Supporting Information for

Ni₅Fe₅/Al₂O₃ catalytic hydrogenolysis of lignin: mechanism investigation and selectivity regulation

Zhensheng Shen[a,b], Wei Wang[a,b], Lun Pan[a,b,c], Zhenfeng Huang[a,b], Xiangwen Zhang[a,b,c], Chengxiang Shi[a,b,*] and Ji-Jun Zou[a,b,c,*]

[a] Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

[b] Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

[c] Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China

[*] Corresponding author.

E-mail address: cxshi@tju.edu.cn, jj_zou@tju.edu.cn

This supporting document includes:

Number of Tables: 1

Number of Figures: 11

Total pages: 14

Experimental

Catalyst Preparation

Ni$_5$Fe$_5$/Al$_2$O$_3$ (Nb$_2$O$_5$, TiO$_2$, ZrO$_2$) were prepared by the incipient wetness method. 0.2476g Ni(NO$_3$)$_2$·6H$_2$O, 0.3617g Fe(NO$_3$)$_3$·9H$_2$O are dissolved in a certain volume of deionized water to form a uniform solution and then slowly added to 1g of oxide carrier. After aging at room temperature for 12h, maintain at 60°C for 12h to remove excess water. Then the prepared catalysts were calcined at 500°C for 3 h and reduced by 10% H$_2$/90% Ar at 400°C for 3 h in a tubular furnace. The synthesis of Ni$_{10-x}$Fe$_x$/Al$_2$O$_3$ is the same as the above method, except that the feeding ratio of Ni and Fe precursors is different.

Catalyst characterization

The X-ray powder diffraction pattern was recorded by an X-ray diffractometer (XPERTPRO, PANalytical B.V.), Cu target Kα X-ray, λ= 0.154 nm, operated at 40 kV, 200 mA, measuring range 2θ = 5°~80°, the step length is 0.02°, and the scanning speed is 5°/min. The scanning electron microscope images (SEM) were recorded by field emission scanning electron microscope (Apero S LoVac, FEI). The transmission electron microscope (TEM) and high-resolution image (HRTEM) of the catalyst were obtained using the JEM-F200 field emission electron microscope operating at 200 kV. The instrument is equipped with STEM dark field detector. The specific surface area of samples was determined by the American Micromerics ASAP 2020 nitrogen physical adsorption/desorption analyzer. Before the experiment, 0.1 g of the sample was degassed at 300°C and 10^{-4} Pa for more than 8 h, and the liquid nitrogen temperature was -196°C; The specific surface area of the catalyst was calculated by Brunauer-Emmett-Telle (BET) method. NH$_3$ temperature programmed desorption (NH$_3$-TPD) was determined on the chemisorption instrument. Put 50 mg of the dried catalyst in the sample test tube, purge it for 2 h in an inert atmosphere of 300°C, and cool it to 50°C. In an NH$_3$/Ar atmosphere, adsorb it for 2 h to saturation, and then purge it for 1 h in an Ar atmosphere of 50 mL/min, and then raise the temperature from 50°C left to right at a heating rate of 10°C/min to 700°C in an Ar atmosphere of 50 mL/min. The H$_2$ temperature programmed reduction (H$_2$-TPR) curve was determined by an automatic chemisorption instrument (AutoChem II 2920, American Mike Instrument). Purge 100 mg of sample in Ar (30 mL/min) at 300°C for 30 minutes, and then cool to room temperature. Use the reducing gas containing 5% H$_2$/95% Ar, the flow rate is 30 mL/min, the heating rate is 10°C/min, and the room temperature rises to 700°C. Use

the TCD detector to monitor the consumption of H_2. X-ray photoelectron spectroscopy (XPS) is recorded by an X-ray photoelectron spectroscopy analyzer (K-Alpha+, Thermo).

Catalyst activity tests

The reduction catalytic fractionation of beech sawdust and the conversion of model compounds were carried out in a 100 ml Hastelloy high-pressure reactor. For each reaction, add 1 g of wood powder, 0-0.2 g of catalyst, and 20 ml of methanol to the reactor, and then replace the gas in the reactor with pure N_2 and pure H_2 three times respectively, and pressurize with H_2 to the target pressure (0-4 Mpa). After that, raise the temperature to the target temperature (190-270°C) at 5°C/min and maintain a certain reaction time (1-5 h). After the reaction, immediately cool the reactor to room temperature with ice water. After the reactor is opened, the solid-liquid mixture is separated by suction filtration., and weigh the solid product (solid residue after reaction and catalyst) after drying overnight at 100°C; After the solvent is removed by the rotary evaporator, the liquid product is extracted with dichloromethane and water for three times, and the dichloromethane phase (lignin oil) is dried overnight at 45°C and then weighed. GC and HPLC analyses (Figure S1) of the pre-extraction, post-extraction and aqueous phase products showed that cellulose hemicellulose derivatives were extracted into the aqueous phase and that the quantification of lignin oil was accurate. Using n-decane as the internal standard, the product was quantified by gas chromatography (GC, Shimadzu 2010 plus), equipped with a hydrogen flame ionization detector (FID) and HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). The heating process is 40°C for 1 minute, then increase to 150°C at the rate of 10°C/min for 2 minutes, and then increases to 300°C at the rate of 20°C/min for 10 minutes. The product was identified by a GC-MS combination (GC-MS, Shimadzu QP 2010S). The yield and selectivity of the product are calculated by the following formula:

