# **Supporting Information**

# Selective Conversion of Lignin to Ethylbenzene

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#### **Experimental Section**

**Chemicals:** Corncob lignin (Shandong Longlive Co., Klason lignin content: 80 wt.%), n-dodecane (Sinopharm, > 98% GC assay), hydroconiferyl alcohol (J&K, > 99% GC assay), methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate (Alfa Aesar, > 97% GC assay), Na<sub>2</sub>SiO<sub>3</sub> (Sinopharm, SiO<sub>2</sub>: 4.82 mol·L<sup>-1</sup>, Na<sub>2</sub>O: 1.39 mol·L<sup>-1</sup> NaOH (Sinopharm, AR), hexadecyl trimethyl ammonium bromide (Sinopharm, AR), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sinopharm, AR), AlCl<sub>3</sub> (Sinopharm, AR), NH<sub>3</sub>·H<sub>2</sub>O (Sinopharm, AR), urea (Sinopharm, AR), Tetrahydrofuran (J&K, 99.8%, HPLC/spectro,non(BHT), DMSO-d<sub>6</sub> (99.9%, Cambridge Isotope Laboratories), Acetone-d<sub>6</sub>, (99.9%, Cambridge Isotope Laboratories), Chloroform-d (99.8%, Cambridge Isotope Laboratories), Silicalite-1, HZSM-5(300), HZSM-5(70), HZSM-5(5) were all purchased from the Catalyst Plant of Nankai University. Air, H<sub>2</sub> and N<sub>2</sub> gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

**Synthesis of the Ni catalysts supported on HZSM-5:** In a typical experiment, The Ni catalysts supported on HZSM-5(5) were synthesized by DP method. Nickel nitrate (10.2 g) was firstly dissolved in the deionized water (250 mL), and one part of this solution (210 mL) was suspended with HZSM-5(5) (2.0 g) and then heated to 70 °C. The rest latter solution (40 mL) was dissolved with urea, and then drop-wise added into the former HZSM-5(5) suspension. Afterwards, the mixture was held at 90 °C with stirring for 10 h. After cooling down, the solid was filtered, and washed by distilled water. Finally, the samples were dried at 100 °C overnight, calcined in flowing air at 400 °C for 4 h (flowing rate = 100 mL·min<sup>-1</sup>, heating rate: 2 °C·min<sup>-1</sup>).

## Catalyst characterization

**Characterization of lignin raw material:** Organic elemental analysis (C, H, N, and S) of lignin was analyzed by the classical oxidation method in a Vario EL III instrument. Determination of the Klason lignin content in the crude sample: Firstly, the corncob lignin (1.0 g) was extracted by an ethanol-benzene mixture (volume ratio: 1:2) in a Soxlet apparatus for 4 h. Then the as-received sample was dried, and added into a  $H_2SO_4$  solution (15 mL, 72 wt%) at 25 °C, stayed at stirring for 4 h. Afterwards, the concentrated  $H_2SO_4$  solution was diluted to 3 wt%, and then reacted under reflux with stirring for another 4 h. Finally, the solid was filtered, washed by hot water until neutralized, dried under vacuum at 105 °C for 12 h, and weighted.

The Klason lignin content = 
$$\frac{mass_{residue \ soild}}{mass_{corncob \ lignin}} \times 100\%$$
 (1)

**Characterization of the Ni catalysts and parent materials:** The Ni contents were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP–AES) with a Thermo IRIS Intrepid II XSP emission spectrometer after dissolving the catalyst in a HF solution. XRD measurement was conducted on a Rigaku Ultima IV X-ray diffractometer (35 kV and 25 mA) using Cu Ka radiation (k = 1.5405 Å). The Brunauer–Emmett–Teller (BET) specific surface areas were measured by using nitrogen adsorption at 77 K on a Belsorp-Max instrument. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) was detected on a Tecnai G<sup>2</sup> f30 microscope. The IR spectra of adsorbed pyridine (IR-Py) were recorded with a Nicolet NEXUS 670 FTIR spectrometer equipped with an in-situ IR cell. The samples were activated in vacuum at 673 K for 1 h before equilibrated with pyridine at 423 K, then evacuated at 423 K for 1 h. 2D HSQC and <sup>13</sup>C NMR spectra were measured at 500 MHz in d<sub>6</sub>-DMSO (or Acetone-d<sub>6</sub> and Chloroform-d) using TMS signal.

**Identification and Quantitation of the products:** Liquid products were analyzed on a gas chromatograph (GC) equipped with GC-MS (Shimadzu QP-2010 Ultra). Quantification of liquid yields used undecane as an internal standard. Analysis for gaseous products was performed on a GC equipped with a thermal conductivity detector (TCD) and (TDX-01: 30 cm × 3 mm, TDX-01: 2 m × 3 mm) columns, as well as a flame ionization detector (FID) and a HP-PLOT Q (50 m × 0.53 mm × 25 µm) capillary column.



## **Catalytic testing**

**Catalytic tests of hydrodeoxygenation of lignin:** A typical experiment for hydrodeoxygenation of lignin was carried out as follows: 2.0 g lignin, 0.5 g Ni/S-1 catalyst, *n*-dodecane (80 mL) were charged into a batch autoclave. The reactor was firstly flushed with  $H_2$  for three times, and to 6 MPa  $H_2$  at ambient temperature, and then heated up to 300 °C and the reaction started at a stirring speed of 700 rpm. The liquid products were *in situ* sampled during the catalytic run, and then the

liquid products were analyzed by GC and MS. After reaction, the remaining solid was filtrated and dried at 110 °C overnight.

