Supporting Information

Polyphenylene as an Active Support for Ru Catalyzed Hydrogenolysis of 5-Hydroxymethylfurfural

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1. Supporting figures

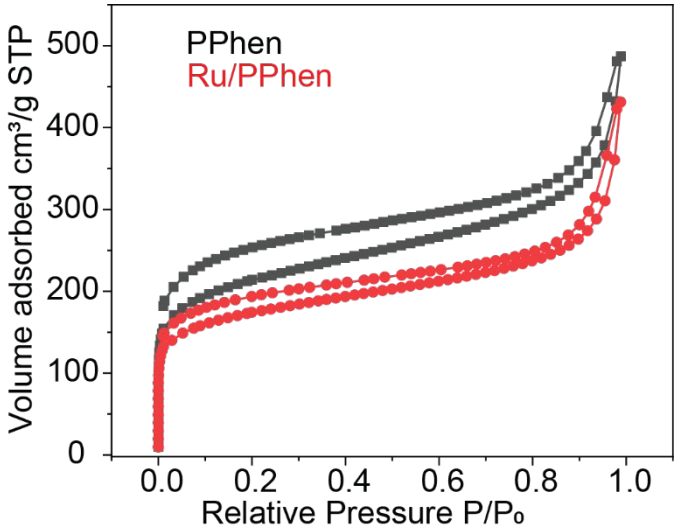

Figure S1. N_2 physisorption isotherm of PPhen (black) and Ru/PPhen (red).

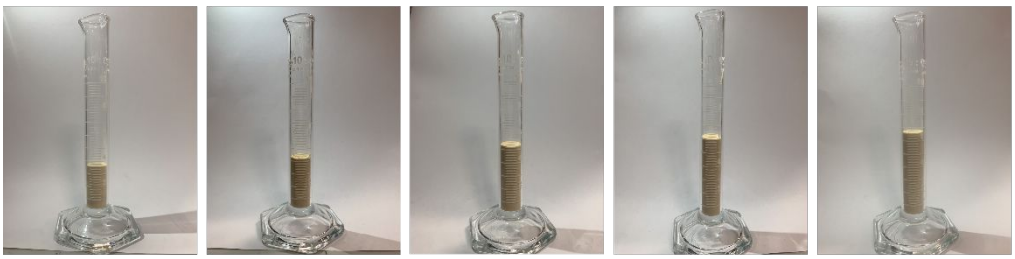

Figure S2. Swelling test of PPhen with ethanol. 200 mg of PPhen is used and mixed with certain amount of ethanol.

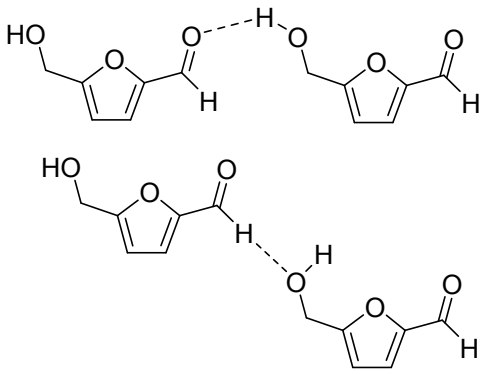

Figure S3. Illustraton of the intermolecular hydrogen bond.