$$Phenolic\ monomers\ yield = \frac{Mass\ (total\ monomers)}{Mass\ (lignin)} * 100\% \tag{1}$$

$$X\ monomer\ selectivity = \frac{Mass\ (X\ monomer\ selectivity)}{Mass\ (total\ monomers)} * 100\% \tag{2}$$

$$Lignin\ oil\ yield = \frac{Mass\ (Lignin\ oil)}{Mass\ (lignin)} * 100\% \tag{3}$$

$$Solid\ residue\ yield = \frac{Mass(solid\ residue)}{Mass\ (beech\ sawdust)} * 100\% \tag{4}$$
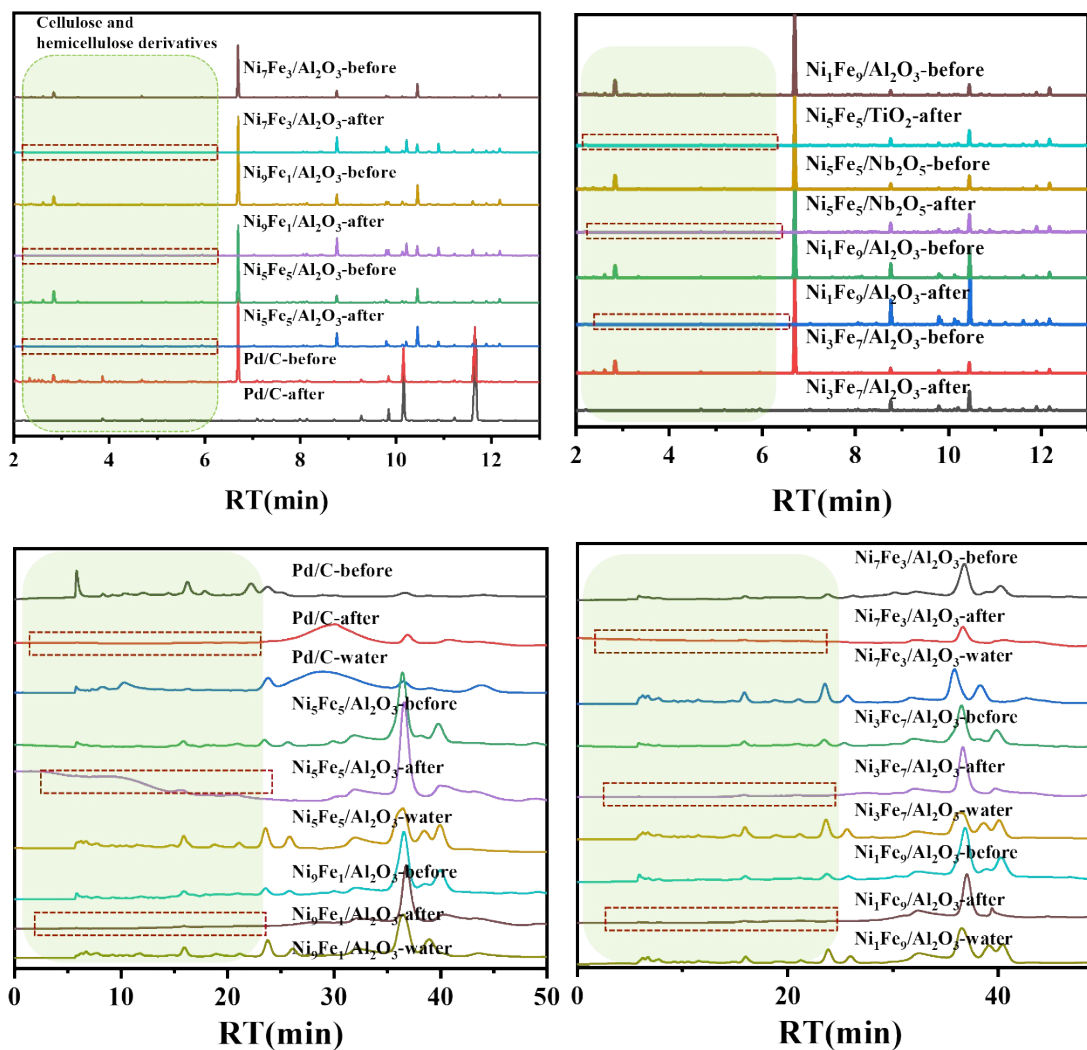
Figure S1 GC (a, b) and HPLC (c, d) chromatograms of the pre-extraction, post-extraction and aqueous phases.

