Supplementary Material (ESI) for Chemical Communications

Supporting information

Hydrodeoxygenation of Bio-Derived Phenols to Hydrocarbons using Raney Ni and Nafion/SiO_2 Catalysts

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Chemicals

All chemicals were obtained from commercial companies: phenol (Merck, 99.5% GC assay), guaiacol (Fluka, >98.0% GC assay), catechol (Aldrich, crystalline, >99.0% GC assay), 2,6-dimethoxyphenol (Aldrich, >98.0 GC assay), 4-*n*-propylphenol (SAFC, >97.0% GC assay), 4-methylguaiacol (Aldrich, 99.0 % GC assay), 4-ethylguaiacol (Aldrich, >98.0% GC assay), 4-*n*-propylphenol (Aldrich, >99.0 GC assay), 4-*n*-propylguaiacol (SAFC, >99.0% GC assay), 4-allyl-2,6-dimethoxyphenol (Alfa Aesar, 98.0% GC assay), Pd/C (Aldrich, loading 5 wt% Pd, S_{BET}: 845 m^2g^{-1}), Nafion water suspension (Aldrich, 10 wt%), Nafion/SiO_2 (Aldrich, loading 13 wt% Nafion), Zeolite H-beta (CP-814 E, Zeolyst, S_{BET}: 700 m^2g^{-1}, V_1=0.195 cm^3g^{-1}, SiO_2/Al_2O_3=25), Zeolite H-Y (CBY 720, Zeolyst, S_{BET}: 720 m^2g^{-1}, V_1=0.286 cm^3g^{-1}, SiO_2/Al_2O_3=30), nickel aluminum alloy (Alfa Aesar, Raney type 50/50), Raney Ni®2400 (Aldrich), Raney Ni®4200 (Aldrich), Ni/SiO_2 (Aldrich, loading 60 wt% Ni), Ni/ASA (Aldrich, loading 65 wt% Ni), hydrogen (Air Liquide, >99.999%).

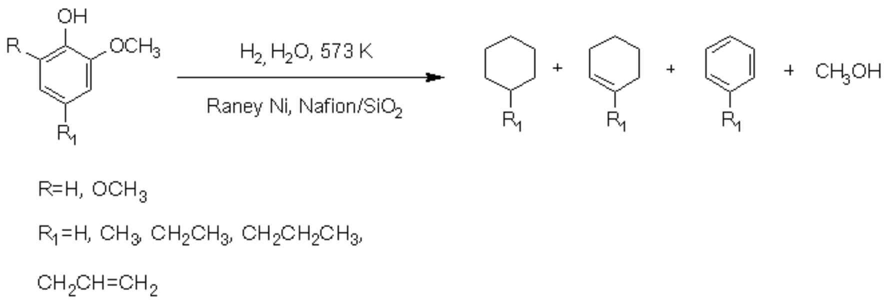
Raney Ni catalyst preparation

The Raney Ni catalyst preparation was carried out according to the literature.[1] The starting nickel aluminum alloy powders were heated to about 773 K in hydrogen for 2 h. Then the powders were cooled to room temperature and treated with 20 wt% aqueous sodium hydroxide in a 250 ml beaker immersed in thermostated water at 373 K for 1 h. The extracted catalysts were washed with distilled water at room temperature until neutralized. The samples were finally washed with absolute ethanol for three times, and transferred to stoppered tubes for storage in absolute ethanol at room temperature.

