

Supporting Information

Tuning Optimal Ni Nanoparticles and Acid Sites onto Silica Alumina for Liquefaction and Hydrodeoxygenation of Lignin to Cyclic Alkanes

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General Information

Chemicals: Corncob lignin (Shandong Longlive Co., Klason lignin content: 80 wt.%), *n*-dodecane (Sinopharm, > 98% GC assay), benzyl phenyl ether (TCI, >98% GC assay), diphenyl ether (Sinopharm, CP), guaiacol (Sinopharm, > 98% GC assay), 4-methylguaiacol (J&K, > 99% GC assay), 4-ethylguaiacol (TCI, > 97% GC assay), 2,6-dimethoxy-4-methylphenol (Alfa Aesar, > 97% GC assay), (2-bromoethyl)-benzene (J&K, > 98% GC assay), phenol (Sinopharm, AR), Na₂SiO₃ (Sinopharm, SiO₂: 4.82 mol·L⁻¹, Na₂O: 1.39 mol·L⁻¹), ZrO₂ (Shanghai maikun Co.), ZnO (Shanghai maikun Co.), TiO₂ (Shanghai maikun Co.), MgO (Shanghai maikun Co.), Al₂O₃ (Shanghai maikun Co.), SiO₂ (Shanghai maikun Co.), NaOH (Sinopharm, AR), hexadecyl trimethyl ammonium bromide (Sinopharm, AR), Ni(NO₃)₂·6H₂O (Sinopharm, AR), AlCl₃ (Sinopharm, AR), NH₃·H₂O (Sinopharm, AR), urea (Sinopharm, AR), Ce(NO₃)₃·6H₂O (Sinopharm, AR), 1,4-dioxane (Sinopharm, AR), benzene (Sinopharm, AR), methylbenzene (Sinopharm, AR), naphthane (Sinopharm, GR), ethanol (Sinopharm, AR), ethylene glycol (Sinopharm, AR), tetrahydrofuran (Sinopharm, AR), dimethyl sulfoxide (Sinopharm, AR), and dimethyl sulfoxide-d⁶ (J&K, 99.9%). Air, H₂ and N₂ gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Synthesis of benzyl 2-phenylethyl ether (β-O-4 model compound): phenol (18.8 g, 0.2 mol) and hexadecyl trimethyl ammonium bromide (3.2 g, 0.1 mol) were firstly added into an aqueous solution of NaOH (500 mL, 20 wt.%) with stirring. The mixture was then heated to 60 °C with stirring for 0.5 h, and subsequently (2-bromoethyl)-benzene (18.5 g, 0.1 mol) was added. The suspension reacted at 80 °C for 12 h. After that, the organic phase was extracted by diethyl ether. The remaining liquid part was evaporated, and further reacted with an aqueous NaOH solution (10 wt.%, 250 mL) at 60 °C for 24 h in order to remove the residual phenol. Following the extraction by diethyl ether and sequential evaporation procedures, the final product was purified by distillation under vacuum. Purity: 99.5% (detected by GC), M_w: 198 g·mol⁻¹, Formula: C₁₄H₁₄O. The ¹H and ¹³C NMR spectra are displayed in Fig. S5.

Synthesis of amorphous-silica-alumina support: The amorphous-silica-alumina (ASA) support was prepared by the co-gelification method. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and Na_2SiO_3 were used as precursors, and $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added into the mixed precursor solutions in order to adjust the pH attaining 8.0. For realizing full decationization, the as-received co-gelificated gel was ion-exchanged with $\text{CH}_3\text{COONH}_4$ for three-times, and then dried at 100 °C for 24 h. Prior to use, it is calcined in flowing air (flowing rate: 100 mL·min⁻¹) at 550 °C for 4 h.

