One-pot preparation of biochar supported Ni-Mo_2C catalyst for selective hydrogenation of lignin

Yuan-Ying Wang, Li-Li Ling, Hong Jiang*

CAS Key Laboratory of Urban Pollutant Conversion, Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

Corresponding author:

Dr. Hong Jiang, Fax: +86-551-63607482; E-mail: jhong@ustc.edu.cn

Table S1 The nickel and molybdenum content of catalysts prepared by one-pot method (Ni-Mo_2C/C, Ni/C and Mo_2C/C) and catalyst prepared by chemical reduction method (Ni-MoO_2/C) detected by flame atom absorption method.

sample	Ni-Mo_2C/C	Ni/C	Mo_2C/C	Ni-MoO_2/C
Ni content（wt%）	14.20	48.89	0	5.25
Mo content（wt%）	11.83	0	16.33	22.31

Table S2 The elemental composition of the catalysts tested by elemental analyzer (VARIO EL III, Elementar, Germany).

Catalyst	Elemental composition (wt.%)		
	N	C	H
Ni-Mo_2C/C	0.51	45.97	1.59
Ni/C	0.21	51.55	1.07
Mo_2C/C	0.82	33.1	2

Table S3 The surface properties of one-pot prepared catalysts characterized by BET.

Textural characteristic	Ni-Mo_2C/C	Ni/C	Mo_2C/C
BET surface area （m^2/g）	220.47	150.20	208.04
BJH average pore diameter （nm）	10.6	10.9	6.0
Pore volum （cm^3/g）	0.162	0.243	0.110

Table S4 The element contents of Ni-Mo_2C/C catalyst detected by XPS.

Element	Mo	C	N	O	Ni
Mass ratio %	19.73	60.71	7.14	8.45	3.96

Table S5 Compounds and peak areas in liquid products determined by GC-MS. Reaction conditions: 1.0 g of lignin, 0.25 g of Ni-Mo_2C/C catalyst, initial 2.0 MPa H_2, 100 mL isopropanol, 523 K, 2 h.

RT[a] (min)	Compounds	Peak area (%)
11.96	Phenol	1.62
15.18	2-methoxy-phenol	2.71
16.02	2-ethylhexanoic acid	1.61
17.48	4-ethylphenol	11.36
18.20	2-methoxy-4-methylphenol	1.53
19.06	2,3-dihydrobenzofuran	0.58
20.58	4-ethyl-2-methoxyphenol	9.68
21.59	2-methoxy-4-vinylphenol	0.85
22.51	2,6-dimethoxyphenol	6.27
22.94	2-methoxy-4-propylphenol	0.61
23.60	2,3,4,5-tetrahydroxypentanal	0.92
24.08	1-(2-methylenecyclopropyl)benzene	0.97
24.91	4-hydroxy-3-methoxybenzoic acid	2.16
25.13	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	1.84
25.56	unidentified	2.57
26.02	1-(4-hydroxy-3-methoxyphenyl)ethanone	1.05
26.79	5-tert-Butylpyrogallol	4.73
26.98	Homovanillyl alcohol	0.48
28.58	4-allyl-2,6-dimethoxyphenol	0.62
28.74	4-propyl-1,1'-diphenyl	1.36
28.96	3-hydroxy-4-methoxybenzoic acid	0.41
29.79	2-methylindene	0.73
29.98	4-hydroxy-3,5-dimethoxybenzaldehyde	0.93
30.03	benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	0.96
30.36	(2E)-4-(4-hydroxy-3-methoxyphenyl)-2-butanone oxime	0.81
30.55	benzenepropanoic acid, 4-hydroxy-, methyl ester	0.40
30.89	4-allyl-2,6-dimethoxyphenol	1.05
31.54	1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone	8.66
32.23	3,5-Dimethoxy-4-hydroxyphenylacetic acid	0.45
32.49	methyl 2-hydroxy-2-(4-methoxyphenyl)acetate	0.83
33.40	(1,1'-Biphenyl)-2,2'-dicarboxaldehyde	0.68
33.95	4-hydroxy-3,5-dimethoxybenzoic acid	0.92
34.25	3,5-dimethoxy-4-hydroxyphenylacetic acid	1.28
34.67	methyl (3,4-dimethoxyphenyl)(hydroxy)acetate	0.57
35.50	unidentified	1.09
35.83	unidentified	4.40

