

ISCI, Volume 15

Supplemental Information

**Design of Nickel Supported on Water-Tolerant
Nb₂O₅ Catalysts for the Hydrotreating of Lignin
Streams Obtained from Lignin-First Biorefining**

Glauco F. Leal, Sérgio Lima, Inês Graça, Heloise Carrer, Dean H. Barrett, Erico Teixeira-Neto, Antonio Aprigio S. Curvelo, Cristiane B. Rodella, and Roberto Rinaldi

Supplemental file

Design of nickel supported on water-tolerant Nb₂O₅ catalysts for the hydrotreating of lignin streams obtained from lignin-first biorefining

Glauco F. Leal,^{a,b,c} Sérgio Lima,^a Inês Graça,^a Heloise Carrer,^c Dean H. Barrett,^{c,e} Erico Teixeira-Neto,^d Antonio Aprigio S. Curvelo,^b Cristiane B. Rodella,^c Roberto Rinaldi^{a,*}

^a Department of Chemical Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, United Kingdom.

^b Department of Physical Chemistry, Institute of Chemistry of São Carlos, University of São Paulo, Av. Trabalhador São Carlense, 400, São Carlos, SP, 13566-590, Brazil.

^c Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, SP, 13083-970, Brazil.

^d Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, SP, 13083-970, Brazil.

^e School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

*Corresponding author: R. Rinaldi, e-mail: rrinaldi@ic.ac.uk.

Transparent Methods

Catalysts synthesis

Niobia synthesis by hydrothermal method. TT-Nb₂O₅ nanorods were prepared by dissolving ammonium niobium oxalate (5.22 g; 99.9%, CBMM) in deionized water (65 mL) and H₂O₂ (15 mL, 30%, Synth) in a molar ratio H₂O₂:Nb of 10, forming a yellowish solution.(Leal et al., 2019) This solution was then transferred to a 150 mL stainless steel reactor equipped with a PTFE liner, for a hydrothermal treatment at 175°C for 15 h. The hydrothermal treatment produced a white precipitate of Nb₂O₅. The solid was separated by filtration and washed with deionized water several times. Next, the solid was dried overnight in an oven at 60°C. To obtain the final support (TT-Nb₂O₅), the material was calcined in a muffle at 380°C for 2 h.

Preparation of Ni/Nb₂O₅ catalysts. Ni was deposited on the Nb₂O₅ material by employing a deposition-precipitation ammonia evaporation method.(Leal et al., 2019) Typically, Nb₂O₅ (1.0 g), (NH₄)₂CO₃ (2.0 g, Sigma-Aldrich) and NiCO₃·2Ni(OH)₂·xH₂O (in quantities to provide a 5, 10, 15, and 25 wt% Ni, 99.9%, Sigma-Aldrich) were dispersed in deionized water (20 mL). To the mixture, an aqueous NH₄OH solution (20 mL, 26-30%, Sigma-Aldrich) was added. The suspension was then kept under magnetic stirring at 90°C for 3 h, under N₂ flow. The solid was centrifuged and washed with deionized water several times until the filtrate showed a neutral pH value. Next, the solid was dried at 110°C overnight in an oven. The dried Ni/Nb₂O₅ catalyst precursor was reduced in a tubular oven under H₂ flow. The sample was heated up to 320°C with a heating ramp of 5°C min⁻¹, and kept at 320°C for 1.5 h under H₂ atmosphere. The reduced Ni/Nb₂O₅ catalyst was cooled down to room temperature

under Ar flow and stored under Ar atmosphere in a glove box. The catalysts were referred to as %Ni/Nb₂O₅, where %Ni represents the nominal Ni loading on Nb₂O₅.

Catalyst characterizations

Ni loading. Ni loading on Nb₂O₅ (Table 1) was determined by inductively coupled plasma – mass spectroscopy (ICP-MS) analysis on an Agilent Technologies 7900 ICP-MS system. For the analysis, a catalyst sample (5 mg) was suspended in HNO₃ (10 mL, >68%, Fisher Chemical) and digested under microwave irradiation at 200°C for 15 min by using a CEM MARS6 microwave oven. After digestion, an aliquot of the solution (0.1 mL) was diluted 10-times in deionized water (9.9 mL). The solution was then analyzed on the ICP-MS. For each sample, the determination of Ni and Nb was carried out in triplicate.

