

## Supporting Information

### Fabricating nickel phyllosilicate-like nanosheets to prepare a defect-rich catalyst for one-pot converting lignin into hydrocarbons under mild condition

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### EXPERIMENTAL

#### Materials

Nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), sodium borohydride ( $\text{NaBH}_4$ ), 2-phenylethyl phenyl ether ( $\text{C}_{14}\text{H}_{14}\text{O}$ ), cyclohexane ( $\text{C}_6\text{H}_{12}$ ), ethylcyclohexane ( $\text{C}_8\text{H}_{16}$ ), cyclohexanol ( $\text{C}_{16}\text{H}_{12}\text{O}$ ), ethylbenzene ( $\text{C}_8\text{H}_{10}$ ), n-dodecane ( $\text{C}_{12}\text{H}_{26}$ ), hexadecane ( $\text{C}_{16}\text{H}_{34}$ ) and phenol ( $\text{C}_6\text{H}_6\text{O}$ ) were purchased from Aladdin Industrial Co., Ltd. Corncob enzymatic lignin was purchased from Shandong Longlive Co., Ltd. Ludox-HS-40 colloidal silica (40 wt%  $\text{SiO}_2$ ) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. Sodium hydroxide ( $\text{NaOH}$ ) was purchased from Guangdong Guanghua Sci-Tech Co., Ltd. Ammonium hydroxide ( $\text{NH}_4\text{OH}$ , 28% in water), Acetone ( $\text{C}_3\text{H}_6\text{O}$ ) and Ethanol ( $\text{C}_2\text{H}_6\text{O}$ ) were purchased from Guangzhou chemical reagent factory.  $\text{SiO}_2$  (Aerosil 200) was purchased from Evonik Industries AG. All the chemicals were used without purification.

#### Synthesis of Ni-PS and $\text{Ni}(\text{OH})_2$ precursors

The Ni-PS was prepared through a reduction-oxidation strategy. Typically, nickel nitrate (1.69 g) and HS-40 colloidal silica (780  $\mu\text{L}$ ) were dissolved in 50 mL deionized water in a 250 mL three-necked flask. 20 mL of aqueous solution containing 0.879 g sodium borohydride ( $\text{NaBH}_4$ ) with  $\text{NaBH}_4/\text{Ni}$  molar ratio of 4 and 0.1 g sodium hydroxide ( $\text{NaOH}$ ) was added dropwise to the above mixed solution under nitrogen

atmosphere and vigorous stirring to form the black precipitates. After stirring for 2 h to completely reduce the metal cations, the reduced black aqueous solution was exposed to air. The solution was left under stirring for another twelve hours at room temperature and the color of suspension gradually became green during exposure to ambient air. The products were collected by filtration and washed several times with water and ethanol, and finally dried at 50 °C overnight, denoted as Ni-PS. For comparison, Ni(OH)<sub>2</sub> was prepared by the similar method as mentioned above, but without any silica source added.

### **Catalyst preparation**

Ni-PS samples were reduced in a 8 vol.%H<sub>2</sub>/Ar flow at 450, 500 and 550 °C for 3, 4.5 and 6 h to clarify the effects of reduction degree on the structure and composition of Ni-PS. The obtained samples were denoted as Ni/Ni-PS-450, Ni/Ni-PS-500 and Ni/Ni-PS-550. Ni(OH)<sub>2</sub> samples were reduced in a 8 vol.%H<sub>2</sub>/Ar flow at 400 °C for 3 h and was denoted as Ni/NiO-Ni(OH)<sub>2</sub>. For comparison, Ni/Ni-PS-AE and Ni/SiO<sub>2</sub>-IMP were prepared by a modified ammonia evaporation (AE) and impregnation method (IMP) with a Ni loading of 36 and 20 wt %, respectively. The reduction temperature was selected based on the H<sub>2</sub>-TPR profiles (**Figure S9**), and the procedures were carried out as follows:

The preparation of Ni/Ni-PS-AE: 2.48 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and a 25 wt% ammonia aqueous solution (NH<sub>3</sub>/Ni molar ratio = 8) dissolved in 50 ml deionized water, then the solution was mixed and stirred for 15 min. A certain amount of colloidal silica (HS-40) colloidal silica was then added to the solution and stirred for 12 h. All the above operations were performed at room temperature. Then the suspension was heated in a water bath preheated to 80 °C to allow for the evaporation of ammonia until the pH value of the suspension decreased to 6–7. Then the resultant precipitate was filtered, washed with distilled water, and then dried at 80 °C for 12 h. The green solid was received and calcined at 600 °C in air. The calcined sample was reduced in a 8 vol.%H<sub>2</sub>/Ar flow at 500 °C for 4.5 h.

