

## Electronic Supporting Information (ESI)

### Hydrodeoxygenation of lignin derived phenolics over hydrous ruthenium oxide based catalyst: Role of surface water molecules and acidity of support

Adarsh Kumar <sup>a,b</sup>, and Bhaskar Thallada <sup>a,b\*</sup>

<sup>a</sup> Thermo-catalytic Process Area (TPA), Material Resource Efficiency Division (MRED), CSIR-Indian Institute of Petroleum (IIP), Dehradun-248005, Uttarakhand, India.

<sup>b</sup> Academy of Scientific and Innovation Research (AcSIR), Kamla Nehru Nagar Ghaziabad, Uttar Pradesh, India.

\* Corresponding author

Bhaskar Thallada, Email: tbhaskar@iip.res.in, thalladab@yahoo.com

Ph:+911352525820

**Table S1:** Effect of reaction time on guaiacol conversion and product selectivity.

Time, h	Conversion, %	Selectivity, %			
		Cyclohexanol	2-methoxy cyclohexanol	Phenol	Cyclohexane
0.08	2.5	50	20	30	0
0.25	11	49	18	32	0
0.5	73	71	24	5	0
0.75	100	79	21	0	0
1.0	100	89	11	0	0
1.25	100	88	6	0	6



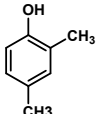
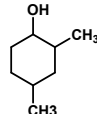
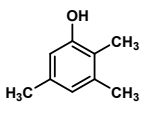
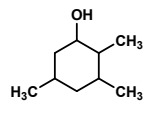


**Experimental conditions:** Guaiacol - 0.5 mmol, Catalyst - HRO@Y (50 mg), Water - 12.5 ml, P - 2.0 M Pa, T - 160 °C



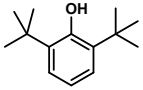
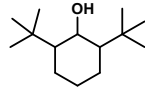
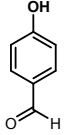
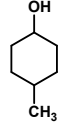
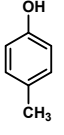
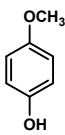

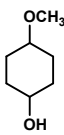
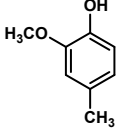
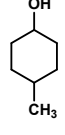
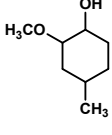
**Table S2:** Effect of catalyst amount on guaiacol conversion and product selectivity.

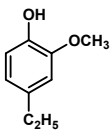
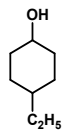
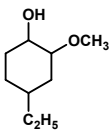
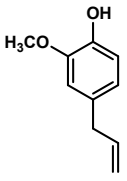
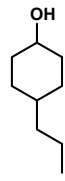
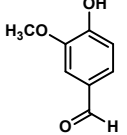

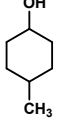
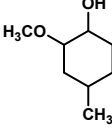
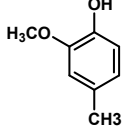
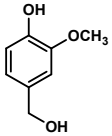
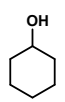
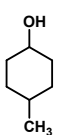
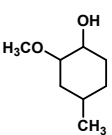
Catalyst amount, mg	Conversion, %	Selectivity, %		
		Cyclohexanol	2-methoxy cyclohexanol	Others
10	73	63	37	0
20	83	81	19	0
30	93	83	17	0
40	100	85	15	0
50	100	89	11	0
60	100	94	6	0
70	100	91	5	4

**Experimental conditions:** Guaiacol - 0.5 mmol, Catalyst - HRO@Y, Water - 12.5 ml, P - 2.0 M Pa, T - 160 °C, Time - 1 h

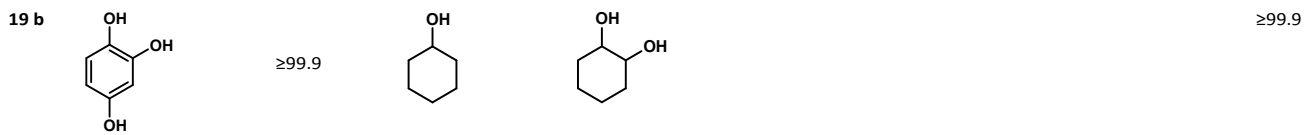
**Table S3:** Scope of HRO@Y for different lignin model compounds.

Entry	Reactant	Conversion, %	Selectivity,%	Total selectivity of cyclohexanol and alkylated cyclohexanol, %
1 a		≥99.9	 [≥99.9] <sup>c,d</sup>	≥99.9
2 a		≥99.9	 [≥99.9] <sup>d</sup>	≥99.9
3 a		≥99.9	 [≥99.9] <sup>d</sup>	≥99.9
4 a		≥99.9	 [≥99.9] <sup>d</sup>	≥99.9

5 a		≥99.9			≥99.9
			[≥99.9] <sup>d</sup>		
6 a		≥99.9			≥99.9
			[≥99.9] <sup>d</sup>		
7					
a		≥99.9	[67.3] <sup>c,d</sup>	[32.7] <sup>c,d</sup>	67.3
b		≥99.9	[≥99.9] <sup>c,d</sup>	[0] <sup>c,d</sup>	≥99.9
8 a		≥99.9			96
			[96] <sup>c,d</sup>	[4] <sup>d</sup>	
9 a		≥99.9			90.4
			[90.4] <sup>c,d</sup>	[9.6] <sup>d</sup>	

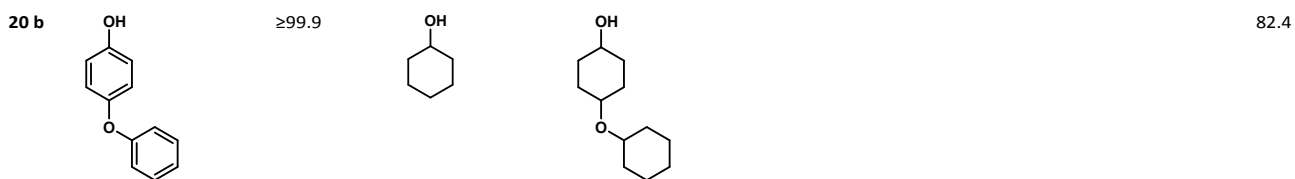
10 a		≥99.9			78.9		
			[78.9] <sup>d</sup>	[22.1] <sup>d</sup>			
11 a		≥99.9			≥99.9		
			[≥99.9] <sup>d</sup>				
12							
a		≥99.9	[6.9] <sup>c,d</sup>	[62.3] <sup>c,d</sup>	[1.5] <sup>d</sup>	[29.3] <sup>d</sup>	69.2
b		≥99.9	[7.6] <sup>c,d</sup>	[81.8] <sup>c,d</sup>	[10.6] <sup>d</sup>	[0] <sup>d</sup>	89.4
13 a		≥99.9					95.6
			[11.7] <sup>c,d</sup>	[83.9] <sup>c,d</sup>	[4.4] <sup>d</sup>		

14		≥99.9				97.7		
b			[97.7] <sup>d</sup>	[2.3] <sup>d</sup>				
15								
a		89	[4.9] <sup>c,d</sup>	[75.3] <sup>c,d</sup>	[12] <sup>d</sup>	[2.2] <sup>d</sup>	[5.6] <sup>d</sup>	80.2
b		≥99.9	[6.7] <sup>c,d</sup>	[83.2] <sup>c,d</sup>	[10.1] <sup>d</sup>	[0] <sup>d</sup>	[0] <sup>d</sup>	89.9
16								
a		59.9	[81] <sup>c,d</sup>	[19] <sup>d</sup>				81
b		≥99.9	[89.7] <sup>c,d</sup>	[10.3] <sup>d</sup>				89.7
17		≥99.9					≥99.9	
			[88] <sup>c,d</sup>	[12] <sup>d</sup>				
18		≥99.9					≥99.9	
b			[75.5] <sup>c,d</sup>	[24.5] <sup>d</sup>				