Table S1. Catalysts composition and notation information.

Catalysts	Support	Theoretical Ni:Fe (wt/wt)	Experimental Ni:Fe (wt/wt)
Ni_5Fe_5/Nb_2O_5	Nb_2O_5	5:5	3.66:3.03
Ni_5Fe_5/TiO_2	TiO_2	5:5	3.89:3.16
Ni_5Fe_5/ZrO_2	ZrO_2	5:5	3.26:2.70
Ni_{10}/Al_2O_3	Al_2O_3	10:0	7.02:0
Ni_9Fe_1/Al_2O_3	Al_2O_3	9:1	5.91:0.65
Ni_7Fe_3/Al_2O_3	Al_2O_3	7:3	5.06:2.28
Ni_5Fe_5/Al_2O_3	Al_2O_3	5:5	3.65:4.05
Ni_3Fe_7/Al_2O_3	Al_2O_3	3:7	2.07:4.49
Ni_1Fe_9/Al_2O_3	Al_2O_3	1:9	0.68:6.52
Fe_{10}/Al_2O_3	Al_2O_3	0:10	0:6.72
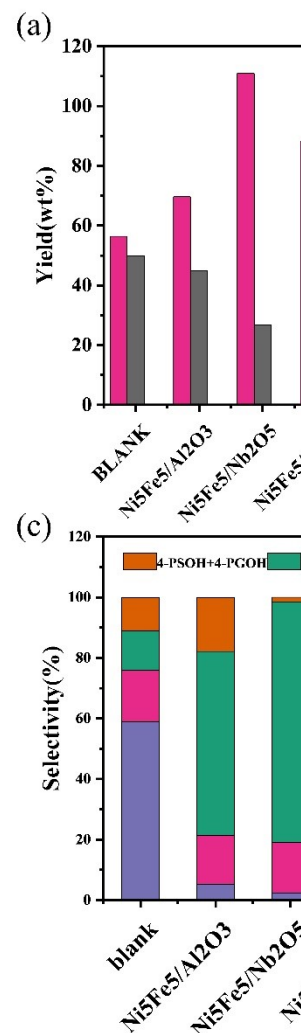
Figure S2. (a) Lignin oil yield and solid residue of different catalysts; (b) Monomers yield of different catalysts; (c) Selectivity of different catalysts; (d) Lignin oil yield and solid residue of different catalysts.
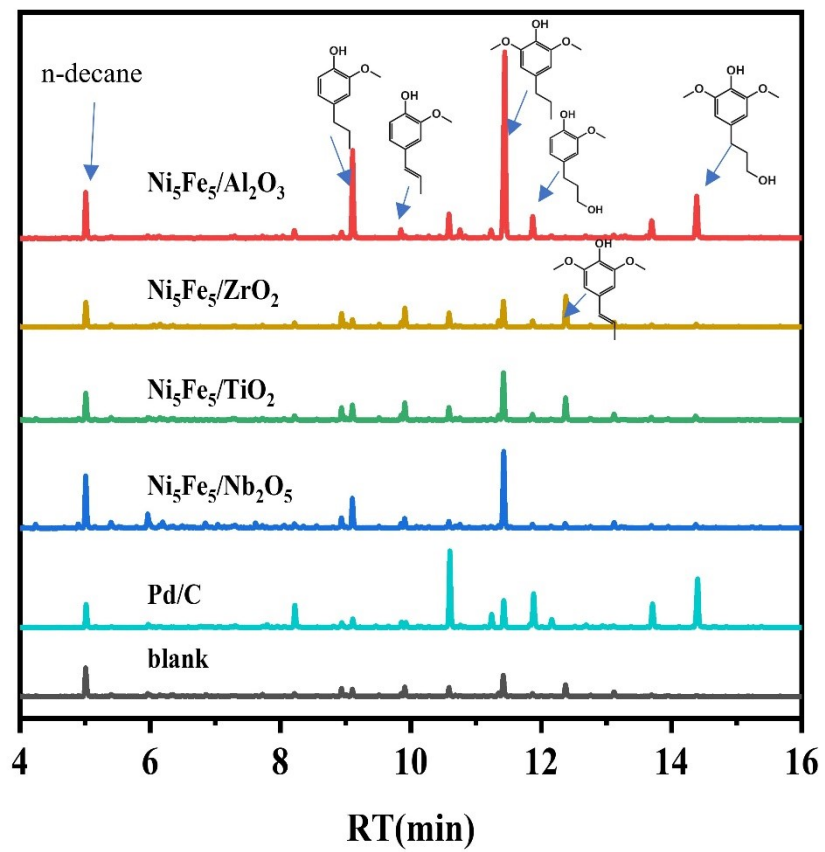
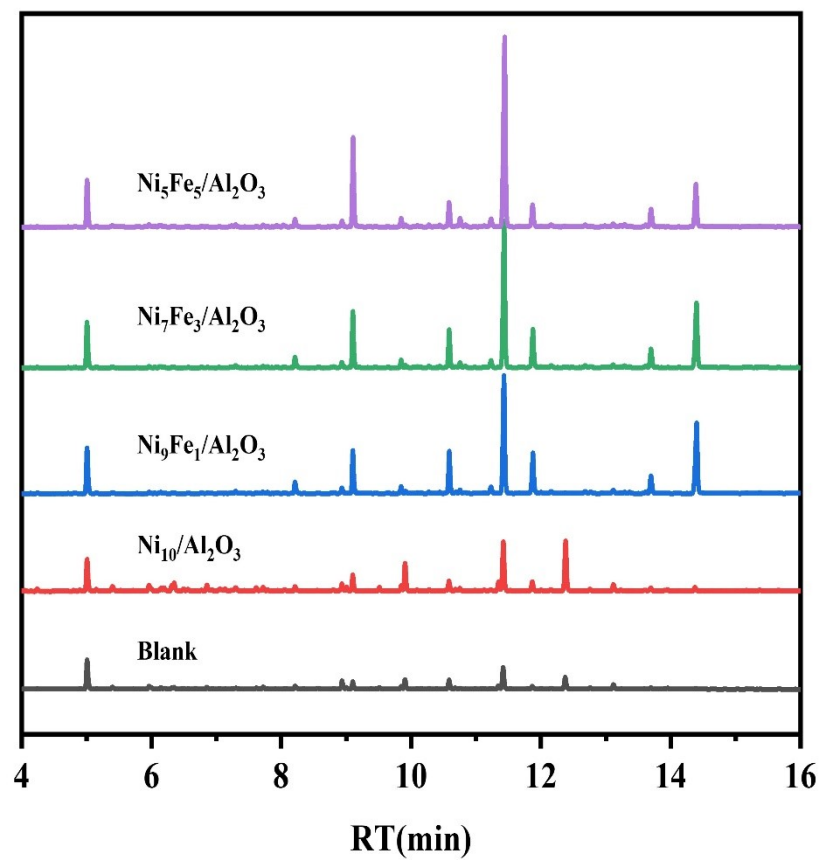Figure S3 GC spectra of the lignin-derived monomers