The preparation of Ni/SiO<sub>2</sub>-IMP: 2.0 g SiO<sub>2</sub> (Aerosil-200) was impregnated with Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution (2.48 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O dissolved in 50 mL deionized water)

and stirred overnight. After removing the solvent, the catalyst precursor was dried at 80 °C overnight. The dried catalyst precursor was reduced in a 8 vol.%H<sub>2</sub>/Ar flow flow at 400 °C for 3 h.

### **Catalyst characterization**

The Brunauer-Emmett-Teller (BET) surface areas ( $S_{BET}$ ) of the catalysts (approximately 0.1 g of sample) were determined by nitrogen physisorption at liquid N<sub>2</sub> temperature using an Autosorb iQ automated gas sorption analyzer (Quantachrome, USA).

The X-ray powder diffraction (XRD) patterns were obtained on a BRUKER D8 Advancer diffractometer (Bruker, Germany) using Cu K $\alpha$  radiation over a 2 $\theta$  range of 20-70°.

The morphology of the samples was observed by Field emission scanning electron microscopy (FESEM, Merlin, Germany).

Transmission electron microscopy (TEM), high resolution transmission electron microscope (HR-TEM) and energy-dispersive X-ray spectrometry (EDS) scanning of samples were performed on a JEM-2100F microscope (JEOL, Japan) operating at 200 kV.

XPS measurement of catalysts was carried out on an ESCALAB 250Xi spectrometer (Thermo, USA) with Al K $\alpha$  radiation (1486.8 eV) to determine the surface atomic ratios and valence states of elements. The C1s peak has been fixed at binding energy (BE) of 284.8 eV to subtract the surface charging effect.

The Ni, Si, and B content of the catalysts was determined by inductively coupled plasma optical emission spectrometry (ICP–OES) using an Agilent 725 spectrometer (Agilent, USA).

The pyridine adsorption FT-IR spectra (Py-IR) were conducted on a Thermo IS10 spectrometer (Thermo, USA) to probe the accessible surface acid sites.

The X-ray absorption fine structure spectra (XAFS) Ni K-edge were collected at BL07A1 beamline of National Synchrotron Radiation Research Center (NSRRC). The data were collected in fluorescence mode using a Lytle detector while the

corresponding reference samples were collected in transmission mode. The samples were grinded and uniformly daubed on the special adhesive tape. The contents of Ni<sup>0</sup> during the different reduction conditions were estimated by linear combination fitting of XANES spectra using Ni foil and NiO as references. Temperature-programmed reduction (TPR) profiles were carried out using a BELCAT instrument (BEL, Japan) equipped with TCD detector. Prior to measurement, the catalyst was pretreated with Ar at 200 °C for 1 h to remove traces of water and then cooled to 50 °C. TPR analysis on catalyst was performed using 5% H<sub>2</sub>/Ar with a flow rate of 30 mL/min, and the temperature was raised from 50 to 800 °C with the heating rate of 10 °C /min.

In order to measure the amount of active sites of the acid catalysts, temperature-programmed desorption (TPD) experiment was performed with Micromeritics AutoChem II 2920 (Micromeritics, USA) using NH<sub>3</sub> gas with a mass spectrometer detector. Before each TPD measurement, 100 mg of catalyst was loaded into a quartz tube, the catalyst was outgassed for 1 h in Ar at 200 °C, and then cooled down to 100 °C. After that, the outgassed catalyst was exposed to NH<sub>3</sub> for 1 h at a flowrate of 50 mL/min. Subsequently, the sample was flushed for 1 h under He at a flow rate of 50 mL/min to remove physisorbed NH<sub>3</sub> molecules. For the TPD measurement, the catalyst was heated up with a rate of 10 °C /min from 100 °C to 800 °C under He gas flow to desorb ammonia. The outlet gas was analyzed by an on-line mass spectrometer. In order to avoid the peak from water fragmentation, the fragment with m/e = 16 was used for the ammonia desorption peak.

