

Supporting information

Selective production of indane and its derivatives from lignin over a modified niobium-based catalyst

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Experimental section

Materials

Al_2O_3 , ZrO_2 and 5wt% Pd/C catalyst were purchased from Aladdin Chemical Co., Ltd and Al_2O_3 sample was calcinated at 500 °C for 6 h before use. All chemicals used here were purchased from Sinopharm Chemical Reagent Co. Ltd, except for RuCl_3 and 4-methylphenol, which were purchased from Aladdin Reagent Co. Ltd. All purchased chemicals were of analytical grade and used without further purification. Birch, beech, and pine samples were purchased from Shandong Province, China. The lignin oil is prepared according to the literature. [1]

Catalysts preparation and characterization

Nb_2O_5 support was synthesized according to the procedure in literature.[2] In a typical process, ammonium oxalate and self-prepared niobium oxalate were dispersed in deionized water, treated by hydrothermal method at 180 °C for 1 day, and calcinated at 400 °C for 4 h under air with a linear heating ramp of 10 °C min^{-1} .

The 2 wt% Ru/ Nb_2O_5 catalyst was prepared by a typical wetness impregnation method. Typically, RuCl_3 (0.2 g of a 10 wt% aqueous solution of RuCl_3) was dispersed with Nb_2O_5 (1 g), and the resulting material was dried at 60 °C for 12 h, reduced in a 10% H_2/Ar flow at 400 °C for 4 h, and then purged with N_2 for 1 h. The preparation of 2 wt% Ru/ ZrO_2 and Ru/ Al_2O_3 were same as above.

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCA LAB-250 spectrometer with monochromatic Al $K\alpha$ radiation.

Diffused Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of CO adsorption as well as the adsorption of 4-methylphenol were collected with a NICOLET iS50 FT-IR spectrometer equipped with an MCT/A detector. For Ru/ Nb_2O_5 sample, the catalysts were firstly *in situ* reduced in the cell in H_2 at 400 °C for 30 min and cooled to 35 °C in N_2 , and a background was recorded. Then 4-methylphenol with N_2 was bubbled into the cell for 30 min, blowing with N_2 for 60 min and the adsorption spectra of 4-methylphenol was recorded. For Ru/ Nb_2O_5 - CH_2Cl_2 sample, after reduced in H_2 and cooled to room temperature, CH_2Cl_2 with N_2 was bubbled into the cell for 30 min, blowing with N_2 for 60 min and a background was recorded. Then 4-methylphenol with N_2 was bubbled into the cell and the adsorption spectra of 4-methylphenol was recorded. For the adsorption of CO, the steps are same as above, except the change of 4-methylphenol with CO.

Hydrogen temperature-programmed desorption (H₂-TPD) was carried out in a quartz tube reactor on a Micromeritics Chemi-Sorb 2720 instrument equipped with a thermal conductivity detector (TCD). In the case of H₂-TPD program, the Ru/Nb₂O₅ sample (100 mg) was sealed and treated in a gas mixture of H₂ and Ar (1:9, v/v) at 400 °C. Subsequently, Ar was flowed into the reactor and cooled down to 40 °C for the adsorption of H₂. After flushing with Ar until a stable baseline was obtained, the temperature was raised to 600 °C with a heating rate of 10 °C min⁻¹. For Ru/Nb₂O₅-CH₂Cl₂ sample, the steps are same as above, except the adsorption of CH₂Cl₂ before adsorbing hydrogen.

Depolymerization of lignocellulosic biomass and separation of lignin oil

In a typical depolymerization reaction, the autoclave (50 mL) was charged with a suspension of 1000 mg of feedstock, 100 mg of Pd/C, and 30 µL of tridecane as internal standard in 20 mL of methanol. The reactor was sealed, purged with hydrogen several times, filled with 3 MPa hydrogen and then heated to 250 °C with continuous stirring at 700 rpm for 3 h. After reaction, the reactor was quenched in a water bath to stop the reaction immediately.

The mixture after biomass depolymerization was filtered to remove (hemi)cellulose and Pd/C solid residue, and methanol in the liquid phase was removed by rotary evaporation. Then the residues were extracted with ethyl acetate and water to obtain an ethyl acetate phase. After removal of ethyl acetate by rotary evaporation, the lignin oil was obtained. The lignin oil was diluted with ethyl acetate (5 mL) and analyzed by GC-MS (Agilent 7890A-5975C) and GC (Agilent 7890B). The yield of products is defined as follows:

Phenolic monomers yield (wt%) = weight of phenolic monomers / weight of lignin oil*100%

Here, Lignin phenolic monomers were analyzed by the NBO method according to the literature.^[3]

Reaction of lignin oils and model compounds

Typically, catalyst (0.10 g), lignin oil (0.10 g), dichloromethane (50 µL), tridecane (30 µL) as internal standard, and deionized water (15 mL) were charged to a 50 mL stainless steel autoclave. After the reactor was purged with hydrogen for three times, 0.5 MPa hydrogen was charged. Then the reactions were carried out at 250 °C with continuous stirring at 700 rpm for 20 h. After reaction, the reactor was quenched in a water bath to stop the reaction immediately. The solution was extracted with ethyl

acetate to obtain organic phase, and analyzed by GC-MS (Agilent 7890A-5975C) and GC (Agilent 7890B). The reaction of lignin model compounds was same as above. The yield of products is defined as follows:

Products Yield (mol%) = mol of product/mol of monomer *100%

Phenolic monomers yield=weight of phenolic monomers / weight of lignin oil *100%

Aromatic alcohol monomers yield=weight of aromatic alcohol monomers / weight of lignin oil *100%

