Supporting Information

Hydroxyalkylation/alkylation of 2-methylfuran and furfural over niobic acid catalysts for the synthesis of high carbon transport fuel precursors

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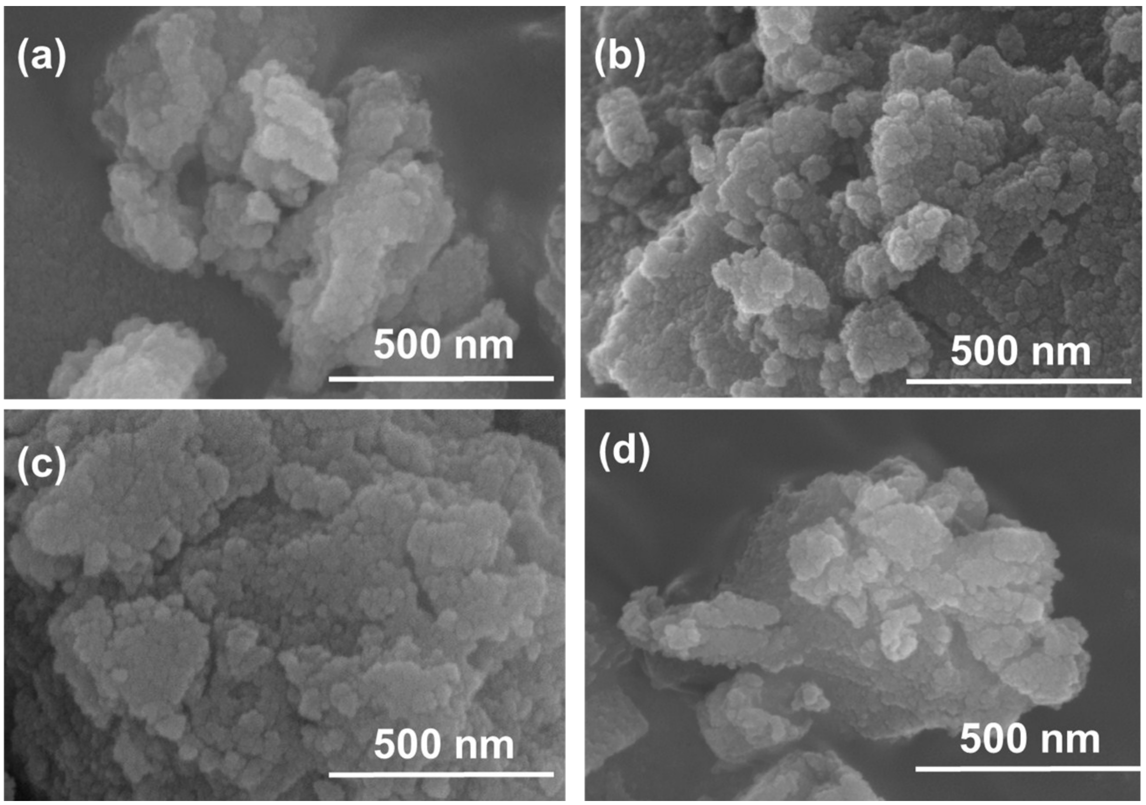


Fig. S 1. SEM images of (a) NAC_{100}, (b) NAC_{200}, (c) NAC_{300}, and (d) NAC_{500}.

The degradation of the niobic acid catalysts (NAC) started with a mild curve from room temperature to around 100°C which is attributed to the physically adsorbed water. The additional weight loss up to 400°C corresponds to the build-up of the inorganic amorphous network and fragments of organic molecules.

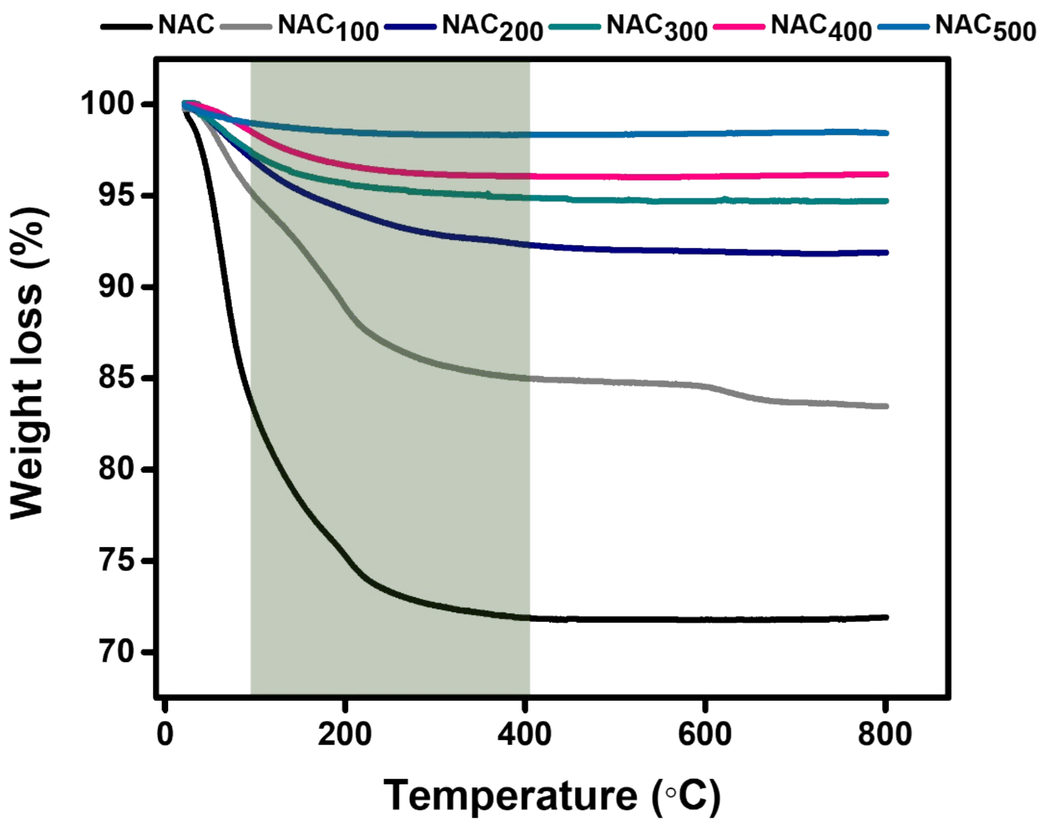


Fig. S 2.TGA curves of the niobic acid catalysts calcined at different temperatures (100-500°C).

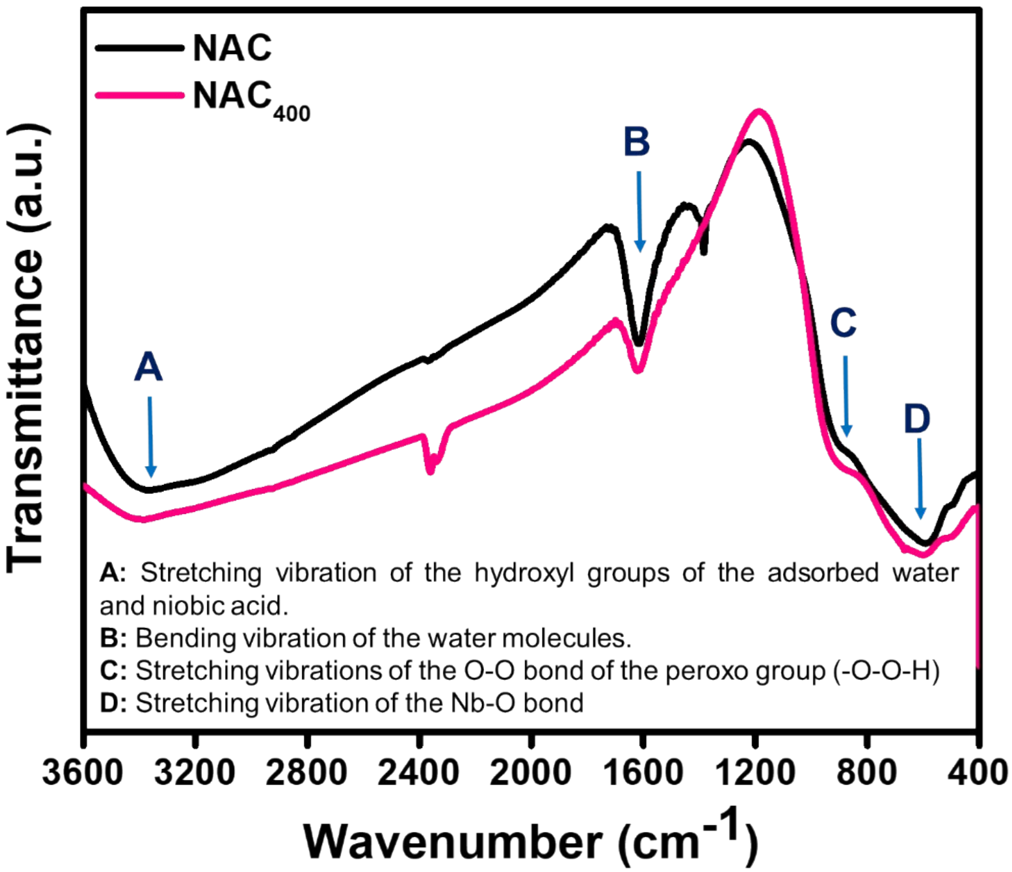


Fig. S 3. FT-IR spectra of NAC and NAC_{400}.