36.81	unidentified	1.55
37.27	4,4'-ethylidenediphenol	0.53
38.55	unidentified	5.54
39.32	unidentified	2.46
39.42	2-(2'-methoxyphenyl)-2-(2'-hydroxyphenyl)propane	1.22
39.61	1-(4-isopropyl-1,6-dimethyl-5,6,7,8-tetrahydronaphthalen-2-yl)ethanone	0.94
39.68	6-acetyl-5-hydroxy-2,7-dimethyl-1,4-naphthoguinone	1.46
42.13	3-ethoxy-4-methoxybenzaldehyde	0.64
42.40	unidentified	1.96
43.09	dip-tolyl naphthalene-1,5-dicarboxylate	0.99

[a] Retention time

Table S6 FTIR spectra peak position and assignments of Ni-Mo_2C/C catalyst, original lignin, SR of Ni-Mo_2C/C catalytic reaction and LP of Ni-Mo_2C/C catalytic reaction.

Wavelength (cm)	3365	2800 and 3000	1600	1240 and 1100
Substance	−OH	C−H	C=O	C−O
Ni-Mo_2C/C	none	none	none	none
original lignin	obviously	obviously	slightly	obviously
SR	barely	slightly	barely	slightly
LP	obviously	dramatically	dramatically	dramatically