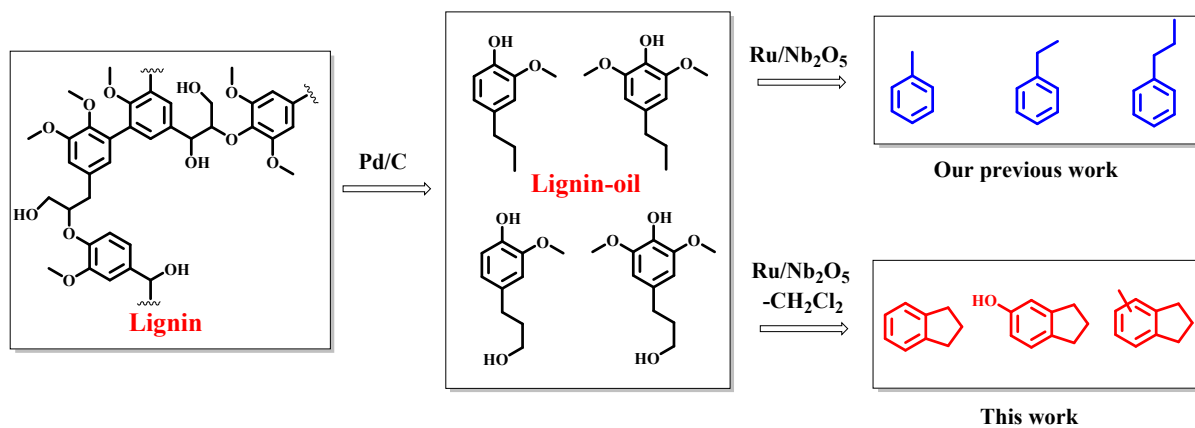
Procedure for the syntheses of model compounds of lignin monomers

3-(4-hydroxyphenyl)propanol (A): A dry 500 mL three-necked flask equipped with a mechanical stirrer and a reflux condenser was charged with LiAlH₄, THF and 3-(4-hydroxyphenyl) propanoic acid. The mixture was stirred at 70 °C overnight. After the solution was cooled to ambient temperature, NaOH aqueous solution was added dropwise into the flask until the solution is alkaline, and then MgSO₄ was added. After filtrating the solution, the filtrate was evaporated under reduced pressure to remove THF and the pH of solution was adjusted to less than 1. The aqueous phase was extracted with ethyl acetate (3*50 mL) and the combined organic phase were concentrated under reduced pressure to obtain final products. (see Scheme S1)

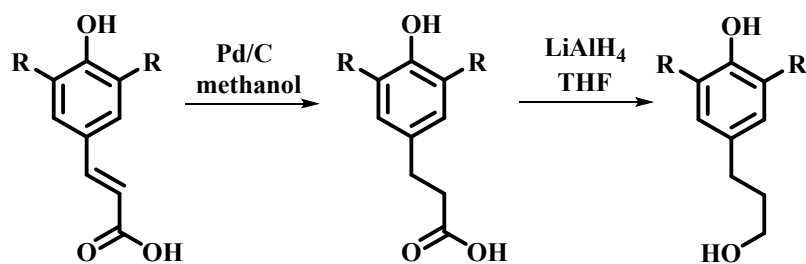
4-(3-hydroxypropyl)-2-methoxyphenol (B): The process was same as above with the exception of the substrate, 3-(4-hydroxy-3-methoxyphenyl) propanoic acid is used here.

4-(3-hydroxypropyl)-2,6-dimethoxyphenol (C): The process was same as above with the exception of the substrate, 3-(4-hydroxy-3,5-dimethoxyphenyl) propanoic acid is used here.

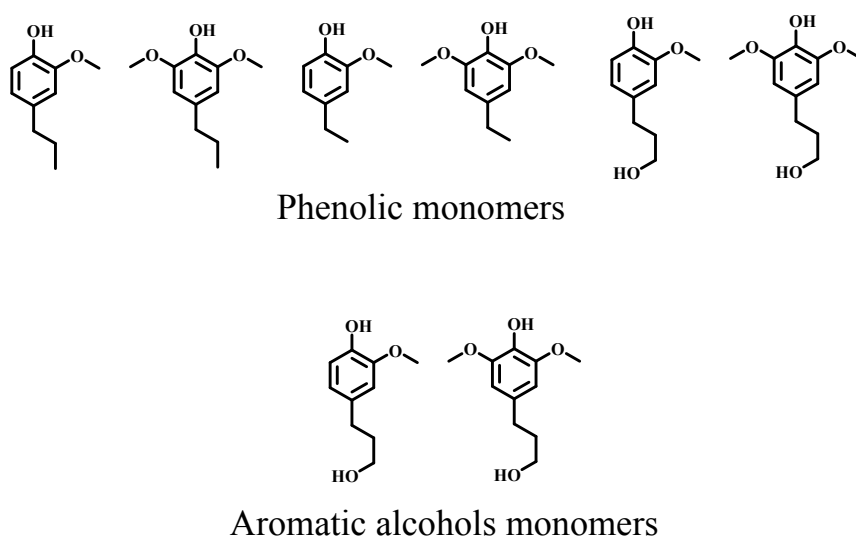
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (400 MHz, CDCl₃) spectrums of compound A, B and C were recorded in Fig. S1-Fig. S6.



