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Cu-Mo doped Zeolite ZSM-5 catalyzed conversion of lignin to alkyl phenols with high selectivity

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Supporting Information

Table of Content

1. TEM analysis of catalyst:

The particles of synthesized zeolite HZSM-5 were found to be nearly spherical in morphology in the range 2-10 µm (Fig S1 A-B). These particles were not electron transparent , hence no clarity could be obtained for zeolite particles in TEM analysis (Fig S1 C). However, for Cu/Mo-ZSM-5, TEM micrographs showed metal deposition outside the zeolite (Fig S1 D).

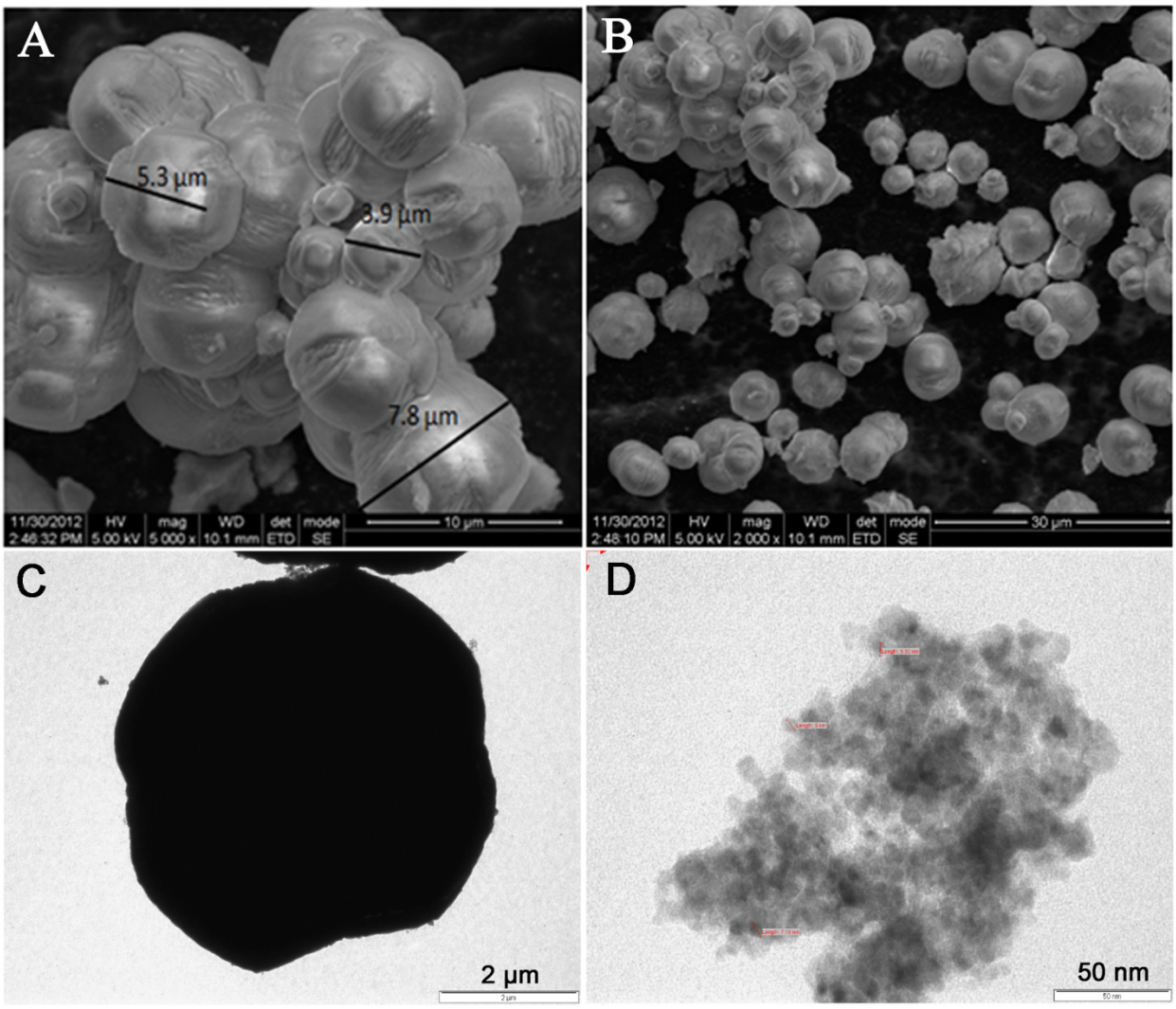

Figure S1 A-B) SEM microgarphs of ZSM-5 and C-D) TEM micrographs of Cu/Mo-ZSM-5.