Powder X-Ray diffraction. X-Ray diffraction (XRD) measurements were performed on the XPD beamline at the Brazilian Synchrotron Light Laboratory (LNLS), operating at an energy of 8keV ($\lambda = 1.5498 \text{ \AA}$). XRD patterns were collected in a 2θ angular range from 15 to 90° with a Mythen – 1K linear detector (Dectris) installed at 1 m from the sample. Crystalline phases were identified by comparison with JCPDS files. Ni crystallite size was estimated by using the Scherrer equation, with the full-width at half-maximum (FWHM) of the peaks being determined by fitting the data in a pseudo-Voigt function.

Scanning transmission electron microscopy. Scanning transmission electron microscopy (STEM) was performed in the LNNano facilities, CNPEM, Brazil. Acquisition of High-Angle Annular Dark-Field (HAADF) images was performed in an

FEI Titan Themis aberration-corrected scanning electron microscope operating at 300 kV. The samples were prepared by applying the catalyst powders directly over TEM standard specimen holder.

Textural properties. The surface area was determined by adsorption-desorption isotherms of N₂ at -196°C in an Autosorb 1C (Quantachrome). The samples were pretreated at 120°C overnight under vacuum. The specific surface area was determined by the BET method.

Temperature-programmed reduction of Ni/Nb₂O₅. The reduction of the Ni/Nb₂O₅ catalyst precursor was analyzed by H₂ temperature-programmed reduction (TPR). The precursor samples (50 mg) were pre-treated at 150°C for 1 h under He flow (50 mL min⁻¹). TPR analysis was then performed from room temperature to 1000°C at a heating rate of 10°C min⁻¹ under 5% H₂/He flow (50 mL min⁻¹). H₂ was monitored by a mass spectrometer OmniStar™ GSD 320 O1 (Pfeiffer Vacuum).

ATR-FTIR pyridine adsorbed on Ni/Nb₂O₅. The acidic properties of niobium oxide support were evaluated by attenuated total reflection Fourier Transform infrared spectroscopy (ATR-FTIR) of adsorbed pyridine (Py). FTIR spectra were collected on an FTIR spectrometer from Perkin Elmer (Spectrum Two) in the range from 400 to 4000 cm⁻¹ at a resolution of 0.5 cm⁻¹. For signal accumulation, 32 scans were collected. Initially, the samples in powder form were dried at 150°C for 1h, under N₂ flow, in a three-neck rounded bottle flask (50 mL) equipped with a heating mantle. N₂ carried pyridine (Py) vapor was introduced into the flask for the adsorption of pyridine on Nb₂O₅ and reduced Ni/Nb₂O₅ samples. Next, the sample was exposed to Py vapor at 150°C for 1 h. Then, the flask was purged with N₂ at 120°C, for 30 min, to remove

physisorbed Py. After cooling to room temperature, the sample was transferred to an eppendorf and the FTIR spectra were collected with the ATR probe. The spectrum of adsorbed Py was obtained by subtracting the spectrum of the sample with chemisorbed Py from that of the treated sample without pyridine.

Quantification of Brønsted and Lewis acid sites by FTIR of adsorbed pyridine on Nb₂O₅. The acidic properties of the niobium oxide were evaluated by FTIR of the samples adsorbed with pyridine (Py). The FTIR spectra were collected using a Nicolet FT-IR-6700 spectrometer in the range from 4000 to 1000 cm⁻¹ with a resolution of 2 cm⁻¹ and 128 scans for signal accumulation. The samples were prepared as a thin pellet through pressing sample powder. The sample pellet was transferred into a homemade IR cell equipped with CaF windows. First, the sample was dehydrated at 120 °C under dynamic vacuum (2·10⁻⁵ mbar) for 22 h. After cooled down to room temperature, the sample spectrum was obtained. Then, the sample was exposed to Py vapor until the equilibrium with vapor pressure and cooked at 150 °C for 20 h. Next, the system was cooled down to room temperature and kept under dynamic vacuum (2·10⁻⁵ mbar) for 30 min to remove the physisorbed Py and collected the FTIR spectrum. The quantification of acid sites was done using the Lambert-Beer equation ($A_i = \epsilon_i \cdot c \cdot d$) using the integrated absorbance (A_i) and the Integrated Molar Absorption Coefficient (ϵ_i). (Barzetti et al., 1996) The bands in 1444 cm⁻¹ ($\epsilon_i = 2.22 \text{ cm } \mu\text{mol}^{-1}$) and 1540 cm⁻¹ ($\epsilon_i = 1.67 \text{ cm } \mu\text{mol}^{-1}$) (Emeis, 1993) were used to quantify Lewis Acid Sites (LAS) and Brønsted Acid Sites (BAS), respectively.