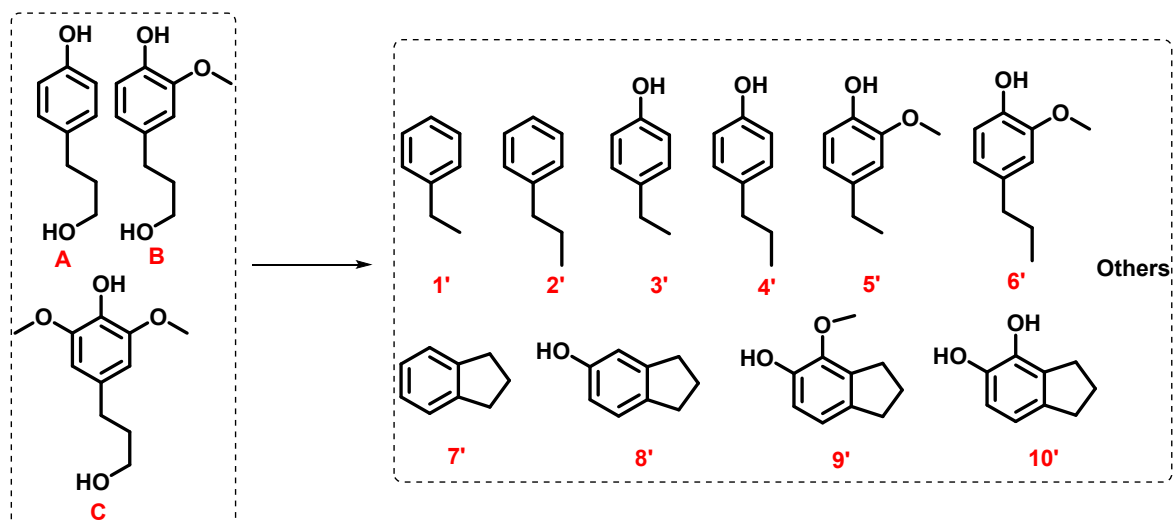
Scheme S1. Scheme for the conversion of lignin into indane and its derivatives.



Scheme S2. Synthesis of three lignin model compounds.



Scheme S3. The structures of phenolic monomers and aromatic alcohols monomers.



Scheme S4. View of the chemical structures for all possible intermediates and products during the conversion of three lignin model compounds.

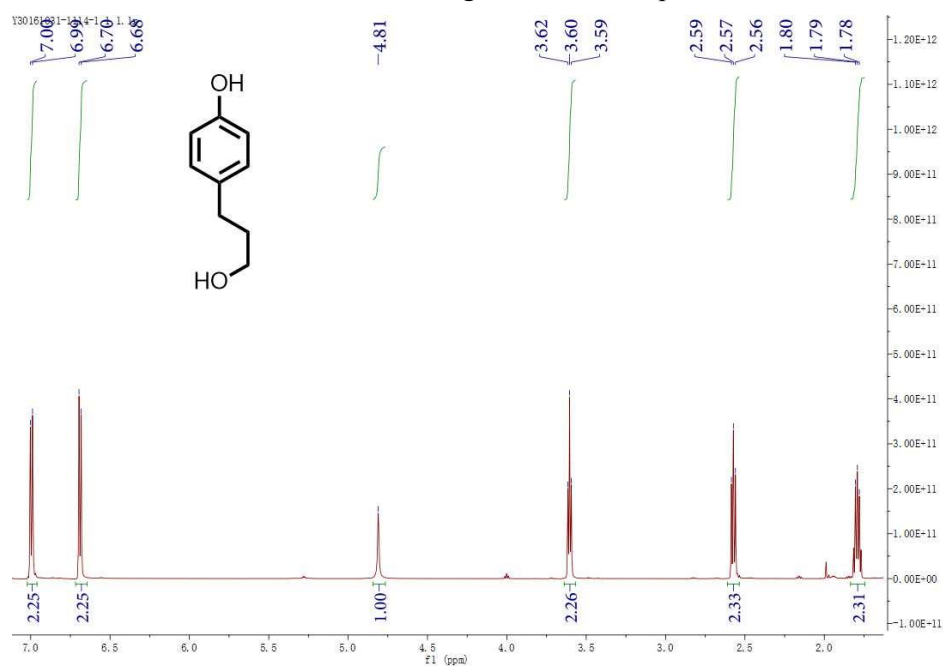


Fig. S1 ^1H NMR (400 MHz, CDCl_3) spectrum of compound A.

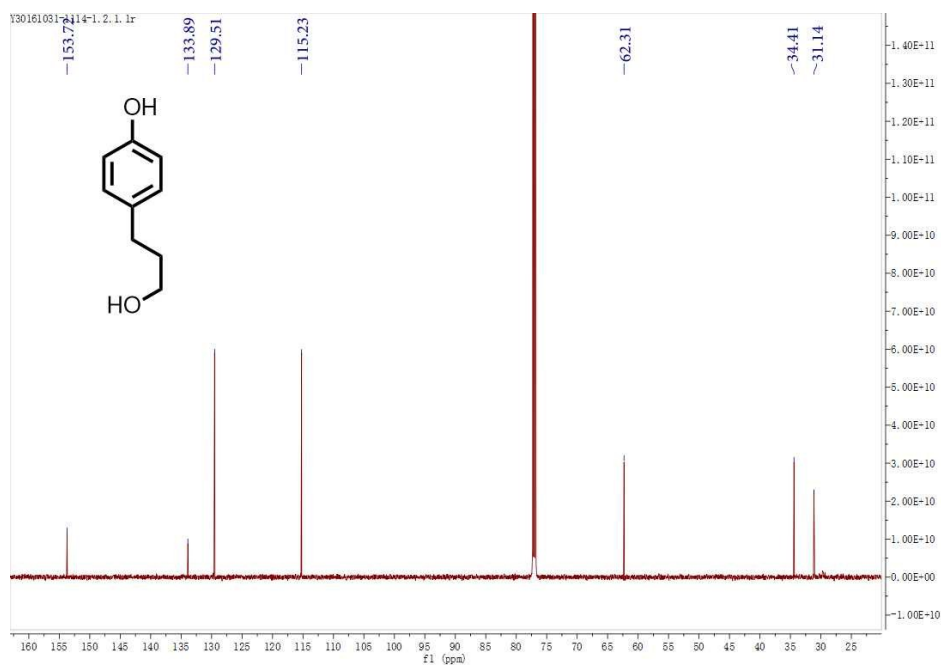


Fig. S2 ^{13}C NMR (400 MHz, CDCl_3) spectrum of compound A.

