Supporting Information

Conversion of High Concentration of Lignin to Cyclic Alkanes by introducing Pt/HAP into Ni/ASA Catalyst

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Experimental Section

Chemicals:

Corncob lignin (Shandong Longlive Co., Klason lignin content: 80 wt.%), n-dodecane (Sinopharm, > 98% GC assay), $Al(NO_3)_3·9H_2O$ (Sinopharm, AR), Na_2SiO_3 (Sinopharm, 30%SiO_2), $NH_3·H_2O$ (Sinopharm, AR), NH_4Cl (Sinopharm, AR), alcohol (J&K, > 99% GC assay), AR), $Ni(NO_3)_2·6H_2O$ (Sinopharm, AR), urea (Sinopharm, AR), $PtCl_4$ (J&K, 58%), $RuCl_3$·3H2O (J&K, 59.5%), $PdCl_2$ (J&K, 59.5%), Hydroxylapatite (Aladdin, ≥ 97%,＜ 100 nm partical size (BET)), SiO_2 (J&K, 99.8%), Al_2O_3 (Chengdu Makaxi Chemical Co. , Ltd., AR), HZSM-5 (Nankai University, Si/Al ratio = 5), MgO (Shanghai mcqueen Co. , Ltd., AR), 1,4-dioxide (Sinopharm, AR), N,N-Dimethylformamide (Shanghai Richjoint Chemical Reagent Co. , Ltd., AR), Tetrahydrofuran (J&K, 99.8%, HPLC/spectro, non(BHT)), DMSO-d_6 (Innochem, 99.9%,), Acetone-d_6, (Innochem, 99.9%), Chloroform-d (Innochem, 99.8%), Air, H_2 and N_2 gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Synthesis of amorphous-silica-alumina (ASA) support:

ASA was prepared by the co-gelification method. $AlCl_3·6H_2O$ (156.0 g) and Na_2SiO_3 (58.4 g) was dissolved in the deionized water (1000 mL), stirring for two hours, then $NH_3·H_2O$ was added into the mixed solution to change the pH to 9.0 under stirring. After stirring for one hour, the sample was washed with deionized water until neutral. Afterwards, the samples were dried at 100 °C overnight. The ground support was ion exchanged with NH_4Cl for three times, Dried at 100 °C overnight. Prior to use, the calcined ASA in flowing air at 550 ℃ for 4h (flowing rate = 100 $mL·min^{-1}$, heating rate: 2 $°C·min^{-1}$).

Synthesis of the Ni catalysts supported on ASA:

In a typical experiment, the Ni catalysts supported on ASA were synthesized by deposition precipitation 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 ASA (2.0 g) and then heated to 70 °C. The rest solution (40 mL) was dissolved with urea, and then drop-wise added into the former ASA suspension. Afterwards, the mixture was held at 90 °C with stirring for 10 h. After cooling down, the solid was separated by vacuum filtration, and the sample was washed serval time with deionized water. Finally, the samples were dried at 100 °C overnight. The ground sample was calcined at 400 ℃ for 4h (flowing rate = 100 $mL·min^{-1}$, heating rate: 2 $°C·min^{-1}$) and reduced with hydrogen at 450 ℃ for 4h (flowing rate = 100 $mL·min^{-1}$, heating rate: 2 $°C·min^{-1}$).

Synthesis of the Ni-X(X=Pd, Pt, Ru) catalysts supported on ASA:

The NiX supported on ASA catalysts were synthesized by co-deposition precipitation method. Using Pd-Ni/ASA as an example, $Ni(NO_3)_2·6H_2O$ and $PdCl_2$ were firstly dissolved in the deionized water (250 mL), and one part of this solution (210 mL) was suspended with ASA (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 ASA suspension. Afterwards, the mixture was held at 90 °C with stirring for 10 h. After cooling down, the solid was separated by vacuum filtration, and the sample was washed serval time with deionized water. Finally, the samples were dried at 100 °C overnight. The ground sample was calcined at 350 ℃ for 4h (flowing rate = 100 mL·min^{-1}, heating rate: 2 °C·min^{-1}) and reduced with hydrogen at 460 ℃ for 4h (flowing rate = 100 mL·min^{-1}, heating rate: 2 °C·min^{-1}).

