals and fuels has been studied in catalyst research because utilization of these biomass-based materials is expected to contribute to future human society based on green and carbon-neutral concepts. Moreover, enhancement of biomass usage is highly desired to reduce reliance on conventional fossil fuel resources, which are limited and entail high CO₂ emissions.

Furaldehydes such as 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde (furfural) are regarded as platform materials for cellulose-based and hemicellulose-based biorefinery transformations. Therefore, many efforts have been devoted to the generation of such furaldehydes with economical and environmental-friendly methodologies.^{1–5} HMF, a hexose (C6)-derived furaldehyde, is regarded as a promising building block to produce valuable chemicals because it possesses two functional groups (formyl and hydroxyl group) in a furan ring. Selective oxidation,^{6,7} hydrogenation,^{8,9} reductive amination,¹⁰ reductive cleavage,^{11–13} hydrolytic ring opening,^{14–16} hydrogenative rearrangement,¹⁷ and so on have been examined to afford upgraded HMF derivatives.¹ Ever-increasing interest and challenges to develop HMF utility are anticipated to continue into future investigations in this area.

However, for furfural transformations, a pentose (C5)-derived furaldehyde, production of furfuryl alcohol,^{18,19} levulinic acid (LA) or relative esters,²⁰ diols,^{21–23} and amine^{24,25} are regarded as versatile routes. Unfortunately, such schemes affording value-added chemicals from furfural have not been conducted in as many various ways as the vastly numerous possible HMF transformation styles.^{26–28} Apparently, the structural character of furfural, a formyl group linked on a furan ring at the second position, limits its potential as a starting material. To attenuate the shortcomings of C5 furaldehyde, we have specifically examined direct hydroxymethylation of furfural and its derivatives with a formaldehyde reagent to produce HMF-like derivatives (C6), a furan ring composed of two functional groups.

Catalytic transformation of C5 to C6 furaldehydes has been investigated by very few research groups. Important discussions have been undertaken by Moreau and co-workers about the direct hydroxymethylation of furaldehydes with 37% aqueous formaldehyde in the presence of dealuminated mordenite as a catalyst.^{29–32} They achieved maximum performance of

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approximately 10% yield for HMF production from furfural under a high molecular ratio of formaldehyde/furfural (ca. 240)²⁹ and 67.5% yield for 2,5-bis(hydroxymethyl)furan (BHMF) production from furfuryl alcohol with formaldehyde/furfuryl alcohol of 111.³⁰

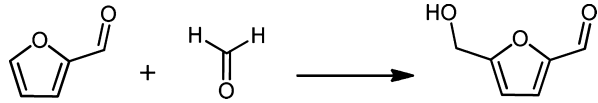
As an attractive reaction route, direct hydroxymethylation of furfurylamine by a mineral acid to afford 5-(hydroxymethyl)-furfurylamine (HMFA) has been examined by some groups. However, the yield only slightly approached a significant value (<10%).^{33,34} On the basis of a similar concept, production of 2,5-furandicarboxylic acid (FDCA) from furfural was also attempted with a homogeneous catalytic system via multiple reactions in 1962.³⁵ It is noteworthy that unique C–H carboxylation of furoic acid to FDCA with CO₂ in the presence of alkali media was generated only very recently.³⁶ However, such C5 to C6 transformation under the control of double functional groups indeed remains a challenging subject.

Herein, we examined heterogeneous acid catalyst-assisted direct hydroxymethylation of furfural and its derivatives with aqueous formaldehyde, in particular, that of furfural to HMF. From the perspective of biomass feedstock issues, transformation of such inedible biomass-based furfural to edible biomass-based HMF is expected to be interesting for various research areas.

RESULTS AND DISCUSSION

Table 1 presents results for hydroxymethylation of furfural to HMF with aqueous formaldehyde over various solid catalysts.