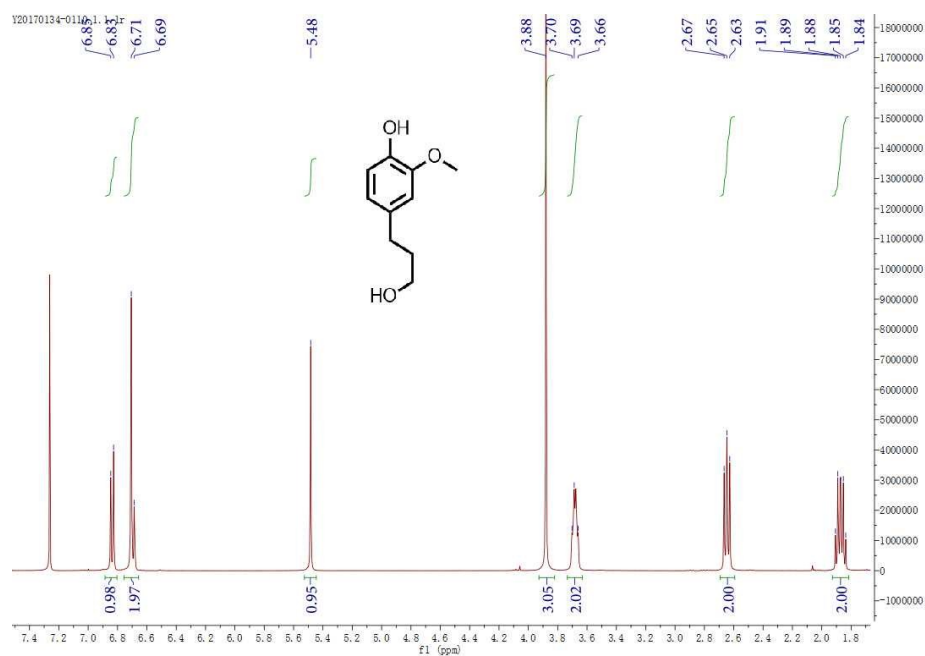


Fig. S3 ^1H NMR (400 MHz, CDCl_3) spectrum of compound B.

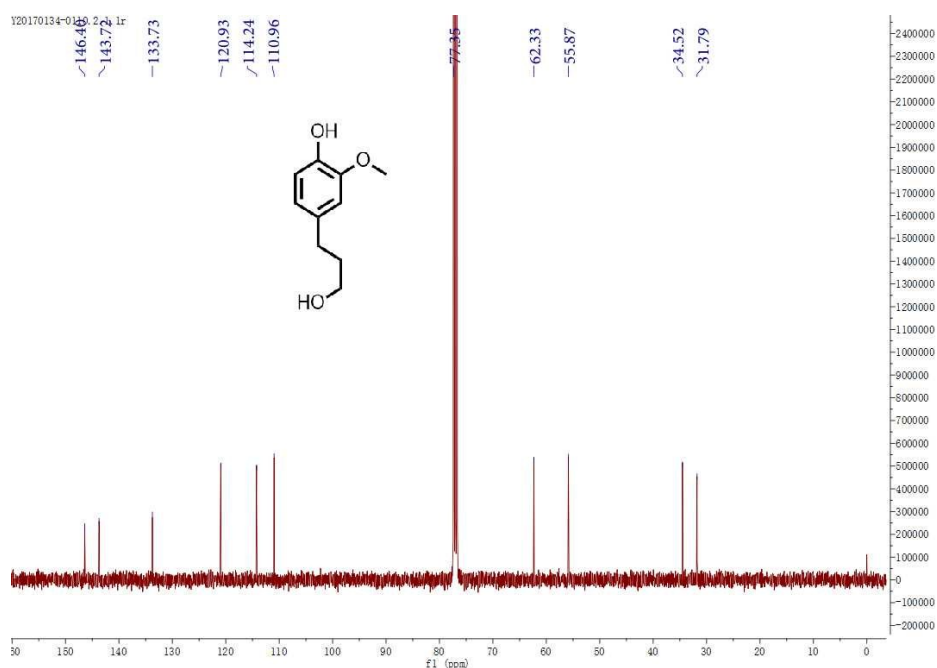


Fig. S4 ^{13}C NMR (400 MHz, CDCl_3) spectrum of compound B.