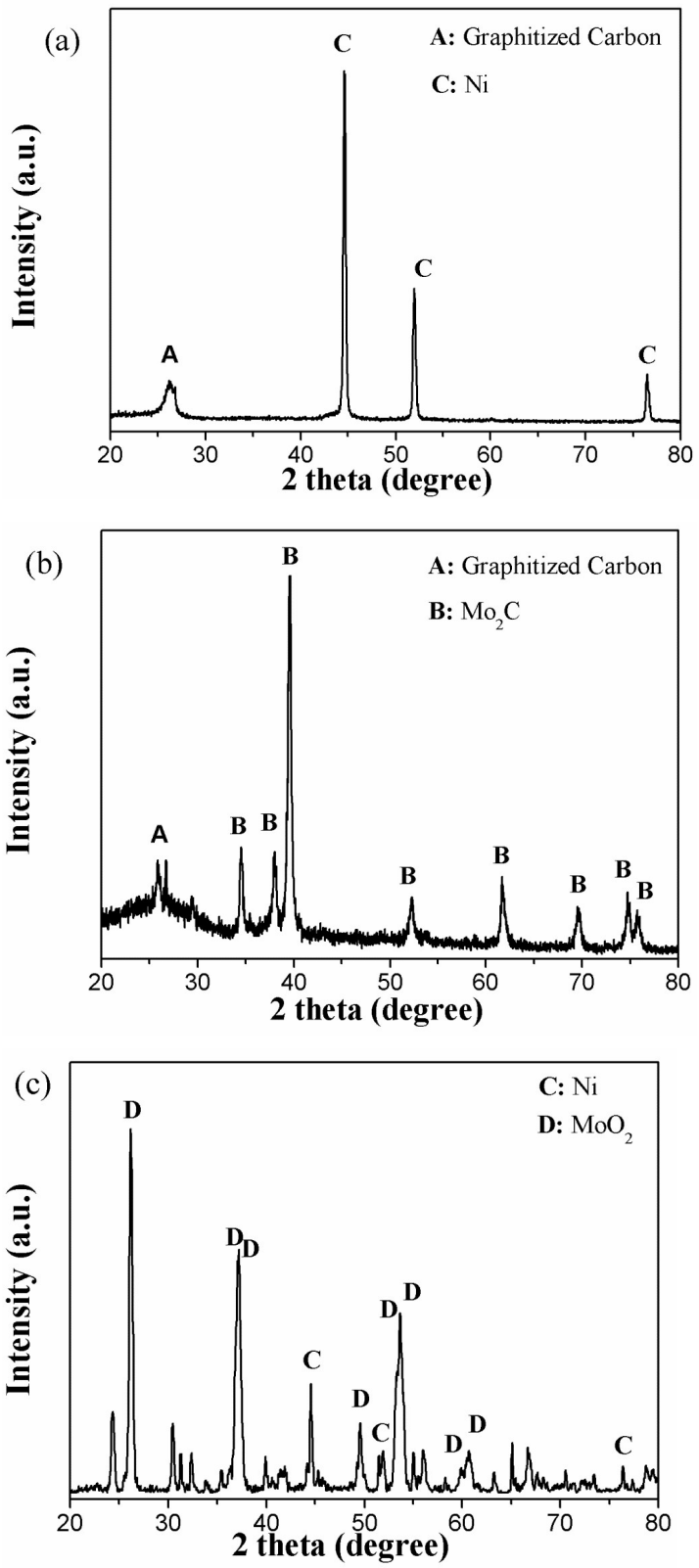

Fig. S1 XRD pattern of pyrolytically prepared Ni /C catalysts (a) and Mo_2C/C (b); XRD pattern of chemically synthesized catalyst Ni-MoO_2/C (c).

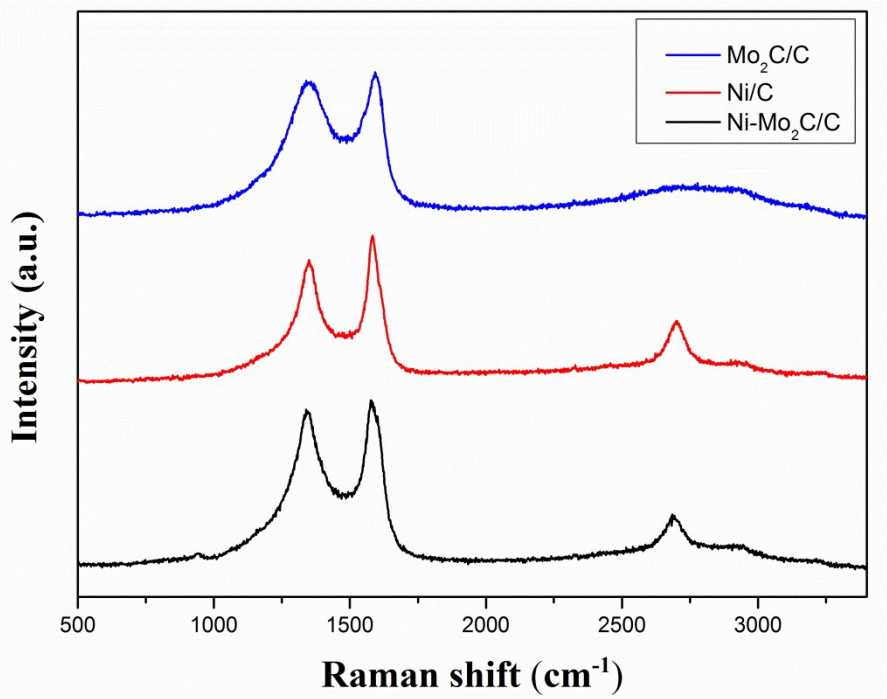

Fig. S2 Raman spectrum of pyrolytically prepared catalysts Ni-Mo_2C/C, Ni/C, and Mo_2C/C.