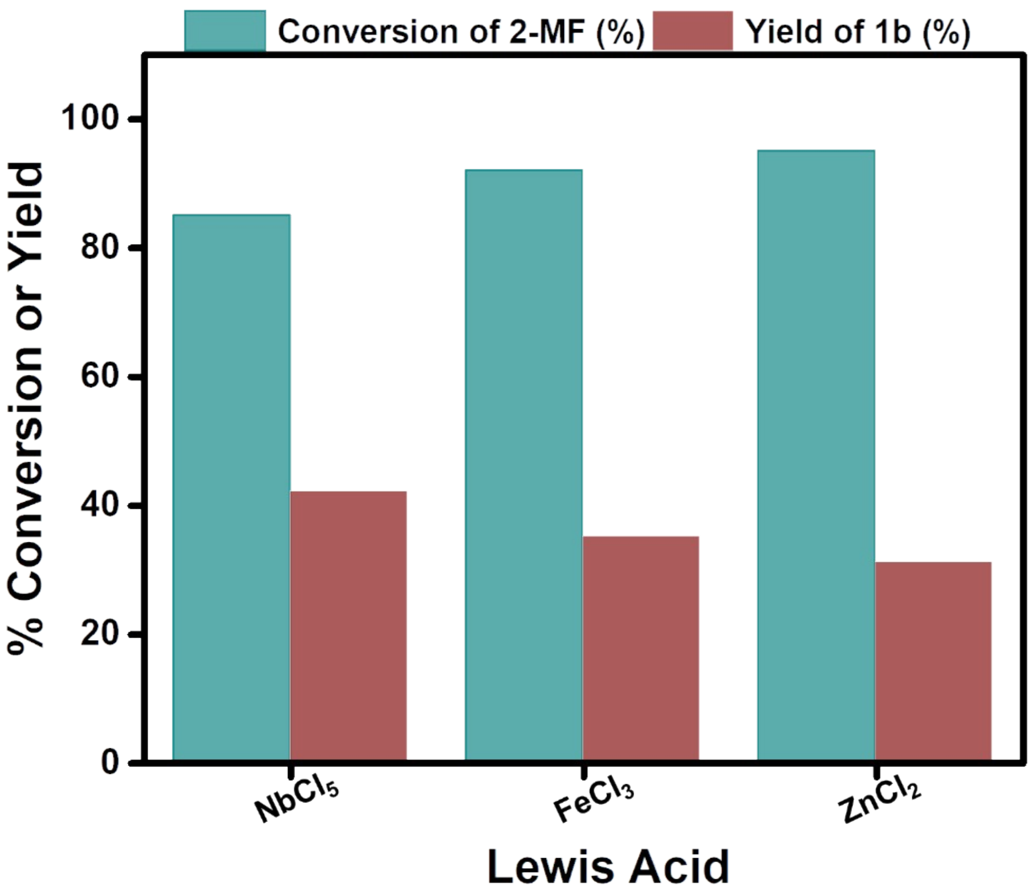


Fig. S 4. HAA condensation of 2-MF with FUR over Lewis acid catalysts. Reaction conditions: 2-MF (3.37 g, 41 mmol), FUR (1.92 g, 20 mmol), catalyst (0.20 g), 80°C, 6 h.

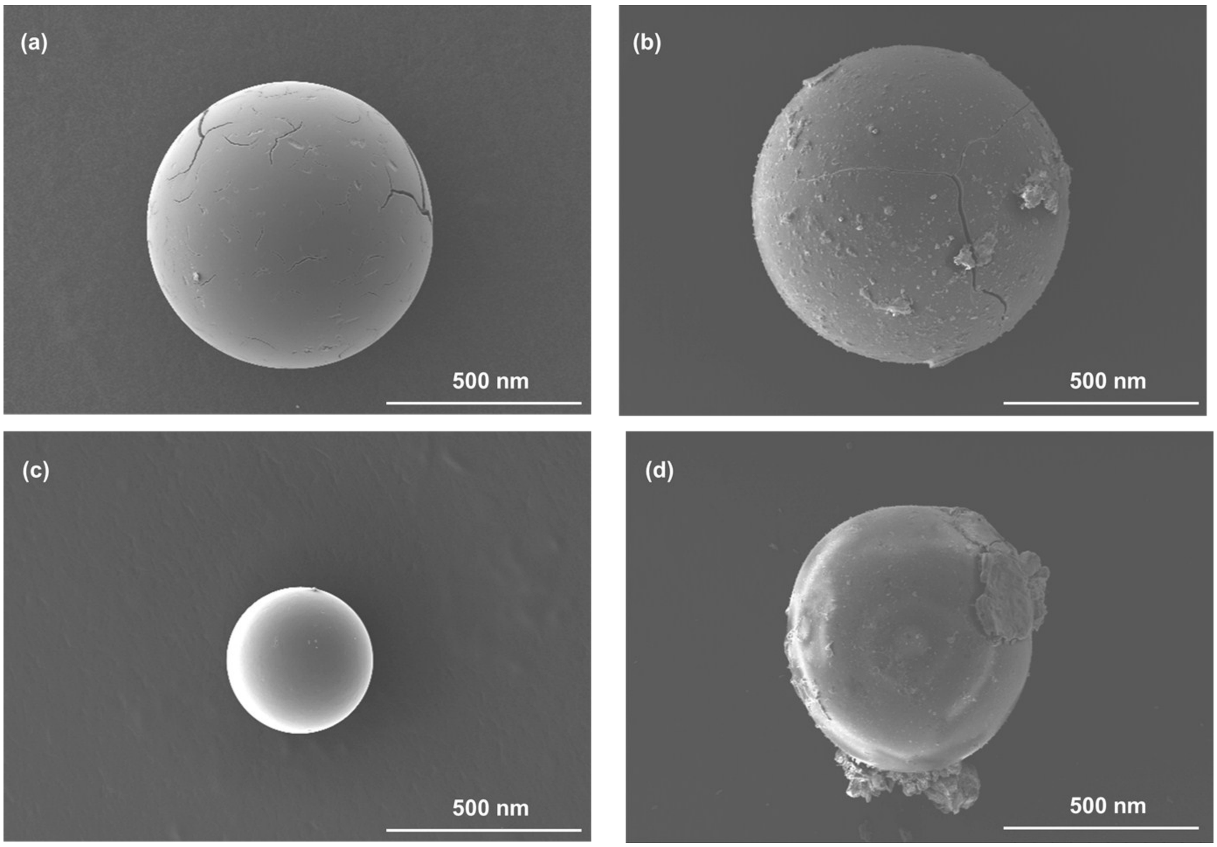


Fig. S 5. SEM images of (a) fresh Amberlyst-15, (b) recycled Amberlyst-15, (c) fresh Amberlyst-36, and (d) recycled Amberlyst-36.