[94.5]<sup>c,d</sup>

[5.5]<sup>d</sup>



[82.4]<sup>c,d</sup>

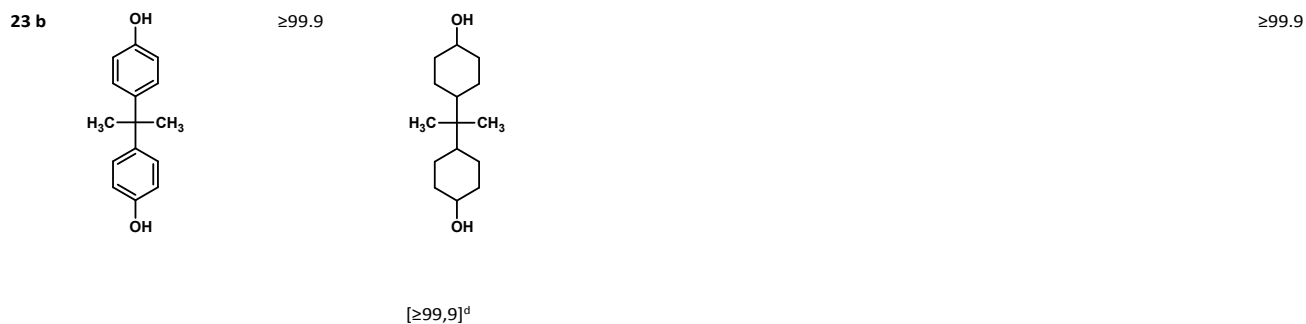
[17.6]<sup>d</sup>



[ $\geq 99.9$ ]<sup>c,d</sup>



[ $\geq 99.9$ ]<sup>d</sup>



Experimental conditions: Catalyst - 60 mg, Reactant - 0.5 mmol, P - 2.0 MPa, T - 160 °C, Water - 12.5 ml

a - 1 hr

b - 2 hr

c - GC yield

d - GC-MS yield

**Table S4:** Physical characteristics of HY zeolite and prepared materials.

S. No.	Catalyst	BET surface area, m <sup>2</sup> .g <sup>-1</sup>	Pore volume, cm <sup>3</sup> .g <sup>-1</sup>	Average pore size, A <sup>o</sup>	Metal, wt% (ICP-AES)	Metal dispersion, %	TOF, h <sup>-1</sup> *
a	HRO@Y	261	0.41	90	4.7	12.5	147.1
b	HRO@Z	201	0.04	49	4.7	18.6	97.1
c	HRO@γ-Al <sub>2</sub> O <sub>3</sub>	110	0.79	146	4.6	21.3	87.7
d	HRO@SiO <sub>2</sub>	379	0.85	68	4.8	17	101.6
e	Ru/Y	233	0.38	89	4.5	-	-
f	S-HRO@Y-5	193	0.37	89	4.6	-	-
g	RuO <sub>2</sub> -HRO@Y	258	0.48	89	-	-	-
h	HY-zeolite	290	0.52	91	-	-	-

\* TOF for guaiacol conversion

**Table S5:** Product distribution of hydrodeoxygenated lignin bio-oil.

Entry	Compound	Selectivity, %
1	Cyclohexanol	23.7
2	Methyl cyclohexanol	16.2
3	Methoxy cyclohexanol	17.8
4	Ethyl cyclohexanol	18.5
5	1-Methoxy-methyl cyclohexanol	5.6
6	Propyl cyclohexanol	11.7
7	1-Hydroxy-4-propyl cyclohexanol	6.5

**Table S6:** Product distribution of hydrodeoxygenated sugarcane bagasse bio-oil.

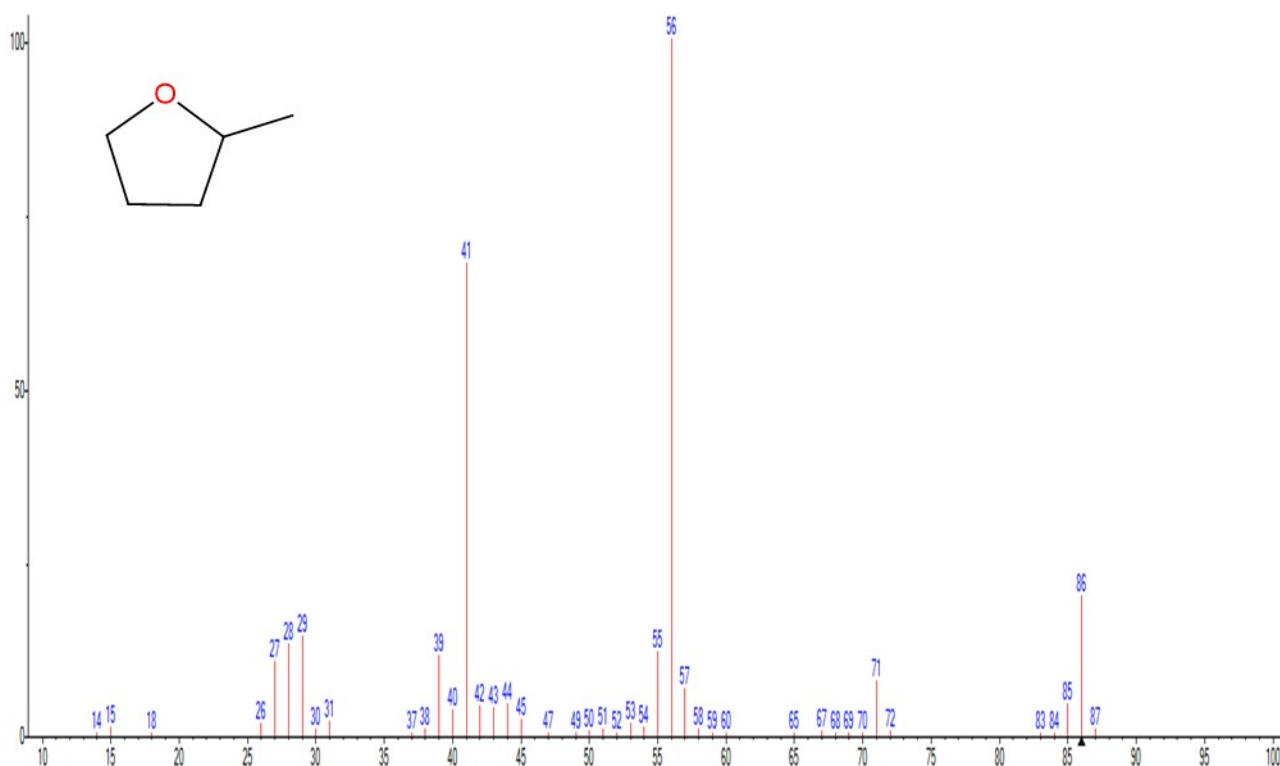
Entry	Compound	Selectivity, %
1	Methyl tetrahydrofuran	1.5
2	Methyl cyclopentanol	4.8
3	Cyclohexanol	21
4	Methyl cyclohexanol	22.3
5	Ethyl cyclohexanol	46.8
6	Propyl cyclohexanol	3.6