Synthesis of the Ni catalysts supported on ZrO₂, ZnO, TiO₂, MgO, SiO₂, Al₂O₃ and ASA: The Ni catalysts supported on carriers of ZrO₂, ZnO, TiO₂, MgO, SiO₂, Al₂O₃, and ASA were synthesized by deposition-precipitation (DP) method²⁶. 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 oxide supports (2.0 g) and then heated to 70 °C. The rest latter solution (40 mL) was dissolved with urea (6.3 g), and then drop-wise added into the former oxide 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⁻¹, heating rate: 2 °C·min⁻¹), and reduced in flowing H₂ at 460 °C for 4 h (flowing rate = 100 mL·min⁻¹, heating rate: 2 °C·min⁻¹).

Synthesis of Ni/ASA catalysts with different deposition-precipitation time

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 latter solution (40 mL) was dissolved with urea (6.3 g), and then drop-wise added into the former oxide suspension. Afterwards, the mixture was held at 90 °C with stirring for different time. 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⁻¹, heating rate: 2 °C·min⁻¹), and reduced in flowing H₂ at 460 °C for 4 h (flowing rate = 100 mL·min⁻¹, heating rate: 2 °C·min⁻¹).

Synthesis of Ni/ASA catalysts with different concentrations of Ce additives: Firstly, nickel nitrate (10.2 g) was dissolved in the deionized water (250 mL) with definite amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (base on the weight percentage of the catalyst). Then the following procedure for DP method was similar to that described in the above-section for synthesis of Ni based supported catalysts.

Experimental section

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. IR spectrum of lignin was recorded on a Bruker Tensor 27 Fourier transform infrared spectrometer. ^1H NMR spectrum of lignin was obtained using a Bruker DPX-400 spectrometer after dissolving the lignin in DMSO-d^6 solution.

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 20 °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.

$$\text{The Klason lignin content} = \frac{\text{mass}_{\text{residue solid}}}{\text{mass}_{\text{corn cob lignin}}} \times 100\%$$

Characterization of Ni catalysts: 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 K α radiation ($k = 1.5405 \text{ \AA}$). 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 G² 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. For determination of metal dispersion, pulse CO chemisorption was tested on a Micromeritics AutoChem 2910. Prior to test, 50 mg catalyst was reduced in a flow of 100 mL min⁻¹ 10 vol% H₂ in He at 500 °C for 2 h and then flushed in He for 1 h. After cooled to ambient temperature in He, the CO gas pulses (5 vol% in He) were introduced in a flow of 100 ml min⁻¹. The changes in the CO gas phase concentration were tracked by TCD.

Identification of the soluble fraction of molecular weight of lignin by gel permeation chromatography: The gel permeation chromatography (GPC) consisted of two Waters HPLC columns, a 2414 refractive index (RI) detector and a Water 1515 isocratic HPLC pump. Tetrahydrofuran was used as the solvent for lignin dissolution and eluent for GPC. The flow-rate was maintained at 1 ml min⁻¹ with a column temperature of 35 °C. The calculation was calibrated with narrowly dispersed linear polystyrene standards.

Catalytic tests of hydrodeoxygenation of lignin: A typical experiment for depolymerization and hydrodeoxygenation of lignin was carried out as follows: lignin (2.0 g), Ni/ASA catalyst (30.1 wt.%, 1.0 g), *n*-dodecane (80 mL) were charged into a batch autoclave (Parr Instrument, 300 mL). The reactor was firstly flushed with H₂ at ambient temperature for three times, and then heated up to 300 °C when 6 MPa H₂ was purged, and the reaction started at a stirring speed of 700 rpm. The liquid products were *in situ* sampled during the catalytic run. After reaction, the remaining solid was filtrated and dried at 110 °C overnight. During the catalytic run, and then the liquid products were analyzed by GC and MS. 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.

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

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

Kinetics of benzyl 2-phenylethyl ether and guaiacol conversion: the procedures were similar and in typical tests, guaiacol (5.0 g) and Ni/ASA (30.1 wt.%, 0.2 g) was used. The reaction was carried out at 300 °C in presence of 6 MPa H₂ at a stirring speed of 700 rpm. The liquid products were in situ sampled every 30 min. During the catalytic run, and then the liquid products were analyzed by GC and MS.