### **Catalyst activity tests**

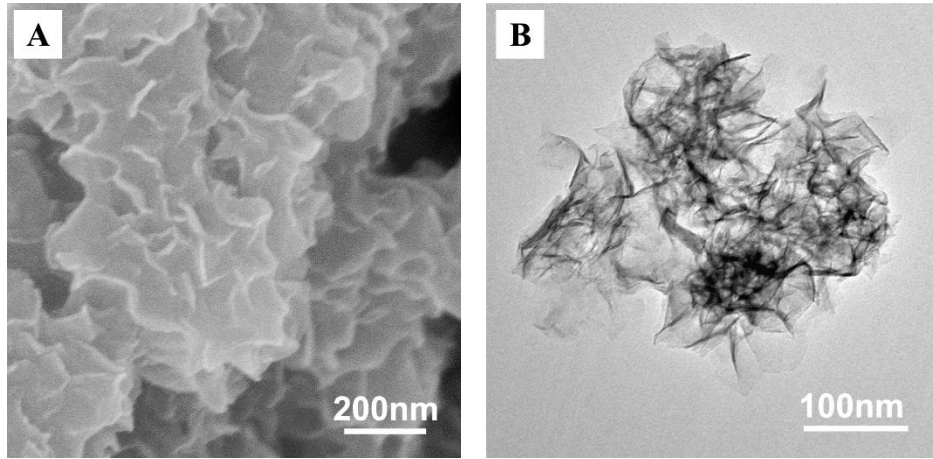
All reactions were carried out in a stainless steel autoclave (250 mL) with a mechanical stirring and the temperature was monitored using a thermocouple (Parr, USA). PPE was chosen as a model compound for the depolymerization and HDO reaction. In a typical experiment, PPE (1 mmol) or enzymatic lignin (0.5 g), 30 g n-dodecane and catalysts were added into the reactor. After purging the reactor with nitrogen three times, the outlet valve was pressurized to maintain the certain pressure of hydrogen at room temperature. Reactions were conducted at a certain temperature for a certain time with a stirring speed of 350 rpm. After reaction, 15 mL

of acetone was added into the reactor at ambient temperature. For the recycling experiments, the spent catalyst was separated by centrifugation, washed three times in ethanol with ultrasonic treatment, and dried at 50 °C for 8 h in a vacuum drying oven for the next run. The liquid products were identified via gas chromatography-mass spectrometry (TRACE 1300-ISQ, Thermo, USA ) and quantified by a gas chromatograph (GC-2010, Shimadzu, Japan) with HP-5 ms capillary column (5% phenyl methyl silox, 30 m × 0.25 mm × 0.25 μm). The oven temperature program started at 50 °C (held for 3 min). The temperature was raised to 150 °C (7 °C min<sup>-1</sup> , held for 10 min), then to 170 °C (7 °C min<sup>-1</sup> ) and finally to 300 °C (20 °C min<sup>-1</sup> , held for 20 min). Hexadecane was used as an internal standard for the quantification of the liquid products. The remaining solid was filtrated and dried at 80 °C overnight. Lignin conversion and the carbon yield of hydrocarbons from lignin were calculated as follows:

$$\text{Lignin conversion} = \frac{\text{Solid mass}_{(\text{before reaction})} - \text{Solid mass}_{(\text{after reaction})}}{\text{mass}_{(\text{raw lignin})}} \times 100\%$$

$$\text{Yield of hydrocarbons} = \frac{\text{Carbon mass}_{(\text{identified liquid product hydrocarbons})}}{\text{mass}_{(\text{raw lignin})} \times \text{Theoretical carbon yield}} \times 100\%$$

Typical composition, organic elemental analysis of lignin and theoretical carbon yield (**Table S3**) was analyzed by the classical oxidation method in a Vario EL cube instrument (Elementar, German) .



**Figure S1** (A) SEM and (B) TEM images of Ni(OH)<sub>2</sub> precursors.

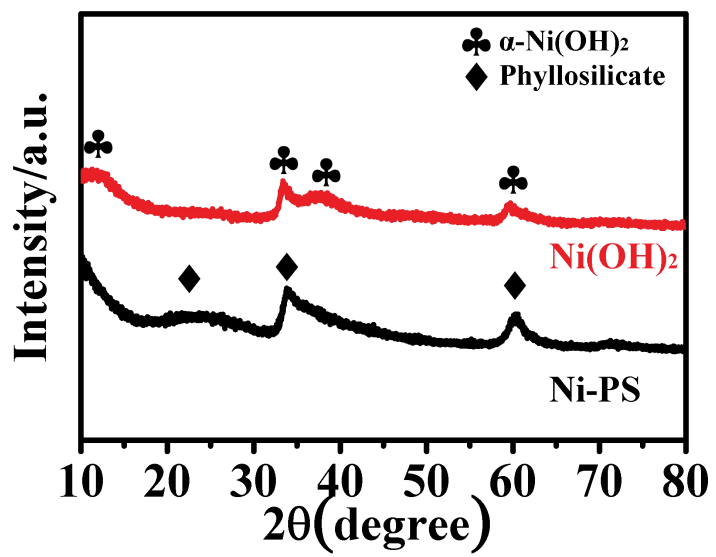


Figure S2 XRD patterns of Ni(OH)<sub>2</sub> and Ni-PS samples.