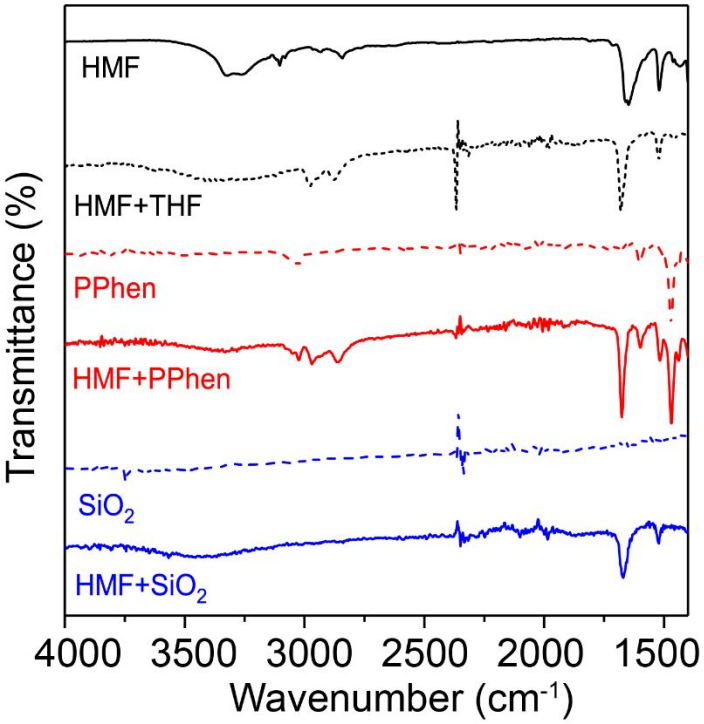

Figure S4. Full range of the IR spectra for HMF over PPhen and SiO_2.

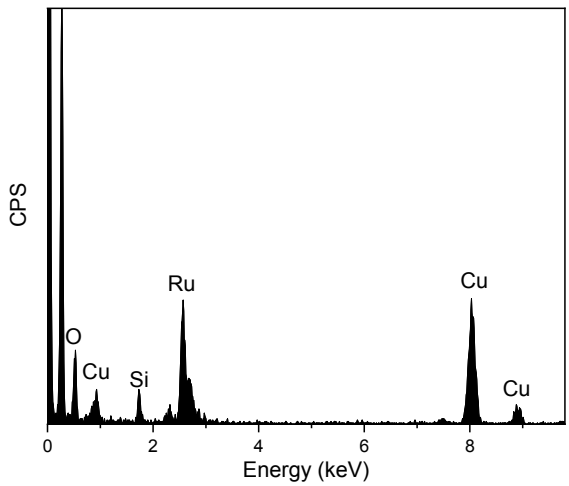

Figure S5. EDS spectrum of Ru/PPhen. The Pd signal should be at 3.3 kev, which is not observed here.

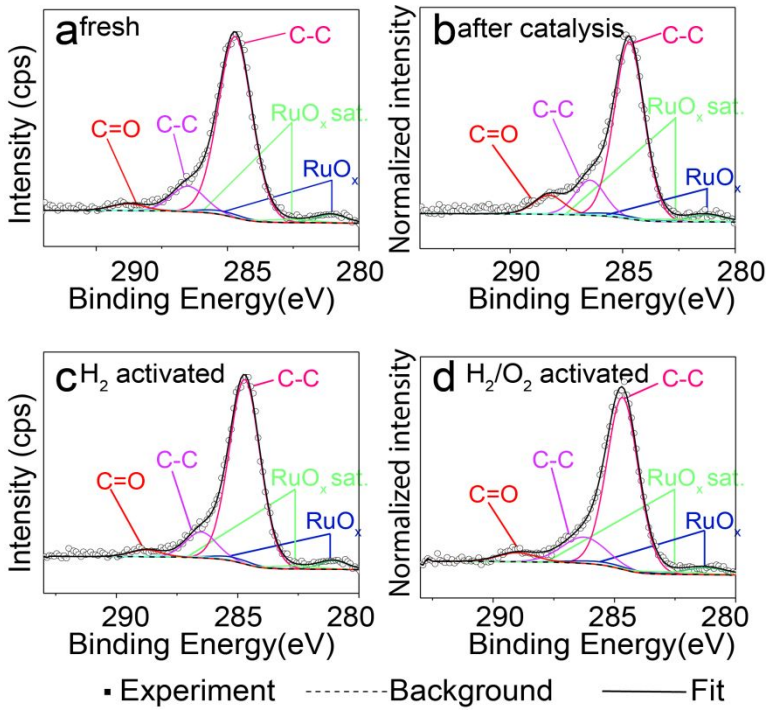

Figure S6. XPS spectra of Ru/PPhen (a) fresh Ru/PPhen, (b) Ru/PPhen after catalysis, (c) Ru/PPhen activated with H_2, (d) Ru/PPhen activated with H_2/O_2.

