Supporting information for

Selective isomerization of β -pinene: a sustainable method for total utilization of turpentine as biomass resource

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Experimental Section

All starting materials and solvents were purchased from Sigma-Aldrich or Thermo Scientific Chemicals and were used without further purification. Data from Gas Chromatography with Flame Ionisation Detection (GC-FID) were recorded using Thermo Scientific Trace 1310 gas chromatograph equipped with a Thermo Scientific TG-17MS column (length 30 m, internal diameter 0.25 mm, film thickness 0.25 µm) or with a Thermo Scientific TG-1MS column (length 30 m, internal diameter 0.25 mm, film thickness 0.25 µm). Gas chromatography-mass spectrometry (GC-MS) was carried out using an JEOL JMS-T200GC AccuTOF GCx equipped with an Agilent DB 5MS column (length 30m, internal diameter 0.25 mm, film thickness 0.25 µm). Mass spectra were acquired in the electron impact mode at 70 eV using an m/z range of 40-500 and 0.5 s recording interval. Compound identification was done by comparison of the mass spectra against a database (NIST), when reference compounds were not available. Nuclear Magnetic Resonance (NMR) spectroscopy data were recorded with the Bruker DPX 400 MHz spectrometer operating at 400 MHz (¹H), 61.4 MHz (²H), 101 MHz (¹³C), assigning chemical shifts in parts per million (ppm). MestReNova 14.2.2 ©2021 (Mestrelab Research S. L.) was used for analysing the spectra. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was conducted using a Perkin Elmer Optima 2000 DV. Solutions were prepared by digestion of catalysts (ca. 10 mg) in agua regia, followed by dilution to 10 ml in 5% HCl solution after removal of solids by centrifugation. Transmission Electron Microscopy (TEM) images were collected using a JEM-2100+ TEM using 'Lacey' carbon covered 200 mesh copper grids, purchased from Agar scientific. Analysis of TEM images were conducted using GATAN DigitalMicrograph3 and ImageJ software. Powder X-ray diffraction (PXRD) patterns were measured on a PANalytical X'Pert PRO diffractometer with a Cu-Ka source (40 kV, 40 mA) with a step size of 0.01° and a 210 s time step from 20° to 60°. XPS data was collected using a Thermo Scientific K-Alpha X-ray spectrometer with a monochromated aluminium source at 1486 eV. High resolution X-ray Photoelectron Spectroscopy (HR XPS) analysis was carried out using CasaXPS software (version 2.3.24) and all fittings obtained using Gaussian-Lorentzian line shapes (SGL(10) for Pd(II) and LA(50) for Pd(0)) and a Shirley baseline, and calibrated to the adventitious C 1s signal at 284.8 eV. Light Emitting Diodes (LEDs) used included Luzchem 365nm 7 LED, Luzchem 455nm 7 LED and Evoluchem 365DX lamp. Thermal Gravimetric Analysis (TGA) was performed using a TA Instruments Q500 TGA with platinum crucibles over a temperature range of 30 to 800 °C (10 °C min⁻¹ ramp) in air.

Palladium nanoparticles supported on TiO_2 (Pd@TiO_2) were prepared by photodeposition. P25 TiO_2 (2.0 g) and PdCl₂ (44.0 mg) were dispersed in Milli-Q water (400 ml) and stirred for 5 min, then sonicated for 15 minutes .The reaction mixture was irradiated using Evoluchem 365nm LED for 5 h, with vigorous stirring, which resulted in a brown slurry. The catalyst was separated via centrifugation and was washed five times, followed by desiccation which resulted in a fine brown powder of Pd@TiO_2 (1.9 g). TEM imaging showed ~2nm Pd nanoparticles on the titania support. ICP-OES gave a weight loading of 1.3% of Pd on TiO_2. The catalyst was kept in a desiccator throughout the project for reliable activity.