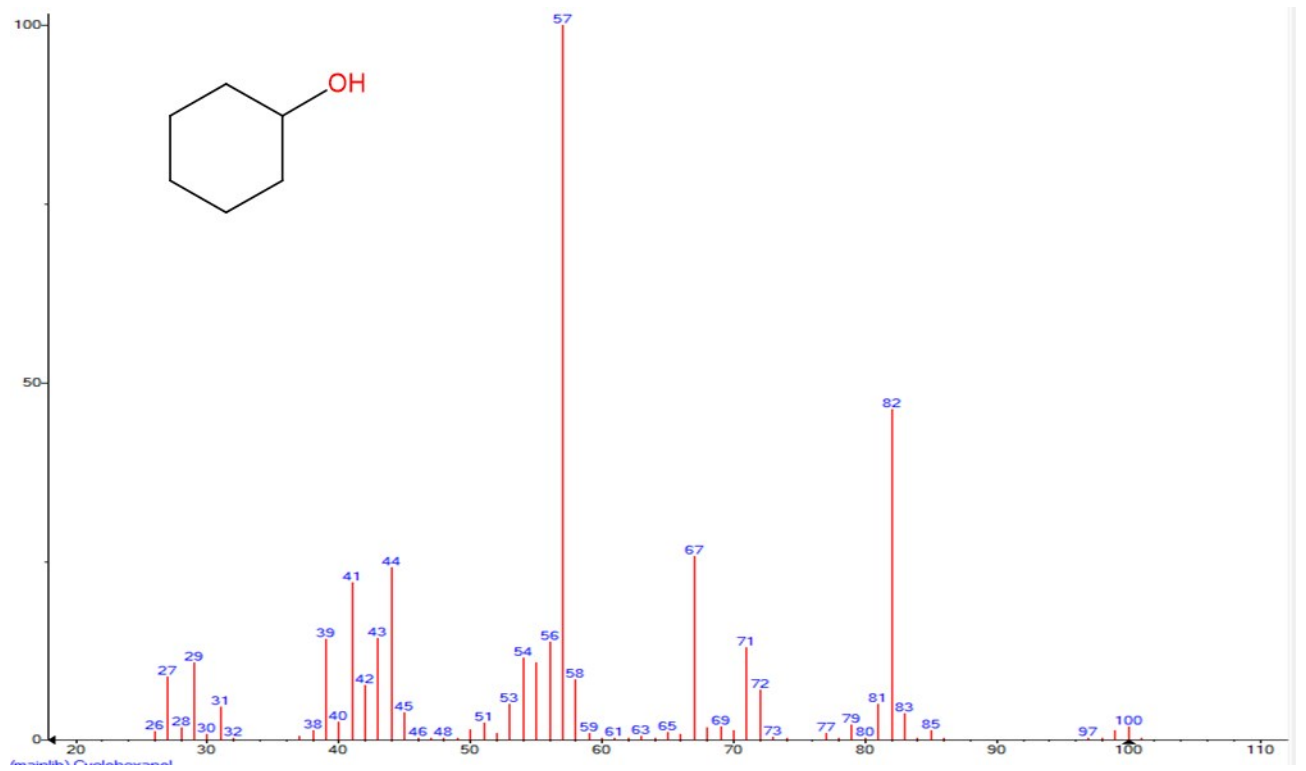
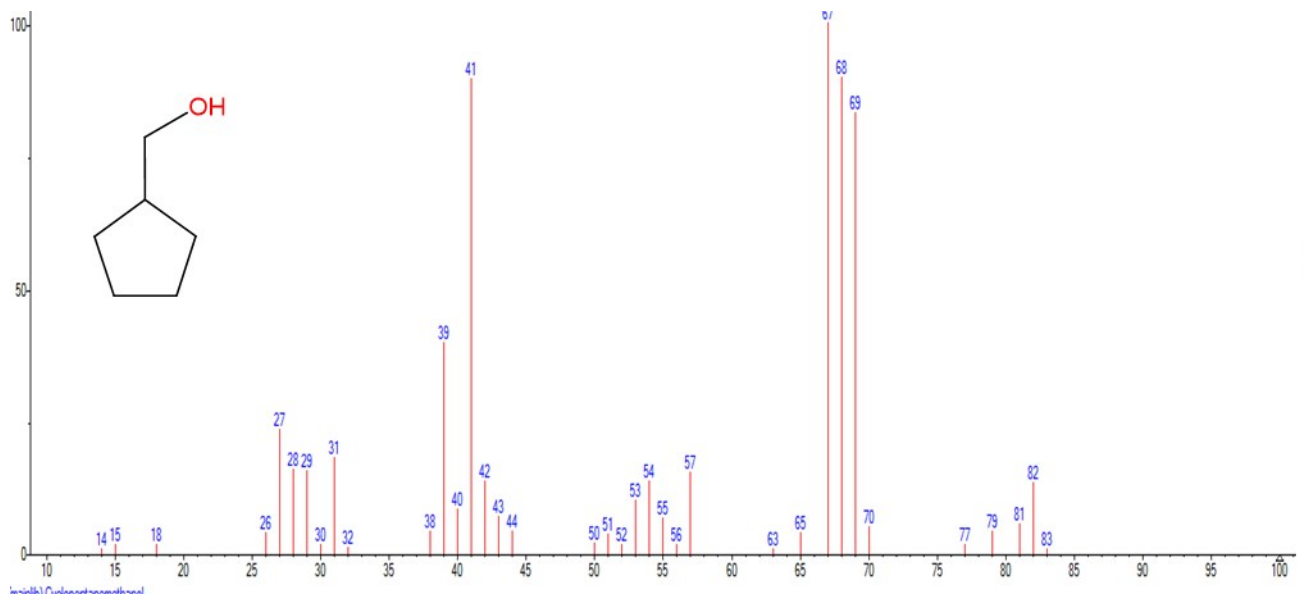


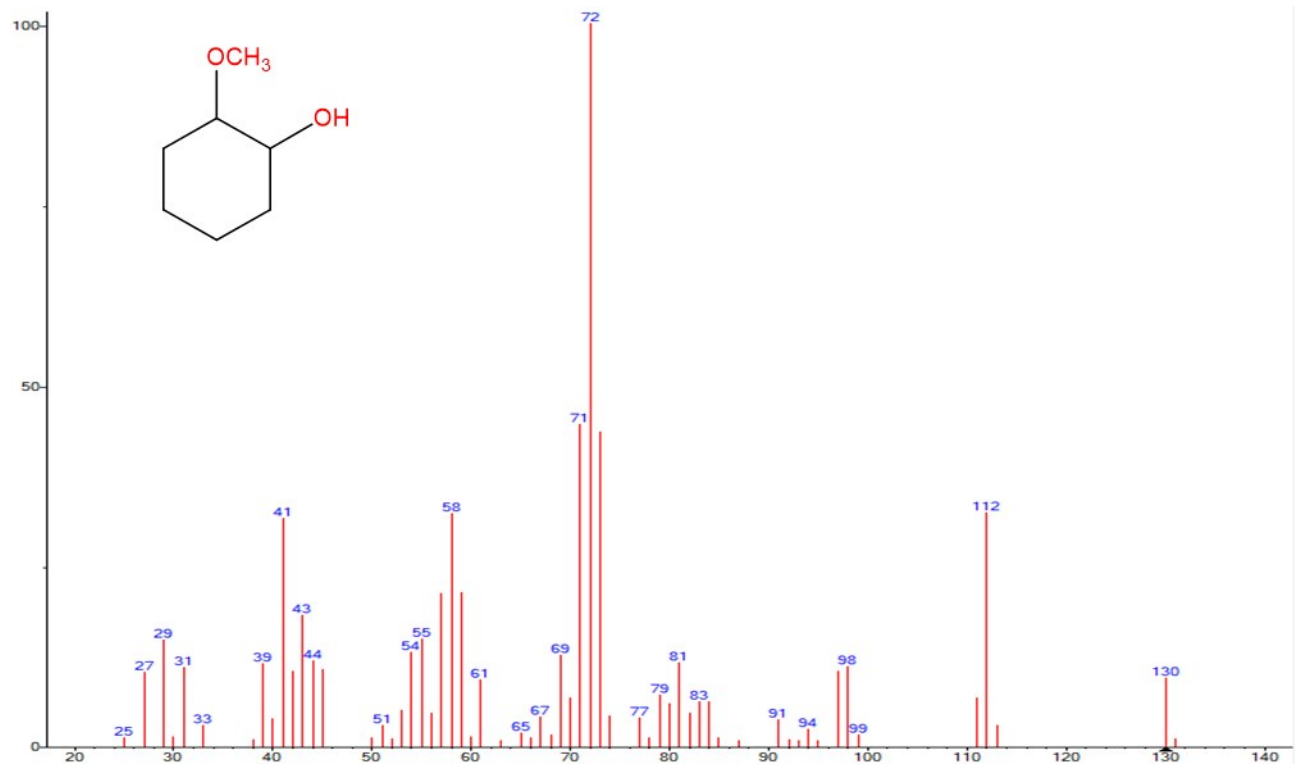
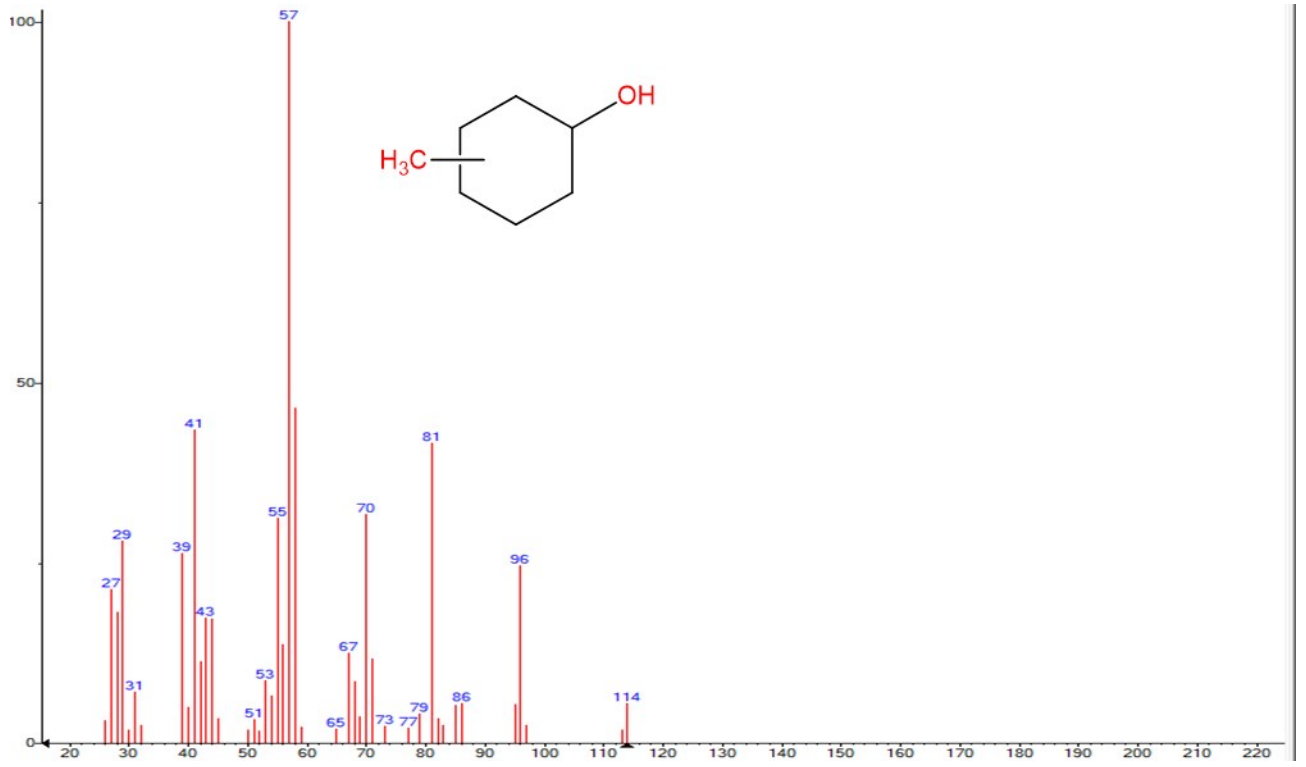
**Table S7:** Comparison of this work with literature reports in the best of our knowledge.