Table 1. Hydroxymethylation of Furfural Toward HMF with Aqueous Formaldehyde^a



entry	catalyst	furfural conv. (%)	HMF yield (%)	HMF sel. (%)
1	Amberlyst-15	70.7	40.4	57.1
2 ^b	Amberlyst-15	66.7	25.2	37.8
3	Amberlyst-35	84.8	37.3	44.0
4	Amberlyst-45	60.4	28.2	46.8
5	Amberlyst-46	45.3	20.4	44.9
6	Nafion NR50	50.7	24.6	48.4
7	zeolite β ^c	60.6	23.0	38.0
8	ZSM-5 ^c	32.8	12.3	37.6
9	mordenite ^c	16.0	2.9	18.4
10	zeolite Y ^c	10.6	<1	
11	WO ₃ ^c	13.4	<1	
12	CeO ₂ ^c	13.2	<1	
13	γ-Al ₂ O ₃ ^c	10.8	<1	
14	TiO ₂ ^c	10.7	<1	
15	ZnO ^c	10.4	<1	
16	ZrO ₂ ^c	10.0	<1	
17	blank	6.5	<1	

^aReaction conditions: furfural (1 mmol, 10 mmol^b), formalin (5 mL), catalyst (200 mg), time (12 h, 15 h^b), temp. (363 K), stirring (500 rpm). ^cCalcined at 773 K for 5 h.

Commercial acidic resins, several types of zeolites, and solid acids were used for the reaction. Conventional solid acids such as WO₃, CeO₂, γ-Al₂O₃, TiO₂ (anatase), ZnO, and ZrO₂ gave no activity for the HMF production (<1% yields) (entries 11–16) via direct hydroxymethylation of furfural. Among zeolite

catalysts, mordenite (SiO₂/Al₂O₃ = 18.3) and zeolite Y (SiO₂/Al₂O₃ = 5.6) were also inactive (entries 9 and 10), although ZSM-5 (SiO₂/Al₂O₃ = 90) and zeolite β (SiO₂/Al₂O₃ = 25) gave mild activity with 12.3% yield and 23.0% yield (entries 7 and 8), respectively. Nafion NR50, a well-known commercial acidic resin catalyst that possesses strong acidity ($H_0 < -12$)^a but low acid amount (0.8 mmol g⁻¹)^a, exhibited a similar value for the activity: 24.6% yield (entry 6).

It is noteworthy that Amberlyst-type acidic resins such as polystyrene resin decorated with sulfuric acid functionalities served higher yield and selectivity for such demanding reaction (entries 1–5). Numerous yields were found over Amberlyst-15 ($H_0 = -2.20$, acid amount; 4.70 mmol g⁻¹)^a with 40.4% (entry 1) and Amberlyst-35 ($H_0 = -2.65$, acid amount; 5.00 mmol g⁻¹)^a with 37.3% (entry 3). The former showed much better selectivity (57.1%) than the latter (44.0%). Note that Amberlyst-15 was composed by monosulfonic acid functionality in a polystyrene unit at the para position (*p*-toluenesulfonic acid), whereas Amberlyst-35 was composed by disulfonic acid functionalities in a polystyrene unit.^a The large-scale reaction also produced a nice quantity of HMF over Amberlyst-15 (entry 2). Unique Amberlyst-46 (acid amount; 0.43 mmol g⁻¹, which was condensed on the outer surface of resin)^a and Amberlyst-45 (acid amount; 2.95 mmol g⁻¹, a high thermal stability; approx. 443 K)^a showed 20.4% yield and 28.2%, respectively (entries 4 and 5).

It is observed that the strong homogeneous acids of H₂SO₄, HCl, and *p*-toluenesulfonic acid served high yields for HMF production with ca. 35% yields with ca. 45% selectivity. Weak homogeneous mineral acids of H₃PO₃ and H₃PO₄ provided a low yield of 7.6 and 14.2%, respectively, but high selectivity (ca. 55%) (see the Supporting Information, Table S2). It would be noted that Amberlyst-15, Amberlyst-35, Amberlyst-45, Amberlyst-46, and Nafion NR50 showed 16.3% conversion (46.9% selectivity), 18.9% conversion (49.4% selectivity), 23.4% conversion (41.7% selectivity), 13.6% conversion (20.3% selectivity), and 16.1% conversion (20.7% selectivity), respectively, at 1 h reaction. Accordingly, Amberlyst-15 has comparable activity to such conventional homogeneous acid catalysts. Earlier reports have described that Amberlyst-15 acts as an effective heterogeneous acid catalyst for hydration,¹⁴ dehydration,^{37,38} esterification,³⁹ and so on.^{40–43}