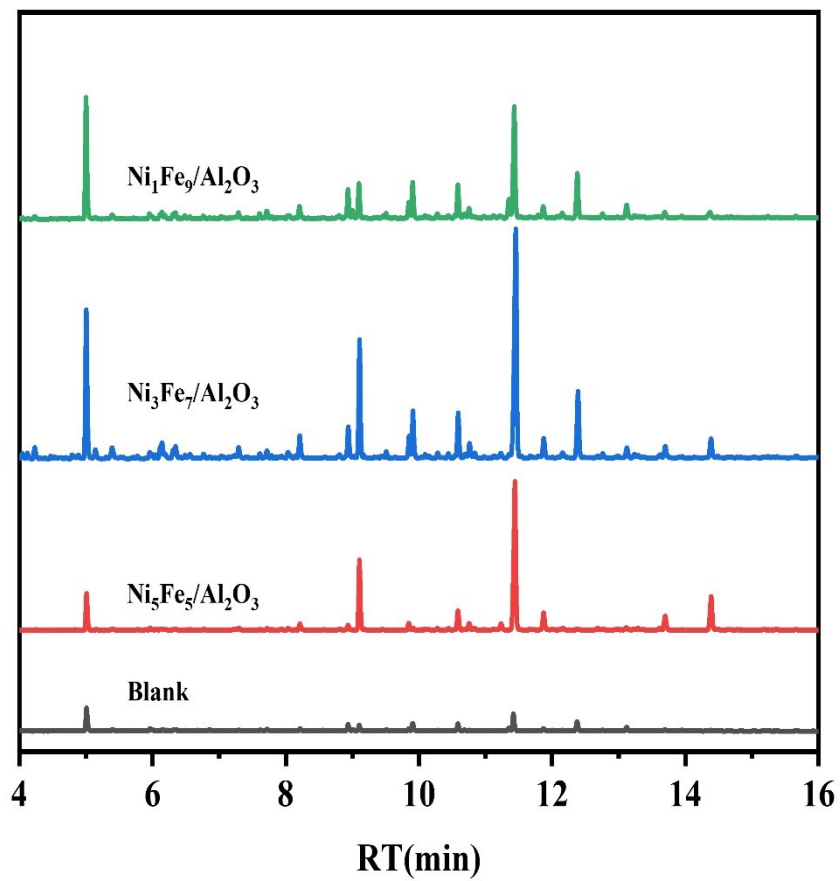Figure S4. GC spectra of the lignin-derived monomers