Catalyst tests

Hydrodeoxygenation of diphenyl ether. The experiments were carried out in a stainless steel batch reactor (250 mL) using a catalyst (0.500 g) suspended in a 0.19 mol L⁻¹ solution of diphenyl ether (13.5 mmol, Sigma-Aldrich, 99%), containing *n*-dibutyl ether (0.052 mol L⁻¹, 3.64 mmol, Acros Organics, > 99%, internal standard for GC analysis) and methylcyclohexane (70 mL, Acros Organics, 99%, solvent) under mechanical stirring at 400 rpm. All processes involving the fresh catalyst manipulation and reactor loading were carried out in a glove box under Ar atmosphere. The reactor was purged with H₂ and loaded with 4 MPa at 25°C. The experiments were performed at 160 or 200°C for 180 min. Reaction mixture aliquots at 0, 15, 30, 60, 90, 120 and 180 min were collected. Recycling experiments were performed at 200°C, under similar operating conditions. Five reaction cycles of 240 min were carried out. After each cycle, the catalysts were separated from the reaction mixture by vacuum filtration, washed with methylcyclohexane and dried in a vacuum oven at 40°C overnight.

The reaction products were analyzed in a gas chromatograph (Shimadzu QP2010 Plus) equipped with a Rxi-1ms capillary column (30 m, 0.25 mm ID, df 0.25 mm). The following temperature program was used: an isothermal step for 5 min at 40°C, increase in temperature at 5.2°C min⁻¹ up to 300 °C and finally an isothermal step for 5 min at 300°C. The quantification was performed using a multi-point internal standard method, through calibration curves based on the response of the flame ionization detector (FID) for each component relative to the internal standard response.

Catalytic Upstream Biorefining to produce the lignin oil stream. The catalytic upstream biorefining (CUB) process was used to deconstruct poplar wood, rendering lignin oil and a holocellulosic pulp.(Ferrini and Rinaldi, 2014) Poplar wood pellets (704 g) and Raney Ni (331 g, wet) were suspended in an aqueous solution of 2-PrOH (4140 mL, 70%, v/v) and placed in a 2 gallon (ca. 9 L) stainless steel batch reactor (Parr Instruments & Co, model number: 4552). The suspension was stirred (75 rpm) for 30 min at room temperature. Then, the reactor was heated to 200°C in 1h under mechanical stirring (700 rpm). The reaction proceeded under autogenic pressure for 3 h. In sequence, the mixture was allowed to cool down to room temperature. The liquor was separated from the solids (Raney Ni in conjunction with the holocellulosic pulp) by filtration through a glass fiber filter (GF6, Ø 90 mm, Whatman). The solids were re-suspended in a 2-PrOH/H₂O mixture in a PE beaker under mechanical stirring. To separate Raney Ni from the suspension, a strong neodymium magnet was externally placed on the bottom of the beaker. The suspension was mechanically stirred, resulting in the detachment of catalyst particles from the pulp, which were magnetically decanted. Keeping the magnet placed on the bottom of the beaker, the catalyst was separated from the pulp suspension by pouring the suspension into a Buchner funnel. The catalyst was recovered by removing the magnet. The liquor was isolated from the pulp by filtration under reduced pressure. The catalyst separation procedure was repeated three times to remove the catalyst content from the pulp fibers. The liquor and the filtrates (obtained from the catalyst separation procedure) were combined. Finally, the lignin oil stream was isolated by removing the solvent from the liquor and filtrates by using a rotoevaporator at 45°C under vacuum.