To optimize details of the reaction system, effects of the formaldehyde concentration (ratio of formaldehyde/furfural) and stirring speed were also monitored with Amberlyst-15. It was clearly observed that high concentrations of formaldehyde in reaction media exhibited the positive effect of hastening the target reaction (see the Supporting Information, Figure S2). Moreover, it was discovered that swelling of the resin catalyst in the solvent had a detrimental effect during mixing in the batch reactor system. However, such diffusion-limited access on the Amberlyst-15 catalyst scarcely influenced the reactivity under our conditions (400–600 rpm stirring) (see the Supporting Information, Figure S3). Other formaldehyde-donating reagents such as 1,3,5-trioxane and para(formaldehyde) gave lower activities under the same conditions (see the Supporting Information, Table S3). Utilization of formaldehyde solution was favorable from the view point of the manufacturing process.⁴⁴

The time-based reaction progression over the Amberlyst-15 catalyst is shown in Figure 1. Both conversion and yield increased together as a function of time up to 15 h; the maximum yield was 43.1% with 57.5% selectivity. Thereafter,

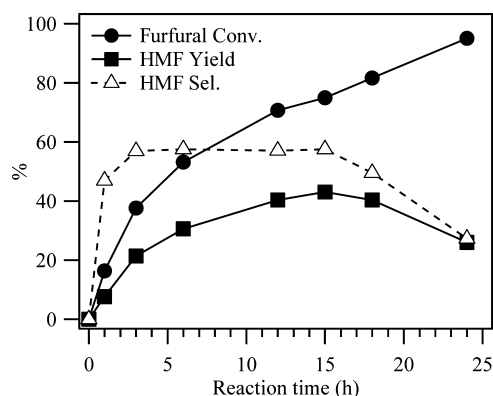


Figure 1. Time-based reaction progression of the hydroxymethylation of furfural to HMF over Amberlyst-15 in a batch reactor. Reaction conditions: furfural (1 mmol), formalin (5 mL), catalyst (200 mg), temp (363 K), stirring (500 rpm).

gradual decreases of HMF yield were observed with a continuous increase of furfural conversion; 43.1% of HMF yield dropped to 26.0% during an additional 9 h reaction. Actually, HMF consumption was expected during the reaction. Because LA was found as a byproduct in the HPLC chart (see the Supporting Information, Figure S1), successive hydrolysis of HMF produced over Amberlyst-15¹⁴ was identified as one of the unfavorable reactions. Formic acid (FA), another product of HMF hydrolysis, was observed only to a slight degree in the HPLC chart because of the peak overlapping with formaldehyde, while the presence of FA was supported by gas chromatography–time-of-flight mass spectrometry (GC–TOFMS) analysis. The time-based reaction progression of HMF consumption under the present condition was investigated (see the Supporting Information, Figure S4). In fact, gradual processing of the transformation of HMF toward LA production was detected; however, over half of the HMF molecules still remained after 12 h stirring. Therefore, it was considered that both HMF production from furfural via hydroxymethylation and HMF consumption to LA via successive hydrolysis competitively occurred and determines the yield of HMF in our study. Compounds of various types were present in the reaction mixture, as suggested by a GC–TOFMS analysis as byproducts. However, it is difficult to identify all reasonable side reactions at this stage. It was also detected that 1,3,5-trioxane and 1,3,5,7-tetroxane were generated during reaction through formaldehyde condensations by GC–TOFMS analysis.^b In addition, according to an earlier report, it was expected that resinification reaction of C5 hydrogen and the protonated carbonyl group and condensation reactions of the carbonyl group with formaldehyde occurred under acidic conditions, leading to resin formation.²⁹