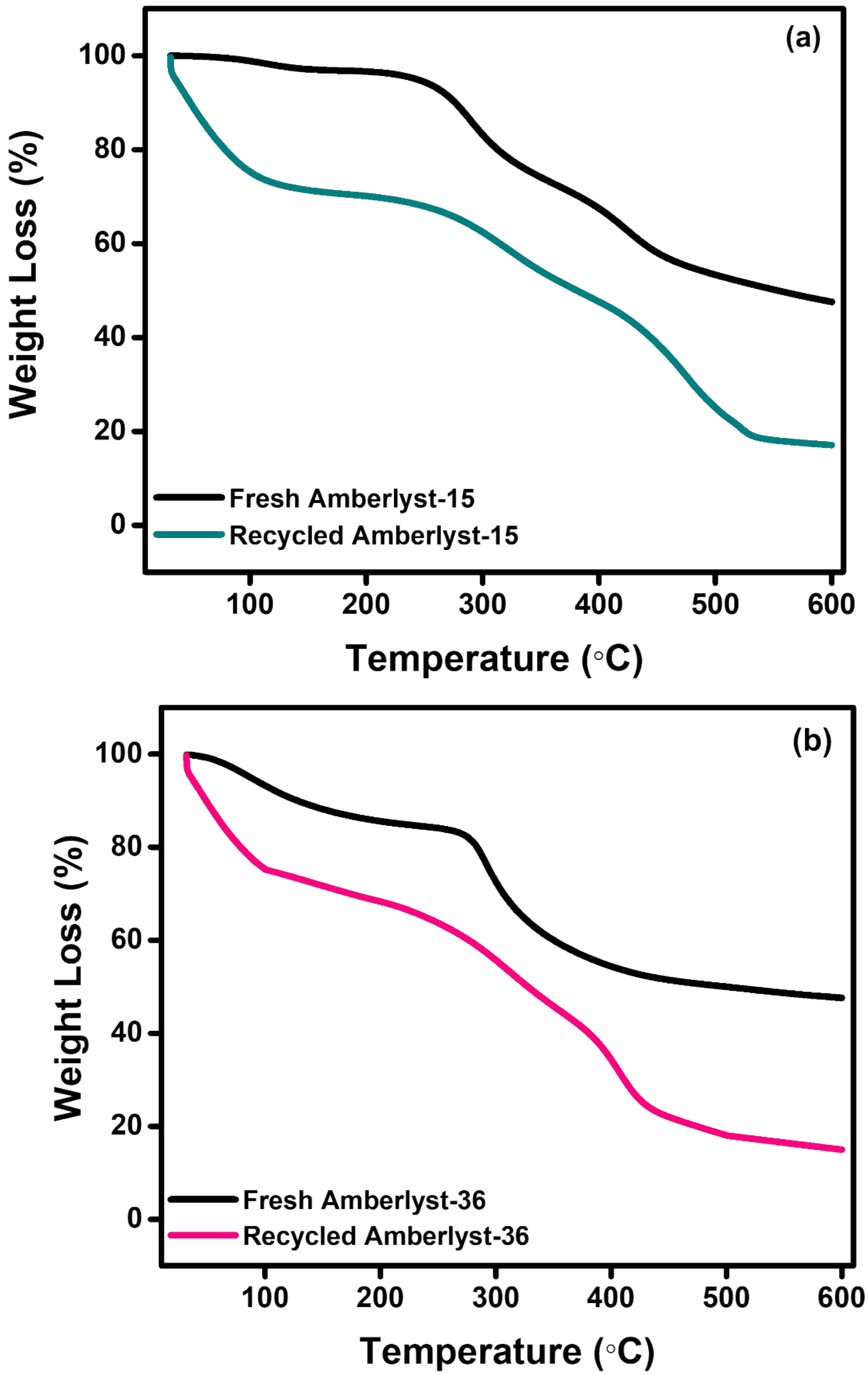


Fig. S 6.TGA curves of (a) fresh and recycled Amberlyst-15, and (b) fresh and recycled Amberlyst-36.

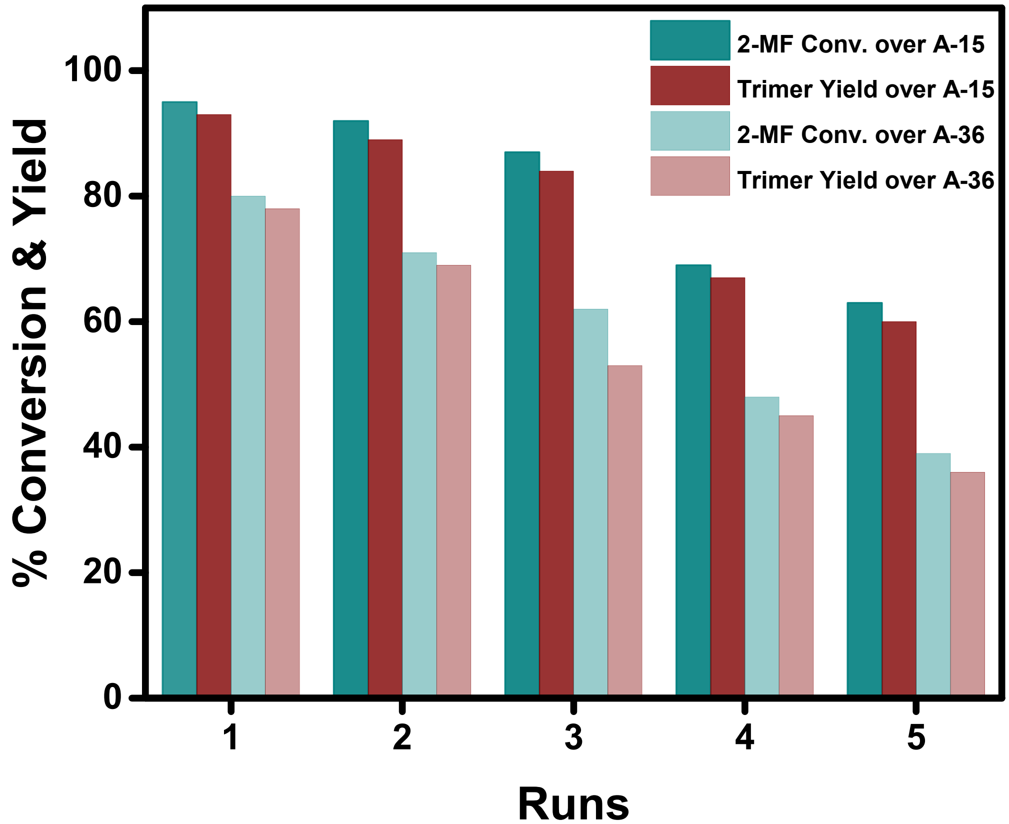


Fig. S 7.Recyclability tests of Amberlyst-15 and Amberlyst-36 for the HAA condensation of 2-MF with FUR. Reaction conditions: 2-MF (3.37 g, 41 mmol), FUR (1.92 g, 20 mmol), catalyst (0.20 g), 80°C, 6 h.

Table S 1. TOFs of the solid acid catalysts.

Catalysts	Acid amount (mmol/g)	Time (h)	2-MF Conversion (%)	HAA rates (mmol g^{-1} h^{-1})	TOF (h^{-1})
Nafion-212	1.10	0.25	25.3	207	188
Amberlyst 15	4.70	0.25	19.9	163	35
Amberlyst 36	5.40	0.25	16.1	132	24
H-Y-80	0.69	1	4.80	10	15
BEA-300	0.20	1	3.20	7	35
CNA	0.75	0.25	2.80	23	31
NAC	1.82	0.25	8.90	73	40
NAC_{100}	1.53	0.25	10.00	82	54
NAC_{200}	1.43	0.25	11.8	97	68
NAC_{300}	1.35	0.25	13.7	112	83
NAC_{400}	1.28	0.25	15.8	130	102
NAC_{500}	0.66	1	3.30	7	11

Reaction conditions: 3.37 g 2-MF (41 mmol), 1.92 g FUR (20 mmol), 80°C, 0.20 g catalyst. The rates of HAA are based from the conversion of 2-MF at the given time.