Table S1. The IR information of band assignments in lignin

Wavenumbers (cm ⁻¹)	Band origin	Wavenumbers (cm ⁻¹)	Band origin
3408	O-H stretch	1357	aliphatic C-H stretch
3006 2937 2848	C-H stretch (methyl and methylene groups)	1330	G ring plus S ring condensed
1695	C=O stretch (ester groups)	1222	C-C, C-O, C=O stretch
1600	Aromatic skeletal vibrations	1126	C-H in-plane (typical for G rings)
1512	Aromatic skeletal vibrations	1170	C=O stretch (conjugated ester groups)
1461	C-H bending vibrations (methyl and methylene groups)	1031	C-O bending vibrations (primary alcohols)
1423	Aromatic skeletal vibrations	835	C-H out-of-plane (S ring)

Table S2. The ¹H-NMR information of peak assignments in lignin

δ (ppm)	assignment
9.9	Protons in formyl groups
7.5	H-2 and H-6 in aromatic rings with a carbonyl group
7.2	Aromatic protons in <i>p</i> -hydroxyphenyl groups
6.8	Aromatic protons in guaiacyl Protons
6.6	Aromatic protons in syringyl Protons
6.3	α -H in β -O-4 units
5.3	α -H in β -5/ α -O-4 units
3.7	Protons in aromatic methoxyl groups
3.3	DMSO (solvent)
2.7	Protons in aliphatic methoxyl groups
2.5	H ₂ O in solvent
2.3	Aromatic acetate
2.0	Aliphatic acetate
1.4- 0.8	Hydrocarbon contaminant

Table S3. Conversion of lignin in different solvents

Solvent	Yield (%)			
	Alcohols +ketones	Aromatics +Olefins	Cycloalkanes +Alkanes	phenols
Ethylene glycol	0	0	0	0
1,4-dioxane	0	0	0	9.47
Benzene	0	0	0	12.34
Toluene	0	0	0	10.31
naphthane	0	0	0	5.82
Ethanol	0	0	0	6.26
Tetrahydrofuran	0	0	0	4.76
Dodecane	2.33	0.36	12.96	2.35

Reaction conditions: lignin (2.0 g), Ni/ASA catalyst (30.1 wt.%, 1.0 g), solvent (80 mL), 250 °C, 4 MPa H₂, 160 min., stirring at 700 rpm.

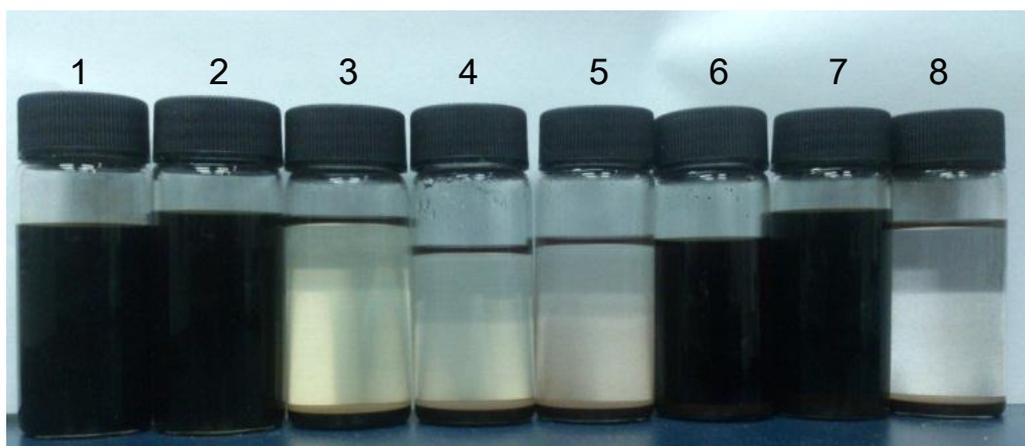


Figure S1. Images of lignin dissolution in different solvents. **1.** Ethylene glycol, **2.** 1,4-Dioxane, **3.** Benzene, **4.** Methylbenzene, **5.** Naphthane, **6.** Ethanol, **7.** Tetrahydrofuran, **8.** *n*-Dodecane