Reusability is one important benefit of the heterogeneous catalysis system against the homogeneous analogue. As shown in Figure 2, the Amberlyst-15 catalyst constantly gave similar performance using a simple procedure through four runs without a marked decrease in reactivity (see the Experimental Section). Therefore, it was expected that deposits on the catalyst surface had a noncrucial impact in the case of Amberlyst-15. It is also an advantage for the resin catalyst that no loss of catalyst weight occurs during recycling procedures. The turn over number for HMF production was estimated to be >1.7 for four runs, and this is implied that the

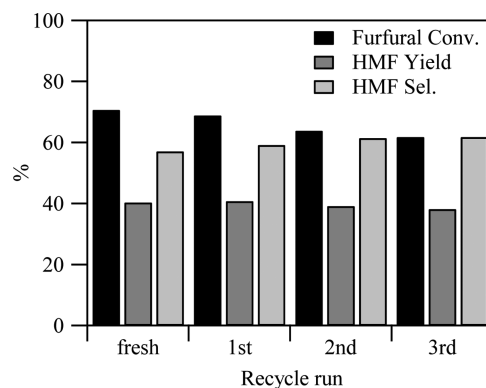


Figure 2. Recycle tests of the Amberlyst-15 catalyst. Reaction conditions: furfural (1 mmol), formalin (5 mL), catalyst (200 mg), time (12 h), temp (363 K), stirring (500 rpm).

acid site on Amberlyst-15 could enhance not only the target reaction but also side and/or over-reactions (vide supra).

A variety of bifunctionalized furans such as BHMF, HMFA, and 5-hydroxymethyl-2-furancarboxylic acid (HMFA) have also been attractive and powerful materials to afford valuable biomass-based chemical intermediates. Therefore, further application of Amberlyst-15-induced hydroxymethylations of three furans was attempted using the Amberlyst-15-catalyzed system. As shown in Table 2, 34.7, 14.3, and 23.8% yields for

Table 2. Hydroxymethylation of Furfural Derivatives with Aqueous Formaldehyde^a

entry	substrate (R)	conv. (%)	yield (%)	sel. (%)
1 ^b	furfuryl alcohol (–CH ₂ OH)	96.4	34.7 (BHMF)	34.6
2 ^{b,c}		79.6	7.1	8.9
3 ^c	furfurylamine (–CH ₂ NH ₂)	92.7	14.3 (HMFA)	15.5
4 ^{c,e}		89.2	15.0	16.9
5 ^d	furoic acid (–COOH)	68.4	23.8 (HMFA)	34.8

^aReaction conditions: substrate (1 mmol), formalin (5 mL), Amberlyst-15 (200 mg), time (15 min^b, 1 h^c, 15 h^d), temp. (313 K^c, 363 K), stirring (500 rpm).

BHMF, HMFA, and HMFA were successively obtained, respectively, from furfuryl alcohol, furfurylamine, and furoic acid used as a substrate (entries 1, 3, and 5). Highly reactive furfuryl alcohol and furfuryl amine were almost entirely consumed (conv. > 92%) within 1 h, although furoic acid gave a lower conversion value (68.4%).^c Apparently, the lower yields for BHMF and HMFA were attributed to the considerably higher reactivity of substrates of furfuryl alcohol and furfuryl amines, whereas the lower value for the HMFA yield is attributable to the lower reactivity of furoic acid (see the Supporting Information, Figure S5). High reactivity of former substrates were not inhibited significantly even at a lower operation temperature of 313 K (entries 2 and 4). According to these results, not only the activation of the fifth position of a furan ring but also prohibitions of side reactions are expected to serve a crucial role for the future catalyst design in this system.