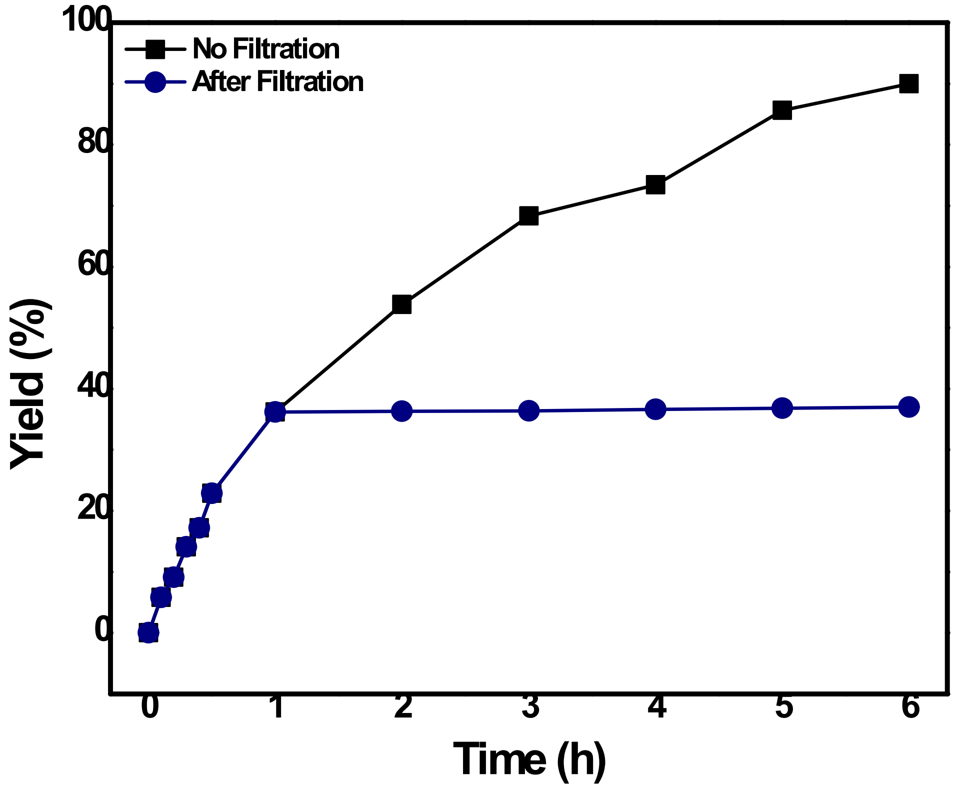


Fig. S 8. Results of the hot filtration test. Catalyst was removed after 1 h and the reaction was continued up to 6 h. Reaction conditions: 3.37 g 2-MF, 1.92 g FUR, 80˚C, 0.5 h, 0.20 g NAC_{400}.

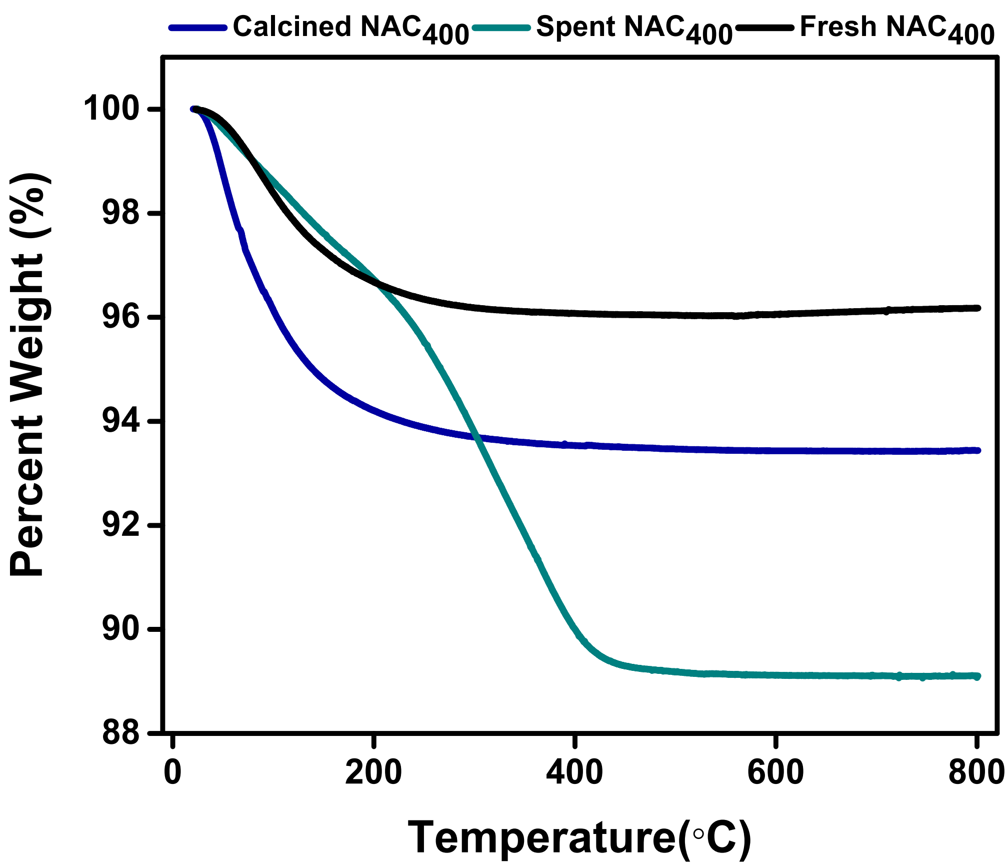


Fig. S 9. TGA curves of the fresh, spent and regenerated NAC_{400}.

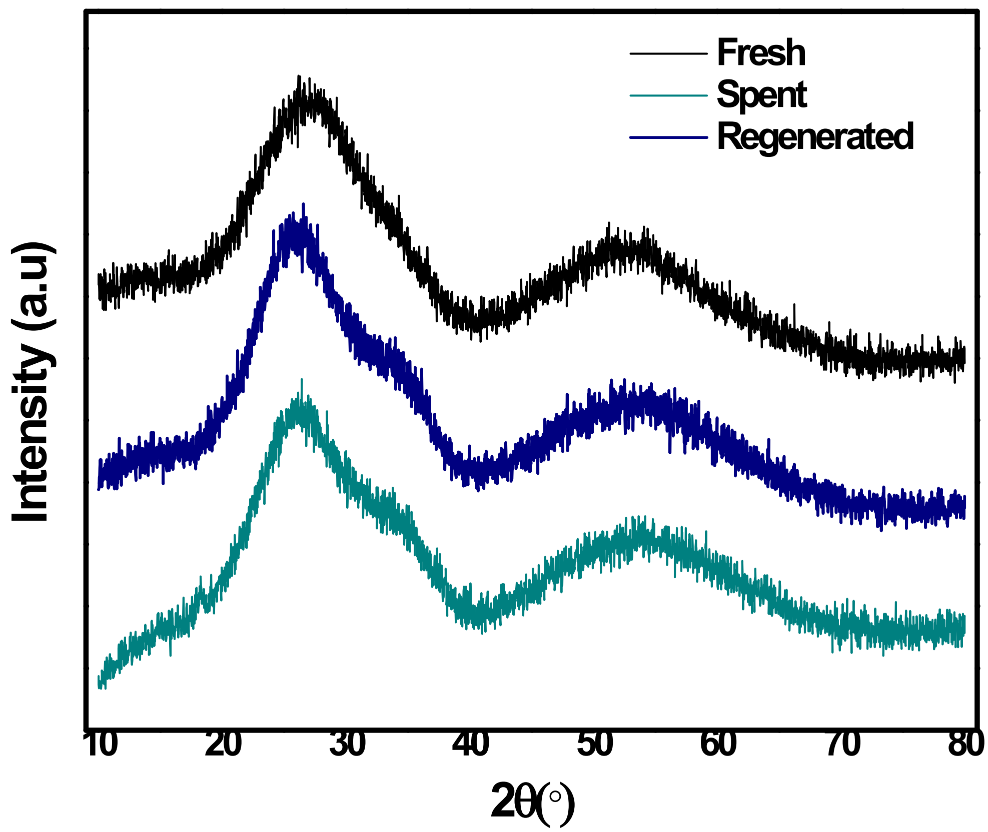


Fig. S 10. XRD patterns of fresh, spent, and regenerated $NAC_{400.}$

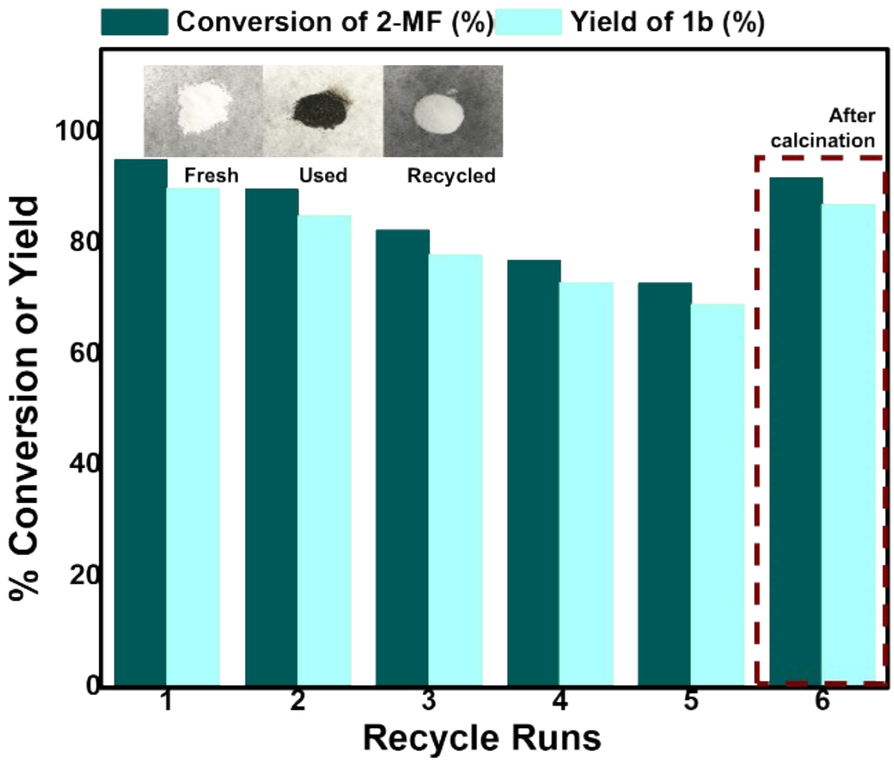


Fig. S 11. Recyclability test of NAC_{400}. Reaction conditions: 2-MF (41 mmol), FUR (20 mmol), 0.20 g NAC_{400}, 80°C, 6 h.