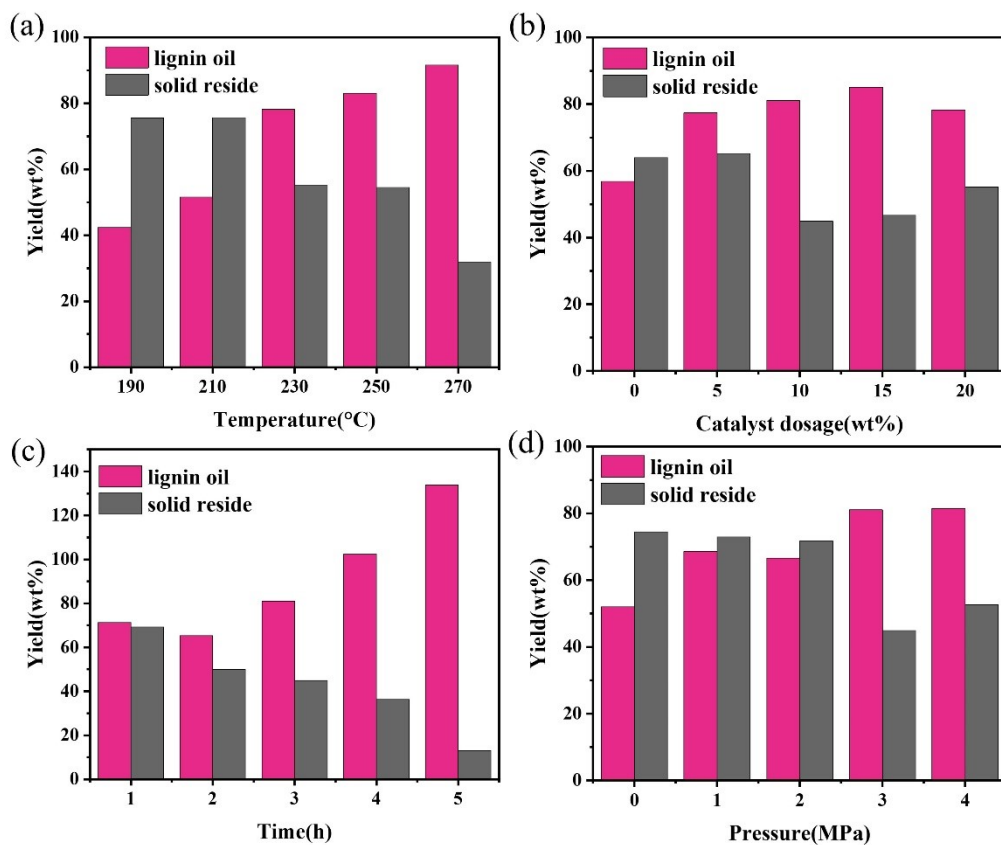Figure S5. GC spectra of the lignin-derived monomers