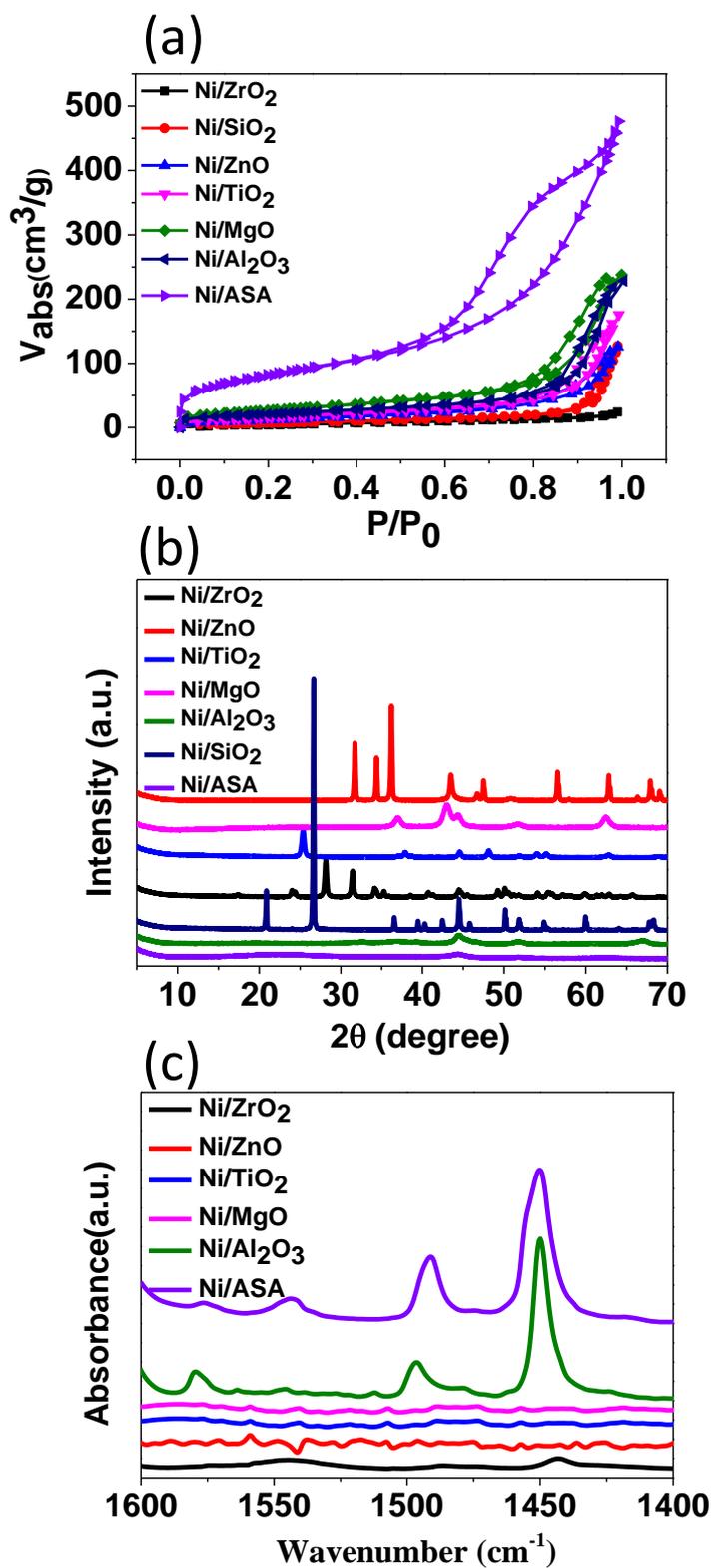
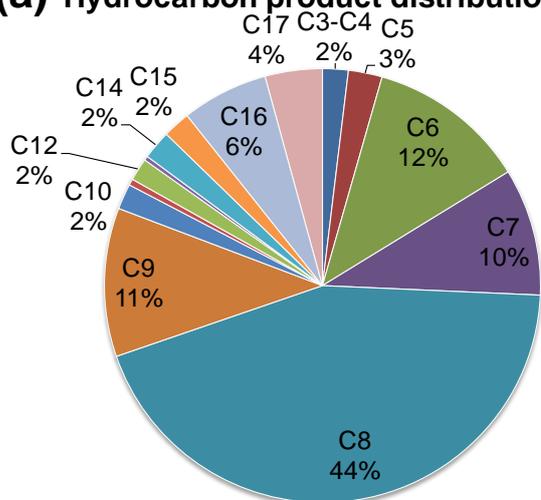