Hydrodeoxygenation of lignin oil. The produced lignin oil (2.000 g), *n*-pentane (70 mL), 15%Ni/Nb₂O₅ (0.400 g) were placed in a 600 mL stainless Parr batch reactor. All steps involving the fresh catalyst manipulation and reactor loading were performed inside a glove box under Ar atmosphere. The reactor was then pressurized to 7 MPa with H₂ (measured at room temperature). The pressure vessel was then heated up to 300°C and the reaction proceed for 16 h under mechanical stirring (400 rpm). In sequence, the mixture was allowed to cool down to room temperature. Then, the liquid fraction was separated from the residual solid, composed of catalyst and lignin residues, by filtration. Finally, to isolate the liquid products, the solvent of the collected liquid fraction was evaporated at 25°C by using a centrifugal evaporator (Centrifan™ PE, KDScientific). To recover the spent catalyst for recycling, the mixture of catalyst and lignin residue was washed with methanol. This procedure could dissolve about 10% of the polymeric lignin residue. The suspension was filtered. After solvent removal, the lignin residue soluble in methanol was set apart for characterization. In turn, the washed solid residue (catalyst containing lignin residue insoluble in methanol) was dried at 40 °C overnight under vacuum and weighed to determine the net conversion of lignin. The net conversion of the lignin oil was calculated by Eq. S1:

$$Net\ conversion = \left(1 - \frac{mass_{washed\ solid\ residue} - initial\ mass_{catalyst}}{mass_{lignin\ oil}} \right) \times 100 \quad (S1)$$

The liquid products and the solid residue soluble in methanol were analyzed by CHNS/O elemental analysis, GPC and GC-FID/MS.

Analysis of lignin oil products

GC-FID/MS analysis. An aliquot of each sample (20.0 mg) and the external standard (di-*n*-butyl ether, the internal standard for GC analysis, 3.0 mg) were dissolved in MeOH (1 mL). The sample was filtered (membrane filter 0.45 µm). The sample solutions were analyzed by GC-MS 2010 Plus (Shimadzu) equipped with a capillary column DB-1MS (30 m, 0.25 mm ID, df 0.25 µm). The following temperature program was used: an isothermal step for 5 min at 40 °C, increase in temperature at 5.2°C min⁻¹ up to 300°C and, finally, an additional isothermal step for 5 min at 300°C. Quantification of selected components was performed by using the FID response. The response factor of the products was determined from calibration curves (for cyclohexane, cyclohexanol, 4-ethylcyclohexanol, phenol, 4-ethylphenol, 2-methoxy-4-ethylphenol, 2-methoxy-4-propylphenol, 2,6-dimethoxyphenol, 2,6-dimethoxy-4-methylphenol, 4-(3-hydroxypropyl)-2-methoxyphenol, 4-allyl-2,6-dimethoxyphenol) or by using the Effective Carbon Number method (ECN, for 2,6-dimethoxy-4-ethylphenol, 2,6-dimethoxy-4-propylphenol) relative to 2,6-dimethoxy-4-methylphenol. (Scanlon and Willis, 1985)

Gel permeation chromatography analysis. To analyze the apparent molecular weight distribution in lignin products, the products (20 mg) were dissolved in a solution of anhydrous dimethylformamide (DMF) containing 0.1 wt% LiBr (1 mL) and filtered (membrane filter 0.45 µm) prior to injection. The GPC analyses were performed at 60°C with a Shimadzu HPLC Prominence system equipped with three columns (Polargel-M guard 50x4.6mm, Polargel-M 300x7.5mm, Polargel-L 300x7.5mm, Agilent), and by using DMF + LiBr 0.1 wt% as the eluent (1.0 mL min⁻¹). For detection,

a Shimadzu SPD-M20A diode-array detector (PDA) was used. All responses were normalized by the sample weight. The system was calibrated with polystyrene standards (200 to 60 000 Da, Aldrich).

CHN/O elemental analysis. CHN/O elemental analyses of the products were carried out in an Elementar VarioMI-CRO Cube analyzer, by using 1-2 mg of the sample. Each sample was analyzed in triplicate, and the average value was taken. The oxygen content in the samples was estimated by subtraction ($\%O = 100 - \%C - \%H - \%N$).