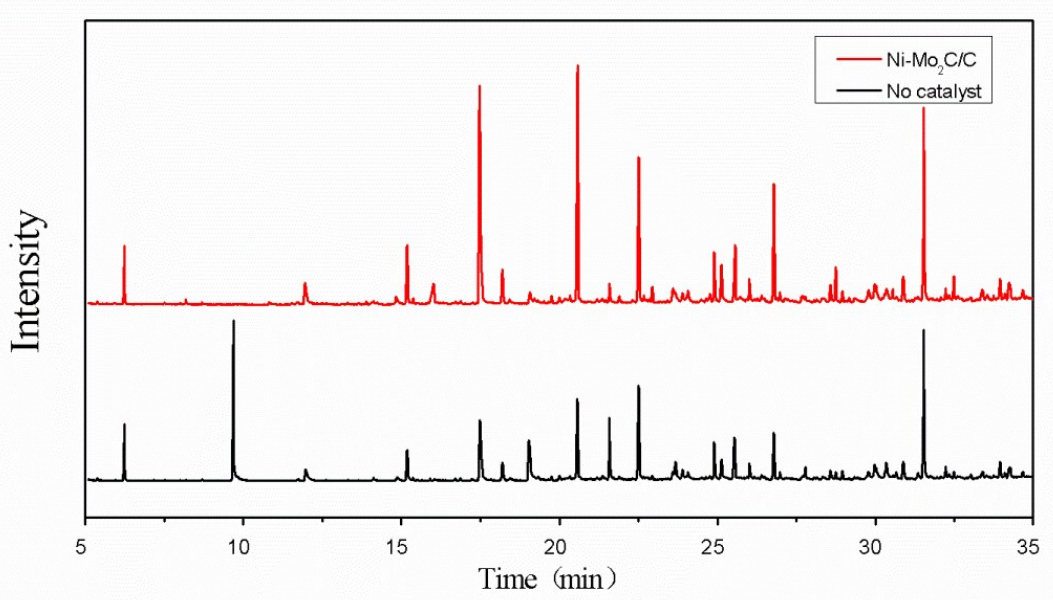

Fig.S3 The distribution of the products in liquid phase with Ni-Mo_2C/C and without catalyst detected by GC-MS. Reaction conditions: 1.0 g of lignin, initial 2.0 MPa of H_2, 100 mL of isopropanol, 523 K, 2 h.

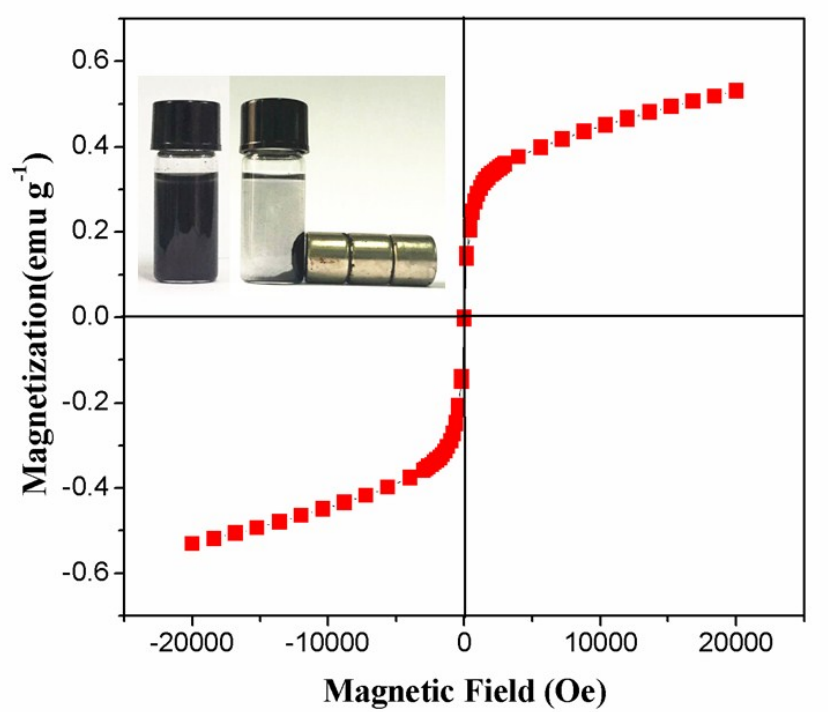

Fig.S4 Magnetic hysteresis loop of Ni-Mo_2C/C catalyst recorded at 300 K, the photographs (inset) show that the catalyst can be separated by a magnet in 30 minutes.