Degassed solvent (4 ml) and the terpene were added to $Pd@TiO_2$ under inert conditions. The reaction mixture was sonicated for 15 min and then irradiated using the Luzchem 365 nm LED or 455 nm LED with continuous stirring at room temperature with varying times/intensity as stated in the main text. The reaction was followed by GC-FID analysis and the products were quantified using tridecane as an external standard.

Catalyst characterisation



Figure S1. Transmission electron microscopy image of the Pd@TiO₂ catalyst used for this study showing Pd nanoparticles (dark spots) on the surface of the larger TiO₂ particles a) before reaction and b) after reaction. Inset: Histogram showing Pd nanoparticle size distribution.



Figure S2. PXRD pattern of Pd@TiO₂ showing diffraction peaks corresponding to anatase formation of anatase (JCPDS card no. 21-1272) and rutile (JCPDS card no. 21-1276) faces of TiO₂. Diffraction peaks corresponding to Pd species (Pd NP or PdO) are not detected, potentially due to the low metal loading in the material.



Figure S3. The emission spectrum of the 455 nm LEDs employed for the photoisomerisation of β -pinene. The filled area (blue) shows the portion of irradiance with sufficient energy to overcome the Pd@TiO₂ band gap.



Figure S4. The diffuse reflectance spectrum of the photodeposited Pd@TiO₂ used in this study.



Figure S5. HR XPS spectra for 3d Pd region showing the surface of $Pd@TiO_2$ before and after one reaction using different solvents (a-e) and after 4 catalytic cycles as per Figure 2 (f).

Thermogravimetric Analysis



Figure S6. Thermogravimetric analysis (TGA) of Pd@TiO₂ before reaction (black) and after reaction conducted in dark conditions (red). Each thermogram has three characteristic transitions: i) loss of volatile solvents adsorbed on the catalyst surface at 60 °C, ii) evaporation and/or decomposition of organic molecules between 60 and 400 °C, iii) decomposition of more amorphous carbon between 400 and 600 °C, and iv) oxidation of Pd around 900 °C.

Entry	Catalyst	Mass change / %				
Lintry	Catalyst	Event i	Event ii	Event iii		
i	Before reaction	0.58	1.95	0.26		
ii	After reaction	1.33	2.84	0.55		
iii	Difference	0.75	0.89	0.29		

Table S1. Percentage mass changes extracted from the TGA thermogram shown in Fig. S2.

Solvent Screening

		Pd@TiO ₂ , solvent 365 nm, 5 min	-	
Entry	Solvent	Polarity index	Conversion (%)	Yield (%)
i	MeCN	5.8	11 ^[a]	<1
ïi	IPA	3.9	99	91
iii	Toluene	2.4	8 ^[a]	<1
iv	Heptane	0	14 ^[a]	<1

Table S2. Screening of solvents for reaction conditions explored in Table 1, entry iv.

^[a] Conversion attributed to adsorption to the catalysts surface.

Leaching Test

Degassed IPA (4 ml) and β -pinene (0.25 mmol) were added to Pd@TiO₂ under inert conditions. The reaction mixture was sonicated for 15 min and then irradiated using a Luzchem 365 nm LED with an intensity of 1.3 Wcm⁻², under continuous stirring for 5 minutes. The reaction mixture was then centrifuged to remove the catalyst, and the reaction supernatant was weighed. The solvent was then removed by rotary evaporation, and the remaining organic material was ashed overnight at 400 °C. The resultant material was then digested in aqua regia at 175 °C for 30 minutes in a microwave reactor. The resultant solution was then made to up to 10 ml in a volumetric flask, and then analysed via ICP-OES. The total amount of Pd detected in the solution was 0.08 µg, compared to the 100.48 µg of Pd present on 8 mg on the original catalyst. The LOD and LOQ for the ICP-OES analysis was found to be 0.05 µg and 0.07 µg, respectively.

Kinetic studies



Figure S7. Kinetic analysis of the isomerisation of β-pinene under air. Reaction conditions: β-pinene (0.25 mmol), Pd@TiO₂ catalyst (8 mg, 0.4 mol%), 4 ml IPA, LED irradiation centred at 365 nm, 1.3 Wcm⁻². Yields calculated via GC-FID using tridecane as external standard.