To investigate a key factor for the direct hydroxymethylation of furfuraldehydes, the initial rates for HMF production among

four types of Amberlyst resin catalysts were monitored with the same amount of acid sites in a reaction media. Figure 3 shows

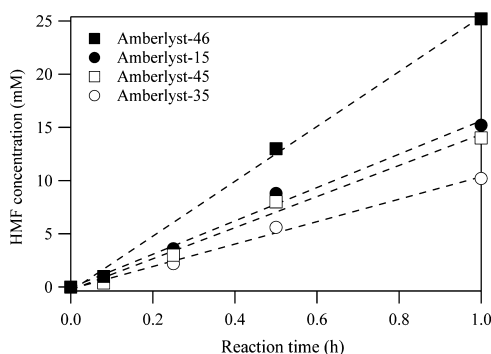


Figure 3. Time-based reaction for HMF production over Amberlyst-type resin catalysts. Reaction conditions: furfural (1 mmol), formalin (5 mL), acid site (0.94 mmol), time (1 h), temp (363 K), stirring (500 rpm). Dashed lines represent the linear approximation result.

the time-based reaction for HMF production over Amberlyst-type resin catalysts within 1 h reaction. It was observed that the reactivity was of the following order: Amberlyst-46 > Amberlyst-15 \approx Amberlyst-45 > Amberlyst-35. Interestingly, the unique Amberlyst-46 gave 1.62 (1.78) times faster activity than Amberlyst-15 (Amberlyst-45) and 2.46 times faster than Amberlyst-35, at initial stage of the reaction. However, during 24 h reaction, other three Amberlyst resin catalysts did not achieve the higher activity than Amberlyst-15; that is, 43.1% yield with 57.5% selectivity (Figure S6).

As an advanced study, application of the liquid flow system for continuous production of C6 furfuraldehydes through the heterogeneous catalyst bed was demonstrated further. Flow reactor systems have been demonstrated in various organic transformation reactions.^{45,46} As presented in Figure 4A, HMF productions over Amberlyst-15 in a flow reactor gave constant values of around 35.5% yield and 48% selectivity;^d that is, 70 mM HMF solution was provided constantly from a 200 mM furfural solution during 24 h. BHMf production is also apparently applicable for a flow reactor system (see the Supporting Information, Table S5). However, from the view point of selectivity, both HMF and BHMf values obtained in the flow reactor were lower than that in a batch reactor system in the case of Amberlyst-15. While in the case of Amberlyst-46, an increase in selectivity was observed in the flow reactor in comparison with that in a bath reactor system, the constant value was around 20% yield with 59% selectivity (Figure 4B). According to these observations, a new catalyst and/or reactor design to transcend the present reactivity derived from sulfuric functionalized resin catalyst, especially Amberlyst-15 and/or Amberlyst-46, is needed for the next generation in this area.^e

CONCLUSIONS

In summary, direct hydroxymethylation of furfural to HMF proceeded smoothly with the highest values of 43.1% yield and 57.5% selectivity in the presence of Amberlyst-15 in a batch reactor system. This catalytic system was reusable and applicable for other transformations of C5 to C6 furfuraldehydes under mild conditions. In addition, such sulfuric functionalized resin-catalyzed direct hydroxymethylation of furfuraldehydes successfully occurred in a liquid-flow reactor system with good performance. These achievements are expected to open

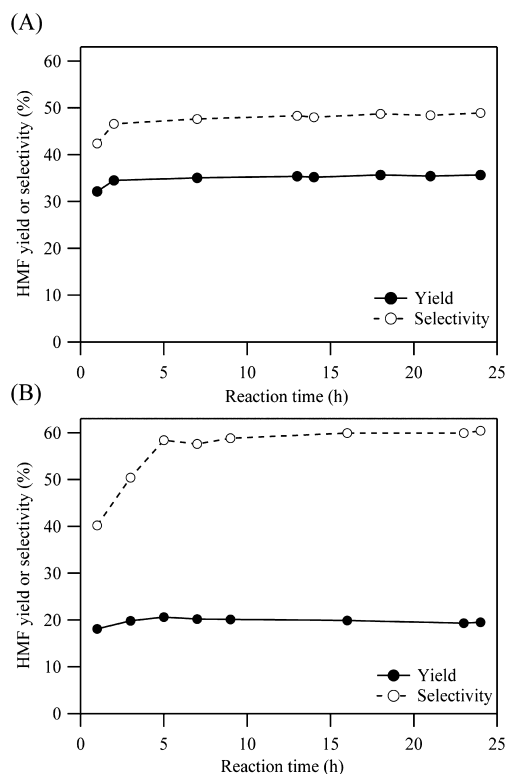


Figure 4. Time-based reaction for HMF production in a flow reactor by using (A) Amberlyst-15 and (B) Amberlyst-46. Reaction conditions: eluent [furfural (14 mmol)/formalin (70 mL) mixed solvent], catalyst bed (800 mg) in a SUS tube (100 mm \times ϕ 5), temp (363 K), flow rate (0.04 mL·min⁻¹).

new avenues for inedible biomass utilization to produce highly valuable chemicals not only in the area of academic investigations but also in industrial studies.