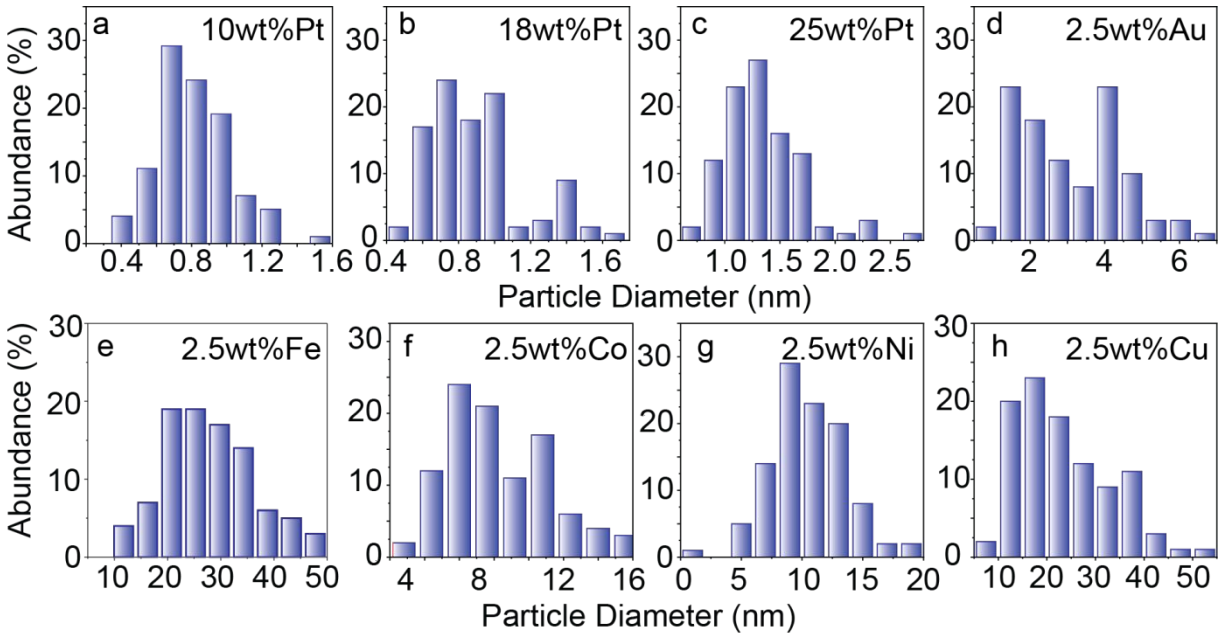

Figure S7. Particle size histogram for (a) 10wt% Pt/PPhen, (b) 18wt% Pt/PPhen, (c) 25%wt% Pt/PPhen, (d) 2.5wt% Au/PPhen, (e) 2.5wt% Fe/PPhen, (f) 2.5wt% Co/PPhen, (g) 2.5wt% Ni/PPhen and (h) 2.5wt% Cu/PPhen.

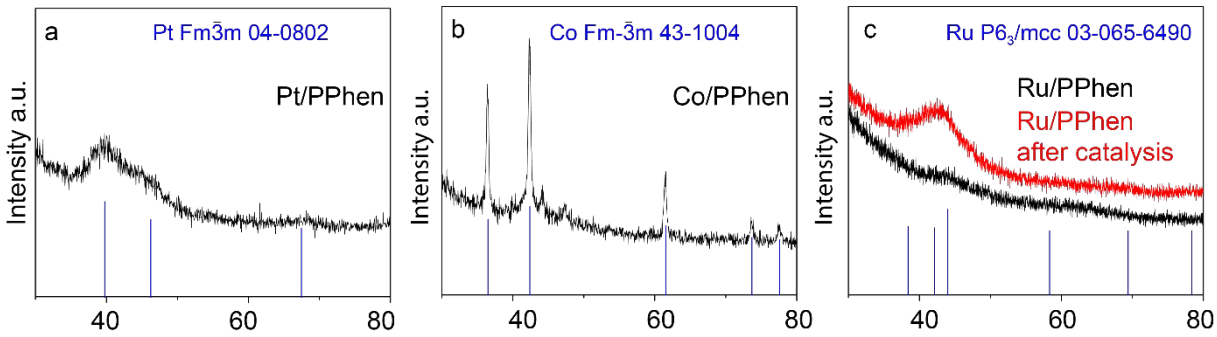

Figure S8. XRD patterns for (a) Pt/PPhen, (b) Co/PPhen and (c) Ru/PPhen.