Figure S6. Influences of reaction parameters on lignin oil yield and solid residue. (a) Temperature; (b) Catalyst dosage; (c) Time; (d) Pressure.
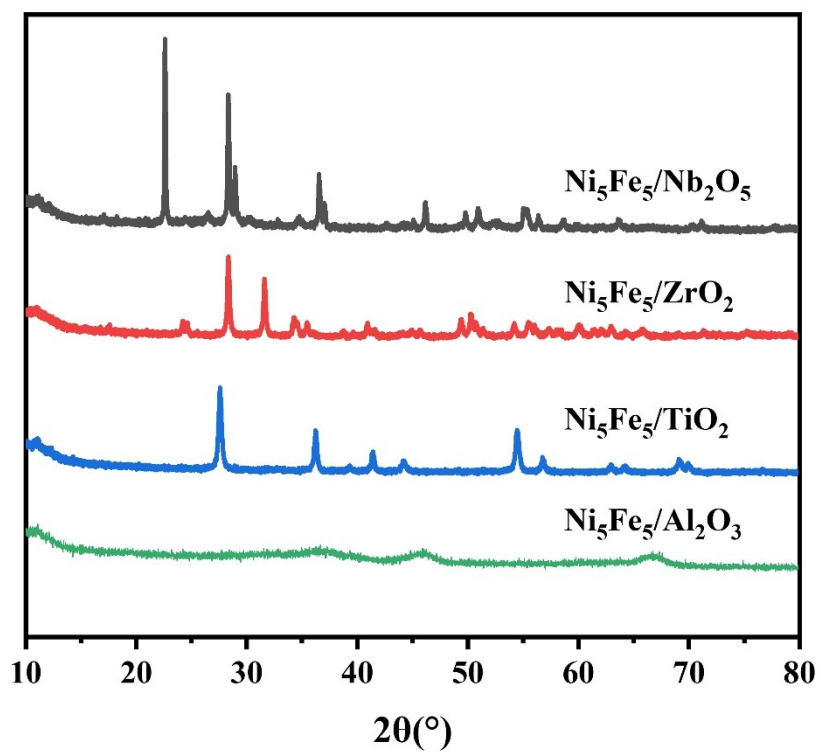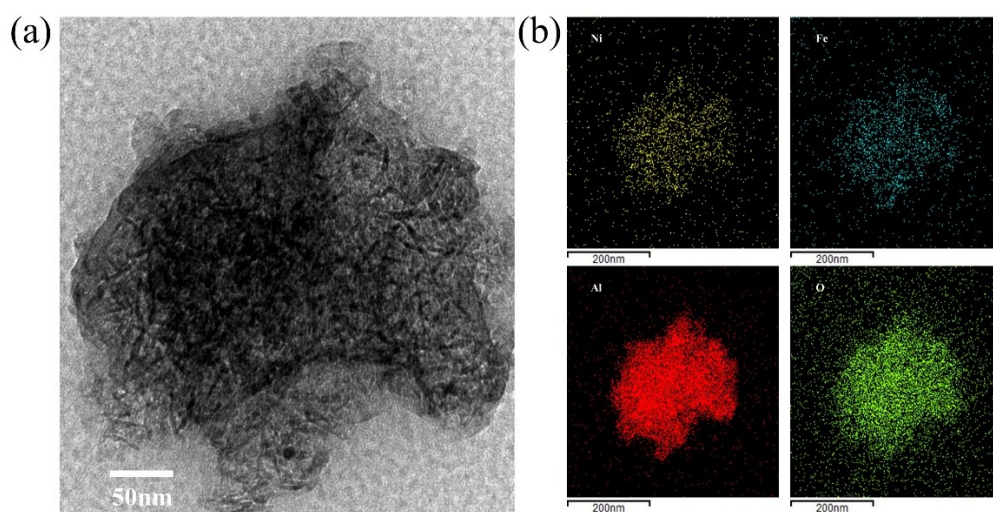
Figure S7. (a) XRD of different catalysts.

