Supplementary Material

Stabilization of Fast Pyrolysis Liquids from Biomass by Mild Catalytic Hydrotreatment: Model Compound Study

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Table S1. Recently researches on PL model compounds hydrotreatment

Model compound	Catalyst	Reaction conditions	Conversion	Product selectivity	Reference
Hydroxyacetone	Ni/HZSM-5-γ-Al2O3	300 ˚C, 1.6MPa H2	100%	78.09% long chain alkanes 2.21% aromatic hydrocarbon	[1]
Hydroxyacetone	Ru/TiO2	70 ˚C 6.21 MPa H2, WHSV 20 h-1	93.6%	99.9%, 1,2-Propanediol 0.1% methane	[2]
Furfural	Ni/MMO-NO3	110 ˚C, 3MPa H2	100%	97% furfural alcohol 3% tetrahydrofurfuryl alcohol	[3]
	Ni/MMO-CO3		100%	1% furfural alcohol 99% tetrahydrofurfuryl alcohol	
Furfural	PhP-Hf (1:1.5)	120 ˚C, 2-propanol as hydrogen donor, 2h	99.2%	98.4% furfural alcohol	[4]
Furfural	Pt–Fe/MWNT	100 ˚C, 30 bar H2	95.2%	91.8% furfural alcohol 2.0% tetrahydrofurfuryl alcohol 5.2% 2-furaldehyde diethyl acetal 1.0% others	[5]
	Pd–Ni/MWNT		92.7%	2.1% furfural alcohol 78.2% tetrahydrofurfuryl alcohol 8.9% 2-furaldehyde diethyl acetal 10.8% others	
Furfural	α-MoC	150 ˚C, 2MPa H2, 6h	96.5%	81.8% 2-methyl furan 5.9% furfuryl alcohol 12.3% others	[6]
	β-Mo2C		66.9%	48.9% 2-methyl furan 38.9% furfuryl alcohol 12.2% others	
	γ-Mo2N		21.0%	5.6% 2-methyl furan 61.8% furfuryl alcohol 1.0% tetrahydrofurfuryl alcohol 31.6% others	
Phenol	Ru/Nb2O5- MC	250 ˚C, 2 bar H2	100%	~80% benzene	[7]

Phenol	Thiol-5wt%Rh/SiO2	Room temperature, 1 atm H2	100%	93% cyclohexanone	[8]
Phenol	20Ni3Fe1/ MCSs	250 °C, 5MPa, 10h	100%	93.8% cyclohexane	[9]
Phenol	Pd/ZrO2	300 °C, atmospheric pressure H2	9.09%	41.29% benzene 1.58% cyclohexanol 50.34% cyclohexanone 6.78% C12 hydrocarbon	[10]
	PdAg/ZrO2		12.99%	4.79% benzene 6.32% cyclohexanol 80.70% cyclohexanone 2.68% C12 oxigenated 5.34% C12 hydrocarbon	
	PdCu/ZrO2		13.54%	11.79% benzene 7.15% cyclohexanol 74.91% cyclohexanone 1.68% C12 oxigenated 4.46% C12 hydrocarbon	
	PdSn/ZrO2		8.91%	29.29% benzene 1.28% cyclohexanol 58.96% cyclohexanone 4.03% C12 oxigenated 6.43% C12 hydrocarbon	
	PdZn/ZrO2		7.74%	7.51% benzene 9.57% cyclohexanol 80.36% cyclohexanone 1.24% C12 oxigenated 1.32% C12 hydrocarbon	
Phenol	Ni/SiO2	300 °C, 5MPa H2, 16h	~98%	~2.3% benzene ~89% cyclohexane ~1% cyclohexene ~6% cyclohexanol	[11]
	Ni/γ-Al2O3		~99%	~3.6% methylpentane ~4.5% benzene	

				~86% cyclohexane ~2.3% cyclohexene ~2.5% others	
Phenol	Pt/ZrO2	300 ˚C, atmospheric pressure H2, W/F 0.01h	9.3%	27.4% benzene 12.8% cyclohexanol 56.6% cyclohexanone 1.8% C5-C6 1.4% C12	[12]
	Pd/ZrO2	300 ˚C, atmospheric pressure H2, W/F 0.02h	8.2%	43.2% benzene 1.7% cyclohexanol 52.6% cyclohexanone 0.1% C5-C6 2.4% C12	
	Rh/ZrO2	300 ˚C, atmospheric pressure H2, W/F 0.01h	8.8%	63.4% benzene 22% cyclohexanone 9.1% C5-C6 0.3% C12 5.2% CH4	
	Ru/ZrO2	300 ˚C, atmospheric pressure H2, W/F 0.07h (0.15h)	8.3% (12.7%)	49.7(74.2)% benzene 0.8(1.7)% cyclohexanol 5.6(6.9)% cyclohexanone 1.1(-)% o-cresol 14.9(8.8)% C5-C6 0.6(-)% C12 27.3(8.4)% CH4	
	Ni/ZrO2	300 ˚C, atmospheric pressure H2, W/F 0.02h	11.4%	26.7% benzene 10.9% cyclohexanol 37.7% cyclohexanone 10.9% o-cresol 0.8% C5-C6 2.8% C12 15.4% CH4	