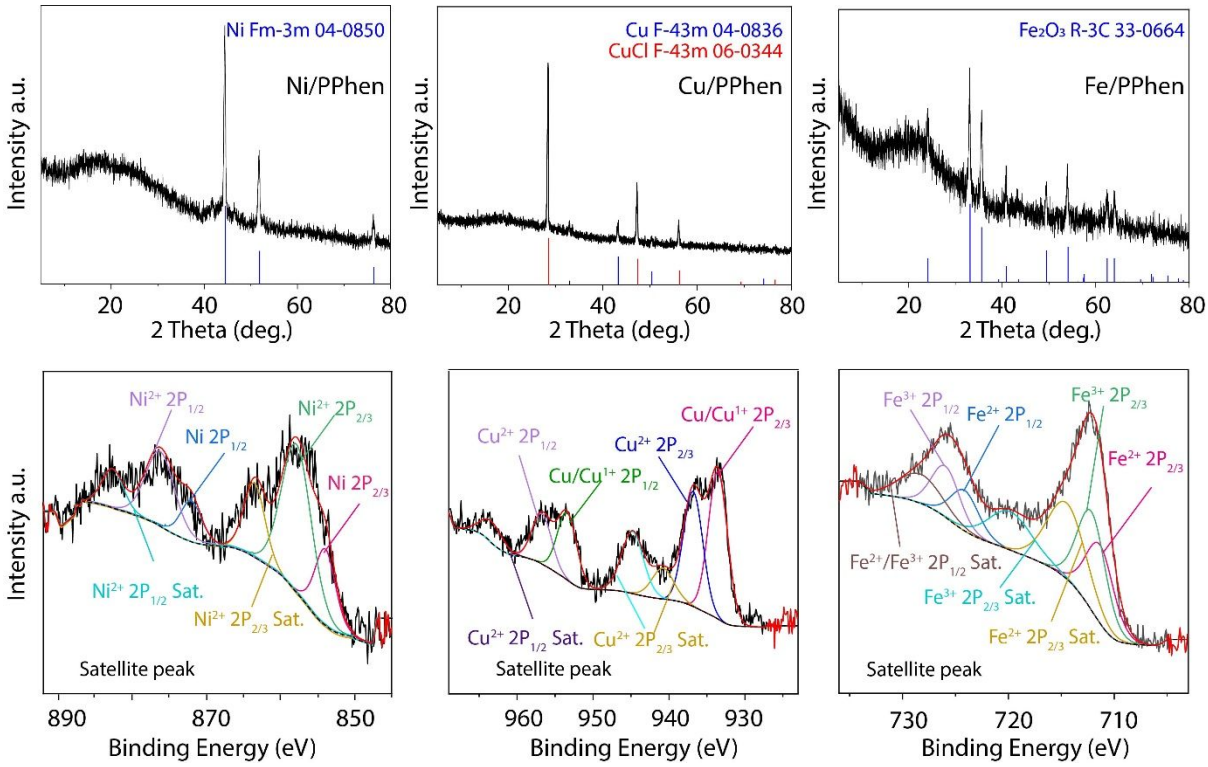

Figure S9 XRD pattern and XPS spectrum of sample Ni/PPhen (left), Cu/PPhen (middle) and Fe/PPhen (right).