2. Lignin Conversion Studies:

Table S1 Product yields in different reaction condition used in the study.

Entry	Solvent Ratio[a] (ml/ml)	Catalyst	NaOH (mmol)	Lignin Conversion[b] (%)	Total EtOAc soluble products (wt%)	THF soluble products[c] (Unconverted Lignin) (wt%)	Gaseous products[d] (wt%)	Char (wt%)
1	30/30	Cu/Mo-ZSM-5	1.7	95.7	60.3	4.0	35.4	0.23
2	45/15	Cu/Mo-ZSM-5	1.7	96.6	62.4	3.1	34.2	0.29
3	15/45	Cu/Mo-ZSM-5	1.7	91.7	53.7	8.0	38	0.27
4	0/60	Cu/Mo-ZSM-5	1.7	89.0	51.5	3.6	37.5	7.4
5	60/0	Cu/Mo-ZSM-5	1.7	82.4	36.5	8.9	45.9	8.7
6	30/30	Cu/Mo-ZSM-5	0	71.1	47	8.2	24.1	20.7
7	30/30	Cu/Mo-ZSM-5	5.2	96	50.9	3.5	45.1	0.47
8	30/30	Cu-ZSM-5	1.7	83.2	61.2	16.3	22	0.53
9	30/30	HZSM-5	1.7	98.5	60.9	1.2	37.6	0.3

[a]water/methanol ratio, [b]Lignin conversion is calculated by deducting EtOAc **insoluble** products (i.e. residual lignin and char), [c] Tetrahydrofuran was used to separate unconverted lignin from char, [d]Gaseous products is calculated by deduction.

3. Catalyst reuse:

Table S2 Cu-Mo/ZSM-5 Catalyst reuse cycles.

Cycle	Lignin conversion (%)	Ethyl acetate soluble products (wt%)	Selectivity of PMT (%)
1	95.7	19.9	70.3
2	95.1	19.4	69.8
3	94.9	20.3	70.1
4	73.4	12.5	55.6

For reaction entry 1 in Table S1.

Catalyst was calcined at 500 °C for 3 hr before reuse in each cycle. The BET surface area and average pore volume of calcined Cu-Mo/ZSM-5 catalyst before reuse is shown in Table S3. The surface area and pore volume were found to decrease in each cycle. This indicated amorphization of the zeolite in each cycle as also confirmed by XRD diffractograms (Fig. S2). Hence, catalyst lost its activity in the fourth cycle.

Table S3 BET surface area and average pore volume of calcined catalyst before reuse.

Cycle	BET surface area (m^2/g)	Average pore volume (cm^3/g)
1	281.7	0.19
2	223.3	0.17
3	164.4	0.16
4	90.5	0.09

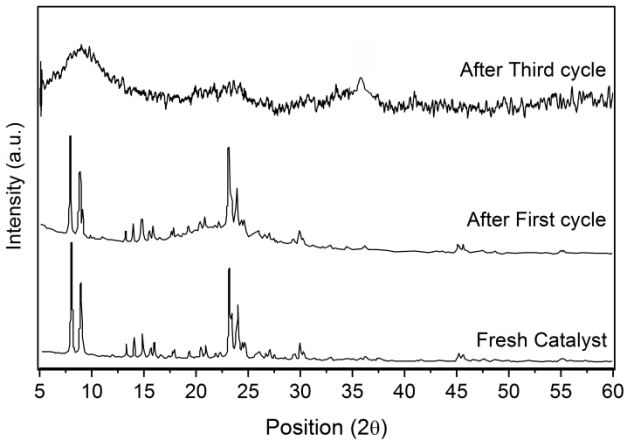

Figure S2 XRD spectra of HZSM-5 (Fresh and after use).