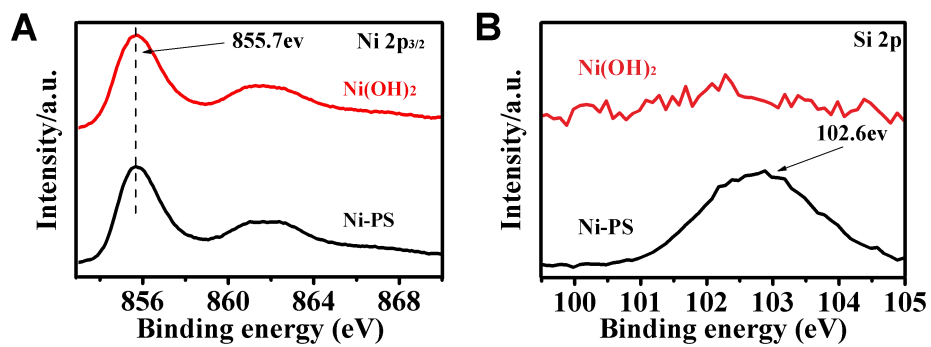
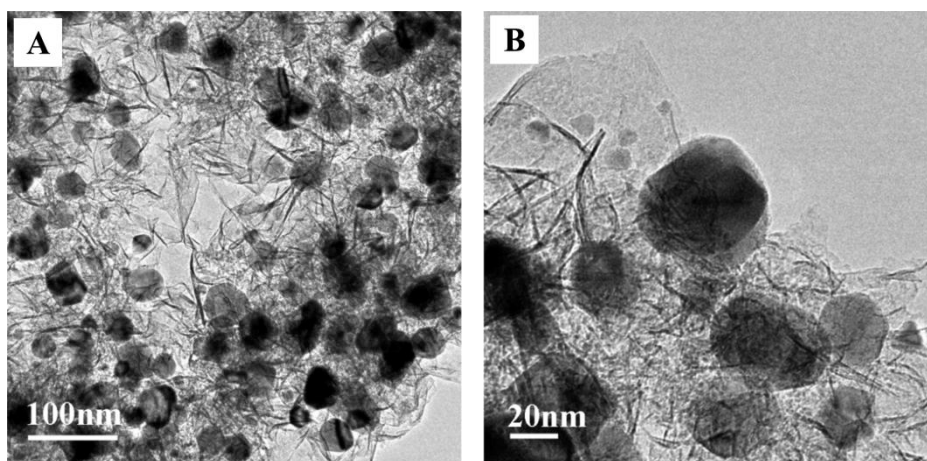
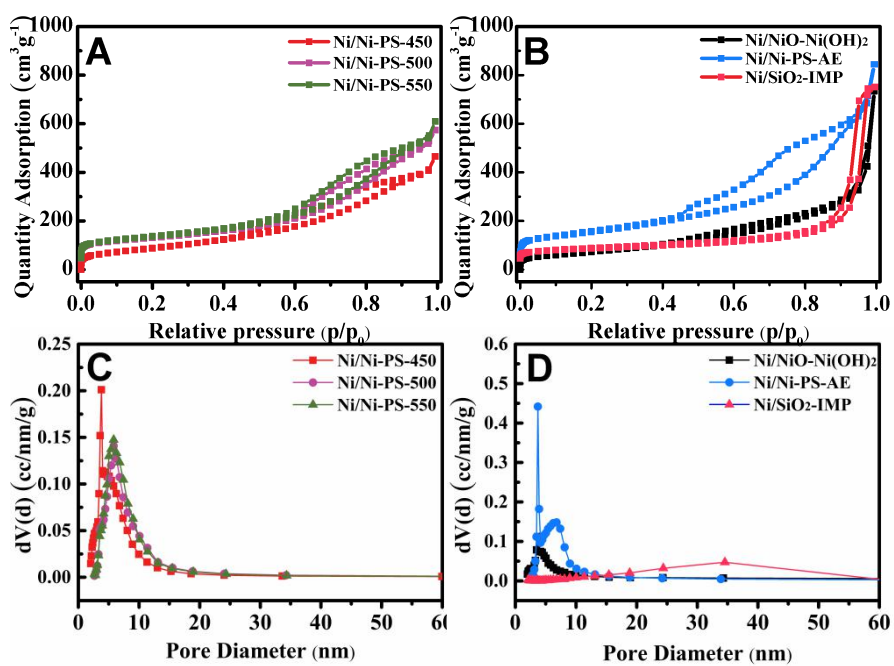


Figure S3 (A) Ni 2p<sub>3/2</sub> and (B) Si 2p XPS spectra of Ni-PS and Ni(OH)<sub>2</sub> precursors.