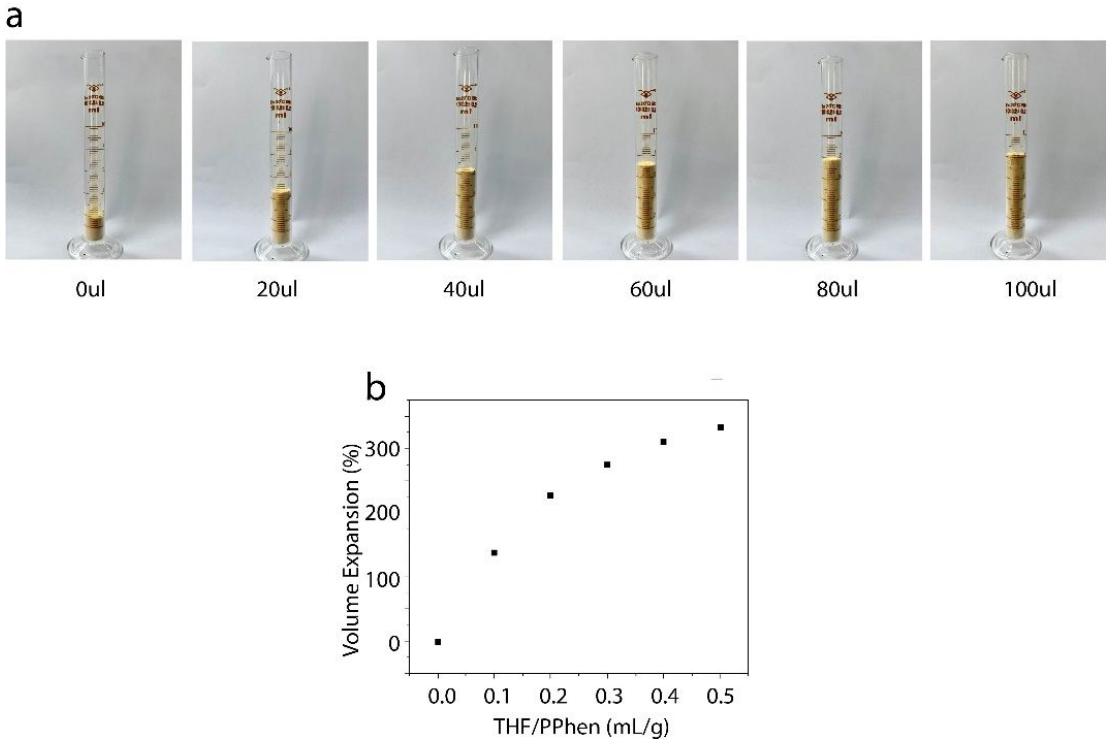

Figure S10 a. swelling test of PPhen with THF. **b.** PPhen volume expansion as a function of ethanol/PPhen ratio.

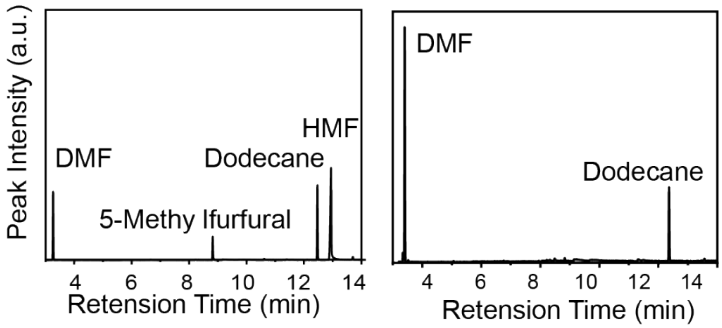

Figure S11. GC-MS chromatograms at Ru/HMF molar ratio of (a) 0.5%, (b) 2.8%.