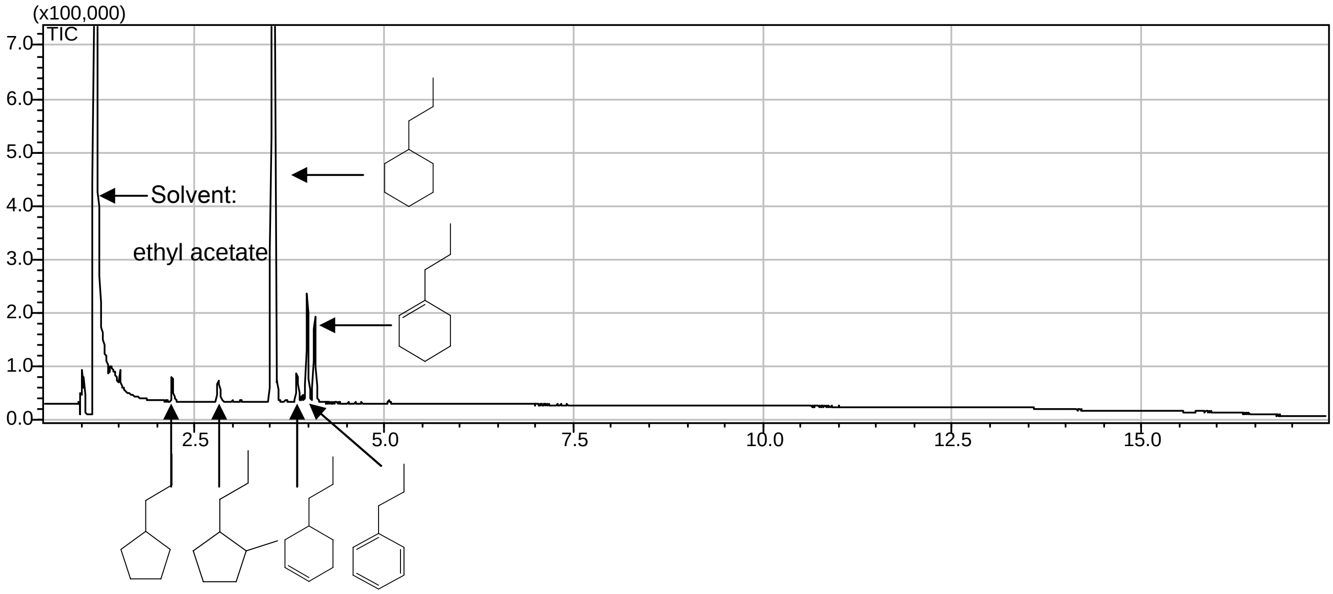
The bulk composition of Raney Ni contains 88.1 wt% Ni and 11.9 wt% Al. $S_{(BET)}$: 140 m^2g^{-1}, pore volume: 0.14 $ml\cdot g^{-1}$, mean pore diameter: 29.1 Å, mean crystallite size: 43.0 Å.