**Figure S4** (A) TEM and (B) HR-TEM image of Ni/NiO-Ni(OH)<sub>2</sub> catalysts.



**Figure S5**  $N_2$  adsorption/desorption isotherms of the (A) Ni/Ni-PS catalysts and (B) other nickel-based catalyst. Pore size distributions of the (C) Ni/Ni-PS catalysts and (D) other nickel-based catalyst.

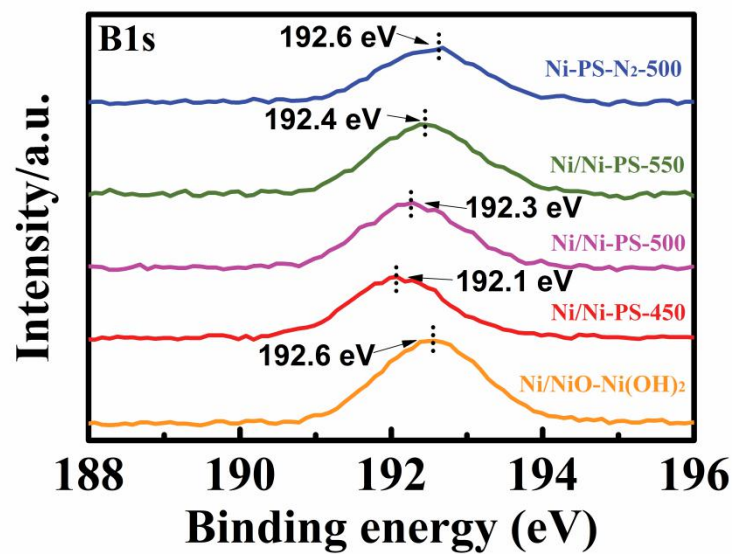


Figure S6 B1s XPS spectra of Ni-Ps-N<sub>2</sub>-500, Ni/Ni-PS and Ni/NiO-Ni(OH)<sub>2</sub> catalysts.