Synthesis of the Pt catalysts supported on HAP:

The Pt/HAP were synthesized by ion exchange method. HAP (1g) was added to 100ml solution contained of appropriate amount of $PtCl_4$. The suspension was reflex at 80 ℃ for 8h. After cooling down, the solid was separated by vacuum filtration, and the sample was washed serval time with deionized water. Then the sample was dried at 60 ℃ overnight. The ground sample was calcined at 350 ℃ for 4h (flowing rate = 100 mL·min^{-1}, heating rate: 2 °C·min^{-1}) and reduced with hydrogen at 350 ℃ for 4h (flowing rate = 100 mL·min^{-1}, heating rate: 2 °C·min^{-1}).

Synthesis of the Pt, Pd, Ru catalysts supported on SiO_2 or HZSM-5 or MgO:

In a typical experiment, the catalysts were synthesized by impregnent method. Using Pt/SiO_2 as an example, firstly an $PtCl_4$ solution was prepared, and then was mixed with SiO_2 at continuous stirring at ambient temperature overnight. Afterwards, the sample was rotated to remove water and dried at 60 ℃ overnight. The ground sample was calcined at 350 ℃ for 4h (flowing rate = 100 mL·min^{-1}, heating rate: 2 °C·min^{-1}) and reduced with hydrogen at 350 ℃ for 4h (flowing rate = 100 mL·min^{-1}, heating rate: 2 °C·min^{-1}).

Catalyst characterization:

Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 microscope.

Transmission electron microscopy (TEM) was detected on a Tecnai G^2 f30 microscope.

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 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 mixed HF and aqua regia solution.

2D HSQC and ^{13}C NMR spectra were measured at 500 MHz in d_6-DMSO (or Acetone-$d_{6,}$ and Chloroform-d) using TMS signal.

The temperature programmed desorption (TPD) analysis of catalysts was performed by using TP5080 (Xianquan Instrument, Tianjin) apparatus equipped with a thermal conductor detector (TCD), using a 10% NH_3/N_2 mixture and CO_2 (flowing rate: 30 mL·min^{-1}).

The temperature programmed reduction (TPR) analysis of catalysts was performed by using TP5080 (Xianquan Instrument, Tianjin) apparatus equipped with a thermal conductor detector (TCD), using H_2 (flowing rate: 30 mL·min^{-1}) as reductive gas.

The metal dispersion was detected by CO Pulse chemisorption performed by using a Micromeritics AutoChem 2910 with aTCD detector. Before the text, 50 mg catalyst was reduced in a flow of 100 ml·min^{-1} 10 vol% H_2 in He at 500 °C for 2 h and then flushed with He for 1 h. After cooling down, the CO gas pulses (5 vol% in He) were introduced at a flow rate of 100 ml·min^{-1}. The changes in the CO gas phase concentration were tracked by TCD.

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.

$$\text{Conversion} = \frac{Total\ solid\ mass_{before\ reaction} - Total\ solid\ mass_{after\ raction}}{mass_{(raw\ corncob\ lignin\ )} \times \ (Klason\ lignin\ content)} \times 100\%$$

$$\text{Liquid yield} = \frac{mass_{undecane} \times \dfrac{area_{\ liquid\ product}}{area_{\ undecane}}}{mass_{(corncob\ lignin\ raw\ material)} \times \ (Klason\ lignin\ content) \times \ (theoretical\ yield)} \times 100\%$$

Catalytic reactions：

Unless stated otherwise, reactions were carried out in an autoclave from Anhui Kemi Machinery Technology Co., Ltd. A typical experiment for depolymerization and hydrodeoxygenation of lignin was carried out as follows: lignin, Ni/ASA and Pt/HAP catalysts or Ni/ASA catalyst (lignin : catalysts = 2:1), *n*-dodecane (80 mL) were charged into a batch autoclave. To remove the residual air, the reactor was firstly flushed with N_2 for three times then flushed with H_2 for three times, then 6 MPa H_2 was purged into the reactor at ambient temperature. and then heated up to 300 °C, and the reaction started at a stirring speed of 600 rpm. The liquid products were *in situ* sampled during the catalytic run. After reaction, the remaining solid was filtrated and dried at 100 °C overnight. During the catalytic run the liquid products were analyzed by GC and MS.

2D NMR detecting the products after the hydrodeoxygenation of lignin: lignin (4.0 g), Ni/ASA + Pt/HAP (2 g) catalysts or Ni/ASA catalyst (2 g), *n*-hexane (80 mL) were charged into a batch autoclave, and reacted at 300 °C and 6 MPa H_2 with different reaction time. After reaction, 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 80 °C. The remaining solid phase may consist of the catalyst, the unconverted lignin, and the depolymerized oligomers. The solid catalysts was removed by filtration of the dissolved solid phase using the 1,4-dioxane. The gained solid products in the 1,4-dioxane was distilled at 110 °C to eliminate the 1,4-dioxane and then the solid products from the hydrodeoxygenation of lignin were obtained. In the NMR tests, DMSO-d_6 was used to dissolve the lignin and the derived solid-phase products, while, the liquid products were dissolved by using the mixed solvents of DMSO-d_6： Acetone-d_6： Chloroform-d (2:1:1).