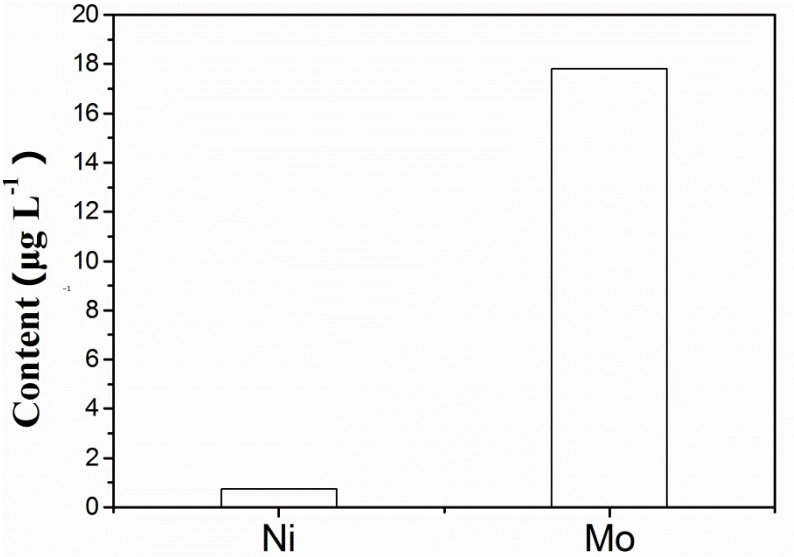

Fig.S5 The Ni and Mo element in liquid after reaction determined by the inductively coupled plasma-sector field mass spectrometry (ICP-SFMS, Plasma Quad 3, Thermo-VG Elemental, UK).

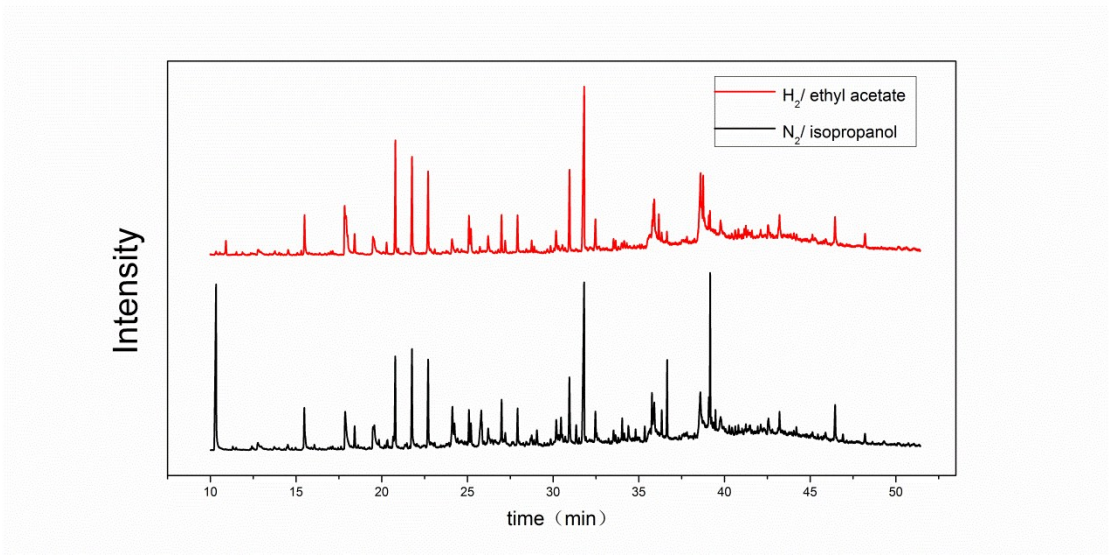

Fig.S6 The distribution of the products in liquid phase under different conditions determined by GC-MS. Reaction conditions: 1.0 g of lignin, 0.25 g of catalyst, initial pressure 2.0 MPa , 100 mL solvent, 523 K, 2 h.