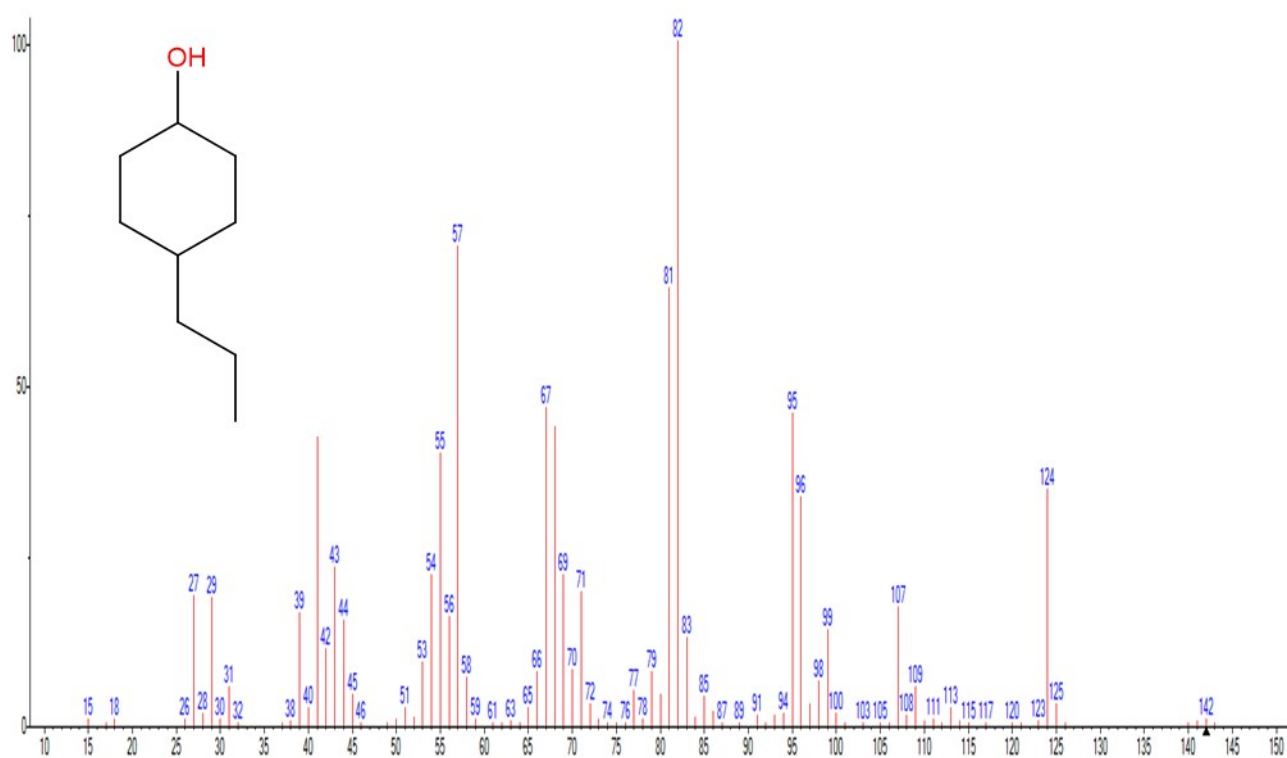
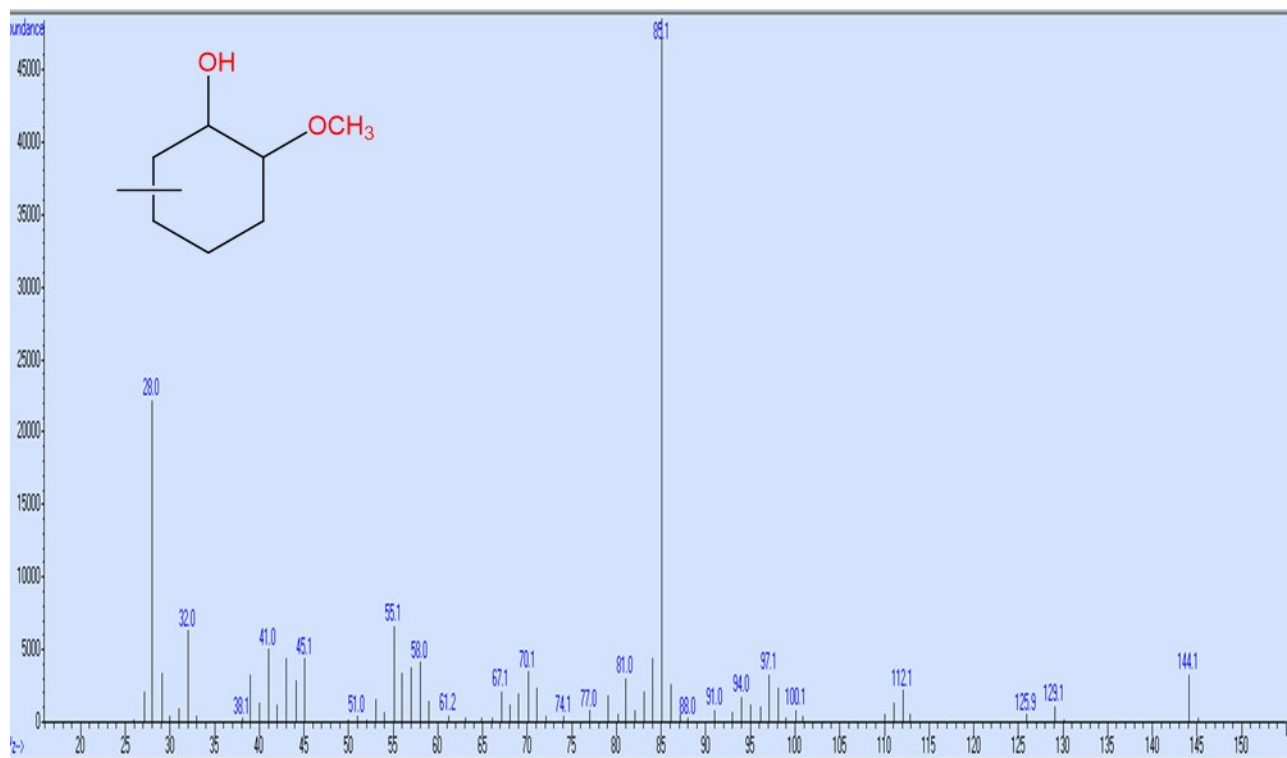
Catalyst	Reactants tested	Reaction conditions	Solvent	Conversion range,%	Alkyl cyclohexanol range, %	Description	Ref.
5 Ru/ZrO <sub>2</sub> – La(OH) <sub>3</sub>	Guaiacol and 5 model compounds	4 MPa, 4h, 200°C	Water	>99	86.9-91.4	Only for 5-6 model compounds	[1]
5 Ru/MgO + NaOH	Guaiacol and 5 model compounds	1.5 MPa, 2h, 150°C	Water	98-100	21-79	Only for 5-6 model compounds	[2]
5 Ru–MnO <sub>x</sub> /C	Guaiacol and three model compounds	1.5 MPa, 2-4 h, 150°C	Water	>99	56-81	Only for 4 model compounds	[3]
.5 Ru/Al <sub>2</sub> O <sub>3</sub>	Guaiacol	1 MPa, 4 h 225 °C	n-hexane	>99	82	Only for guaiacol	[4]
0.5 Ru- 35.5 Co/C	Guaiacol	1.0 MPa, 3 h, 200 °C,	n-dodecane	99.6	94.1	Only for guaiacol	[5]
20 Ni/Nb <sub>2</sub> O <sub>5</sub>	Guaiacol and bio-oil	2.5 MPa, 5 h, 200 °C	Water	93.6	77	Limited to guaiacol, Tested bio-oil but high catalyst loading (20 wt%), amount (500 mg) and time (10 h) was high	[6]
20 Ni/MgO	Guaiacol	3 MPa, 3 h, 160 °C,	Decahydro naphalene	97.74	100	Limited to guaiacol	[7]