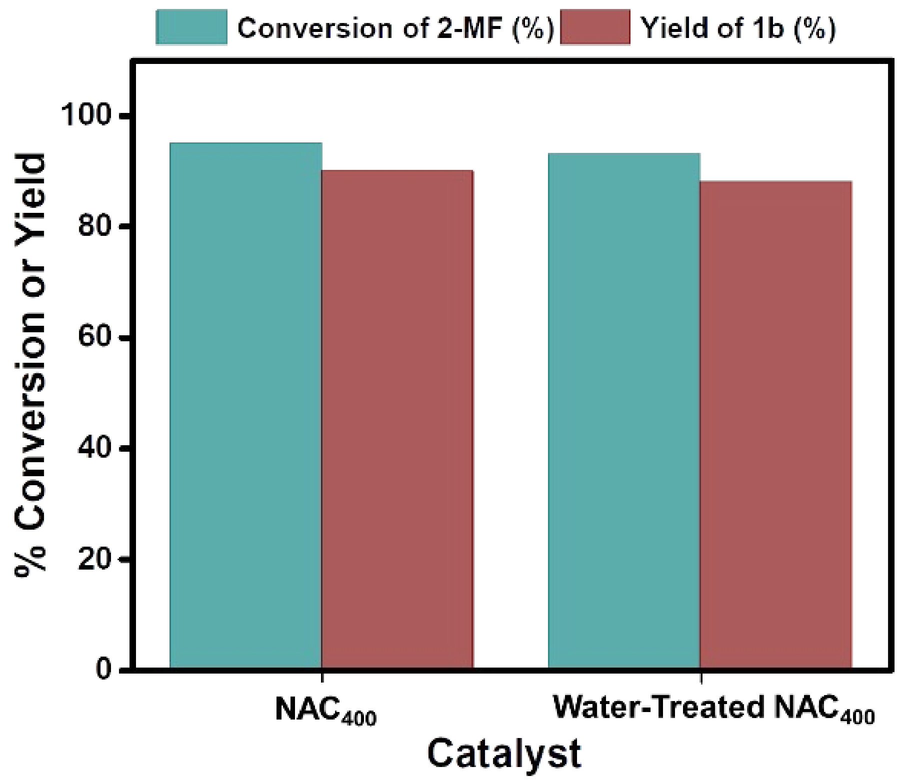


Fig. S 12. HAA condensation of 2-MF with FUR over NAC_{400} and water-treated NAC_{400}. Reaction conditions: 2-MF (3.37 g, 41 mmol), FUR (1.92 g, 20 mmol), catalyst (0.20 g), 80°C, 6 h.

Table S 2. Textural properties and acidity of NAC_{400} and water-treated NAC_{400}.

Catalyst	Surface Area (m^2/g)[a]	Pore Volume (cm^3/g)[b]	Pore Diameter (nm)[b]	Acid Amount (mmol H^+/g catalyst)[c]
NAC_{400}	144	0.24	6.74	1.28
Water-Treated NAC_{400}	140	0.23	6.69	1.25

[a] Calculated from N_2 adsorption-desorption isotherms using BET.

[b] Calculated from N_2 adsorption-desorption isotherms using BJH.

[c] Calculated from NH_3-TPD.

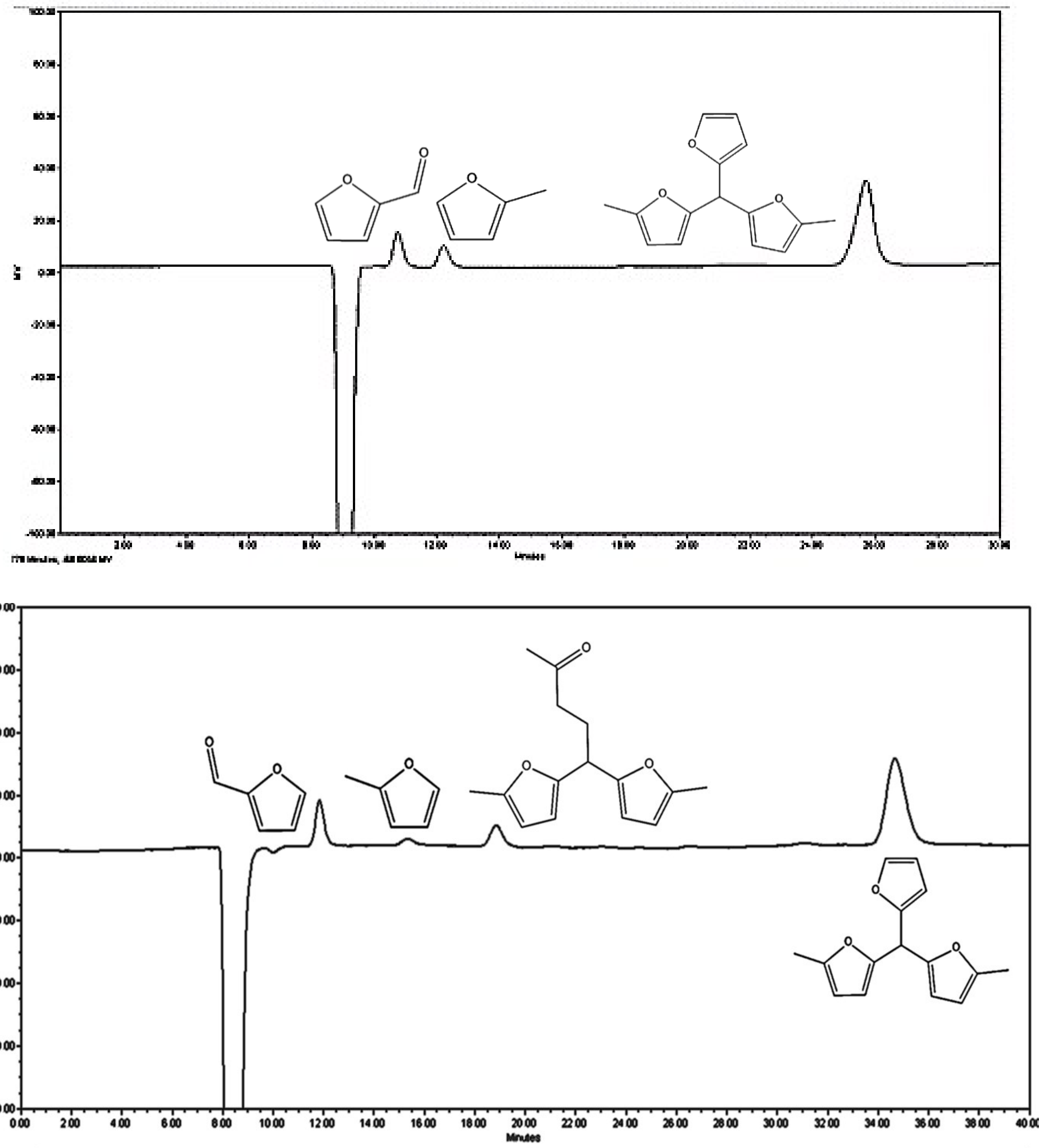
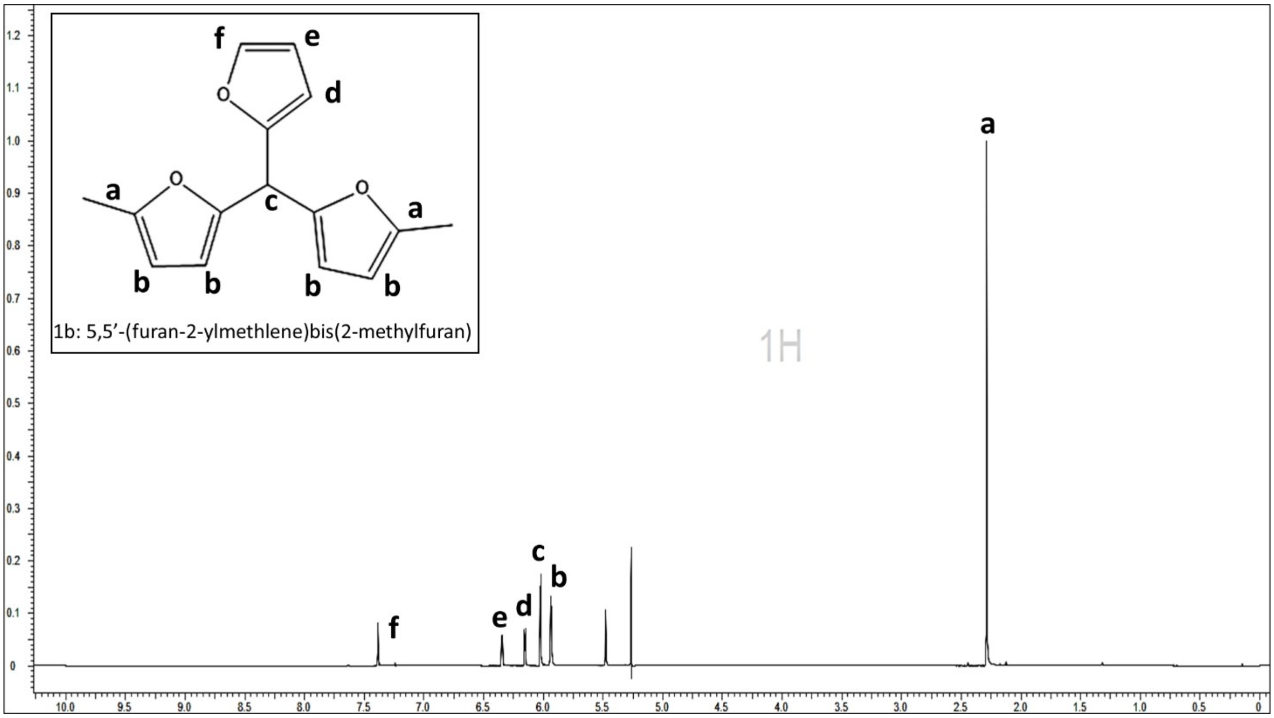