Figure S2. (a) N_2 adsorption and desorption isotherms, (b) XRD patterns, and (c) the IR spectra of adsorbed pyridine of supported Ni catalysts.

(a) Hydrocarbon product distribution



(b) Gas product distribution

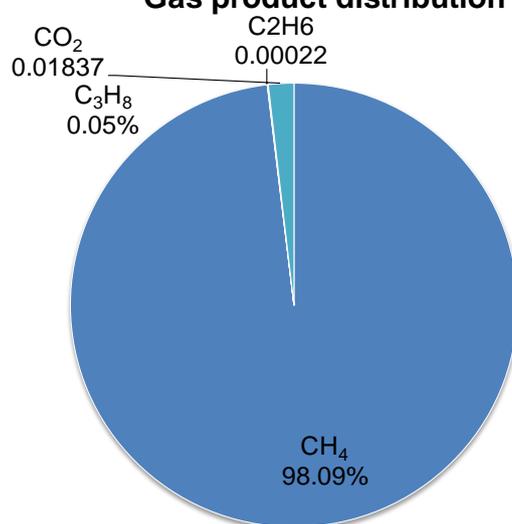


Figure S3. (a) Compositions in lignin derived hydrocarbon product distributions, (b) Gas compositions from lignin conversion. General conditions: lignin (2.0 g), Ni/ASA catalyst (30.1 wt.%, 1.0 g), 300 °C, 6 MPa H₂, dodecane (80 mL), 160 min., stirring at 700 rpm.

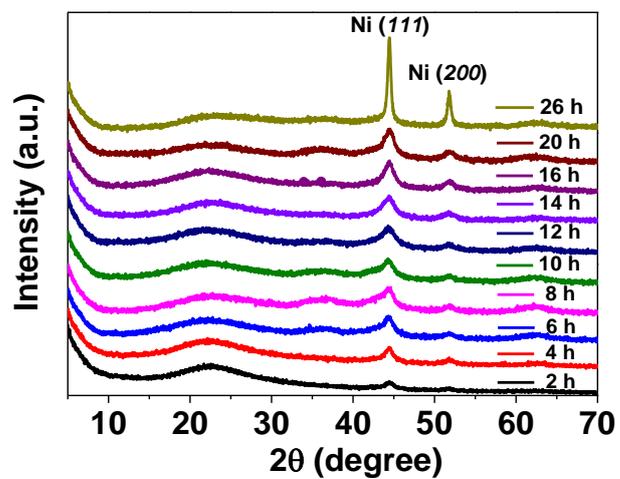


Figure S4. XRD patterns of Ni/ASA as a function of DP times.