EXPERIMENTAL SECTION

The reaction was conducted in a Schlenk flask attached with a condenser. As the general procedure, first, 37% aqueous formaldehyde solution (stabilized with 5–10% methanol; Wako Pure Chemical Inds. Ltd.) (5 mL) and solid catalyst (200 mg) were mixed well under vigorous stirring (500 rpm) at 363 K. Then, furfural (1 mmol) without pretreatment was introduced into the mixture to initiate the target reaction. After 12 h, the catalyst was filtered off using a syringe filter (0.20 μ m; Millex). The filtrate was analyzed using HPLC equipped with an RI detector. Columns were used for furfural/HMF and furoic acid/HMFCA (eluent: 10 mM H₂SO₄ aq, Aminex HPX-87H; Bio-Rad Laboratories Inc.) and furfuryl alcohol/BHMf and furfurylamine/HMFCA reactions (eluent: 10 vol % acetonitrile aq, RSpak DE-413L; Shodex). A GC-flame ionization detector (GC-2014; Shimadzu) and/or GC-TOFMS (JEOL; AccuTOF GCx) equipped with a nonpolar column (DB-1; Agilent J&W) were also used (in part). Conversion and yield values were estimated with the standard lines adjusted by each reference compound. After the reaction, the catalyst was centrifuged, washed with deionized water (1 L), and dried at 383 K overnight before each recycling run for 12 h. It is noteworthy that the reaction condition for each recycling run was the same as the initial condition because the sulfuric functionalized resin catalyst of Amberlyst-15 could be recovered without a significant loss in weight.

The liquid flow reaction was performed using a simple flow reactor system (MCR-1000; EYELA). Further information is presented in the [Supporting Information](#) (see Tables S4 and S5).

Water adsorption isotherm at 298 K was obtained by using BELSORP-max (BEL Japan, Inc.). The samples (0.09 g) were pretreated at 383 K for 2 h under vacuum before measurement.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsomega.8b00120](https://doi.org/10.1021/acsomega.8b00120).

Information on chemicals, HPLC chart, details of reaction activity, and effect of stirring speed and time-based progression of the reaction ([PDF](#))

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

HMF	5-hydroxymethyl-2-furaldehyde
furfural	2-furaldehyde
BHMF	2,5-bis(hydroxymethyl)furan
HMFA	5-(hydroxymethyl)furfurylamine
FDCA	2,5-furandicarboxylic acid
HMFCA	5-hydroxymethyl-2-furancarboxylic acid
LA	levulinic acid
FA	formic acid

■ ADDITIONAL NOTES

^aData provided by the manufacturer.

^bEfficiency of formaldehyde at the hydroxymethylation was hardly estimated by HPLC owing to its high concentration in the reaction mixture.

^cConsidering the activation–deactivation effect onto the fifth position derived from the electron donating–withdrawing group at the second position of the furan ring, –CHO, and –COOH are expected to contribute more to the lower yield rather than –CH₂OH and –CH₂NH₂ functionalities. However, the order in yield was not considerable in relation to this basic phenomenon.

^dDetailed information is presented in [Table S4](#).

^eAccording to our previous report,⁴⁷ we tentatively investigated the water wettability of Amberlyst-15 and Amberlyst-46 by using H₂O adsorption isotherm measurement (see [Figure S7](#)). Because the Amberlyst-46 possessed more hydrophobic nature than Amberlyst-15, it would be expected that surface properties such as hydrophilicity/hydrophobicity will play a crucial role in

the direct hydroxymethylation of furfuraldehydes with aqueous formaldehyde over a sulfuric functionalized resin catalyst.

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