Figure S8 (a) TEM of Ni_5Fe_5/Al_2O_3 catalyst; (b) EDS of Ni_5Fe_5/Al_2O_3 catalyst.
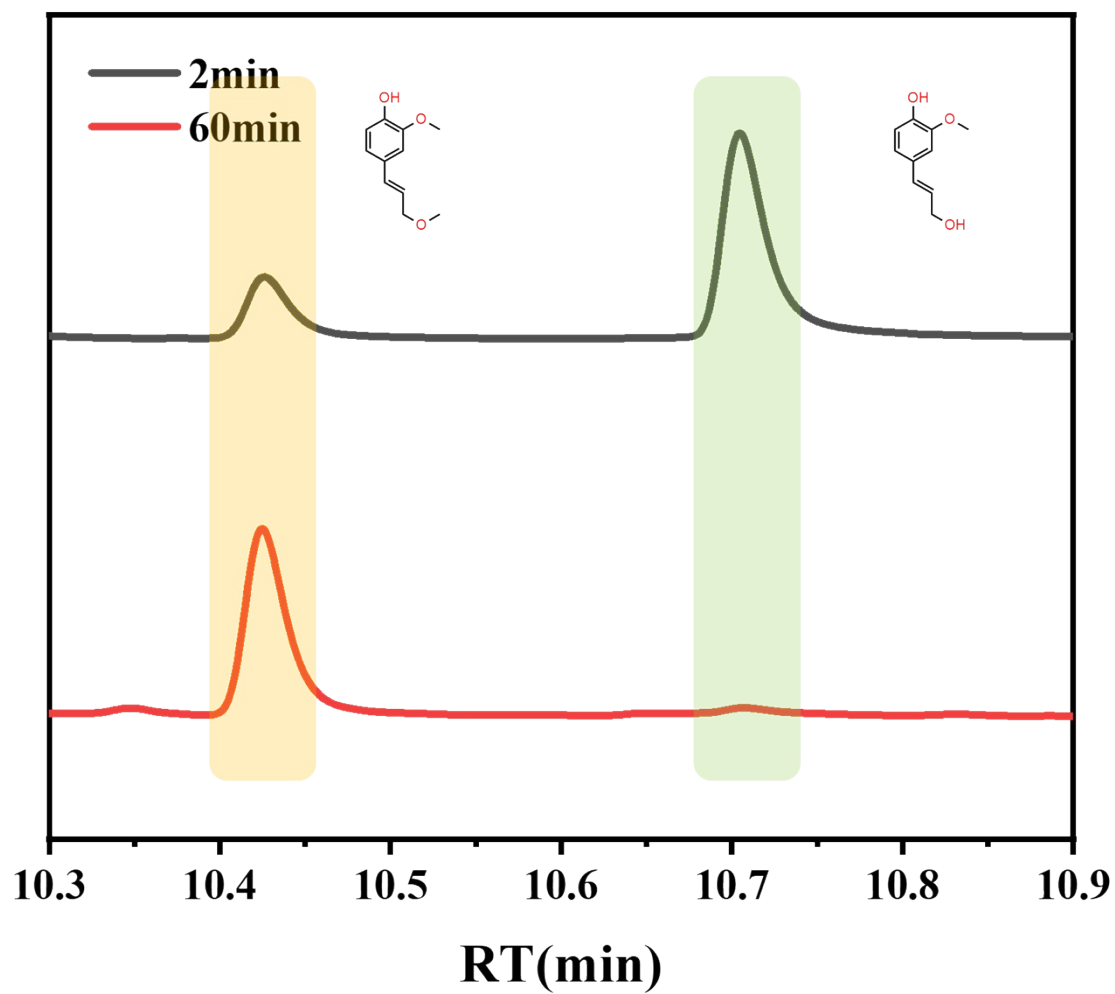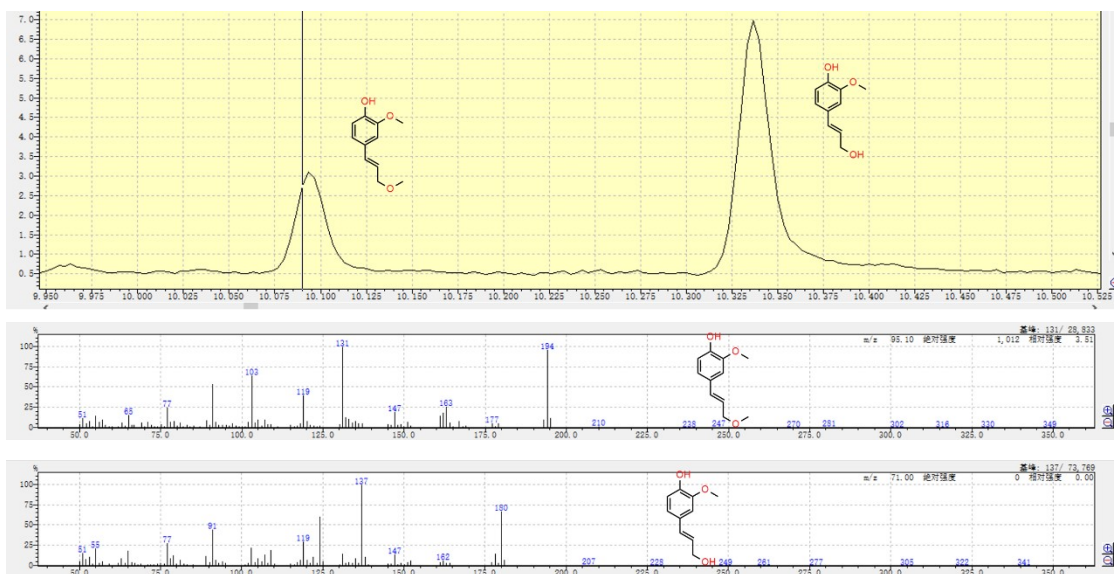
Figure S9. Gas chromatograms