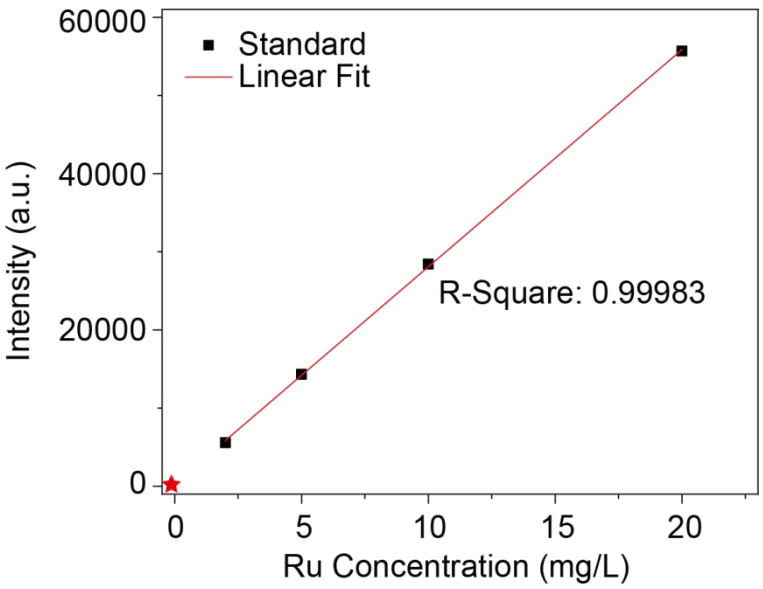

Figure S12. MP-AES measurement of the Ru content in the filtrated solution (marked with red star).

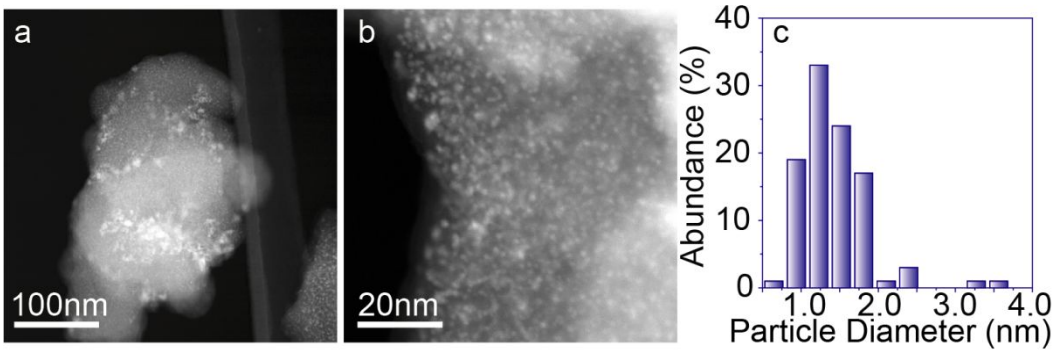

Figure S13 (a,b) HAADF-STEM images of Ru/PPhen after reactvation under H_2.(c) Corresponded size distribution histogram.

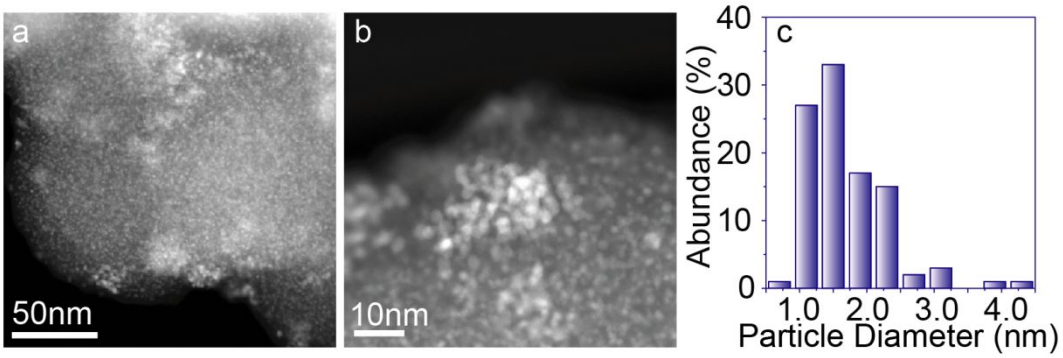

Figure S14 (a) HAADF-STEM images of Ru/PPhen after reactvation under H_2 and O_2 atmospheres. (c) Corresponded size distribution histogram.