Total organic carbon. Total organic carbon content in the aqueous product was determined in a Sievers InnovOx Laboratory TOC analyzer provided by GE Instruments, by diluting 50 μ L of the sample with deionized water to obtain a total volume of 20 mL.

Nitrogen adsorption-desorption measurements

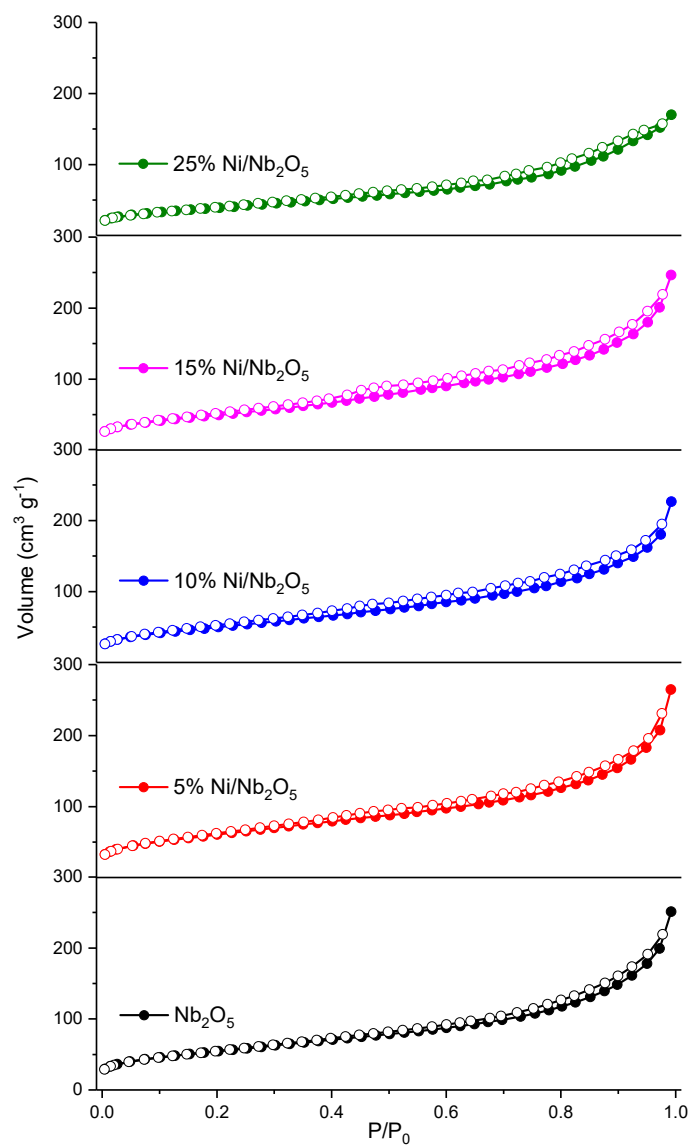


Figure S1. N₂ adsorption-desorption isotherms of the support and Ni/Nb₂O₅ catalysts, related to Table 1.

Table S1. Temperatures of reduction of NiO and Nb₂O₅ species in Nb₂O₅ and Ni/Nb₂O₅ materials, related to Figure 3.

Sample	Reduction temperature (°C)	
	NiO	Nb ₂ O ₅
Nb ₂ O ₅	----	870
5%Ni/Nb ₂ O ₅	339	847
10%Ni/Nb ₂ O ₅	334	847
15%Ni/Nb ₂ O ₅	346	834
25%Ni/Nb ₂ O ₅	338	816

