Preparation of magnetic silica supported Brönsted acidic ionic liquids for the depolymerization of lignin to aromatic monomers

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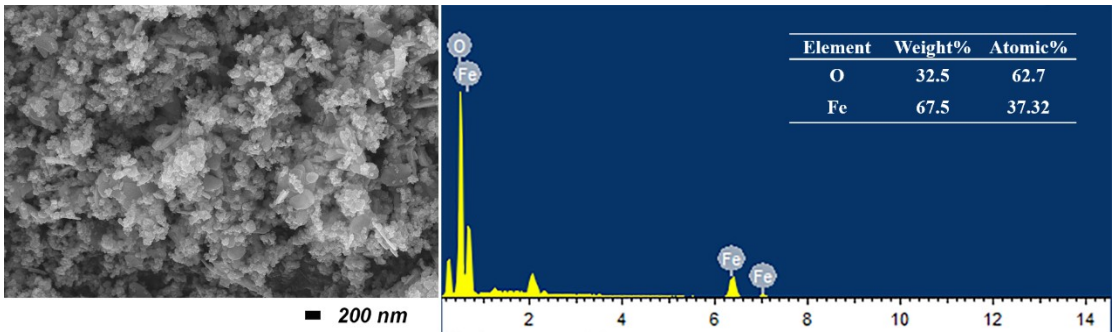

Fig. S1 SEM-EDS image of Fe_3O_4.

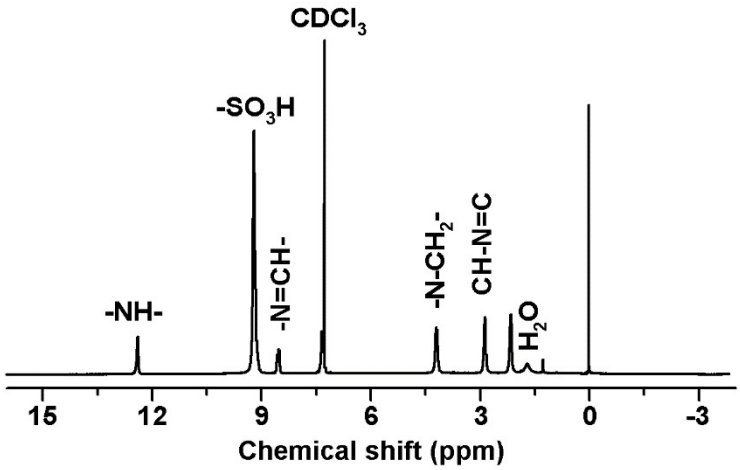

Fig. S2 ^{1}H-NMR spectra of BAIL. [a]

[a] ^{1}H NMR (600 MHz, $CDCl_3$), δ 12.40 (s, 1H), 9.22 (s, 9H), 8.95–8.23 (m, 1H), 7.32 (d, J = 41.5 Hz, 3H), 4.21 (s, 2H), 4.00 – 3.64 (m, 1H), 2.87 (s, 2H), 2.12 (t, J = 28.9 Hz, 2H), 1.79 (d, J = 94.2 Hz, 1H), 1.44 – 1.11 (m, 1H), 0.02 (s, 1H).