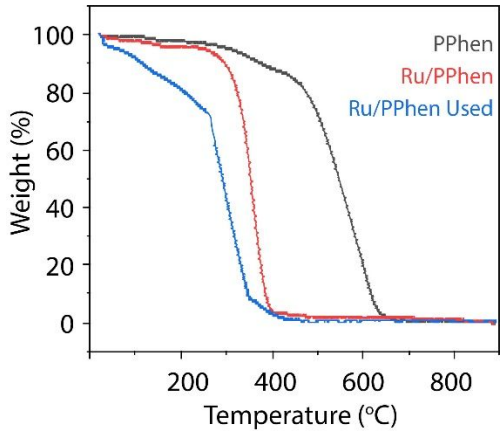

Figure S15. TGA analysis of fresh PPhen (black), Ru/PPhen (red) and Ru/PPhen (blue) after reaction in air.

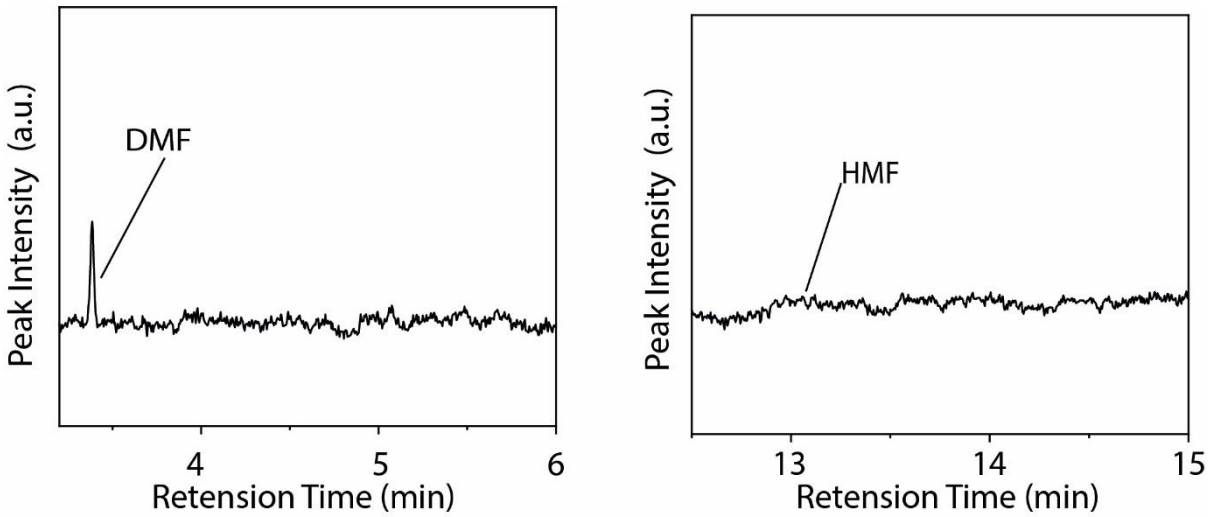

Figure S16. GC-MS chromatograms of the reaction without the presence of THF.

2. Supporting tables

Table S1. Changes of 5-HMF conversion and 2,5-DMF yield at various conditions.

Ru/HMF molar ratio (%)	Temperature (°C)	5-HMF conversion (%)	2,5 DMF yield (%)	Selectivity (%)
0.5	160	38	11.8	31
1.5	160	93	65	70
2.8	160	93	92	99
3.7	160	95	49	52
2.8	100	61	30	49
2.8	120	72	42	58
2.8	140	91	64	70
2.8	180	95	62	65

Table S2. The Performance comparison of the catalyic result of Ru/PPhen with those in the literatures.