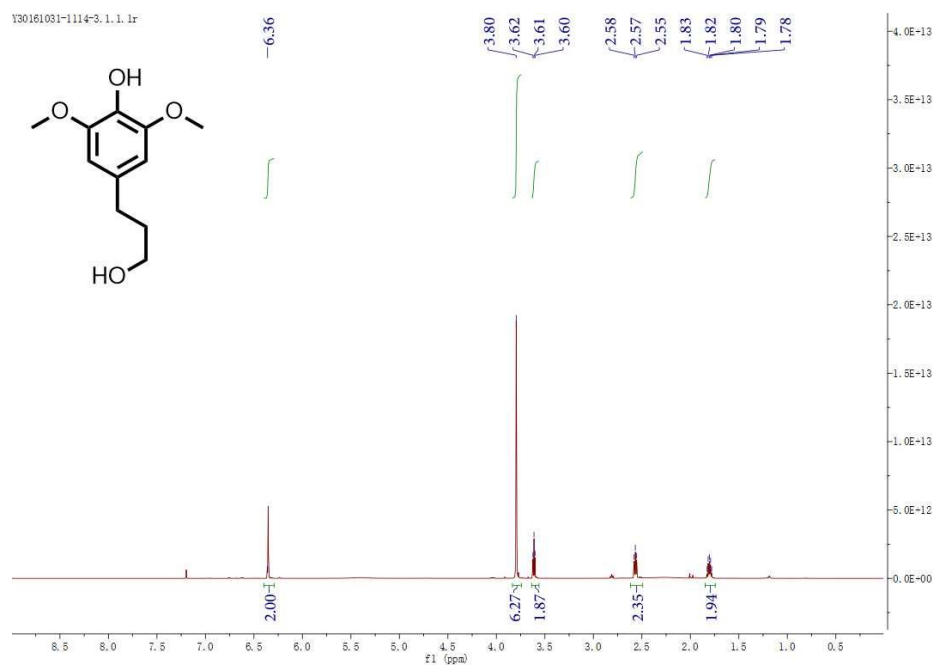


Fig. S5 ^1H NMR (400 MHz, CDCl_3) spectrum of compound C.

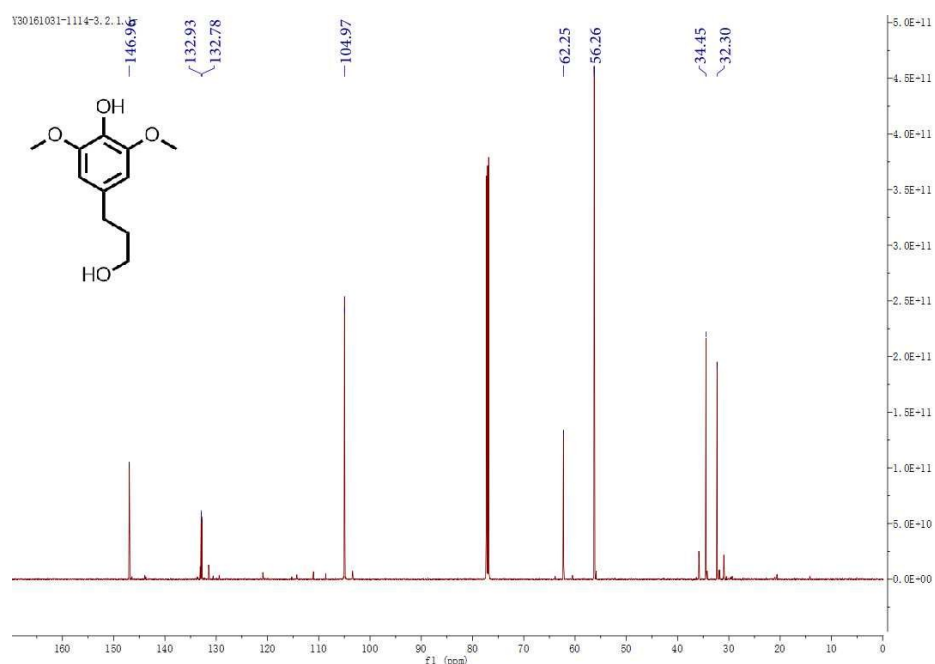


Fig. S6 ^{13}C NMR (400 MHz, CDCl_3) spectrum of compound C.

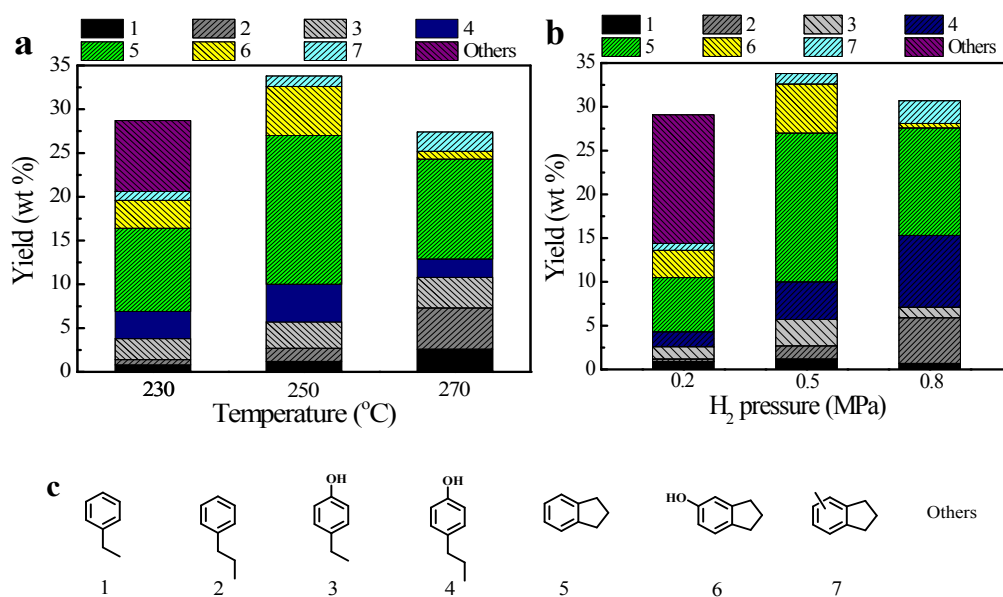


Fig. S7 (a) Effect of reaction temperature on the yield of products from birch-wood lignin oil. Reaction conditions: lignin oil (0.1 g), Ru/Nb₂O₅ (0.1 g), H₂O (15 mL), CH₂Cl₂ (50 μL), 0.5 MPa H₂, 20h. Others include cyclized products with methoxy groups. **(b)** Effect of hydrogen pressure on the yield of products from birch-wood lignin oil. Reaction conditions: lignin oil (0.1 g), Ru/Nb₂O₅ (0.1 g), H₂O (15 mL), CH₂Cl₂ (50 μL), 250 °C, 20h. Others include cyclized products with methoxy groups. **(c)** View of the chemical structures for all possible products.