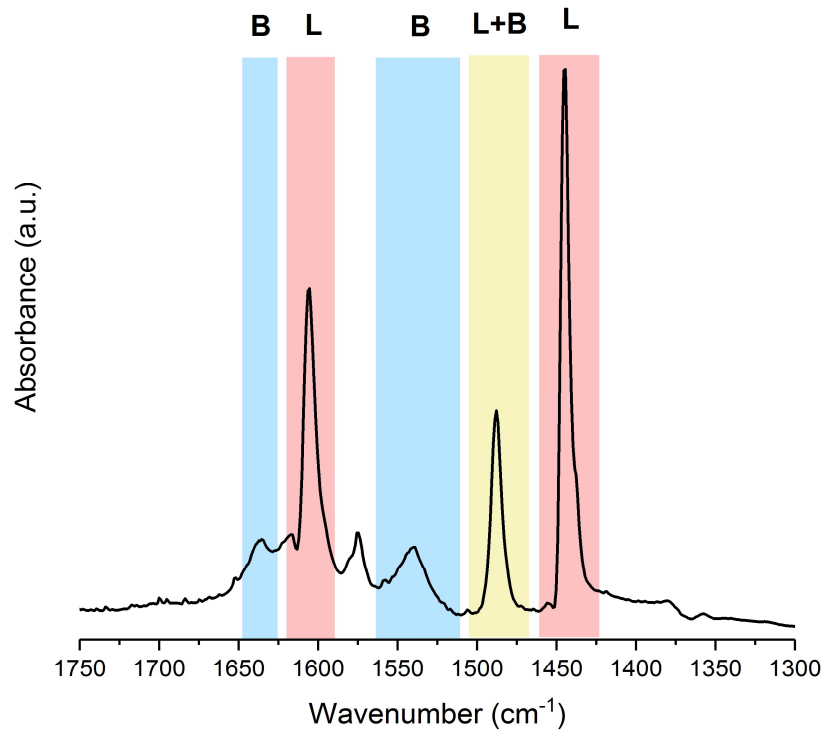


Figure S2. FTIR absorption spectrum of pyridine adsorbed on Nb₂O₅, relate to Figure 4.

Table S2. Amount of Brønsted and Lewis sites in the niobia, relate to Figure S2.

	Area 1444 cm ⁻¹	Lewis acidity (μmol g ⁻¹)	Area 1540 cm ⁻¹	Brønsted acidity (μmol g ⁻¹)
Nb ₂ O ₅	0.466	210	0.239	143

Table S3. Conversion and products distribution of the diphenyl ether hydrogenation reaction in the absence of a catalyst and using only the niobium oxide at 160 °C and 4 MPa H₂ pressure, relate to Table 3.

c1ccc(Oc2ccccc2)cc1 (1) → c1ccc(Oc2CCCCC2)cc1 (2) + C1CCC(CC1)OC2CCCCC2 (3) + Oc1ccc(cc1)c2ccccc2 (4) + c1ccccc1 (5) + Oc1CCCCC1 (6) + C1CCC(CC1) (7)

Catalyst	Conversion (%)	Time (min)	Yield (%)					
			2	3	4	5	6	7
Blank reaction	8	180	1.5	0.3	0.2	0.6	2.8	2.5
Nb(HT)	15	180	4.4	1.1	0.3	1.1	2.3	4