Fig. S 13. HPLC chromatogram of liquid products from the HAA of 2-MF with FUR. Reaction conditions: 80°C, 6 h, 3.37 g 2-MF, 1.92 g FUR and 0.20 g (a) $NAC_{400,}$ (b) Nafion-212.



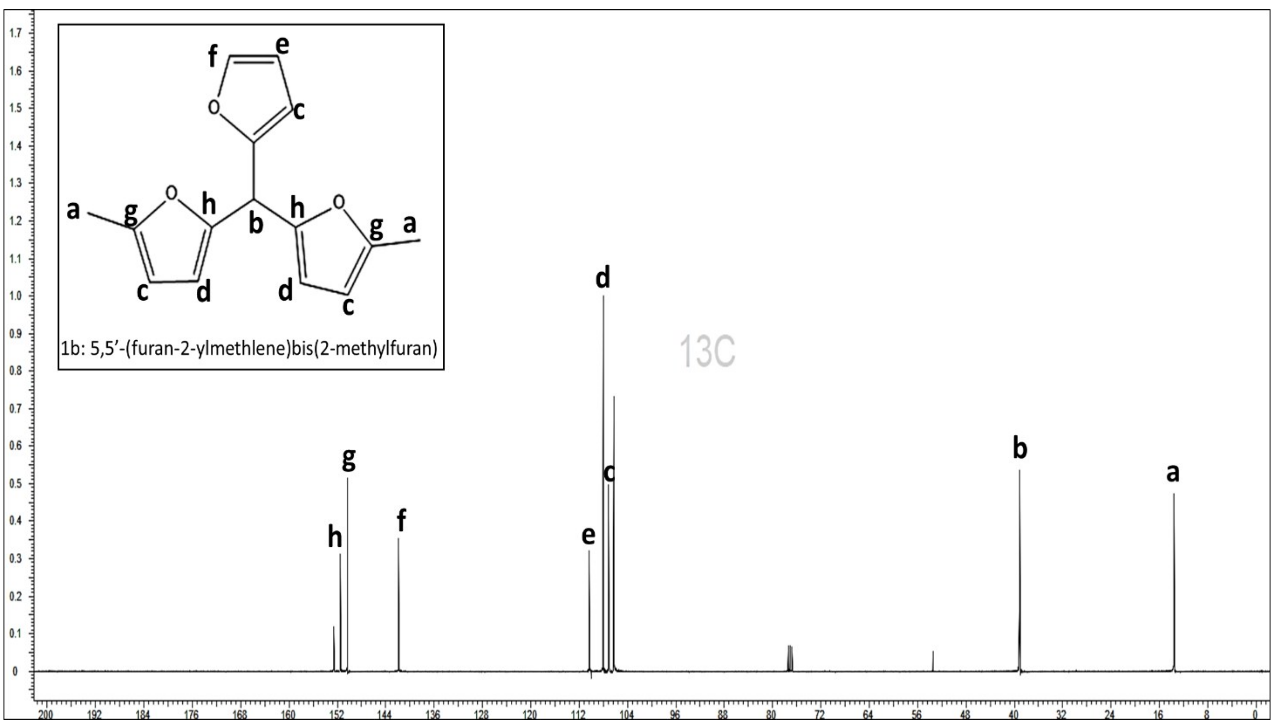


Fig. S 14. ^{1}H and ^{13}C NMR of the 1b prepared by the HAA of 2-MF with FUR.

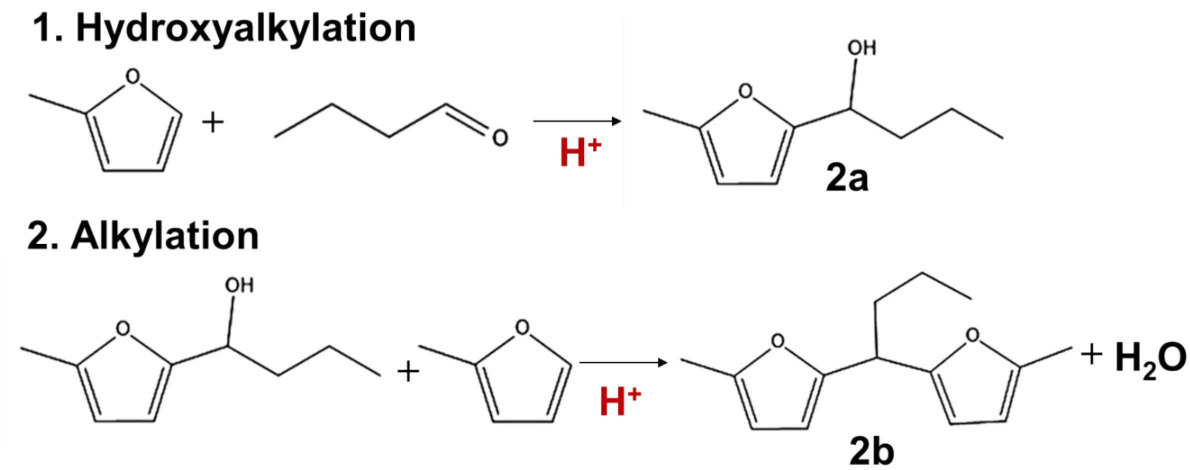


Fig. S 15. Reaction pathway for the HAA of 2-MF with BUT.