10 Ni-10 Co/ $\gamma$ - $\text{Al}_2\text{O}_3$	Guaiacol	5 MPa, 10 h, 200°C	Water	93	85	Limited to guaiacol	[8]
5 HRO@Y	24 phenolic monomers and dimers.  2 real bio-oils	2 MPa, 1 h, 160°C	Water	>99.9	78.9-99.9	Catalyst was able to transform these compounds to cyclohexanol/alkyl cyclohexanols from good (78.9%) to excellent ( $\geq 99.9\%$ ) yield,  For bio-oil conversion was >99.9% and alkyl cyclohexanol(s) yields were >94%	This work









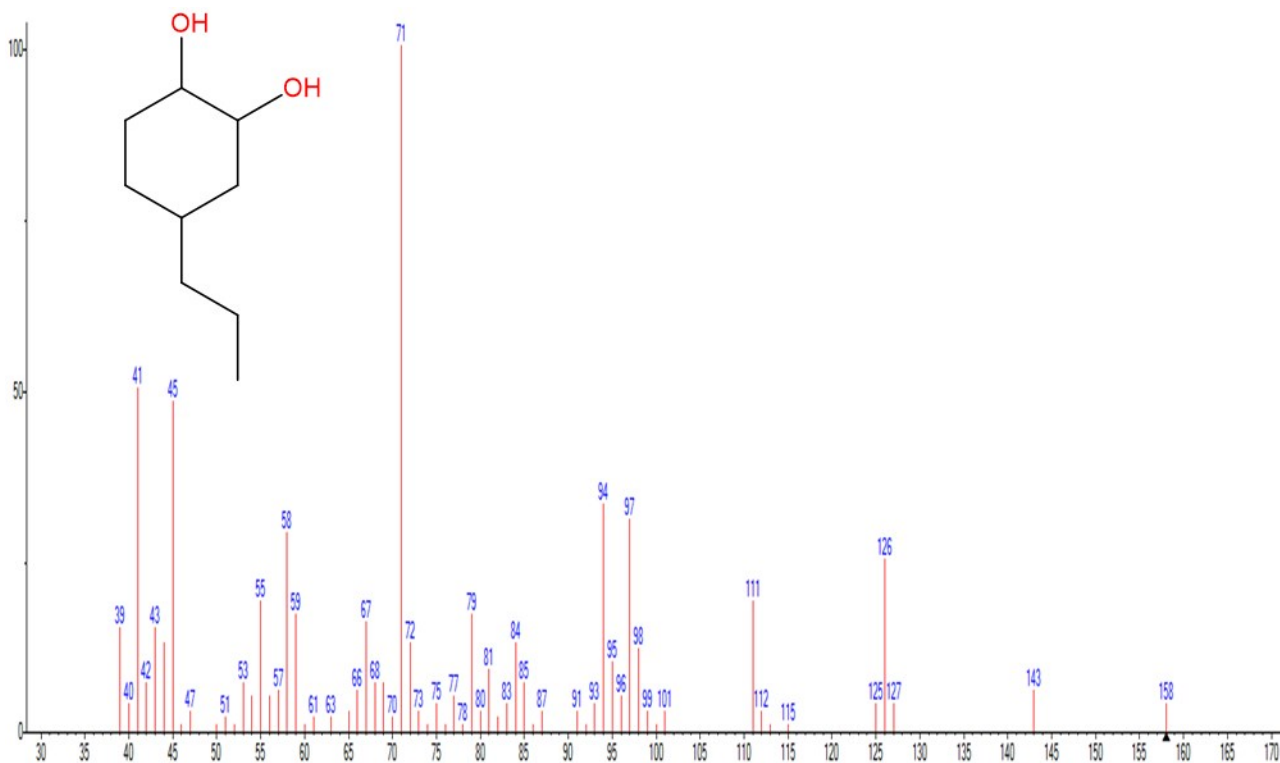
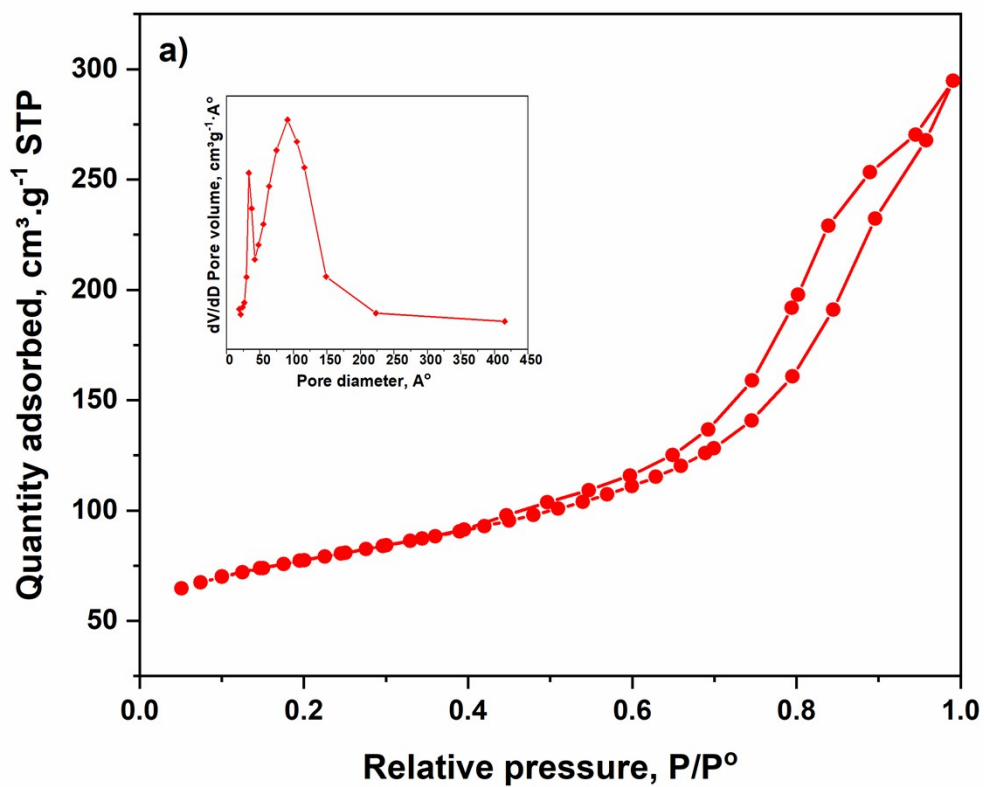
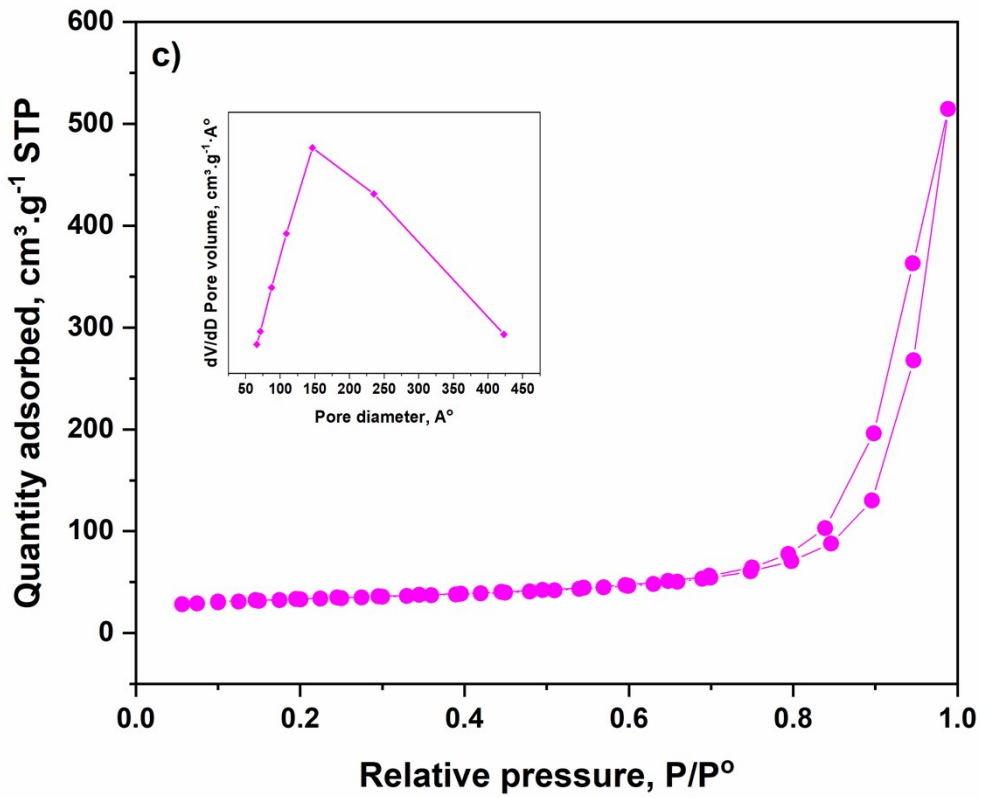
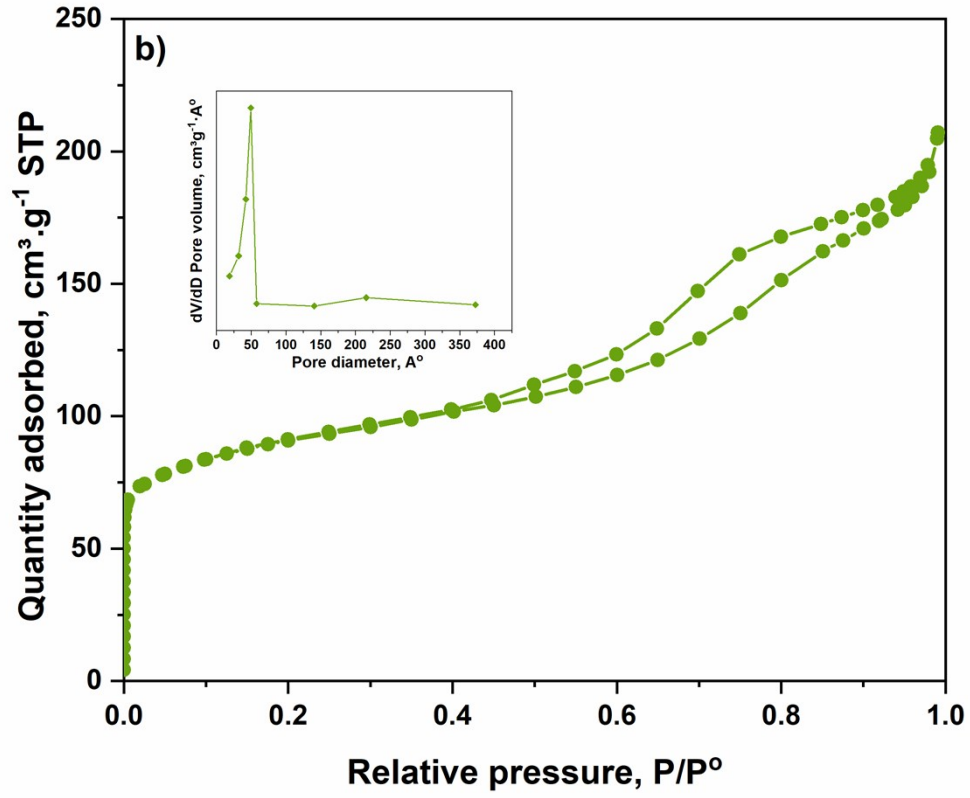
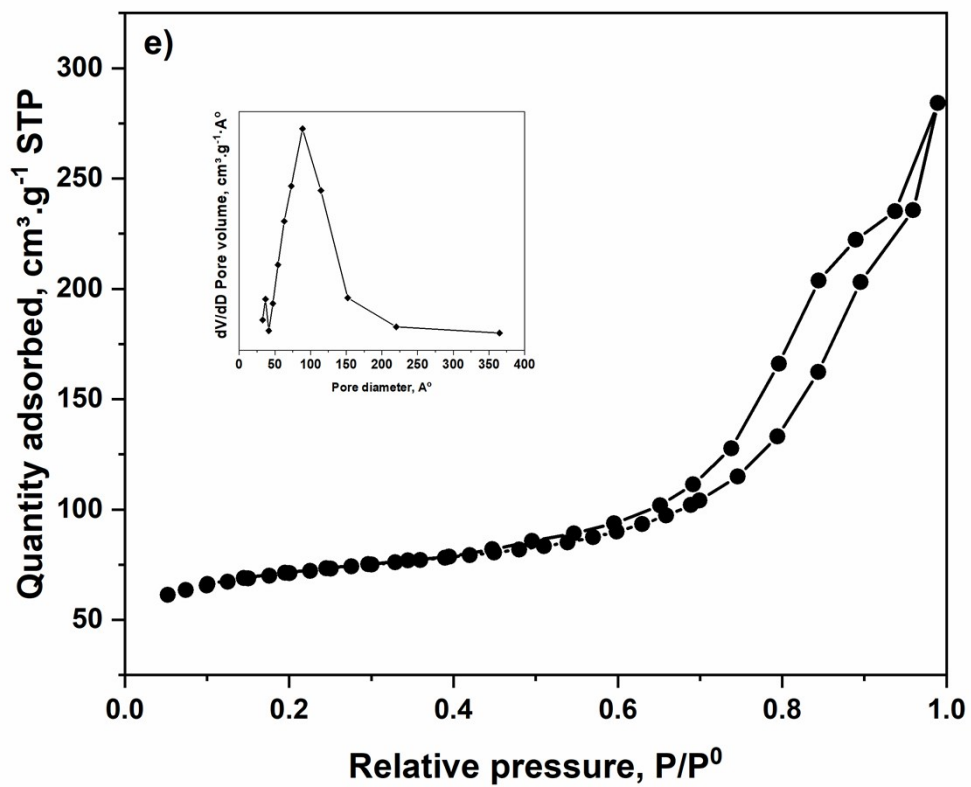
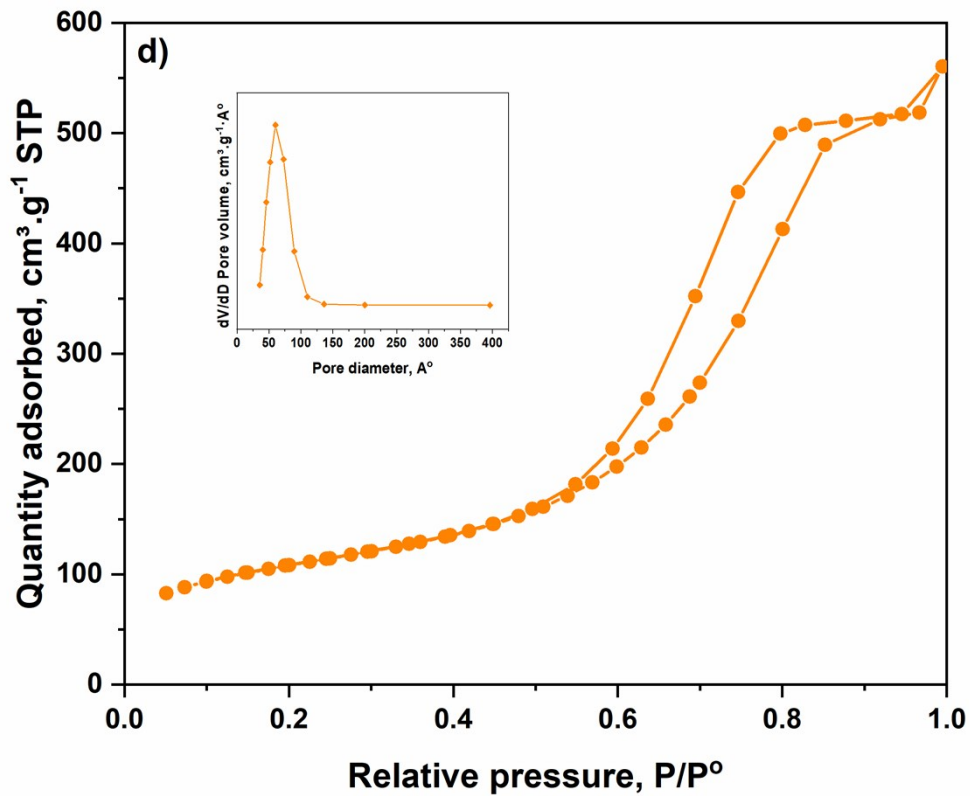