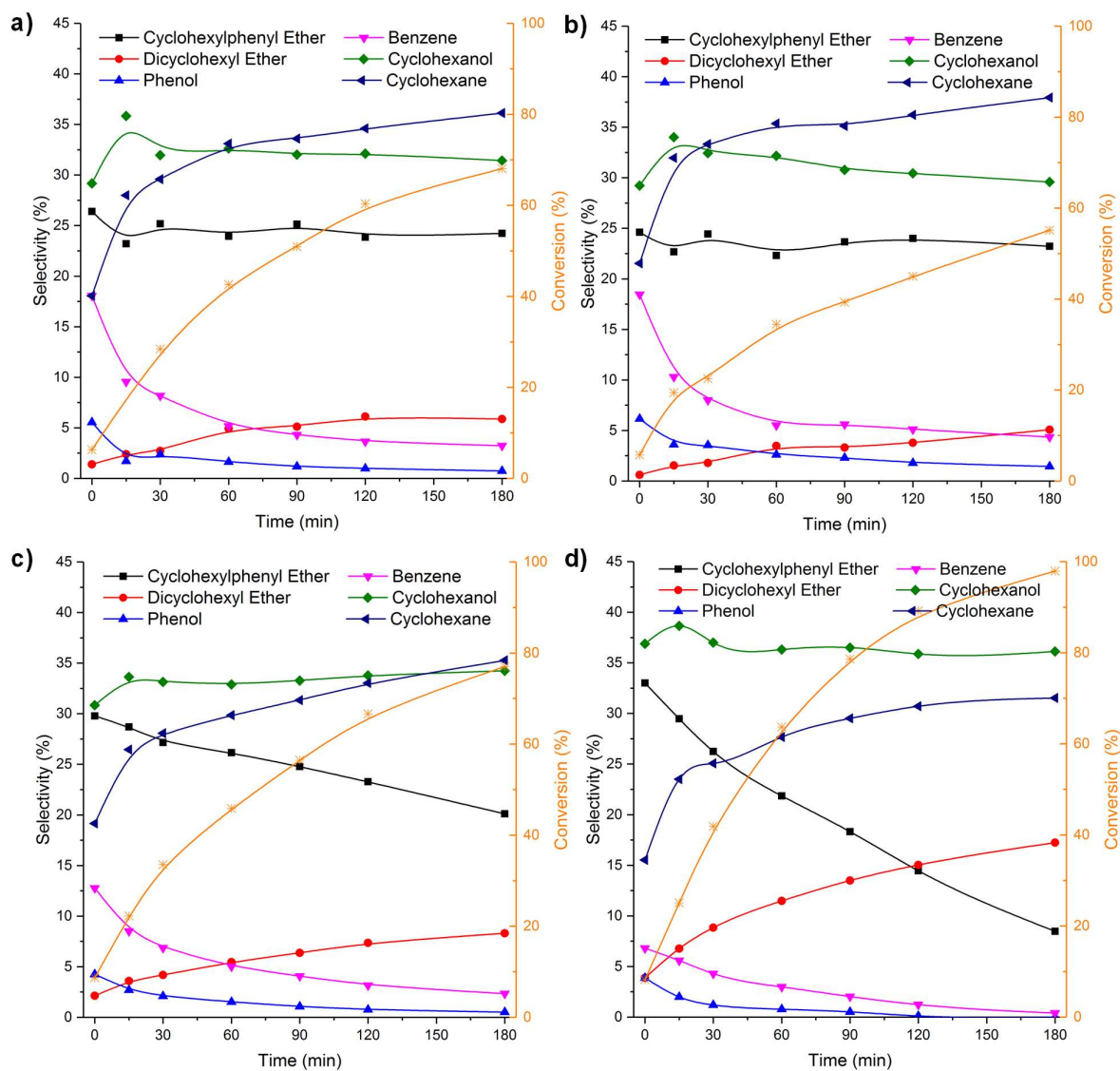
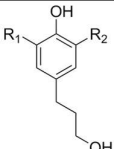
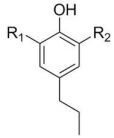
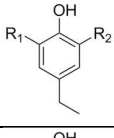
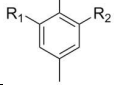
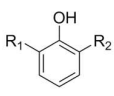
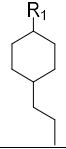
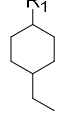
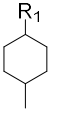
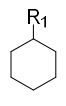


Figure S3. Products selectivity in diphenyl ether hydrodeoxygenation employing as a catalyst: a) 5%Ni/Nb₂O₅; b) 10%Ni/Nb₂O₅; c) 15%Ni/Nb₂O₅ and d) 25%Ni/Nb₂O₅. Conversion of diphenyl ether shown by orange-coded lines, relate to Table 3 and Figure 6.

Table S4. Weight content of selected components in the lignin oil, liquid organic products of the hydrotreating of lignin oil over 15%Ni/Nb₂O₅, and control experiment (no added catalyst) as determined by GC-FID/MS analysis, relate to Figure 13.