**NMR** detecting the products after the hydrodeoxygenation of lignin: lignin (2.0 g), Ni/S-1 catalyst (0.5 g), *n*-hexane (80 mL) were charged into a batch autoclave, and reacted at 300 °C and 6 MPa H<sub>2</sub> with different reaction time. After reaction of 2h, the reacted liquid and solid phase can be achieved by filtration, respectively. The liquid products from the hydrodeoxygenation of lignin were obtained by drying the solvent at 70 °C. The remaining solid phase consist of the catalyst, the unconverted lignin, and the depolymerized oligomers. The solid catalyst was removed by filtration of the dissolved solid phase with using the dioxane solvent. The gained solid products in the dioxane was distilled at 102 °C to eliminate the dioxane and then the solid products were obtained. In the NMR tests, DMSO-d<sub>6</sub> was used to dissolve the lignin and the gained solid-phase products, while, the liquid products were dissolved by using the mixed solvents of DMSO-d<sub>6</sub>: Acetone-d<sub>6</sub>: Chloroform-d (2:1:1).



**Figure S1**: Wide-angle X-ray diffraction (XRD) of Ni/S-1, Ni/HZSM-5(300), Ni/HZSM-5(70), and Ni/HZSM-5(5).



**Figure S2**: TEM images and its Ni particle size distributions of Ni/S-1, Ni/HZSM-5(300), Ni/HZSM-5(70), Ni/HZSM-5(5).



Figure S3: SEM images of S-1, HZSM-5(300), HZSM-5(70), and HZSM-5(5).



**Figure S4**. The nitrogen adsorption-desorption isotherms of Ni/S-1, Ni/HZSM-5(300), Ni/HZSM-5(70), Ni/HZSM-5(5).



**Figure S5**: The Brönsted and Lewis acids of Ni/S-1, Ni/HZSM-5(300), Ni/HZSM-5(70), Ni/HZSM-5(5) determined by the Py-IR.



**Figure S6**: Hydrodeoxygenation of lignin over Ni/HZSM-5 catalysts with different Si/Al ratios. Reaction conditions: lignin 2.0 g, catalyst 0.5 g, dodecane 80 mL,  $H_2 = 6$  MPa, T = 300 °C, t = 2 h.



**Figure S7**: The product distributions from hydrodeoxygenation of lignin over Ni/S-1, Ni/HZSM-5(300), Ni/HZSM-5(70), Ni/HZSM-5(5). Reaction conditions: lignin 2.0 g, catalyst 0.5 g, dodecane 80 mL,  $H_2 = 6$  MPa, T = 300 °C, t = 2 h.



**Figure S8**: The catalyst screening for the dehydrogenation of ethylcyclohexane to ethylbenzene. Reaction conditions: WHSV =  $0.0237 h^{-1}$ , 0.5 MPa H<sub>2</sub>, and 500 °C.



**Figure S9**: The influences of hydrogen pressure on the dehydrogenation of ethylcyclohexane to ethylbenzene over 2wt%Pt-2wt%Sn/Al<sub>2</sub>O<sub>3</sub>. Reaction conditions: WHSV = 0.0237 h<sup>-1</sup>, and 500 °C.



**Figure S10**: The influences of temperature on the dehydrogenation of ethylcyclohexane to ethylbenzene over 2wt%Pt-2wt%Sn/Al<sub>2</sub>O<sub>3</sub>. Reaction conditions: WHSV = 0.0237 h<sup>-1</sup>, and 0.5 MPa H<sub>2</sub>.



**Figure S11**: The influences of WHSV on the dehydrogenation of ethylcyclohexane to ethylbenzene over 2wt%Pt-2wt%Sn/Al<sub>2</sub>O<sub>3</sub>. Reaction conditions: 0.5 MPa H<sub>2</sub>, and 500 °C.



**Figure S12**: Time-on stream performance of hydrodeoxygenation of lignin over Ni/S-1 catalyst. Reaction conditions: lignin 2.0 g, catalyst 0.5 g, dodecane 80 mL,  $H_2 = 6$  MPa, T = 300 °C

Entry	Ni/HZSM-5 (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> )	S <sub>total</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	S <sub>meso</sub> (m²⋅g⁻¹)	S <sub>micro</sub> (m <sup>2</sup> ·g <sup>-1</sup> )
1	5	205	141	64
2	70	268	189	79
3	300	266	195	71
4	+∞	244	139	95

**Table 1**: BET analysis of the synthesized Ni/HZSM-5 catalysts.

Component	Residual	٨eb		Water	Lignin
(wt. %)	sugar	ASII		vvalei	
Sample	3	12		5	80
Element	C		N	6	
(wt. %)	C	11	IN	3	0
Sample	62.4	5.34	0.45		31.8

 Table S2. The composition and elemental analysis of enzymatic lignin.

<sup>a</sup> The remaining part is calculated to be the oxygen content.

**Table S3.** The elemental composition of lignin and calculated theoretical liquid alkane yield.

	Theoretical yield: $C_9H_{18} = 54.1$
$C_{10}H_{10.3}O_{3.8} \to C_9H_{7.3}O_{2.8}(OCH_3)_{1.0}$	wt.%
Lignin unit M <sub>w</sub> = 191 g·mol⁻¹	
Assumed that it contains one $-OCH_3$ group in the	H <sub>2</sub> O = 32 wt.%
lignin unit	
	CH₄ = 8.4 wt.%