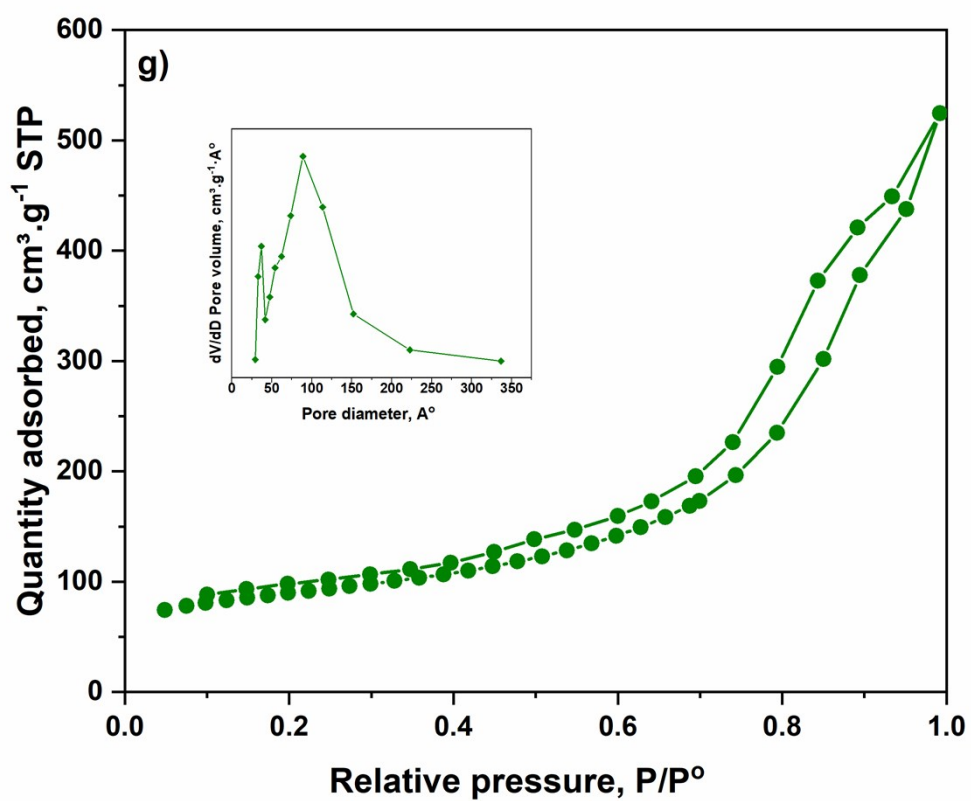
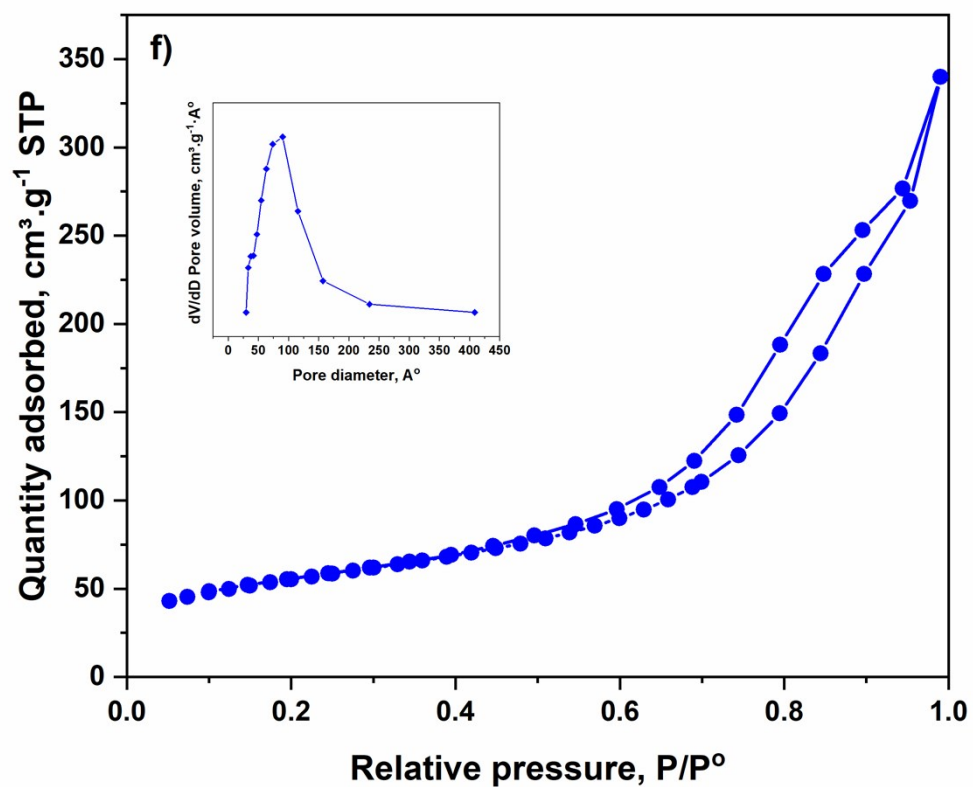
Figure S1: Ion chromatograms of hydrodeoxygenated products of bio-oils.











**Figure S2:** Adsorption-desorption isotherms of as-prepared catalyst; a) HRO@Y, b) HRO@Z, c) HRO@ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, d) HRO@SiO<sub>2</sub>, e) Ru/Y, f) S-HRO@Y-5, g) RuO<sub>2</sub>-HRO@Y.

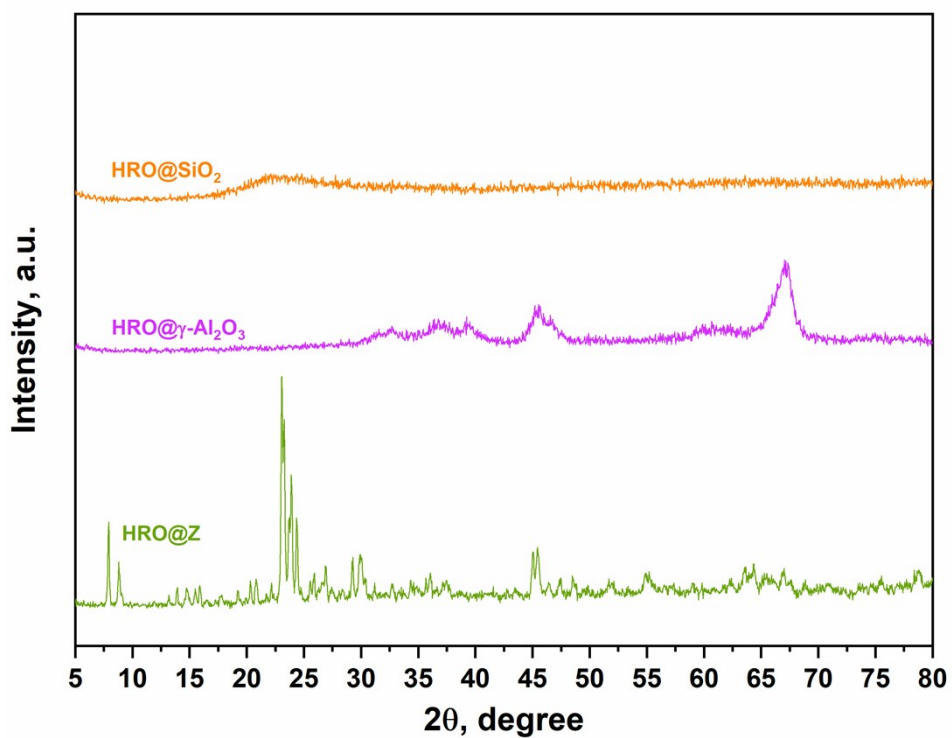


Figure S3: XRD patterns of HRO@SiO<sub>2</sub>, HRO@γ-Al<sub>2</sub>O<sub>3</sub> and HRO@Z.

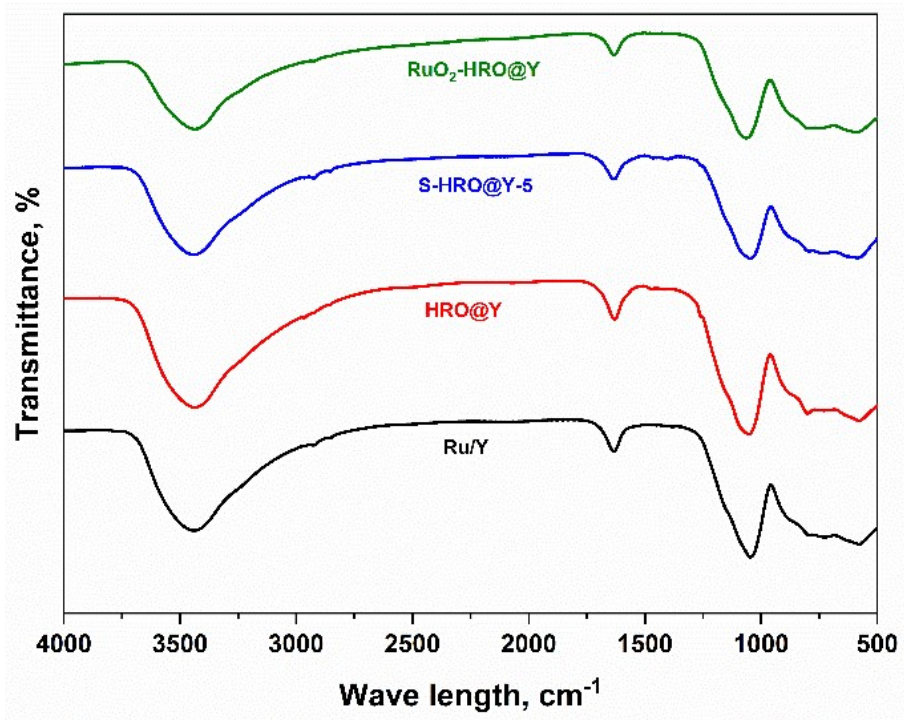


Figure S4: FT-IR spectra of Ru/Y, HRO@Y, S-HRO@Y-5 and RuO<sub>2</sub>-HRO@Y.