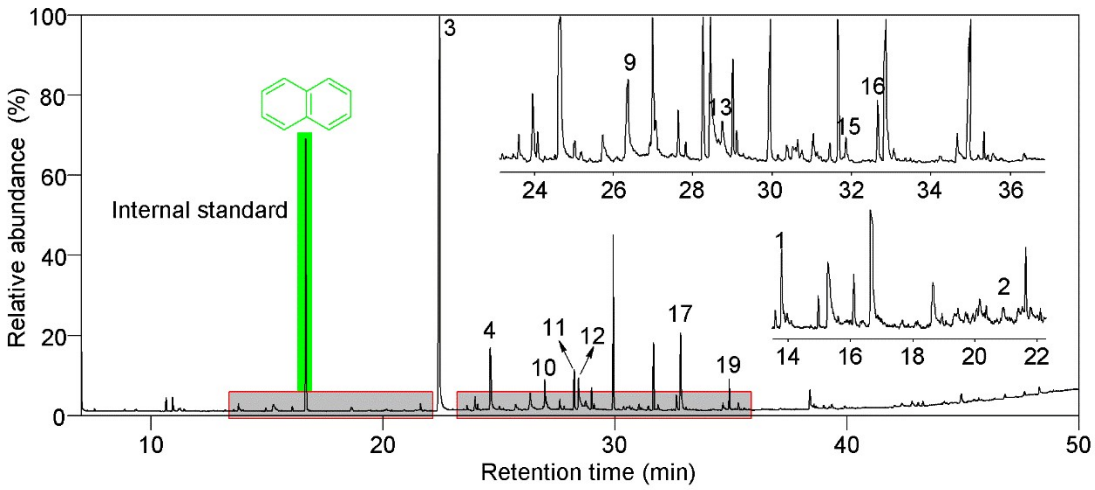

Fig. S3 Total ions chromatogram of liquid products from lignin depolymerization over 40 wt% BAIL (30wt%)-Fe_3O_4@SiO_2 at 160 °C for 3 h. (Identified by GC/MS, naphthalene as the internal standard)

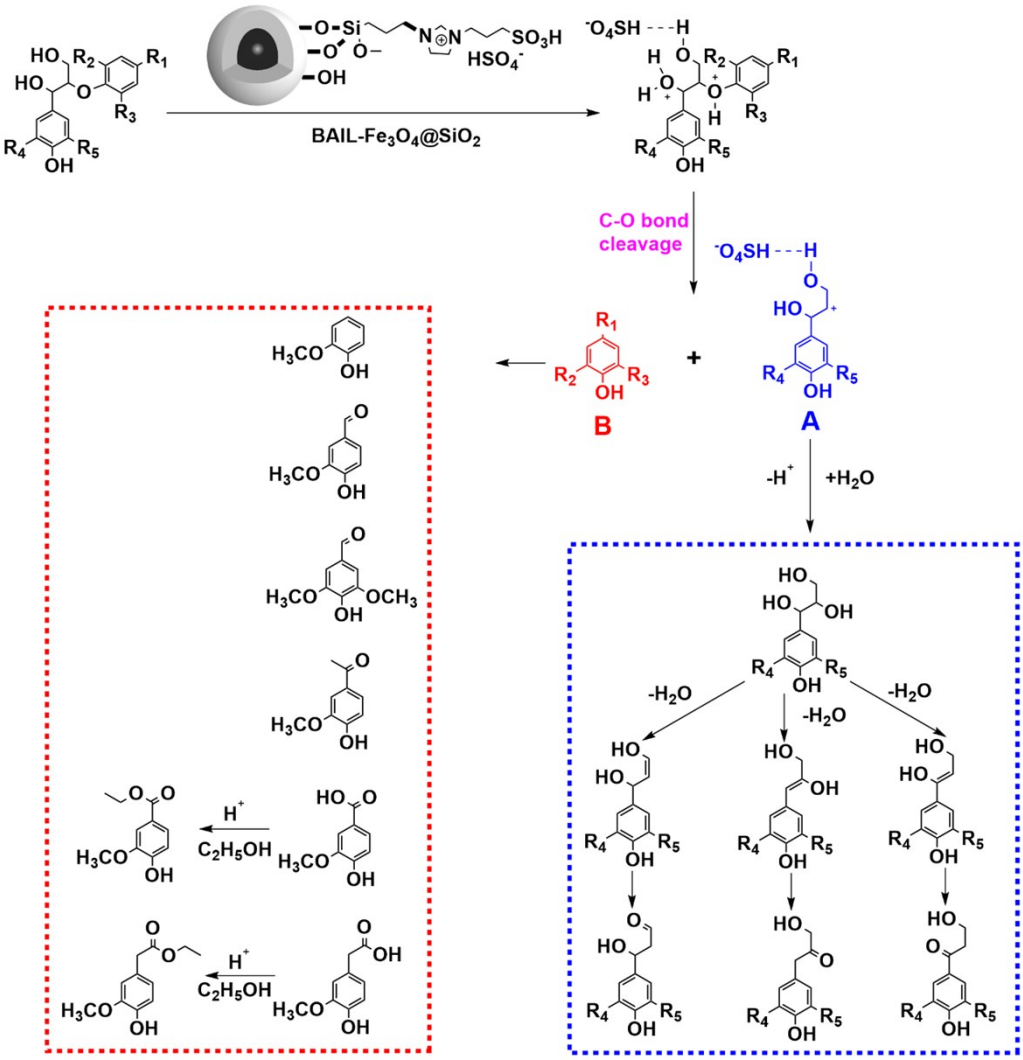

Fig. S4 Possible mechanism proposed for the catalytical depolymerization of lignin over 40 wt% BAIL (30wt%)-Fe_3O_4@SiO_2.