At relatively low temperature (230 °C), the yields of products 5-7 are only 13.7 wt%, with 8.1 wt% cyclized products having methoxy groups (others) due to the weak hydrogenolysis activity. It is reported that cyclized products with methoxy groups tend to polymerize in aqueous solution, [4] which results in the low total yield (28.7 wt%). Increasing temperature (250 °C) leads to an increase of total products yields to 33 wt% and a remarkable decrease in the yields of oxygenated compounds. However, further increasing the reaction temperature to 270 °C, the yields of indane and its derivatives decrease to 14.5 wt% with the increase of products 1-4. This result means that the hydrogenolysis activity (route 2 and route 3 in Scheme 2) was enhanced and the cyclization reaction (route 1 in Scheme 2) was inhibited at high temperature (Fig. S7a).

Besides the reaction temperature, the hydrogen pressure has also influenced the yield of indane (Fig. S7b). 10.1 wt% yields of 5-7 with lots of oxygenated compounds were obtained at 0.2 MPa H₂, which indicates that the hydrogen pressure is not sufficient to convert lignin oils. At 0.5 MPa H₂, the products are composed of 2.7 wt% aromatic hydrocarbon, 7.3 wt% phenolic compounds and 23.7 wt% indane and its derivatives. Increasing the hydrogen pressure to 0.8 MPa H₂ leads to the decrease of total mass yield of aromatic compounds (from 33.8 to 30.7 wt%) and that of indane production (from 23.7 wt% to 15.4 wt%), which may be due to the strong hydrogenolysis activity and weak intramolecular cyclization rate at high hydrogen pressure. These results indicate that high hydrogen pressure was not conducive to the production of indane and its derivatives and the hydrogen pressure should be in a proper range for achieving high yield of products 5-7.

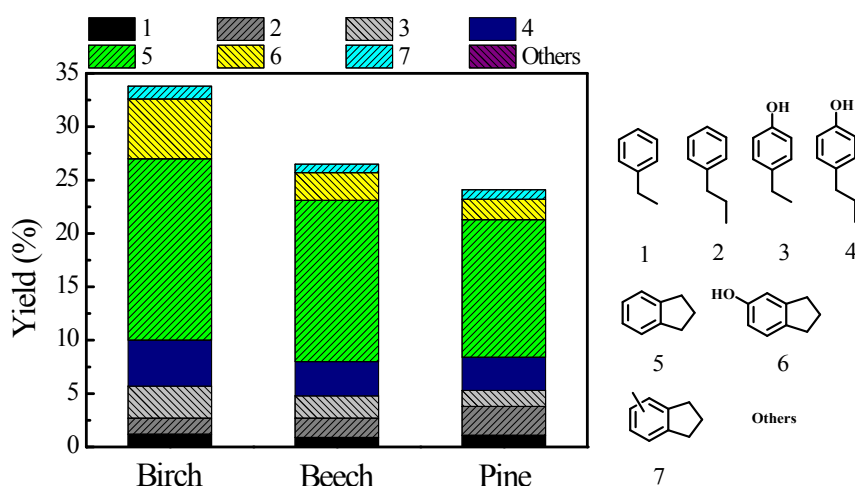


Fig. S8 Effect of different sources of lignin oils on the yield of products. Reaction conditions: lignin oil (0.1 g), Ru/Nb₂O₅ (0.1 g), H₂O (15 mL), CH₂Cl₂ (50 μL), 0.5 MPa H₂, 250°C, 20h. Others include cyclized products with methoxy groups.

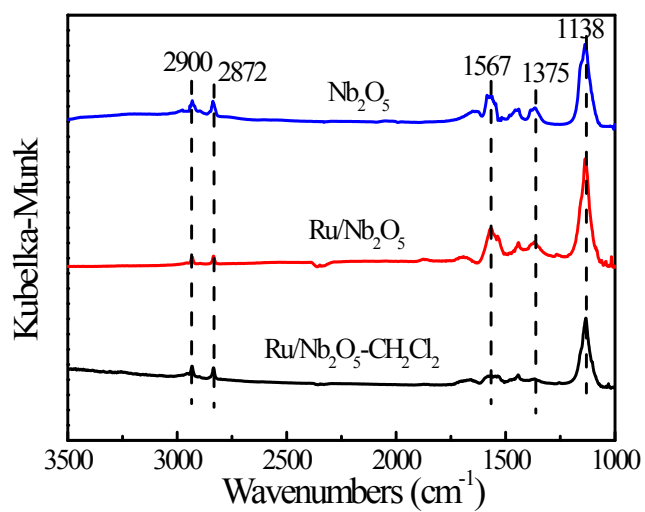


Fig. S9 Fourier-transformed infrared spectra of 4-methylphenol adsorption on Ru/Nb₂O₅ and Ru/Nb₂O₅-CH₂Cl₂ samples recorded in 1000-3500 cm⁻¹.

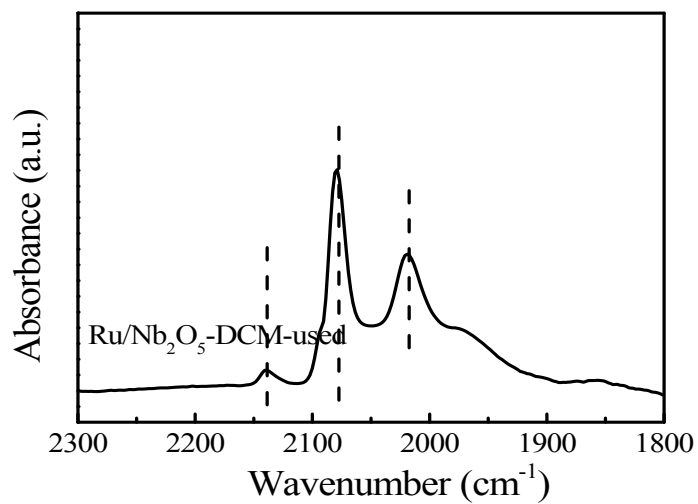


Fig. S10 *in situ* Fourier-transformed infrared spectra of CO adsorption over Ru/Nb₂O₅-DCM-used sample.