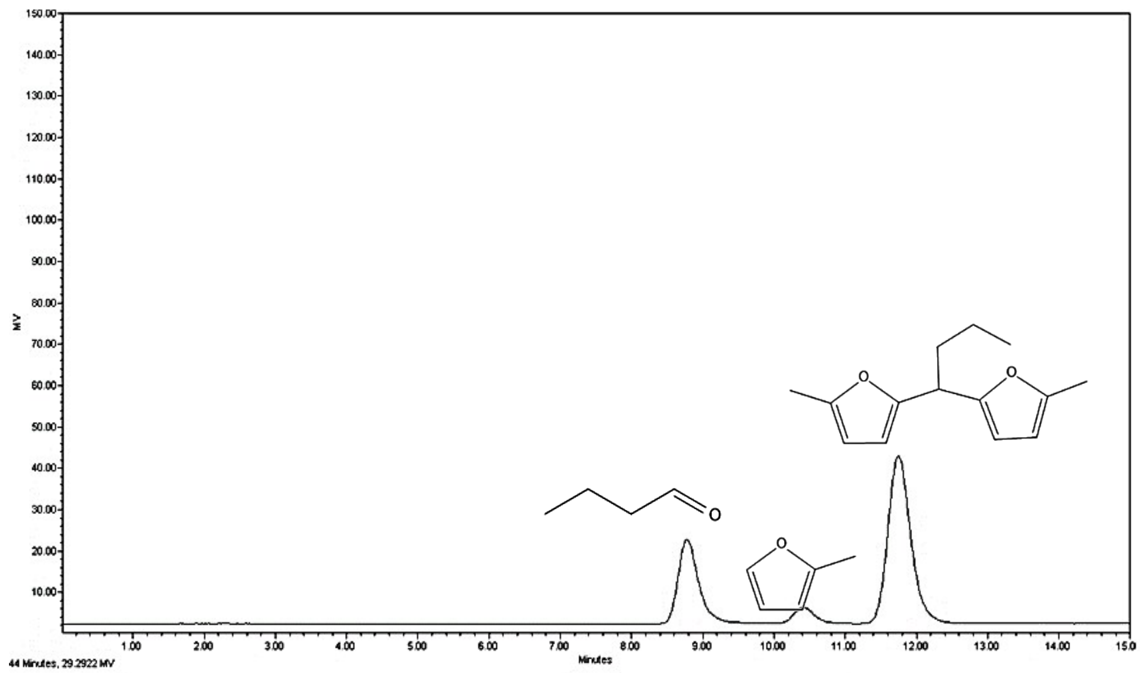


Fig. S 16. HPLC chromatogram of liquid products from the HAA of 2-MF with BUT. Reaction conditions: 80°C, 6 h, 3.37 g 2-MF, 1.44 g BUT and 0.20 g $NAC_{400.}$

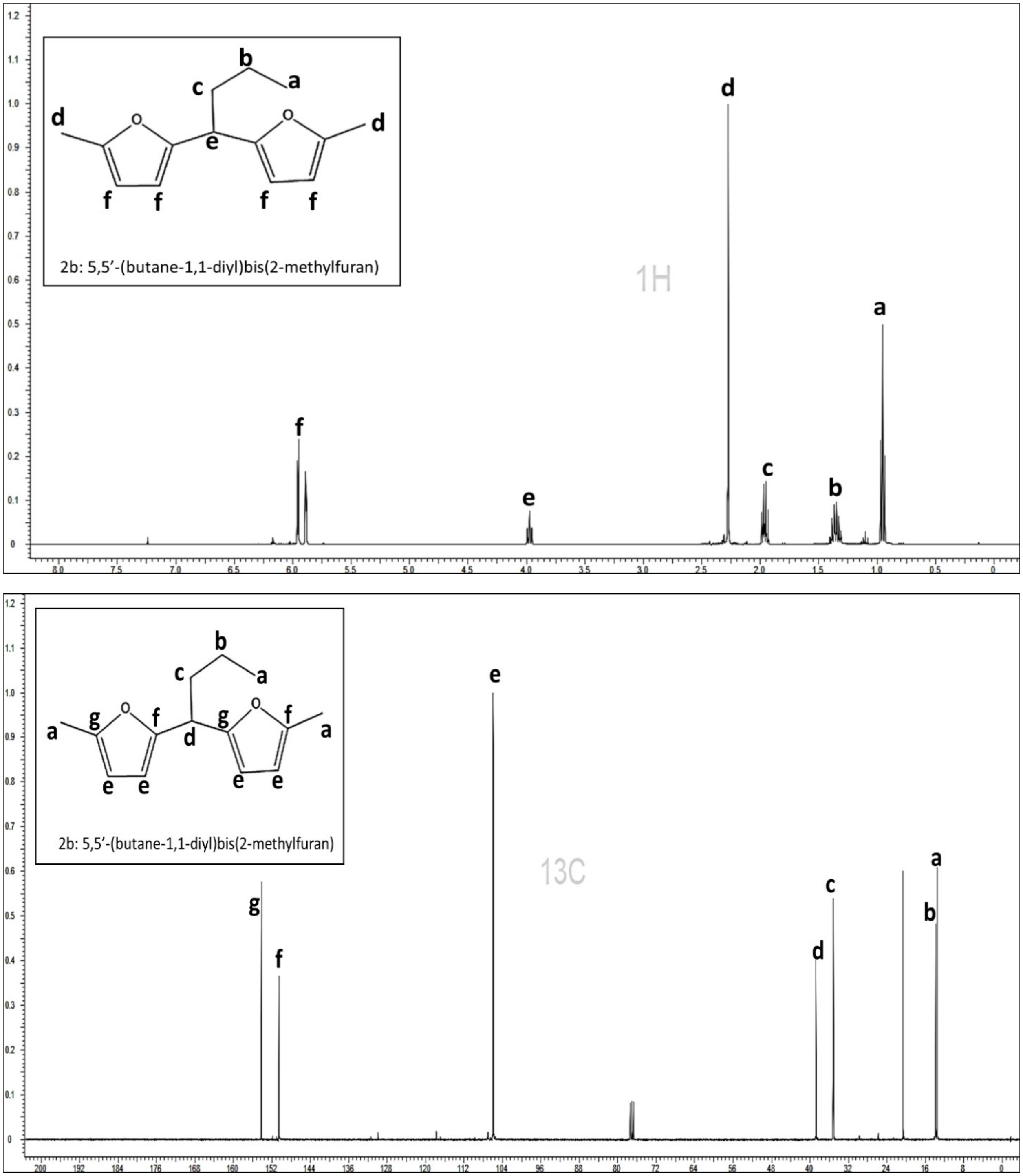


Fig. S 17. ^{1}H and ^{13}C NMR of the 2b prepared by HAA of 2-MF with BUT.

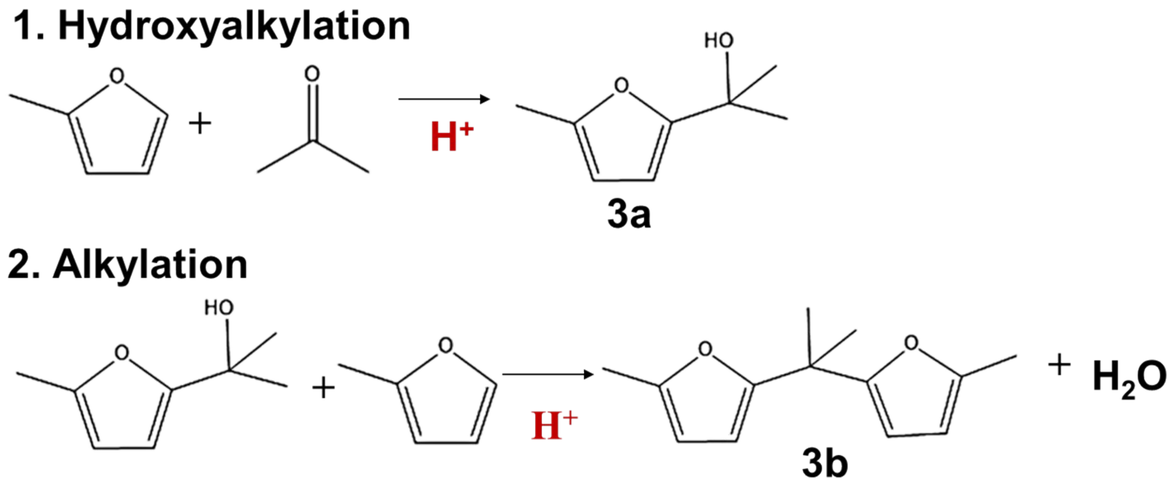


Fig. S 18. Reaction pathway for the HAA of 2-MF with ACE.