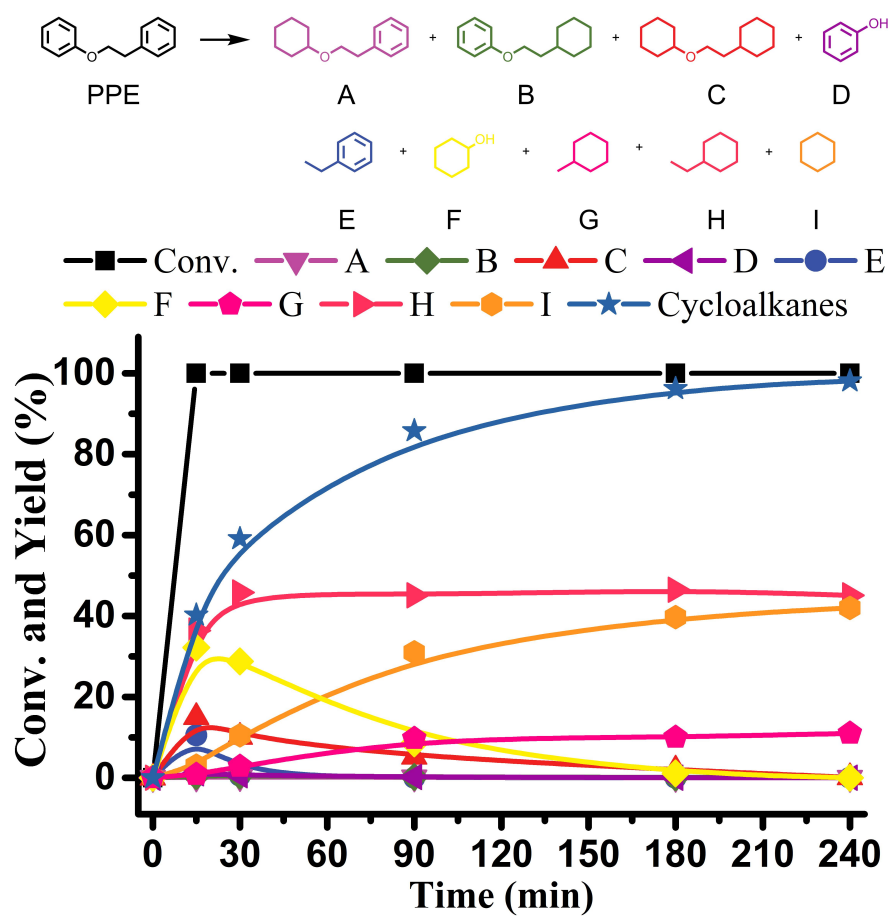
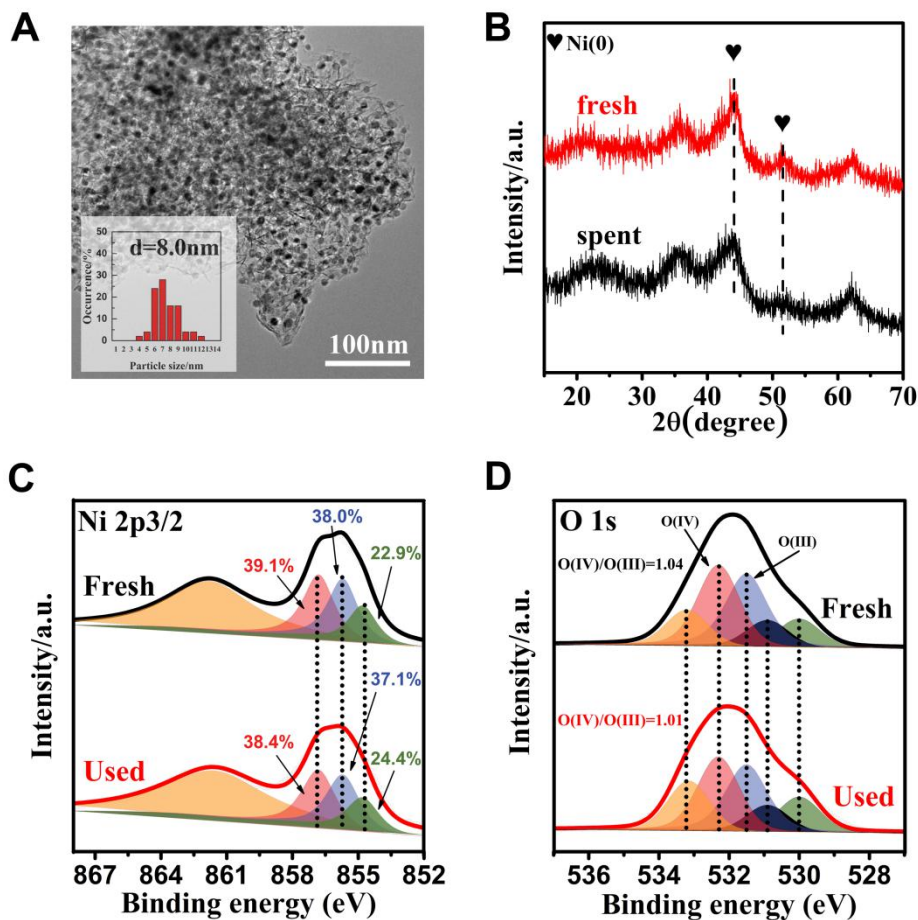
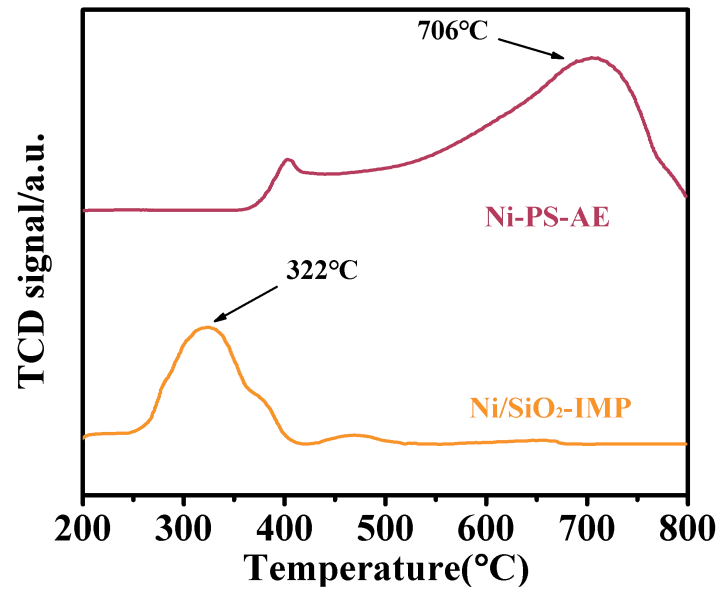


Figure S7 Conversion of 2-phenylethyl phenyl ether and yields of products as a function of reaction time for Ni/Ni-PS-500.

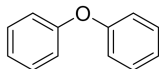
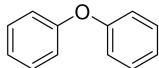
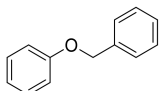
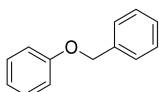
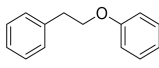
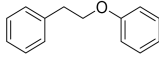
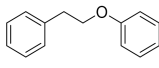


**Figure S8** (A) TEM image of Ni/Ni-PS-500 in catalysts after catalytic cycles, (B) XRD patterns of fresh and spent Ni/Ni-PS-500 catalysts. Ni 2p<sub>3/2</sub> (C) and O 1s XPS (D) spectra of the fresh and spent Ni/Ni-PS-500 catalysts.