Figure S8. Kinetic analysis of the isomerisation of β -pinene under N₂ atmosphere. Left: IPA. Right: deuterated IPA (d₈-IPA). Reaction conditions: β -pinene (0.25 mmol), Pd@TiO₂ catalyst (8 mg, 0.4 mol%), 4 ml IPA, LED irradiation centred at 365 nm, 1.3 Wcm⁻². Yields calculated via GC-FID using tridecane as external standard.



Figure S9. Kinetics for the isomerisation of β -pinene shown in table 3. Reaction conditions: β -pinene a) 0.25 mmol b) 2.5 mmol c) 12.5 mmol), Pd@TiO₂ catalyst a) and b) 8 mg, c) 40 mg, IPA a) 4 ml, b) 3.6 ml, c) 4.7 ml), N₂ atmosphere, LED irradiation centred at 365 nm and working at 0.33 Wcm⁻². Conversions and yields calculated via GC-FID using tridecane as external standard.

NMR spectra of isolated α-pinene



Figure S10. ¹H NMR (400 MHz, CDCI₃) spectrum of isolated α-pinene product, showing only IPA as an impurity.



Figure S11. ¹³C NMR (100 MHz, CDCl₃) spectrum of isolated α-pinene product.

NMR spectra of starting materials



Figure S12. ¹H NMR (400 MHz, CDCl₃) spectrum of α -pinene starting material.



Figure S13. ¹³C NMR (101 MHz, CDCl₃) spectrum of α-pinene starting material.





Figure S15. ^{13}C NMR (101 MHz, CDCl₃) spectrum of β -pinene starting material.



Figure S17. ¹³C NMR (101 MHz, CDCl₃) spectrum of turpentine starting material.

Isotopic studies



Figure S18. ¹H NMR (400 MHz, d₈-IPA) spectrum of product after reaction in deuterated IPA.



Figure S19. ²H NMR (61.4 MHz, d₈-IPA) spectrum of product after reaction in deuterated IPA.

Reusability Studies

Entry	Cycle	Intensity (Wcm ⁻²)	Conversion (%)	Yield (%)
i	1	1.3	100	96
ii	2	1.3	100	94
iii	3	1.3	100	97
iv	4	1.3	100	95
Vi	1	0.33	71	71
vi	2	0.33	94	70
vii	3	0.33	91	79
viii	4	0.33	48	51

Table S3. Reusability tests.^[a]

^[a] Reaction conditions: β-pinene (0.25 mmol), 8 mg Pd@TiO₂ catalyst, 4 ml IPA, N₂ atmosphere, LED irradiation centred at 365 nm for 5 minutes Pd@TiO₂ was removed via centrifugation and dried in a vacuum desiccator before use in the next cycle. Yields calculated via GC-FID using tridecane as external standard.

Substrate Testing

The other terpenes tested demonstrated limited reactivity under the optimised reaction conditions for β pinene isomerisation (Table 4, entries iii-vi). At longer reaction times, however, moderate conversion via isomerisation or hydrogenation processes was observed (Table S4, entries iii-vi). Both the δ^2 and δ^3 isomers of carene underwent isomerisation to interconvert between these forms when the irradiation time was extended to 16 hours (Table S4 entries iii and iv), as with α - and β -pinene, no hydrogenation products were detected even after long irradiation times, which could be attributed to geometry constrains within the molecule that imped interaction with the catalyst surface. The less stable secondary isomers were not observed. Due to its lack of α -H, camphene was found to only undergo hydrogenation (Table S4, entry v). This hydrogenation was found to form both diastereomers suggesting that the photocatalyst can access both sides of the alkene.

Limonene was found to be the most reactive of the other terpenes tested and was observed to undergo oxidation, isomerisation and hydrogenation processes (Scheme S1). The major products were found to be *p*-menth-1-ene –via hydrogenation of the limonene terminal double bond– and γ -terpinene –via isomerisation. The preference for the isomerisation to the γ -terpinene is expected as this is the most stable configuration of cyclohexyl 1,4-diene. The oxidation of limonene to *p*-cymene could be as a result of trace oxygen present in the reaction mixture.