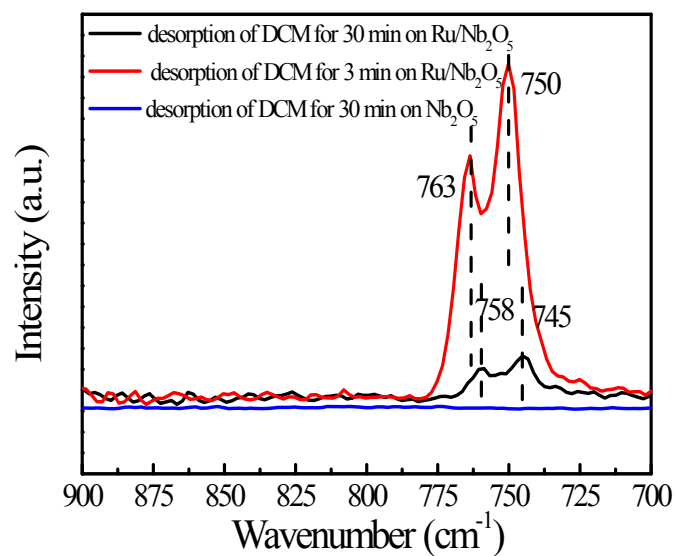


Fig. S11 *in situ* Fourier-transformed infrared spectra of CH_2Cl_2 adsorption over $\text{Ru}/\text{Nb}_2\text{O}_5$ and Nb_2O_5 sample.

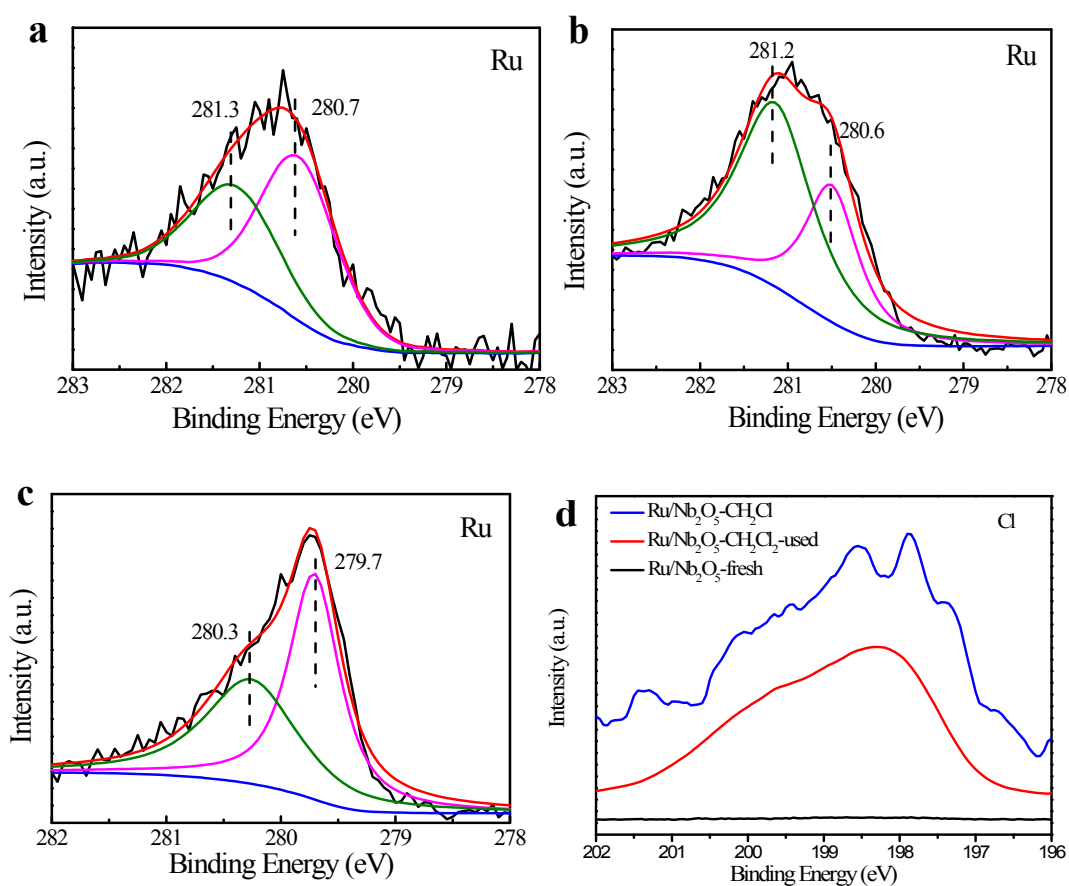


Fig. S12 XPS spectra of Ru $3d_{5/2}$ of (a) $\text{Ru}/\text{Nb}_2\text{O}_5$ -fresh, (b) $\text{Ru}/\text{Nb}_2\text{O}_5$ -used and (c) $\text{Ru}/\text{Nb}_2\text{O}_5$ -DCM-used and (d) Cl $2p$ of three samples.