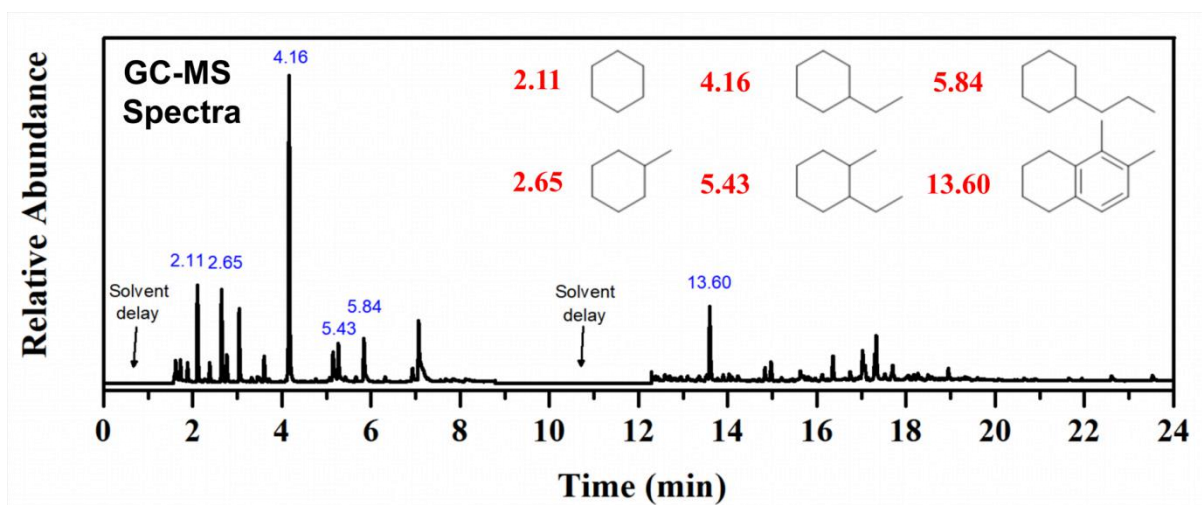




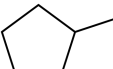


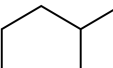
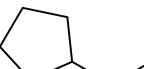
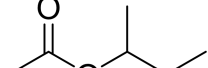
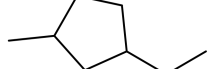
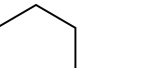
**Figure S9** H<sub>2</sub>-TPR profiles of Ni/SiO<sub>2</sub>-IMP precursors and Ni-PS-AE precursors.

**Table S1** Comparison of the hydrodeoxygenation of dimeric lignin model compounds to cycloalkanes among Ni/Ni-PS and other catalysts.

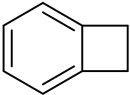
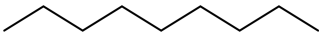
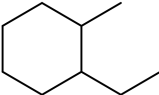
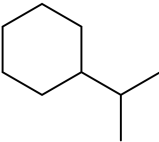
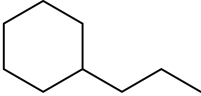
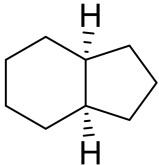
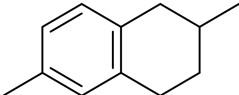
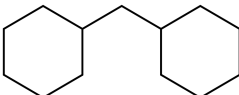
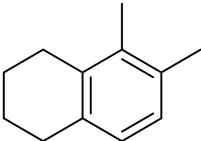
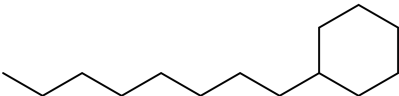
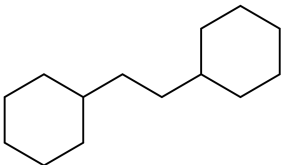
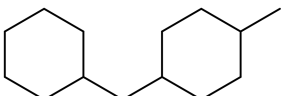
| Entry | Model compound  | Catalyst                              | Temp. (°C) | Pressure (H <sub>2</sub> ) MPa | Cycloalkanes Yield (%) | Ref.      |
|-------|---|---------------------------------------|------------|--------------------------------|------------------------|-----------|
| 1     |  | Ru/TiO <sub>2</sub>                   | 260        | 1                              | 100                    | [1]       |
| 2     |  | Pt/Nb-Al <sub>2</sub> O <sub>3</sub>  | 200        | 3                              | 54                     | [2]       |
| 3     |  | Ru-Cu/HY                              | 250        | 4                              | 68.2                   | [3]       |
| 4     |  | Ru-Re/MWCNT                           | 200        | 2                              | 72                     | [4]       |
| 5     |  | Ir-ReO <sub>x</sub> /SiO <sub>2</sub> | 260        | 3                              | 98                     | [5]       |
| 6     |  | 1Pd10Ni/HZSM-5                        | 220        | 2                              | 99.1                   | [6]       |
| 7     |  | Ni/Ni-PS                              | 160        | 3                              | 98.3                   | This work |