Selected component	Content (wt%)					
	Lignin Bio-oil	1 st Run	2 nd Run	3 rd Run	Control experiment	
	R ₁ = H; R ₂ = OCH ₃	9.7	0	0	0	1.5
	R ₁ = R ₂ = OCH ₃	9.3	0	0	0	0
	R ₁ = R ₂ = H	0.2	0	1.5	1.2	0.3
	R ₁ = H; R ₂ = OCH ₃	0.6	0	3.3	2.9	9.4
	R ₁ = R ₂ = OCH ₃	1.6	0	1.2	1.4	0
	R ₁ = R ₂ = H	0.5	0	2.9	2.2	1.2
	R ₁ = H; R ₂ = OCH ₃	0.6	0	6.3	7.0	8.9
	R ₁ = R ₂ = OCH ₃	1.3	0	0	0	0
	R ₁ = H; R ₂ = OCH ₃	0	0	0.8	0.8	0.7
	R ₁ = R ₂ = H	2.8	0	0.6	0.6	6.6
	R ₁ = H; R ₂ = OCH ₃	0	0	0.9	1.4	4.5
	R ₁ = R ₂ = OCH ₃	0.2	0	0.9	1.4	0.3
Aliphatic double ring products		0	22	3.8	2.3	0
	R ₁ = H	0	16	1.0	1.2	0
	R ₁ = OH	0.6	1.6	11.5	8.9	2.9
	R ₁ = H	0	4.3	0	0	0
	R ₁ = OH	0.7	0	11	13	2.7
	R ₁ = H	0	0.3	0.07	0.1	0
	R ₁ = OH	0	0	1.0	1.2	0
	R ₁ = H	0	0.2	3.0	0.9	1.3
	R ₁ = OH	0	0	7.1	12	1.0
	R ₁ = C ₅ , C ₇	0	4.6	0	0	0
Sum of selected components		28	49	57	58	41

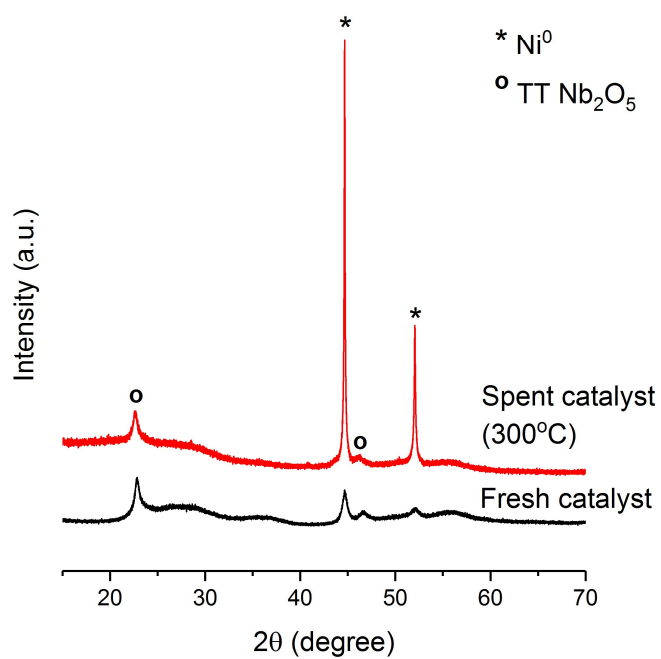


Figure S4. XRD patterns of the 15% Ni/Nb₂O₅ catalyst before and after catalyst recycling at 300 °C (third run), relate to Figure 14.

References

- Barzetti, T., Selli, E., Moscotti, D., Forni, L., 1996. Pyridine and ammonia as probes for FTIR analysis of solid acid catalysts. *J. Chem. Soc. Faraday Trans.* 92, 1401.
- Emeis, C.A., 1993. Determination of integrated molar extinction coefficients for infrared absorption bands of pyridine adsorbed on solid acid catalysts. *J. Catal.* 141, 347–354.
- Ferrini, P., Rinaldi, R., 2014. Catalytic biorefining of plant biomass to non-pyrolytic lignin bio-oil and carbohydrates through hydrogen transfer reactions. *Angew. Chem. Int. Ed.* 53, 8634–8639.
- Leal, G.F., Barrett, D.H., Carrer, H., Figueroa, S.J.A., Teixeira-Neto, E., Curvelo, A.A.S., Rodella, C.B., 2019. Morphological, Structural, and Chemical Properties of Thermally Stable Ni-Nb₂O₅ for Catalytic Applications. *J. Phys. Chem. C* 123, 3130–3143.
- Scanlon, J.T., Willis, D.E., 1985. Calculation of flame ionization detector relative response factors using the effective carbon number concept. *J. Chromatogr. Sci.* 23, 333–340.
- Wang, X., Rinaldi, R., 2016. Bifunctional Ni catalysts for the one-pot conversion of Organosolv lignin into cycloalkanes. *Catal. Today* 269, 48–55.