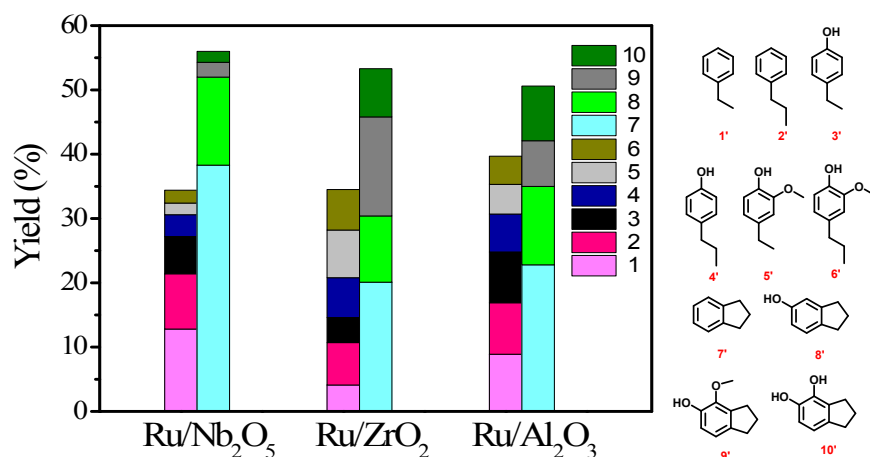


Figure S13 Conversion and products distribution of lignin model compound B over various catalysts. Reaction conditions: substrate (0.1 g), catalyst (0.1 g), H₂O (15 mL), 0.5 MPa H₂, 250°C, CH₂Cl₂ (50 μL), 20h.

Table S1. Yield of lignin oil and lignin monomer from various lignocellulosic biomass.^[a]

Biomass	Mass yield of lignin oils/wt	Phenolic monomers	Aromatic alcohol monomers
	% ^[b]	in lignin oil /wt % ^[c]	in lignin oil /% ^[d]
Birch wood	19.6	49.5	42.7
Beech wood	21.1	43.1	34.5
Pine wood	16.2	41.3	34.3

[a] Reaction conditions: lignocellulosic biomass (1 g), 5 wt% Pd/C (0.1 g), methanol (20 mL), initial H₂ pressure of 3MPa, 250 °C, 3 h. [b] Calculated based on the weight of final liquids. [c] Phenolic monomers yield=weight of phenolic monomers / weight of lignin oil *100% [d] Aromatic alcohol monomers yield=weight of aromatic alcohol monomers / weight of lignin oil *100%

Table S2. Nomenclature for samples

Sample name	Sample information
Ru/Nb ₂ O ₅ -CH ₂ Cl ₂	Ru/Nb ₂ O ₅ treated with CH ₂ Cl ₂
Ru/Nb ₂ O ₅ -DCM	Ru/Nb ₂ O ₅ with the addition of CH ₂ Cl ₂ during reaction

Table S3. Conversion and products distribution of model compound **B** over Ru/Nb₂O₅ catalyst in presence of hydrochloric acid

Substrate	Conv./ %	Yield/%											Carbon Balance/ %
		1'	2'	3'	4'	5'	6'	7'	8'	9'	10'	Others ^[c]	
B	>99	56.3	21.4	-	-	-	-	2.3	-	-	-	10.4	90.4

Reaction conditions: substrate (0.1 g), Ru/Nb₂O₅ (0.1 g), H₂O (15 mL), 0.5 MPa H₂, 250°C, 20h, 0.06 g HCl.

Table S4. Conversion and products distribution of lignin model compound B over Ru/ZrO₂ and Ru/Al₂O₃.

Catalyst	Conv./ %	Yield/%											Carbon Balance/%
		1'	2'	3'	4'	5'	6'	7'	8'	9'	10'	Others ^[c]	
Ru/ZrO ₂ ^[a]	>99	41.3	23.2	-	-	-	-	-	-	-	-	30.7	95.2
Ru/ZrO ₂ ^[b]	>99	4.1	6.6	3.9	6.2	7.4	6.3	20.1	10.3	15.4	7.5	-	87.8
Ru/Al ₂ O ₃ ^[a]	>99	38.8	25.3	-	-	-	-	-	-	-	-	28.4	92.5
Ru/Al ₂ O ₃ ^[b]	>99	8.9	8.0	7.9	5.9	4.6	4.4	22.8	12.2	7.1	8.5	-	89.3

[a] Reaction conditions: substrate (0.1 g), catalyst (0.1 g), H₂O (15 mL), 0.5 MPa H₂, 250°C, 15h. [b]

Reaction conditions: the same as a with the exception of the addition of CH₂Cl₂ (50 μL) and reaction time,

20h here. [c] Others mainly include ring-saturated products with toluene as minor product.

Table S5. The quantitative results of XPS of Ru/Nb₂O₅, Ru/Nb₂O₅-CH₂Cl₂ and Ru/Nb₂O₅-DCM-used.

Catalyst	Binding Energy (eV)	
	Ru ⁰	Ru ⁴⁺
Ru/Nb ₂ O ₅ -fresh	280.7(53.5%)	281.3(46.5%)
Ru/Nb ₂ O ₅ -used	280.6(34.8%)	281.2(65.2%)
Ru/Nb ₂ O ₅ -DCM-used	279.7(54.5%)	280.3(45.5%)

References

- [1] S. V. Bosch, W. Schutyser, S. F. Koelewijn, T. Renders, C. M. Courtin, B. F. Sels. Tuning the lignin oil OH-content with Ru and Pd catalysts during lignin hydrogenolysis on birch wood, *Chem. Commun.* 51 (2015) 13158-13161.
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- [3] L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Heroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph, J. S. Luterbacher. Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization, *Science* 354 (2016) 329-333.
- [4] L. Shuai, B. Saha, Towards high-yield lignin monomer production. *Green Chem.* 19 (2017) 3752-3758.