	Co/ZrO2	300 ˚C, atmospheric pressure H2, W/F 0.08h	10%	16.5% benzene 5.7% cyclohexanol 16% cyclohexanone 38% o-cresol 3.1% C5-C6 5.4% C12 15.4% CH4	
Phenol	15MoO3/ZrO2	350 ˚C, 6MPa H2	48%	97% benzene 2.5% cyclohexene 0.5% cyclohexane	[13]
Phenol	Pd/SiO2	300 ˚C, 1 atm H2, W/F 0.053h	21.3%	13.6% benzene 78.9% cyclohexanone 7.5% cyclohexanol	[14]
	Pd/Al2O3	300 ˚C, 1 atm H2, W/F 0.16h	28.2%	0.3% cyclohexane + cyclohexene 23.4% benzene 62.1% cyclohexanone 14.2% C12	
	Pd/TiO2	300 ˚C, 1 atm H2, W/F 0.053h	22.7%	0.4% cyclohexane + cyclohexene 58.6% benzene 23.4% cyclohexanone 17.6% C12	
	Pd/ZrO2	300 ˚C, 1 atm H2, W/F 0.026h	19.6%	44.5% benzene 51.5% cyclohexanone 2.0% cyclohexanol 2.4% C12	
	Pd/CeO2	300 ˚C, 1 atm H2, W/F 0.026h	21.2%	4.7% benzene 80.7% cyclohexanone 14.6% cyclohexanol	
	Pd/CeZrO2	300 ˚C, 1 atm H2, W/F 0.053h	28.9%	5.9% benzene 73.2% cyclohexanone 20.9% cyclohexanol	

Table S2. The effect of temperature on the hydrotreatment of hydroxyacetone

	Temperature, °C						
	100	120	140	160	180	200	220
Conversion, %	11.9	45.1	74.2	85.1	96.7	101.4	101.3
Selectivity, %							
1,2-propanediol selectivity	99.5	99.6	99.4	100.5	101.5	100.5	101.4
Yield of alcohols, %	11.8	44.9	73.8	85.5	98.2	101.9	102.7

Table S3. The effect of temperature on the hydrotreatment of furfural

	Temperature, °C							
	100	120	140	160	180	200	220	240
Conversion, %	6.5	14.5	29.8	49.3	73.4	94.6	100.5	101.4
Selectivity, %								
Furfuryl alcohol	76.9	64.9	65.2	66.9	58.5	32.9	3.9	0.1
Tetrahydrofurfuryl alcohol	6.2	15.1	17.9	14.9	15.5	17.4	18.1	9.6
Tetrahydrofuran	-	-	-	-	8.0	7.8	6.2	6.9
Methyl furan	-	-	-	-	7.4	23.2	34.9	21.9
Methyltetrahydrofuran	-	-	-	-	2.0	2.4	4.6	7.0
Other	17.0	20.1	16.8	18.1	8.6	16.3	32.3	54.4
Yield of alcohols, %	5.4	11.6	24.8	40.3	54.3	47.6	22.1	9.8

Table S4. The effect of temperature on the hydrotreatment of phenol

	Temperature, °C								
	100	120	140	160	180	200	220	240	250
Conversion, %	0.5	24.1	55.1	65.7	68.6	70.4	72.2	74.6	76.0
Selectivity, %									
Cyclohexanone	53.8	4.3	3.4	2.4	3.1	2.6	3.4	5.1	4.3
Cyclohexanol	46.1	95.5	96.4	97.3	96.5	96.8	92.9	88.6	82.3
Cyclohexane	0.1	0.2	0.2	0.3	0.4	0.6	3.6	6.3	13.4
Yield of alcohols, %	0.2	23.0	53.1	63.9	66.2	68.1	67.1	66.1	62.5

Table S5. The effect of initial H2 pressure on the hydrotreatment of hydroxyacetone

	Pressure, MPa					
	1.51	2.51	3.49	4.50	5.52	6.48
Conversion, %	40.4	56.9	76.5	87.5	100.6	101.5
Selectivity, %						

1,2-propanediol selectivity	99.4	99.6	99.4	101.1	100.9	102.0
Yield of alcohols, %	40.1	56.7	76.0	88.5	101.5	103.6

Table S6. The effect of initial H2 pressure on the hydrotreatment of furfural

	Pressure, MPa					
	1.58	2.53	3.43	4.50	5.40	6.50
Conversion, %	23.1	24.9	29.4	35.5	37.0	43.0
Selectivity, %						
Furfuryl alcohol	60.8	61.8	67.4	61.7	65.9	61.8
Tetrahydrofurfuryl alcohol	8.7	14.6	16.8	17.6	20.6	21.3
Other	30.4	23.6	15.7	15.6	13.5	12.9
Yield of alcohols, %	16.1	19.0	24.8	28.2	32.0	35.7

Table S7. The effect of initial H2 pressure on the hydrotreatment of phenol

	Pressure, MPa					
	1.47	2.52	3.49	4.55	5.51	6.49
Conversion, %	34.8	49.8	56.7	70.7	72.8	74.0
Selectivity, %						
Cyclohexanone selectivity	6.2	3.8	2.7	1.5	0.9	0.5
Cyclohexanol selectivity	93.3	95.9	97.3	98.0	99.0	99.4
Cyclohexane selectivity	0.1	0.2	0.1	0.1	0.1	0.2
Yield of alcohols, %	32.5	47.8	55.2	69.3	72.1	73.6

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