**Table S2** The GC-MS identified liquid products and their retention time after the HDO of enzymatic lignin with Ni/Ni-PS. Reaction condition: 0.5 g enzymatic lignin, 0.2 g of Ni/Ni-PS-500, 6 h, 30 g of n-Dodecane, 240 °C, 3MPa H<sub>2</sub>.

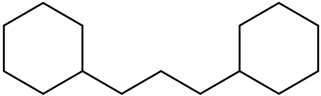
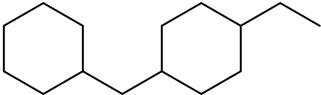
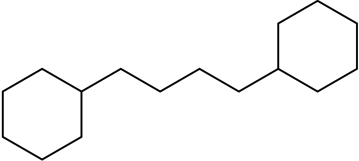
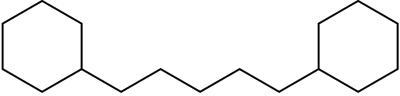


| No. | Compound  | Molecular Formular                            | RT (min) |
|-----|---|---|----------|
| 1   |    | C <sub>5</sub> H <sub>10</sub>                | 1.62     |
| 2   |   | C <sub>6</sub> H <sub>14</sub>                | 1.73     |
| 3   |  | C <sub>6</sub> H <sub>12</sub>                | 1.88     |
| 4   |  | C <sub>6</sub> H <sub>12</sub>                | 2.11     |
| 5   |  | C <sub>7</sub> H <sub>16</sub>                | 2.38     |
| 6   |  | C <sub>7</sub> H <sub>14</sub>                | 2.65     |
| 7   |  | C <sub>7</sub> H <sub>14</sub>                | 2.77     |
| 8   |  | C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> | 3.04     |
| 9   |  | C <sub>8</sub> H <sub>16</sub>                | 3.46     |
| 10  |  | C <sub>8</sub> H <sub>16</sub>                | 4.16     |



|    |   |                |       |
|----|---|----------------|-------|
| 11 |    | $C_8H_8$       | 5.15  |
| 12 |    | $C_9H_{20}$    | 5.27  |
| 13 |    | $C_9H_{18}$    | 5.43  |
| 14 |    | $C_9H_{18}$    | 5.66  |
| 15 |    | $C_9H_{18}$    | 5.84  |
| 16 |    | $C_9H_{16}$    | 6.93  |
| 17 |  | $C_{10}H_{18}$ | 8.13  |
| 18 |  | $C_{12}H_{16}$ | 12.59 |
| 19 |  | $C_{13}H_{24}$ | 13.36 |
| 20 |  | $C_{12}H_{16}$ | 13.60 |
| 21 |  | $C_{14}H_{28}$ | 14.23 |
| 22 |  | $C_{14}H_{26}$ | 14.98 |
| 23 |  | $C_{14}H_{26}$ | 15.63 |

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|    |   |                |       |
|----|---|----------------|-------|
| 24 |  | $C_{15}H_{28}$ | 16.36 |
| 25 |  | $C_{15}H_{28}$ | 17.03 |
| 26 |  | $C_{16}H_{30}$ | 17.70 |
| 27 |  | $C_{17}H_{32}$ | 18.58 |

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**Table S3** Typical composition, organic elemental analysis of lignin and theoretical carbon yield.

| Element (wt.%)   | C    | H   | N   | S | O <sup>a)</sup> |
|--|------|-----|-----|---|-----------------|
| Enzymatic lignin   | 60.1 | 4.6 | 0.7 | 0 | 34.6            |
| Structural unit of lignin <sup>b)</sup> : $C_{10}H_{9.2}O_{4.3} \rightarrow C_9H_{6.2}O_{3.3}(OCH_3)_{1.0}$  |      |     |     |   |                 |
| Theoretical carbon yield = $\frac{\text{carbon mass}(\text{raw lignin}) - \text{carbon mass}(\text{methoxy group})}{\text{mass}(\text{raw lignin})}$ |      |     |     |   |                 |

a): The remaining part is calculated to be the oxygen content.

b): According to previous references<sup>7,8</sup>, assumed that it contains one  $-OCH_3$  group in the lignin unit.

## Notes and references

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