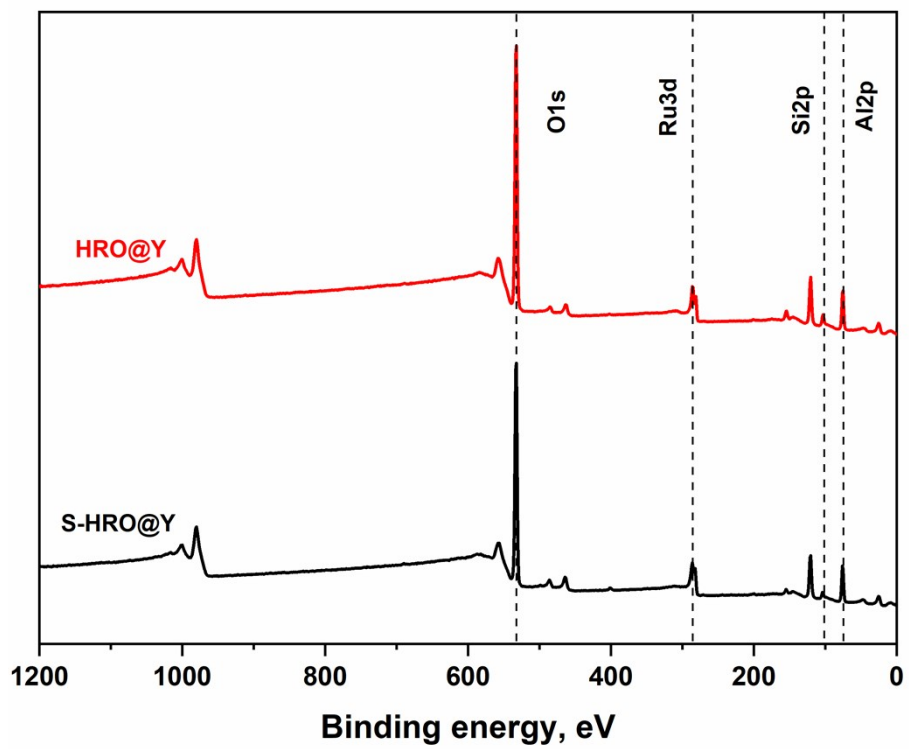


Figure S5: Survey scan of HRO@Y and S-HRO@Y.

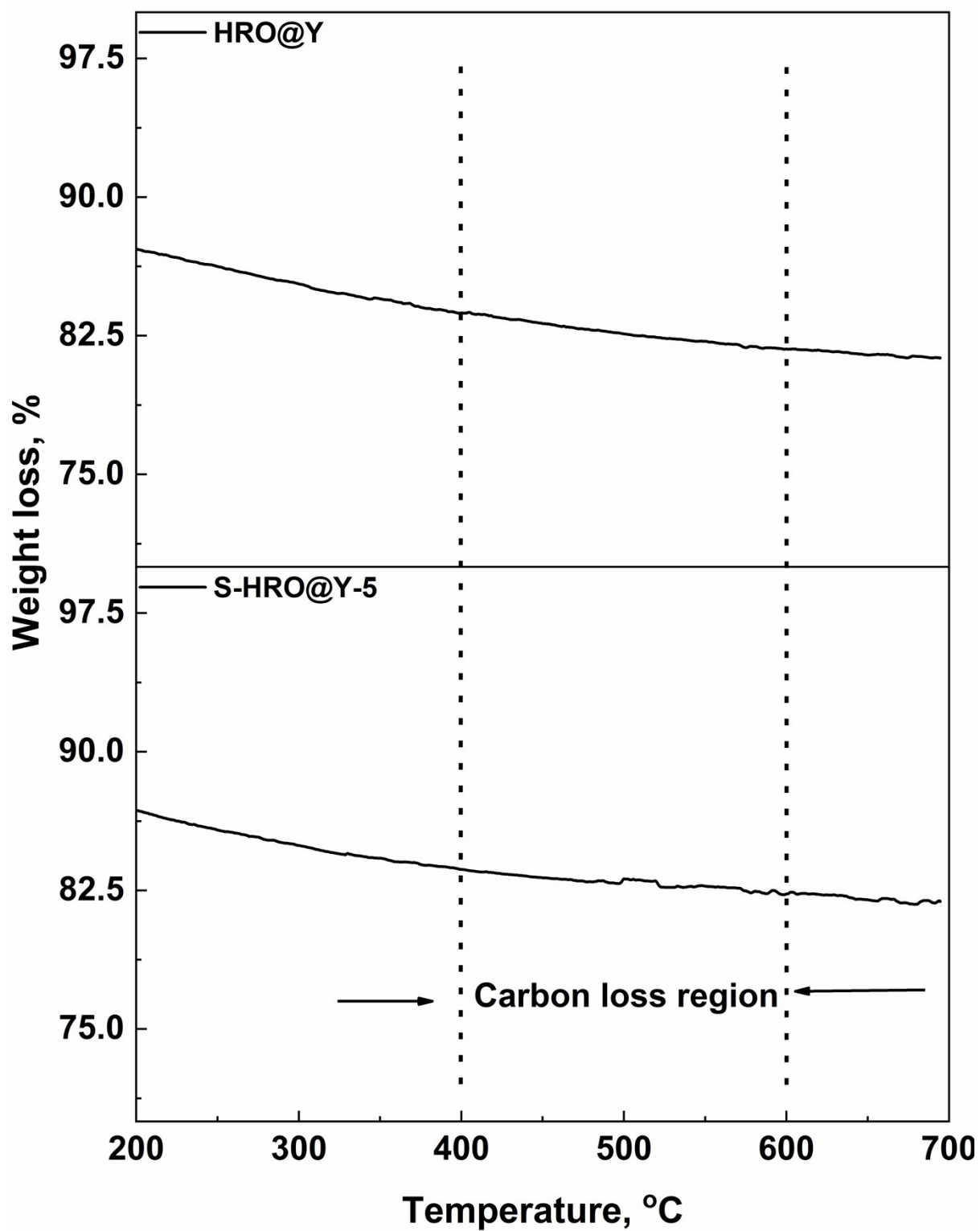


Figure S6: TGA-TPO of HRO@Y and S-HRO@Y.

### Bio-oil production procedure:

Slow pyrolysis of kraft lignin was performed in an up flow cylindrical quartz reactor (length: 450 mm; i.d. 30 mm) at 350 °C. 10 gm lignin and 15 gm SiC were loaded reactor. The particle size of lignin is very small, SiC works as dilution agent and maintains the flow of N<sub>2</sub> from feedstock during pyrolysis. The reactor was purged with 50 ml.min<sup>-1</sup> flow of nitrogen for 10 min prior to pyrolysis to create inert environment, and this flow maintained during pyrolysis which worked as carrier gas to carry out volatiles from reactor. The loaded reactor was fixed to gold coated heating furnace connecting to a PID controller and temperature of reactor increased from room temperature to 350 °C at a heating rate of 20 °C.min<sup>-1</sup>. The reactor temperature was kept constant at 350 °C for 1 h after reaching temperature to confirm that all volatiles had gone out from lignin. Feed bed temperature was chosen as the pyrolysis temperature and pyrolysis vapours was collected in measuring cylinder attached to external condenser having circulatory water at 12 °C. The organic fraction of bio-oil was recovered in ethyl acetate and aqueous fraction removed by the addition of anhydrous sodium sulphate. After evaporation of ethyl acetate in rotatory evaporator, the bio-oil was used for hydrodeoxygenation experiment.

The same procedure was used for the production of bio-oil from sugarcane bagasse however, the pyrolysis temperature and heating rate were 600 °C and 10 °C.min<sup>-1</sup>, respectively.

### Synthesis of Ru/Y zeolite:

5 wt% Ru/Y zeolite was prepared by simple wetness impregnation method. The 0.20 gm RuCl<sub>3</sub> was dissolved in water and this mixture was dropwise added to y-zeolite powder (1.9 gm). The obtained slurry was stirred for 1h at room temperature and after this heated at 80 °C until evaporation of water. The resultant catalyst was used after overnight drying at 120 °C.

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