Phenolic mixture (bio-oil substitute) hydrodeoxygenation

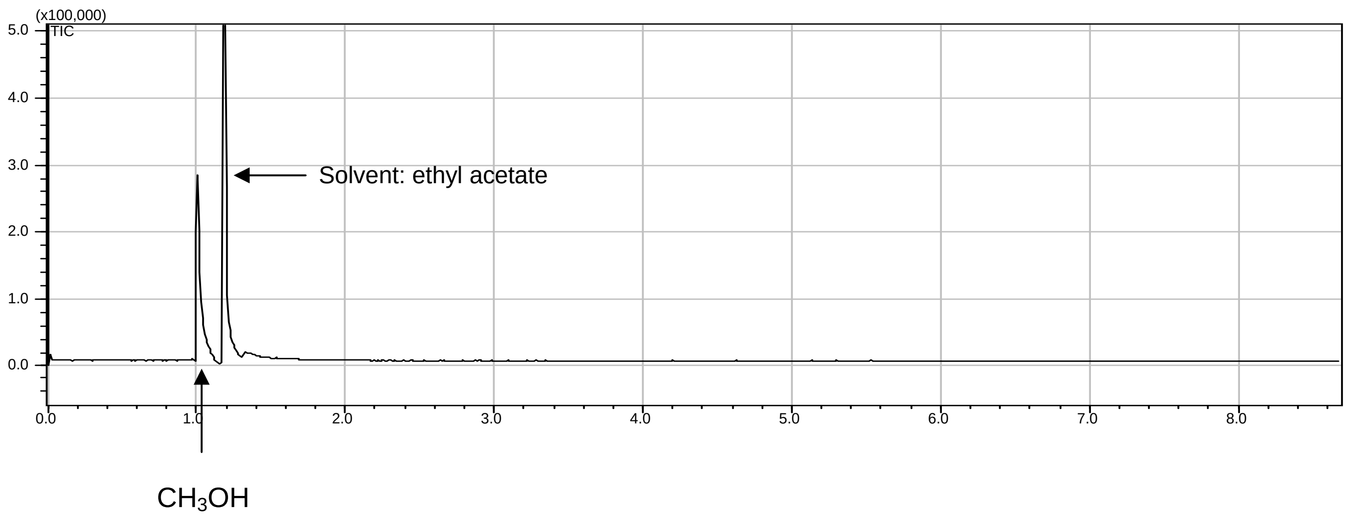
Tests for bio-oil substitute (3.31 g, including 4-*n*-propylphenol (1.36 g, 0.010 mol), 2-methoxy-4-*n*-propylphenol (1.66 g, 0.010 mol), 4-allyl-2-methoxyphenol (1.64 g, 0.010 mol)) were carried out in the presence of Raney Ni (1.00 g), Nafion/SiO_2 (13 wt%, 2.00 g) and H_2O (200 mL) at 573 K with 4 MPa H_2 (room temperature) for 2 h. Ethyl acetate was used to extract the organic mixture and the aqueous phase was also gathered. The aqueous and organic layers were both analyzed by GC and GC–MS. The gas phase products were analyzed by GC.



Scheme S1. Aqueous-phase hydrodeoxygenation of bio-derived phenolic monomers to hydrocarbons and methanol over Raney Ni catalysts and solid acid Nafion/SiO_2.



(a)



(b)

Figure S1. GC-MS product spectrum of (a) organic phase and (b) aqueous phase after aqueous phase hydrodeoxygenation of 2-methoxy-4-*n*-propylphenol over Raney Ni catalysts and solid acid Nafion/SiO_2 at 573 K. Reaction conditions: 2-methoxy-4-*n*-propylphenol (1.66 g, 0.010 mol), Raney Ni (0.30 g), Nafion/SiO_2 (13 wt%, 0.80 g), 573 K, 4 MPa H_2, 2 h, stirred at 1000 rpm.