UV-Vis of the adsorption of lignin on Pt/HAP and Ni/ASA catalysts: lignin (2 mg) was dissolved in the 1,4-dioxane (60 mL), then 0.1g Pt/HAP or Ni/ASA was added to 10 mL of this solution with stirring at ambient temperature for specific time. After separating the liquid phase with a centrifuge, the centrifuged filtrate was analyzed by UV-Vis spectroscopy.

GPC detecting the products after the hydrodeoxygenation of lignin: lignin (0.5g), Ni/ASA + Pt/HAP (1g) catalysts or Ni/ASA catalyst (1 g), or lignin (0.5g), Pt/HAP (1 g), *n*-hexane (80 mL) were charged into a batch autoclave, and reacted at 300 °C and 6 MPa H_2 with different reaction time. After reaction, the reacted solid phase can be achieved by filtration. The solid phase may consist of the catalyst, the unconverted lignin, and the depolymerized oligomers. The solid catalysts was removed out by filtration of the dissolved solid phase using the N,N-Dimethylformamide. Then the N,N-Dimethylformamide solution was detected by GPC.

Recycling tests for hydrodeoxygenation of lignin: Recycling tests for hydrodeoxygenation of lignin: After each recycling reaction, the mixed catalysts were washed with dimethyl sulfoxide (DMSO) to dissolve the unreacted lignin and then subsequently calcined in air, and reduced in hydrogen before next use.

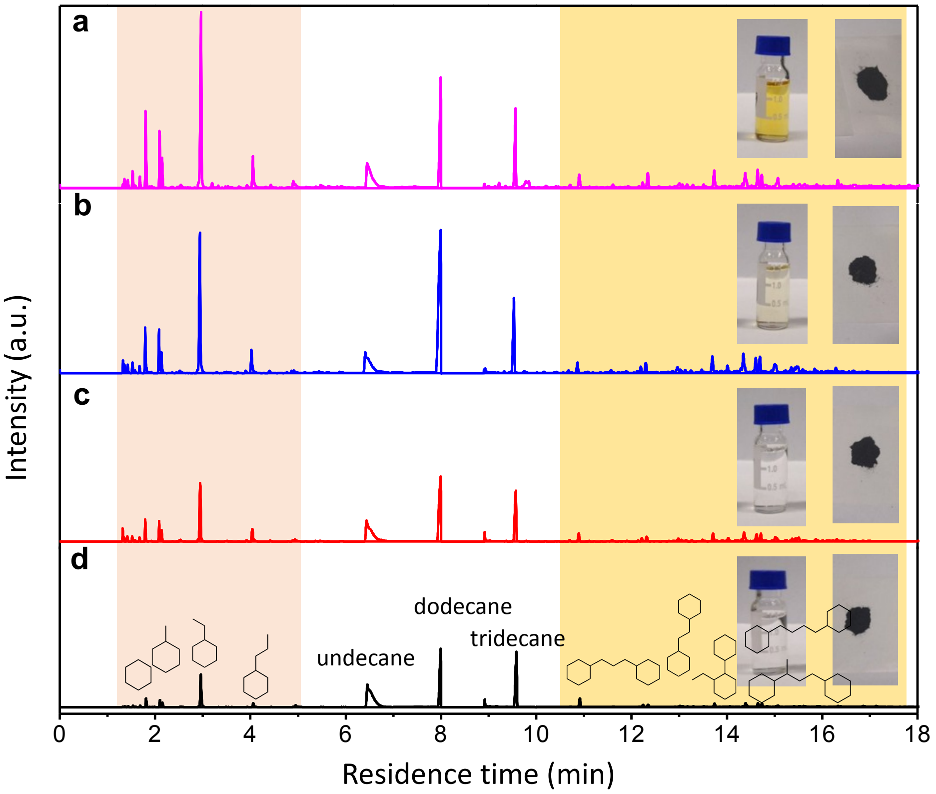

Figure S1: GC spectra for the liquid products after catalytic conversion of lignin at different concentrations with (a) 150 g/L, (b) 100 g/L, (c) 50 g/L, and (d) 25 g/L. Inset images in Fig. S1 are the corresponding reacted solution and used mixed catalyst, respectively. Reaction conditions: a: lignin (12 g), Ni/ASA (3.0 g) and Pt/HAP (3.0 g), 8.5 h. b: lignin (8.0 g), Ni/ASA (2.0 g) and Pt/HAP (2.0 g), 6.5 h. c: lignin (4.0 g), Ni/ASA (1.0 g) and Pt/HAP (1.0 g), 4.5 h. d: lignin (2.0 g), Ni/ASA (0.5 g) and Pt/HAP (0.5 g), 2.5 h. m_{Lignin}/m_{mixed} = 2.0, dodecane (80 mL), 300 °C, 6 MPa H_2, stirring at 600 rpm.