Table S1 Lignin depolymerization products. [a] (Identified by GC-MS)

Classification	Entry [b]	Compounds	Formula	Yield of main products (%)			
				None	40 wt% Fe_3O_4@SiO_2	20 wt% BAIL	40 wt% BAIL (30 wt%)-Fe_3O_4@SiO_2
Phenol	1	2-Methoxyphenol	$C_7H_8O_2$	0.27	0.17	0.7	0.33
	6	2,6-Di-tert-butylphenol	$C_{14}H_{22}O$		0.14		
Aryl aldehyde	2	4-Hydroxybenzaldehyde	$C_7H_6O_2$		0.15		
	3	Vanillin	$C_8H_8O_3$	11.93	12.96	9.38	18.42
	13	4-Hydroxy-3,5-dimethoxybenzaldehyde	$C_9H_{10}O_4$	0.13	0.22		0.75
Aryl ester	7	Methyl 2-(4-hydroxy-3-methoxyphenyl) acetate	$C_{10}H_{12}O_4$			0.8	
	10	Ethyl 4-hydroxy-3-methoxybenzoate	$C_{10}H_{12}O_4$	0.21	0.40	7.97	1.11
	11	Ethyl homovanillate	$C_{11}H_{14}O_4$	0.10	0.18	0.93	1.33
	16	2-Methoxy-4-(2-oxopropyl) phenyl acetate	$C_{12}H_{14}O_4$				0.54
	18	Butyl (4-methylpentyl) phthalate	$C_{18}H_{26}O_4$			0.50	
	19	Dibutyl phthalate	$C_{16}H_{22}O_4$		0.09		0.95
Aryl ketone	4	Apocynin	$C_9H_{10}O_3$	0.95	1.48	2.15	3.06
	17	2-Hydroxy-1-(4-hydroxy-3-methoxyphenyl) ethan-1-one	$C_9H_{10}O_4$				3.18
Aryl acid	9	4-Hydroxy-3-methoxybenzoic acid	$C_8H_8O_4$	0.46	1.01		1.20
	12	Homovanillic acid	$C_9H_{10}O_4$	0.29	0.73		1.91
Aryl alcohol	8	Homovanillyl alcohol	$C_9H_{12}O_3$		0.12		
Heteroatoms-containing aromatic monomers	5	S-methyl 4-(methylthio) benzothioate	$C_9H_{10}OS_2$		0.13		
	14	4-(Methylphenylthio) acetaldehyde diethyl acetal	$C_{13}H_{20}O_2S$	0.13			
	15	Ethamivan	$C_{12}H_{17}NO_3$				0.25

[a] Reaction conditions: 160 °C, 3 h, 0.5 g of lignin, 30 mL of ethanol, and 1 MPa of N_2.

[b] Relative to Fig. S3.

Table. S2 Mass distribution and DBE distribution of the species identified with Q-Exactive Orbitrap MS in the ethanol-soluble products.

Catalyst	Mass distribution of the species identified [a]				DBE distribution of the species identified [b]			Total
	<150	150~250	250~350	350~450	1-3	4-7	⩾8	
None	19	41	39	8	20	56	31	107
BAIL	9	30	17	5	21	30	10	61
Fe_3O_4@SiO_2	13	31	21	7	27	33	12	72
BAIL (30 wt%)-Fe_3O_4@SiO_2	21	43	42	14	14	63	43	120

[a] Number of the species identified with Q-Exactive Orbitrap MS in different molecular mass ranges.

[b] Number of the species identified with Q-Exactive Orbitrap MS in different DBE ranges.