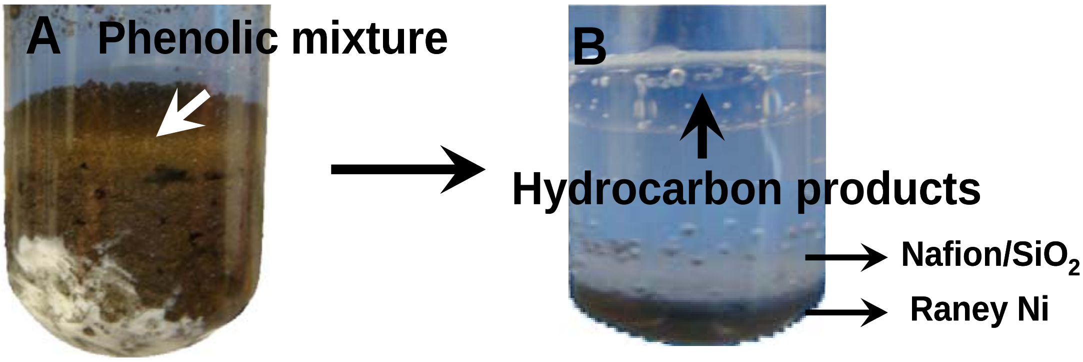
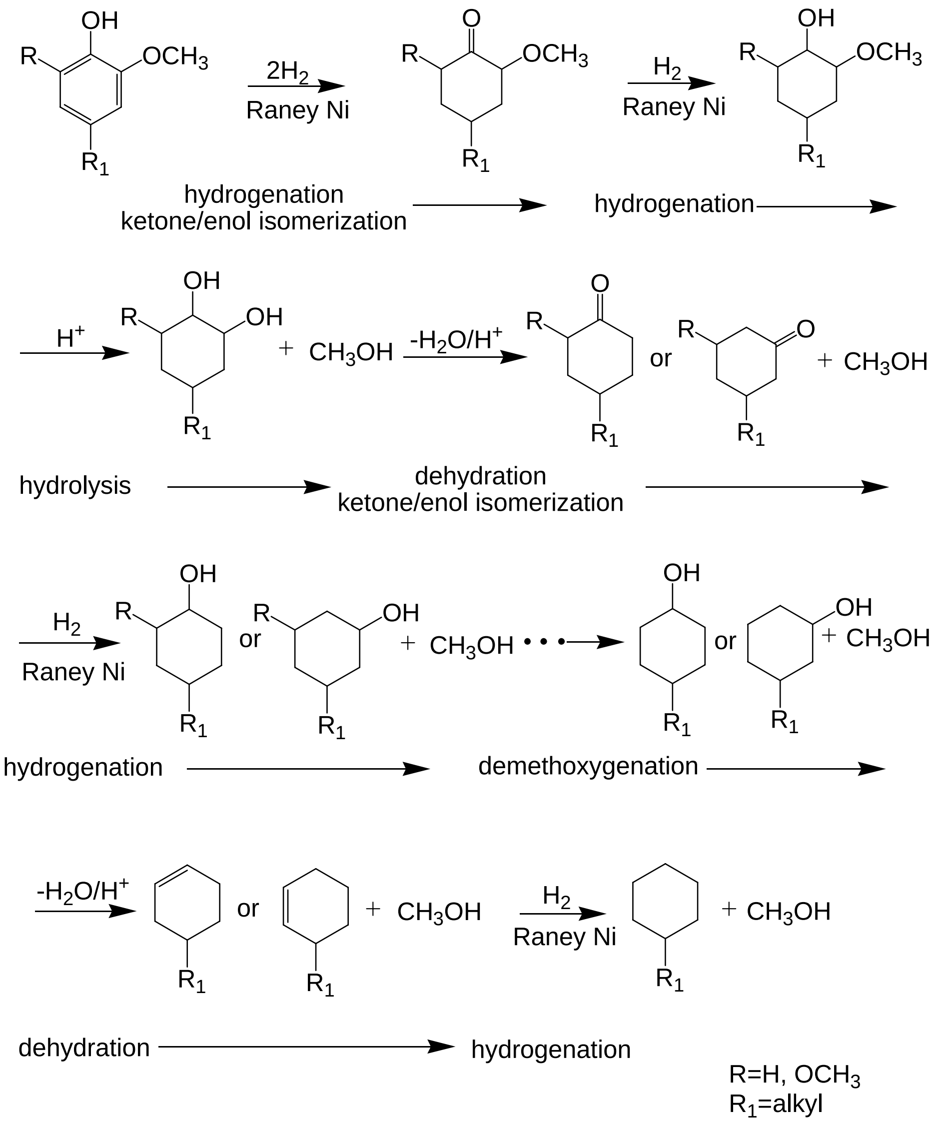
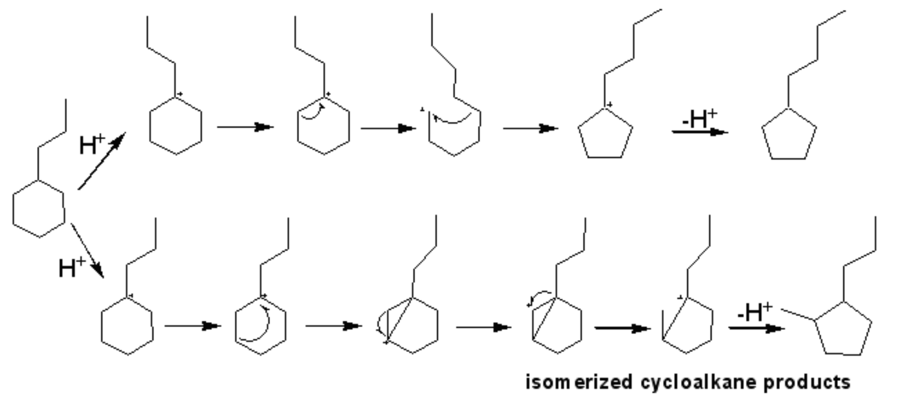