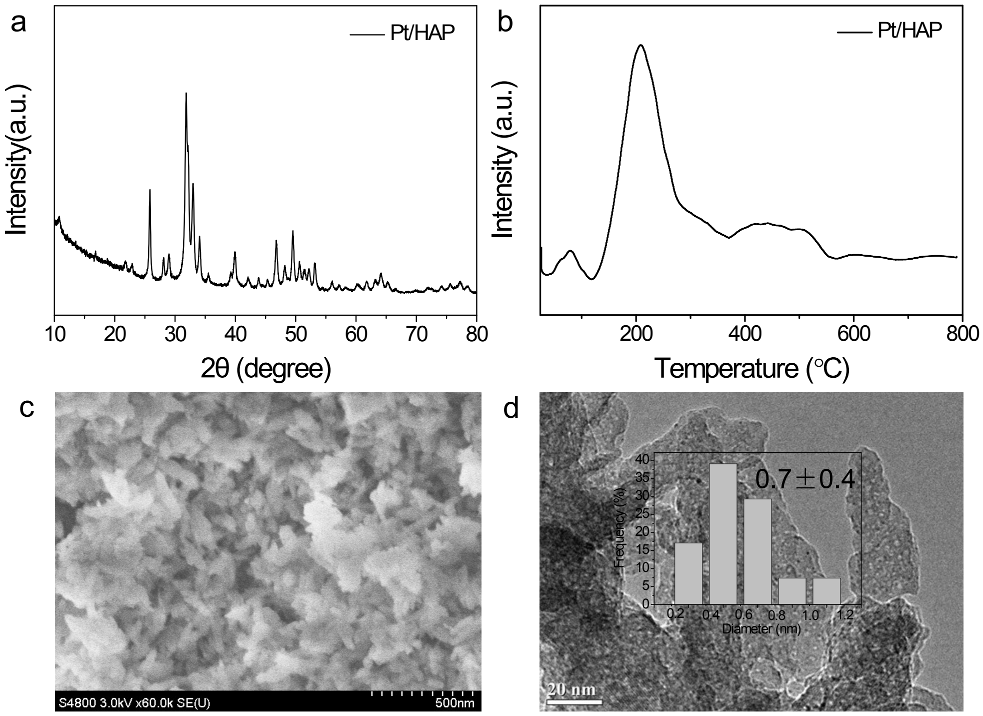

Figure S2: Characterization of Pt/HAP by, (a) XRD, (b) H_2-TPR, (c) SEM, (d) TEM.