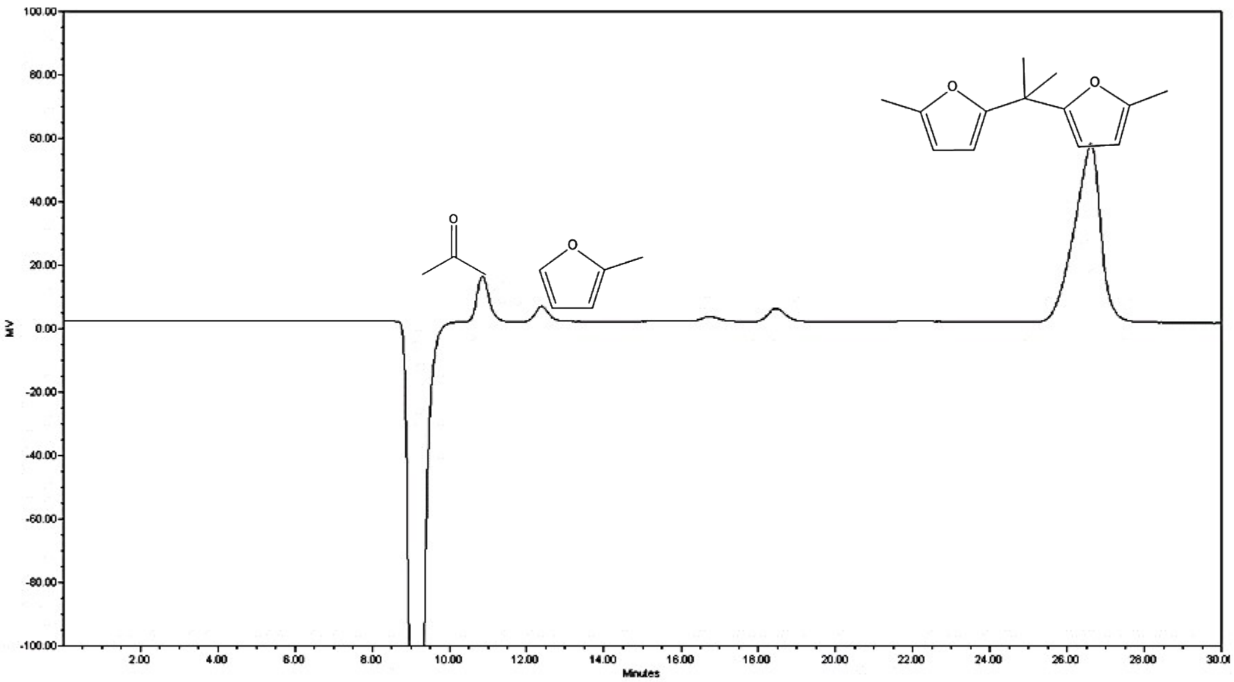


Fig. S 19. HPLC chromatogram of liquid products from the HAA of 2-methylfuran 2-MF with ACE. Reaction conditions: 80°C, 6 h, 3.37 g 2-MF, 1.16 g ACE and 0.20 g NAC_{400}.

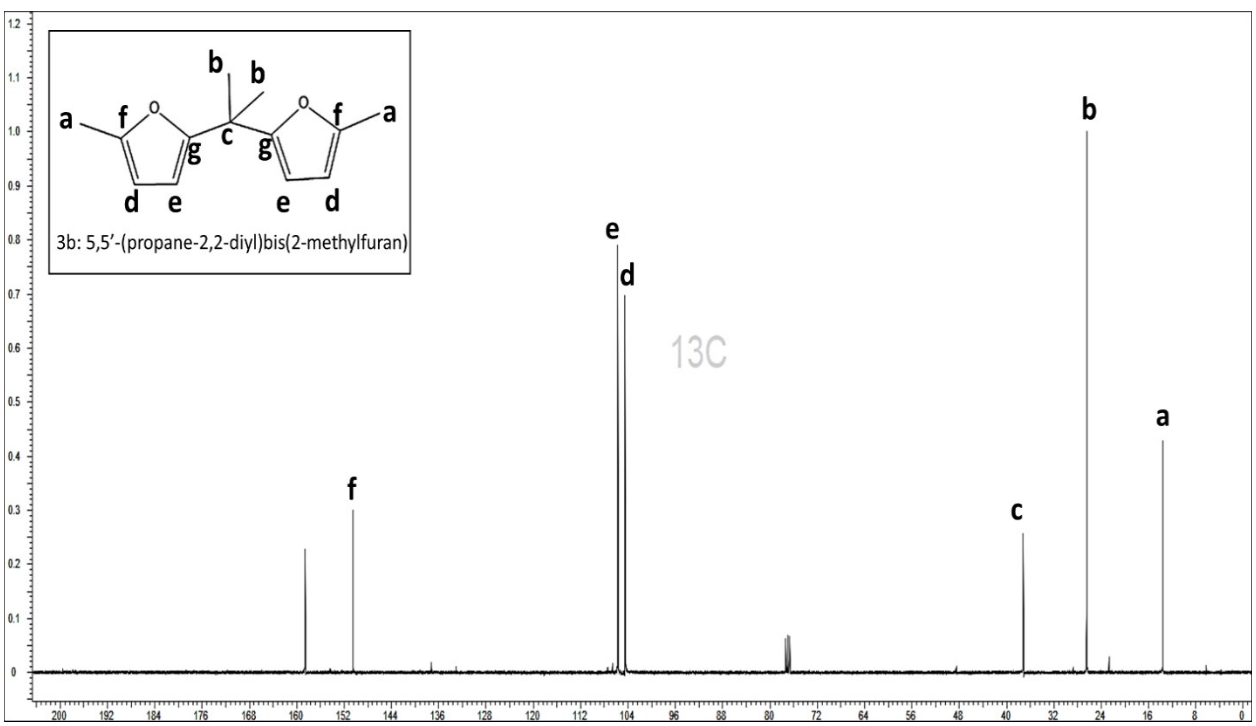


Fig. S 20. ^{1}H and ^{13}C NMR of the 3b prepared by the HAA of 2-MF with ACE.

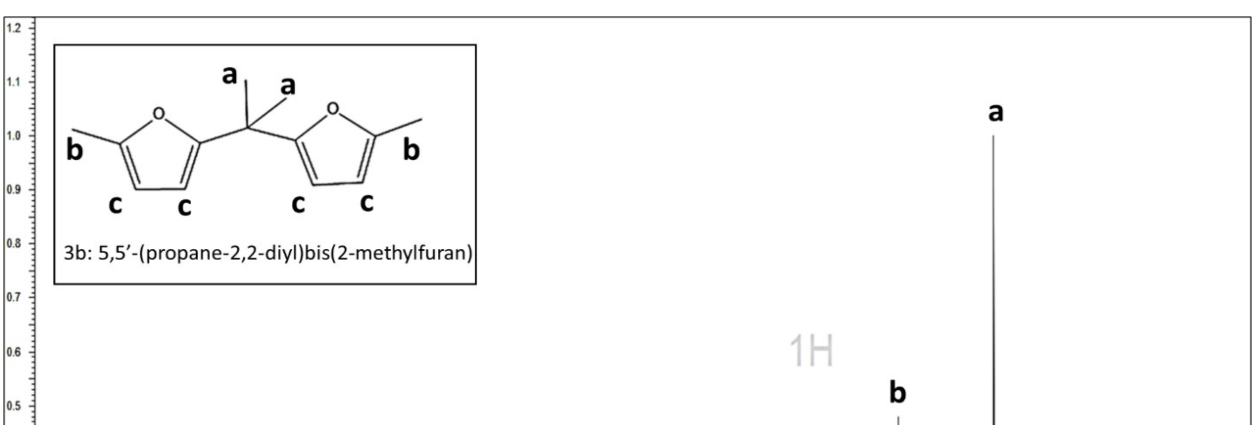


Table S 3. Comparison of the activity of NAC_{400} in the HAA reactions with previous literature.

HAA reaction of 2-MF with FUR						
Entry	**Catalyst**	**Temp. (°C)**	**Time (h)**	**Conversion (%)**	**Yield (%)**	**Ref.**
1	Protonated Titanate Nanotubes (PTNT)	50	4	62 (2-MF)	50	[1]
2	Lignosulfonate-based Acidic Resin	50	2	70.4 (2-MF)	65.4	[2]
3	Lignosulfonate-derived Acidic Carbocatalysts	60	4	96 (FUR)	93	[3]
4	Improved Graphene Oxide Carbocatalyst	60	6	100 (2-MF)	95	[4]
5	NAC_{400}	80	6	95 (2-MF)	90	This work
HAA reaction of 2-Methylfuran with *n*-Butanal						
6	Protonated Titanate Nanotubes (PTNT)	50	4	69.3 (2-MF)	67.6	[1]
7	Lignosulfonate-based Acidic Resin	50	2	78 (2-MF)	75	[2]
8	Lignosulfonate-derived Acidic Carbocatalysts	60	2	99 (n-Butanal)	96	[3]
9	Improved Graphene Oxide Carbocatalyst	60	12	NA	83	[4]
10	NAC_{400}	80	6	91 (2-MF)	88	This work
HAA reaction of 2-Methylfuran with Acetone						
11	Protonated Titanate Nanotubes (PTNT)	50	4	10 (2-MF)	6	[1]
12	Lignosulfonate-based Acidic Resin	50	2	24 (2-MF)	22	[2]
13	Lignosulfonate-derived Acidic	60	24	90 (Acetone)	94	[3]

	Carbocatalysts					
14	Improved Graphene Oxide Carbocatalyst	50	12	NA	90	[4]
15	NAC_{400}	60	6	45 (2-MF)	42	This work

References:

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