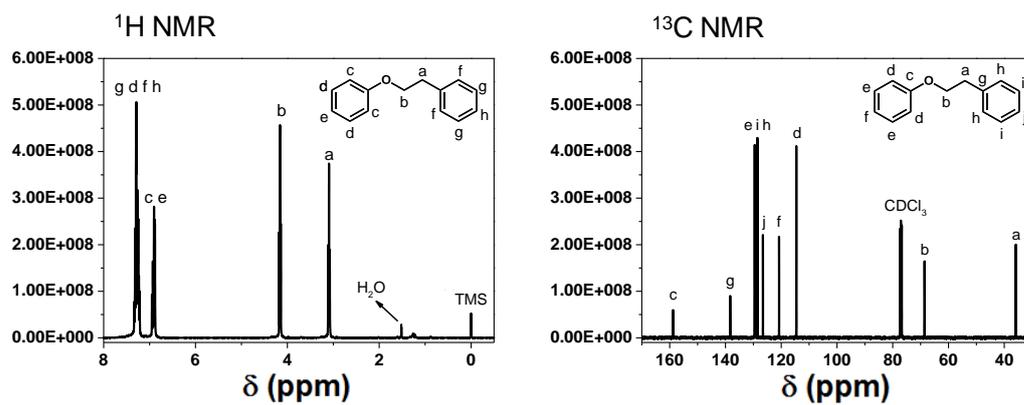


Figure S5. The ¹H NMR and ¹³C NMR spectra of benzyl 2-phenylethyl ether (β-O-4 model compound).

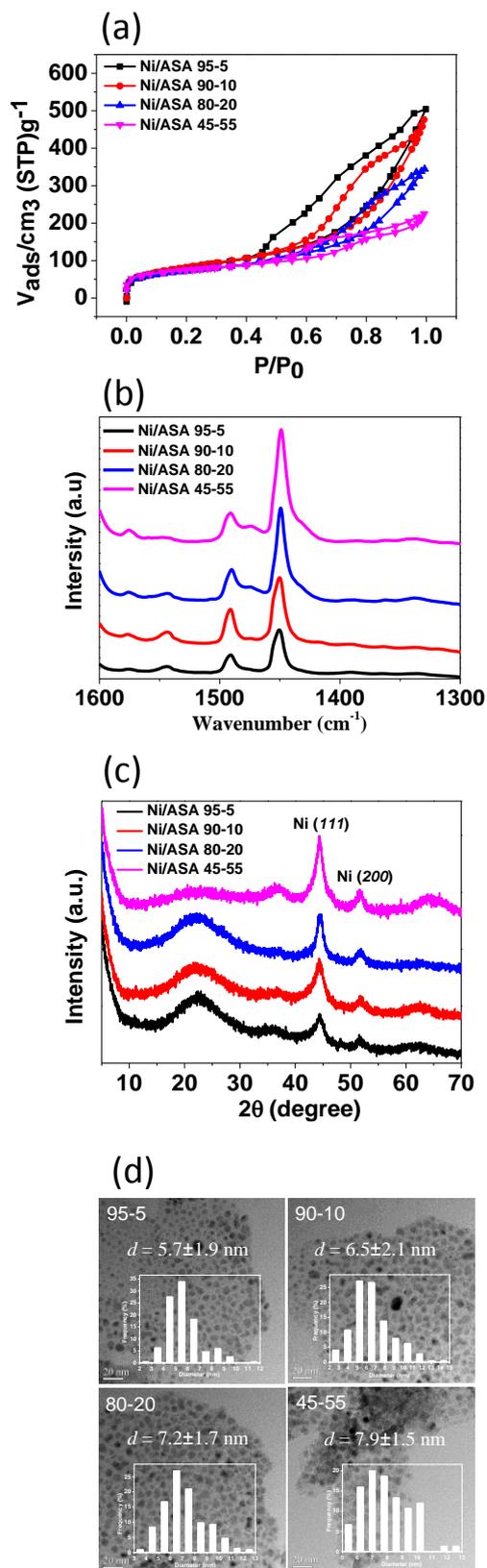


Figure S6. (a) N_2 adsorption and desorption isotherms, (b) IR spectra of adsorbed pyridine, (c) XRD patterns, (d) TEM images of Ni/ASA catalysts with different Al_2O_3 contents.