4. Total Acidity of catalysts:

Total acidity of zeolite samples was measured using a potentiometric method of titration with n-butylamine as reported by **C. Covarrubias *et al.*, *Microporous and Mesoporous Materials,* 2009, 117, 118–125**. n-Butylamime (0.1 N, 0.05 mL) was added to a dispersion of 0.15 g of zeolite sample in 90 mL of acetonitrile. This system was kept under steady stirring for 3 h. The suspension was then titrated using base solution volumes of 0.05 mL each time. The time elapsed before making a potential measurement was 2 min. The electrode potential variation (mV) was measured with a Toshcon CL46+ digital pH/mV meter. The total number of acid sites per gram of catalyst was estimated from the total amount of base added to reach the plateau in the potential vs. milliequivalent (n-Butylamine)/ g catalyst curve, and the acid site density was calculated considering the apparent surface area value of the corresponding zeolite sample.

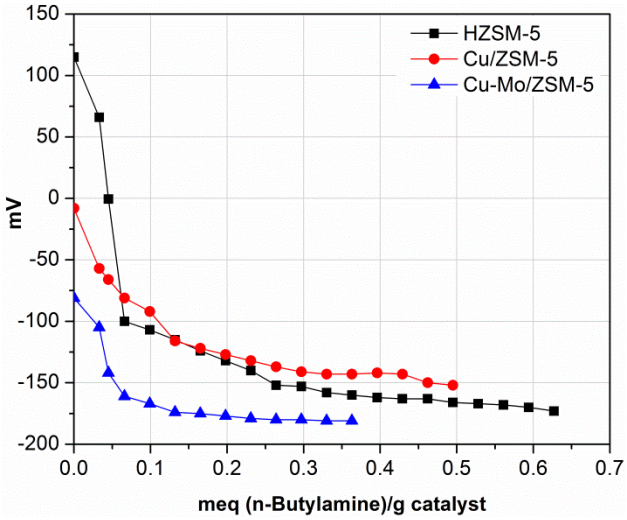

Figure S3 Potentiometric titration curves with n-butylamine for the catalyst used in the study