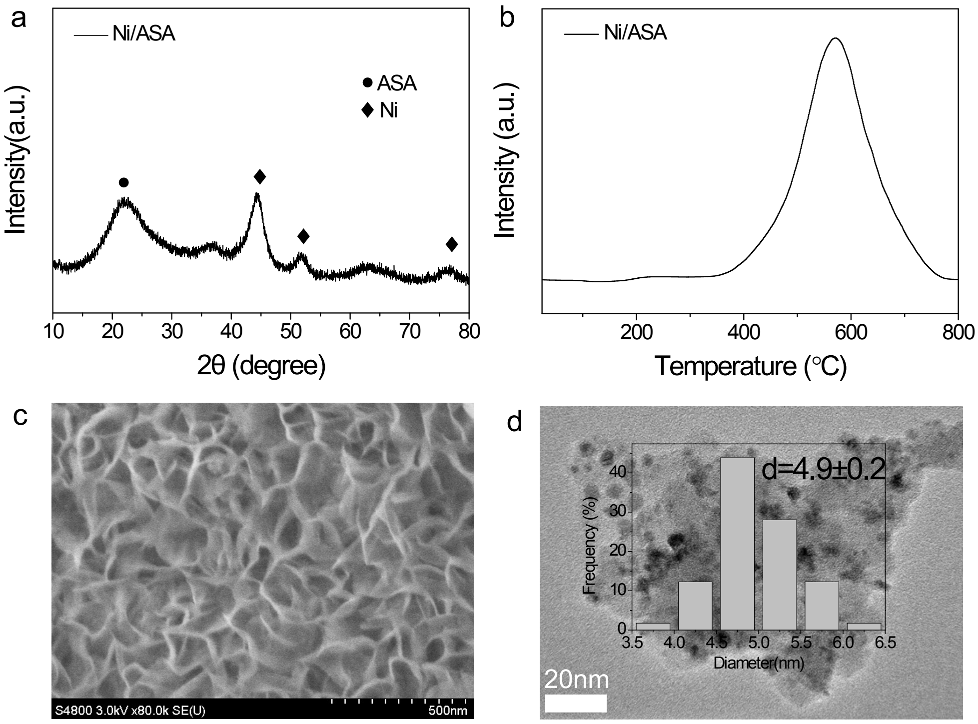

Figure S3: Characterization of Ni/ASA by, (a) XRD, (b) H_2-TPR, (c) SEM, (d) TEM.

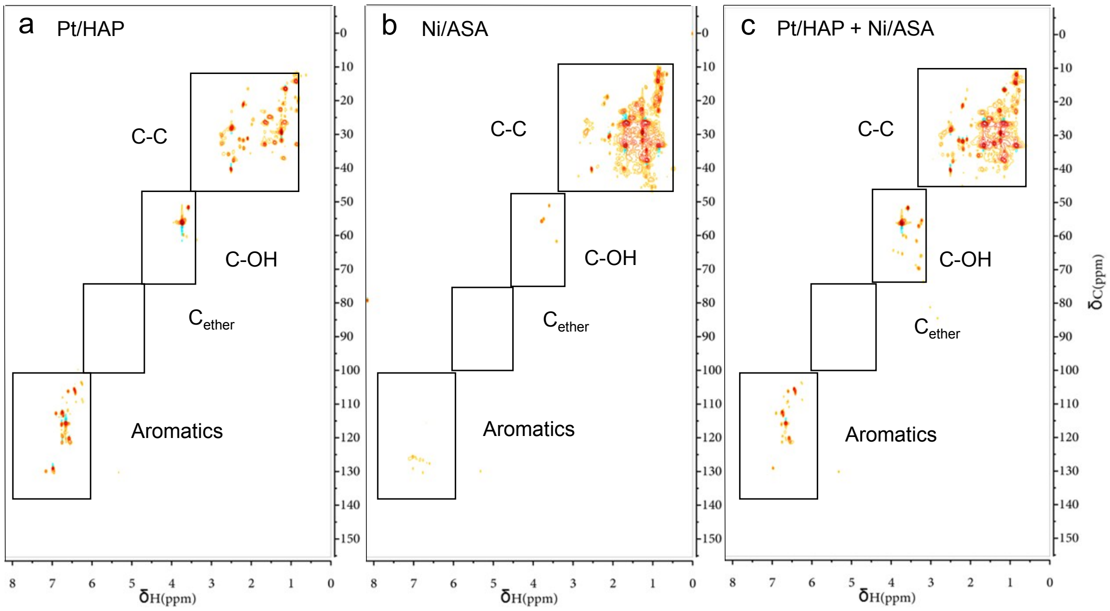

Figure S4. 2D HSQC analysis of liquid products from lignin HDO. The liquid product after 1.5 h catalyzed by (**a**) Pt/HAP, (**b**) Ni/ASA, and (**c**) Pt/HAP + Ni/ASA. Reaction conditions: Lignin (4.0 g), catalyst (2.0 g), dodecane (80 mL), 300 °C, 6 MPa H_2, stirring at 600 rpm.

Table S1: The physicochemical properties of Ni/ASA and Pt/HAP.

Catalyst	Metal loading-ICP (wt%)	Metal Dispersion (%)	Particle size (nm)	Acid amount (μmol·g^{-1})	alkali amount (μmol·g^{-1})	S_{BET}(m^2·g^{-1})		V_{Pore}(cm^3·g^{-1})	
						Micro	Meso	Micro	Meso
Ni/ASA	32	3	4.9 ± 0.2	468	37	0	258.3	0	0.34
Pt/HAP	2	70	0.7 ± 0.4	77	49	0	72.6	0	0.39

Table S2. The elemental composition of lignin and calculated monomer unites determined by GPC.

$C_{10}H_{10.3}O_{3.8} \rightarrow C_9H_{7.3}O_{2.8}(OCH_3)_{1.0}$

Lignin unit M_w = 191 g·mol^{-1}

Monomer unit = 3800/191 ≈ 20