

Electronic Supplemental Information

Full Quantitative Data for Hydrogenation Procedures

Table 1 Product distribution for HMF hydrogenation at full conversion for 50 mg of Ru-black and 200 mg of 1wt% with and without feed pretreatment with Amberlite IRA-400(OH). All reactions were run for 2 hours in 2:1 bi-phasic 1-butanol:water batch reactor at 403 K and 400 psi H₂.(Figure 4)

		Selectivity (%)					
		DHMF	DHMTHF	1,2,6-HT	1,2,5-HT	1,2,5,6-HT	Total
Ru-Black	-	0	46	13	13	11	84
	Pretreated	0	76	6	0	6	87
1 wt% Ru/Vulcan	-	0	50	2	9	28	89
	Pretreated	0	75	1	2	10	89

Table 2 Product distribution for HMF hydrogenation at full conversion for 50 mg of Ru-black and Ru-black with physical mixtures of γ -alumina and magnesium oxide. All reactions were run for 2 hours in 2:1 bi-phasic 1-butanol:water batch reactor at 403 K and 400 psi H₂.(Figure 5)

		Selectivity (%)				
Solid Modifier		DHMTHF	1,2,6-HT	1,2,5-HT	1,2,5,6-HT	Total
-		46	13	13	11	84
Al ₂ O ₃		85	5	3	6	99
MgO		89	3	0	0	91

Table 3 Product distribution for HMF hydrogenation at full conversion for 50 mg of Ru-black and Ru-black with added acids and silica after feed pretreatment with Amberlite IRA-400(OH). All reactions were run for 2 hours in 2:1 bi-phasic 1-butanol:water batch reactor at 403 K and 400 psi H₂. (Figure 6)

		Selectivity (%)				
Modifier		DHMTHF	1,2,6-HT	1,2,5-HT	1,2,5,6-HT	Total
-		76	6	0	6	87
H ₂ SO ₄		9	9	24	11	53
Levulinic Acid		59	10	6	12	87
SiO ₂		64	4	3	18	90

Table 4 Product distribution for HMF hydrogenation at full conversion of HMF for 50 mg of Ru-black in various solvents. All reactions were run for 2 hours at 403 K and 400 psi H₂. (Figure 7)

		Selectivity (%)				
Solvent		DHMTHF	1,2,6-HT	1,2,5-HT	1,2,5,6-HT	Total
Water/1-Butanol		46	13	13	11	84
Water		22	5	32	13	72
THF/Water		50	0	13	15	78
THF-Alcohol		67	5	0	0	72

Table 5 Product distribution for HMF hydrogenation at full conversion of HMF for 200 mg of various loadings of Ru, Pt, and Pd on Vulcan-carbon support. All reactions were run in 2:1 bi-phasic 1-butanol:water batch reactor at 403 K and 400 psi H₂. (Figure 8)

Catalyst	Reaction Time (hr)	HMF Conversion (%)	Selectivity (%)					Total
			DHMF	DHMTFH	1,2,5-HT	1,2,5,6-HT	1,2,6-HT	
1 wt% Ru	2	100	0	75	2	10	1	89
1 wt% Pd	2	100	4	21	6	0	0	32
	12	100	0	25	7	0	0	32
1 wt% Pt	2	64	11	6	3	0	0	21
	12	83	0	11	2	0	0	14
10 wt% Pd	4	100	0	60	4	2	0	66
10 wt% Pt	4	100	0	8	0	4	5	17

Table 6 Chemisorption and reaction information for individual metals for comparison.

Metal Catalyst on Vulcan	Irreversible CO uptake (μmol/g) ^a	Conversion of HMF / Selectivity to DHMF (%/%)	Specific Rate ^b (μmol g ⁻¹ min ⁻¹)	TOF ^c (min ⁻¹)	FAL Conversion ^d (%)
1 wt% Ru	71.4	29/>99	265	3.7	100
1 wt% Pt	42.2	16/>99	141	3.3	67
1 wt% Pd	7.9	98/96	844	107	-

a. Data from Micromeritics ASAP 2020C

b. Specific rate defined as moles of HMF converted per gram of catalyst per minute

c. TOF defined as the specific rate divided by the irreversible CO uptake

d. Furfuryl alcohol was hydrogenated to tetrahydrofuran alcohol using the same conditions in a biphasic reaction for 1 hour at 403 K and 400 psi H₂. This reaction was studied to model DHMF hydrogenation.