5. Product analysis:

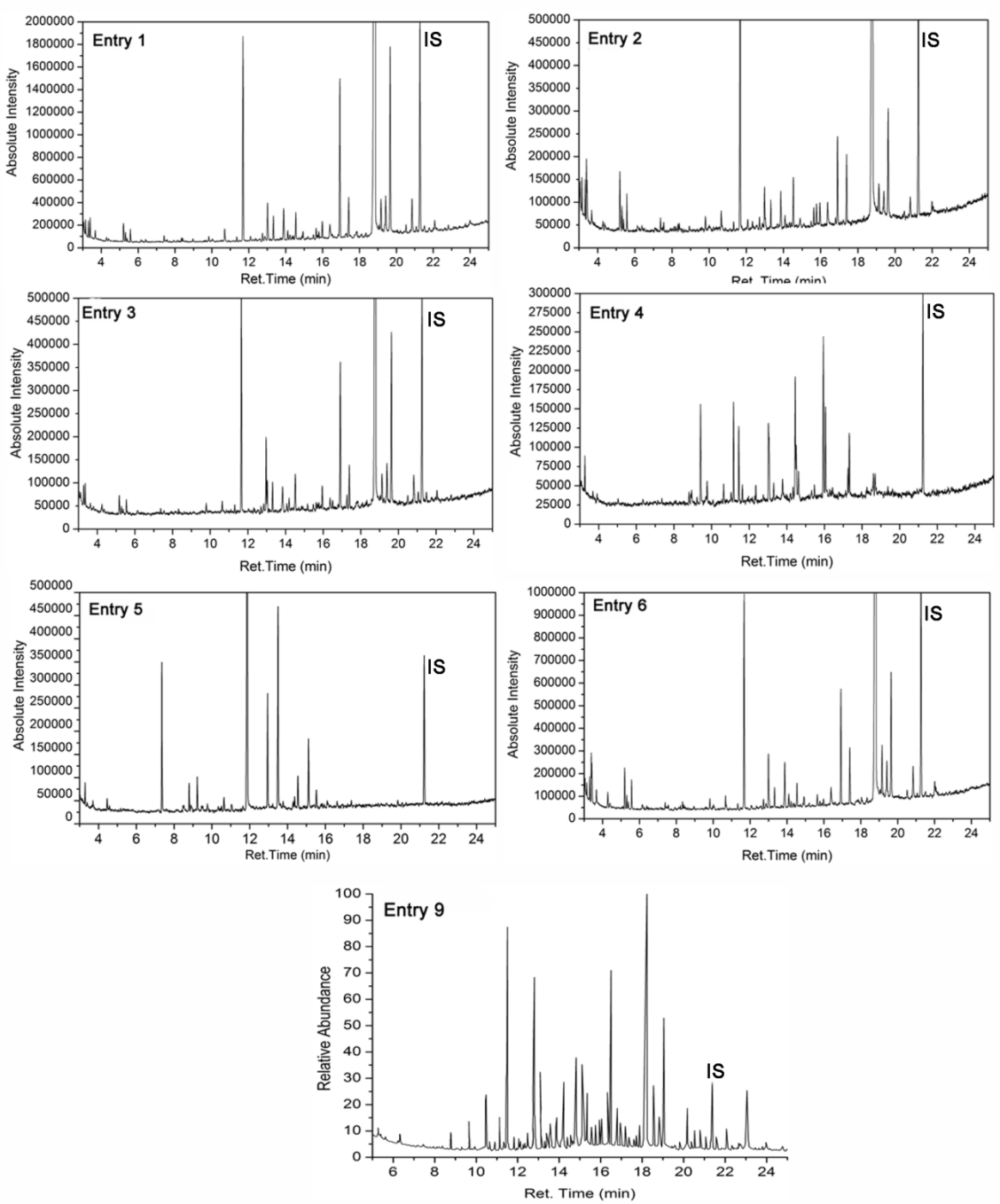

Figure S4 GCMS total ion chromatograms for EtOAc soluble products of reaction entries from Table S1. (IS-Internal Standard)

Table S4 Monomeric products identified from the reaction catalyzed by Cu/Mo-ZSM-5 (entry 1, Table 1).

Product Identified	Selectivity (%)	Product Identified	Selectivity (%)
Phenol,3-methoxy, 2,5,6-trimethyl	70.3	3-acetoxydodecane	0.1
Phenols		[1,1'-Bicyclopropyl]-2-octanoic acid, 2'-hexyl-, methyl ester	0.1
Phenol, 2,4,6-trimethyl	4.5	2,5-heptadienoic anhydride, 2,3,4,5,6-pentamethyl,Z,Z-	0.2
Phenol, 2-ethyl-4,5-dimethyl-	0.4	3,4-Hexanediol, 2,5-dimethyl-	0.1
Phenol, 2,3,4,6-tetramethyl-	0.5	***Cyclic Hydrocarbons***	
3-tert-Butyl-4-hydroxyanisole	5.2	Cyclopentane, 1,3-dimethyl-2-(1-methylethylidene)-, trans-	0.5
2-Ethyl-5-n-propylphenol	1.3	***Cyclic Oxygenates***	
Ethanone, 1-(3,4-dimethoxyphenyl)-	5.1	Cyclopentanone, 2,5-dimethyl-	0.6
1-Propanone, 1-(2,4-dimethoxyphenyl)-	0.7	Cyclohexanol, 2-methyl-, cis-	0.2
Phenol, 2,3,5- trimethyl-	0.8	1-Ethyl-2-(4-methylpentyl)cyclopentane	0.1
Acyclic hydrocarbons		1-Cyclohexene-1-carboxaldehyde, 2,6,6-trimethyl-	3.1
3,5-Decadiene, 2,2-dimethyl-, (Z,Z)-	0.2	3-Acetyl-2,4,4-trimethylcyclohex-2-en-1-one	0.8
1,3-Heptadiene, 2,3-dimethyl-	0.4	p-Benzoquinone, 2,3,5,6-tetramethyl-	0.2
2,4-Heptadiene, 2,4-dimethyl-	0.2	***Others***	
1,4-Hexadiene, 2,3,4,5-tetramethyl-	0.2	2-Butanol, 3-(1-methyl-2-phenylethoxy)-	0.1
Acyclic Oxygenates		Spiro[2,4,5,6,7,7a-hexahydro-2-oxo-4,4,7a-trimethylbenzofuran]-7,2'-(oxirane)	0.2
Pentanoic acid, 4-methyl-	0.2	3,4-Dimethoxytoluene	0.3
3-Hexanone	0.2	p-Benzoquinone, 2,3,5,6-tetramethyl-	0.4
3-Pentanol, 2-methyl-	0.3	Benzene, 1,2-dimethoxy-4-(2-propenyl)-	0.7
Propanoic acid, 2-methyl-	0.1	Benzeneacetamide	0.3
Heptanal	0.1		

Reaction conditions: 0.5 g Lignin, 0.125 g catalyst, 1.7 mmol NaOH, 60 ml Solvent, 220 °C, 7 hr, Inert atmosphere.