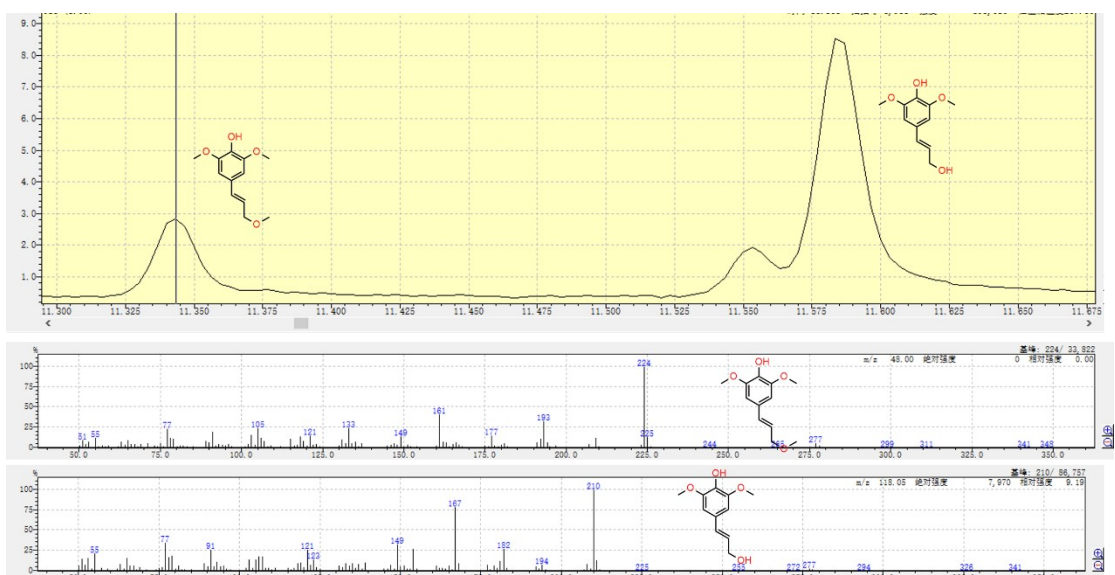Figure S10 Mass spectrometry of intermediate 1D and 2A.
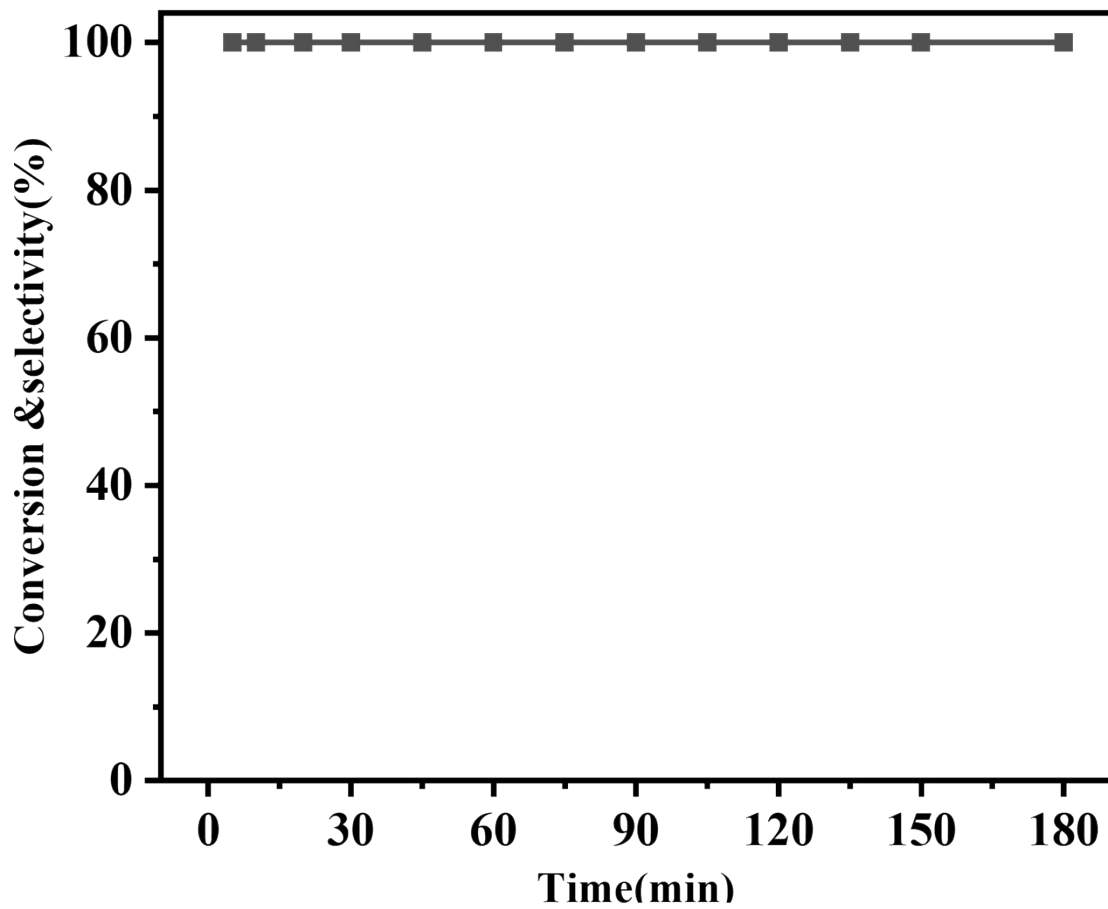

Figure S11 Mass spectrometry of intermediate 3D and 3E.

Figure S12 The conversion curves for bisphenol F.