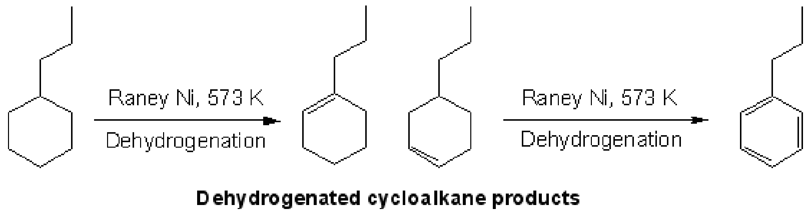
Figure S2. Hydrodeoxygenation of the aqueous phenolic mixture using Raney Ni catalysts and solid acid Nafion/SiO_2 at 573 K and 4 MPa H_2 for 2 h, before reaction (A) and after reaction (B).


2H2
Raney Ni
H2
Raney Ni
hydrogenation
ketone/enol isomerization
hydrogenation
H+
-H2O/H+
+ CH3OH
hydrolysis
dehydration
ketone/enol isomerization
H2
Raney Ni
hydrogenation
demethoxygenation
-H2O/H+
+ CH3OH
H2
Raney Ni
dehydration
hydrogenation
R=H, OCH3
R1=alkyl

(a)


H+
H+
-H+
-H+
isomerized cycloalkane products

(b)



(c)

Figure S3. (a) Proposed reaction pathway for aqueous-phase hydrodeoxygenation of bio-derived phenolic monomers over Raney Ni and Nafion/SiO_2 at catalysts, (b) *n*-propylcyclohexane isomerization with acidic components, (c) *n*-propylcyclohexane hydrogenation/dehydrogenation equilibrium over Raney Ni catalysts at 573 K. The corresponding product analysis (hydrocarbons and methanol) in GC-MS spectrum was provided in Figure S1.

Table S1. Concentration of LAS and BAS calculated from Py-IR for Nafion/SiO_2.

T (K)	Radius (cm)	Weight (mg)	Conc LAS (μmol/g)	Conc BAS (μmol/g)	Total acid conconcentration (μmol/g)
373	0.3175	2.4	0	158	158
423	0.3175	2.4	0	120	120
473	0.3175	2.4	0	69	69

Table S2. Calculation for the potential Brønsted acidity of the solid acids in the experiments.

Acid type	Weight (acid)/g	*n* (Brønsted acidity)/mol
Nafion water suspension (10 wt%)	1.00*10%=0.10	n(-SO_3H)=0.10/($M_{Nafion-unit}$)= 0.10/1000=10^{-4}
Nafion/SiO_2 (13 wt%)	0.80*13%=0.10	n(-SO_3H)=0.10/($M_{Nafion-unit}$)= 0.10/1000=10^{-4}
Zeolite H-Beta[a]	0.080	n(Al)=0.080*(Al content in zeolite %)/27=0.080*3.37%/27=10^{-4}
Zeolite H-Y[b]	0.095	n(Al)=0.095*(Al content in zeolite %)/27=0.095*2.84%/27=10^{-4}

[a] CP-814 E, Si/Al=12.5

[b] CBY 720, Si/Al=15

Reference:

[1] H. Lei, Z. Song, D. Tan, X. Bao, X. Mu, B. Zong, E. Min, *Appl. Catal. A,* **2001,** *214,* 69 – 76.