Catalyst	Reaction Condition					DMF yields (%)
	HMF (mmol)	*T* (°C)	*p* (Bar)	*t* (h)	Metal Loading (mg)	
Ru/PPhen	**0.22**	**160**	**10**	**2 h**	**0.6**	**92**
Cu/ZnO[1]	65.7%	220	15	1 h	1 h	41
Ru/C[2]	3.6	180	8	2	18.2	95
Ru/Co_3O_4[3]	2	130	7	24	40	93.4
Ru/NaY[4]	1	220	15	1	0.5	78
Ru-MoO_x/C[5]	3.96	180	15	1	15	79.5
Ru/HCS[6]	0.16	140	10	2	0.6	90
Ru/SBA-15[6]	0.16	140	10	2	0.6	61
Raney Co[7]	9.42	180	15	15	500	78.5
Co_3O_4[8]	1.4	130	24	10	100	70
Co@C[9]	1.84	180	8	50	20	91.9
CoCu@C[9]	1.99	180	8	50	20	99.4
CoNi@C[9]	1.96	180	8	50	20	97.8
CoZn@C[9]	1.83	180	8	50	20	91.5
CoNi@C[9]	1.96	180	8	50	20	97.8
CoZn@C[9]	1.83	180	8	50	20	91.5
CoAg@C[9]	1.92	180	8	50	20	96.2
CoNi/C[10]	1.8	210	15	24	4.4	61
CuRu/C[11]	24.74	220	68	10	187.5	71
Cu/ZnO[1]	11.9	220	5	15	500	91.8
CuNi/TiO_2[12]	4	200	8	25	30	84.3
Raney Ni[7]	12	180	15	15	500	88.5
Ni-W_2C/AC[13]	12	180	40	3	120	96
Ni_2-Fe_1/CNT[14]	4	200	30	2	5.85	91.3

NiAl-850[15]	12	180	12	4	100	91.5
Fe-N/C[16]	0.5	240	40	5	20	86

Table S3. Fitting results of Ru K-edge EXAFS spectra of Ru/PPhen before and after catalysis[a].

	Scattering	**C.N.**[b]	**R [Å]**[c]	**σ^2**	**ΔE_0 [eV]**
Ru/PPhen before catalysis	Ru-O(1)	1.7 ± 0.2	1.91 ± 0.02	0.003 ± 0.002	-0.45±1.45
	Ru-O(2)	3.4 ± 0.5	2.05 ± 0.01	0.003 ± 0.002	
	Ru-Ru	2.0 ± 0.6	2.73 ± 0.02	0.007 ± 0.002	
Ru/PPhen after catalysis	Ru-O(1)	1.6 ± 0.2	1.91 ± 0.02	0.003 ± 0.003	-1.73±1.16
	Ru-O(2)	3.1 ± 0.5	2.05 ± 0.01	0.003 ± 0.003	
	Ru-Ru	4.1 ± 0.8	2.68 ± 0.01	0.007 ± 0.003	
RuO_2	Ru-O(1)	2.0	1.94		
	Ru-O(2)	4.0	1.99		
	Ru-Ru	2.0	3.10		
Ru foil	Ru-Ru	12.0	2.70		

[a] Fitting

range is 3.4 $Å^{-1} < k < 11.5$ $Å^{-1}$, 1 Å < R < 3 Å.[17-31]

[b] C.N. is the coordination number.

[c] R is the interatomic distance.

Table S4. Reactivation of the Ru/PPhen catalysts.

Cycles	**5-HMF conversion (%)**	**2,5 DMF yield (%)**	**Selectivity (%)**
First run	40	11	28
Recycle	11	4	36
H_2 activation	13	6	46
H_2/O_2 activation	13	7	54

*Reaction condition: 20 mg catalyst, 1 mmol phenylacetylene, 0.176 mmol dodecane, 1 mL water and reacted under 100 ^oC for 24 hours.

Table S5. XPS binding energy of Ru/PPhen before, after catalysis, and reactivation under H_2 and O_2.

		Ru-PPhen Before Catalysis	**Ru-PPhen After Catalysis**	**Ru-PPhen Reactivation under H_2**	**Ru-PPhen Reactivation under H_2 and O_2**
	Name	**Binding Energy (eV)**	**Binding Energy (eV)**	**Binding Energy (eV)**	**Binding Energy (eV)**
C 1s	C-C	284.7	284.7	284.7	284.7
	C-O	286.3	286.4	286.5	286.3
	C=O	288.9	288.3	288.8	289.0
RuO_x	Ru $3d_{5/2}$	281.4	281.3	281.1	281.2
	Ru $3d_{3/2}$	285.6	285.4	285.2	285.4
	Ru $3d_{5/2}$ sat.	282.9	282.9	282.6	282.8
	Ru $3d_{3/2}$ sat.	287.1	287.0	286.8	287.0

3. Reference

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