Scheme S1. Potential products for the hydrogenation, isomerisation and oxidation of limonene. Yields of each observed product after 5 min under the reaction conditions described in table 4 (and Table S4). Values in brackets correspond to yields after 60 min.



Figure S20. EI-MS spectrum of R-limonene extracted from GC-MS analysis of the limonene reaction mixture (Table S4, entry *vi*).



Figure S21. EI-MS spectrum of *p*-menth-1-ene extracted from GC-MS analysis of the limonene reaction mixture (Table S4, entry vi).



Figure S21. EI-MS spectrum of an unidentified monohydrogenated product (potentially isomers *p*-menth-2-ene, *p*-menth-3-ene, or *p*-menth-4-ene) extracted from GC-MS analysis of the limonene reaction mixture (Table S4, entry vi).



Figure S22. EI-MS spectrum of γ -terpinene extracted from GC-MS analysis of the limonene reaction mixture (Table S4, entry vi).



Figure S23. EI-MS spectrum of terpinolene (δ -terpinene) extracted from GC-MS analysis of the limonene reaction mixture (Table S4, entry vi).



Figure S24. EI-MS spectrum of *p*-cymene extracted from GC-MS analysis of the limonene reaction mixture (Table S4, entry vi).

Process mass intensification

Process mass intensities (PMI) in this study were calculated according to Equation S1:

$$Process Mass Intensity = \frac{Total Mass of Reaction}{Mass of Final Product}$$
Eq. S1

Where the total mass of the reaction includes all reagents, reactants, catalysts and solvents, both in the reaction itself and across any work-up steps. However, it does not include the mass required in any chromatographic separation, as this information was not available for previous works, and the technique was not employed within this work.

PMI for homogeneous catalysis approach¹:

 $PMI = \frac{1.362 g [\beta - pinene] + 2.139 g [Na_2Fe(CO)_4] + 53.256 g [THF] + 2.000 g [CuCl] + 49.852 g [water]}{1.076 g [\alpha - pinene yield]} = 177.8$

PMI for homogeneous photocatalysis** approach²:

$$PMI = \frac{0.0026 g [Co(acac)_2] + 0.0016 g [4CzIPN] + 0.0506 g [Hantzsch ester] + 0.0276 g [K_2CO_3] + 1.896g [DMF]}{0.0272 g [\beta - pinene] + 3.988 g [water] + 4.955 g [Hexane] + 6.765 g [EtOAc]} = 663.4$$

**The experimental procedure indicates an extra washing step using brine, but quantities are not specified and therefore not considered in this calculation.

PMI for heterogeneous catalysis[†] approach ³:

$$PMI = \frac{0.1362 \ g \ [\beta - pinene] + 0.00285 \ g \ [Pd] + \uparrow g \ [IL] + 1.261 \ g \ [glycerol] + \uparrow g \ [H_2] + 19.899 \ g \ [CH_2Cl_2]}{0.0954 \ g \ [\alpha - pinene \ yield]} = 223.3$$

⁺The amount of H₂ and choline *N*-tosylalaninate ionic liquid (IL) used is not disclosed in the experimental procedure. No separation attempts were made. Therefore, this calculation underestimates the real PMI.

PMI for this work:

$$PMI = \frac{1.71 \ g \ [\beta - pinene] + 0.04 \ g \ [Pd@TiO_2] + 3.70 \ g \ [IPA]}{1.54 \ g \ [\alpha - pinene \ yield]} = 3.5$$

Table S5. Part I. Qualitative environmental impact of this approach in comparison with other known technologies using suggestions from ref⁴.

Factor ^[a]	Homogeneous catal	ysis ¹	Homogeneous photo	ocatalysis ²	Heterogeneous catalysis ³		Heterogeneous photocatalysis (this work)	
Acidification	Not applicable		Not applicable		Not applicable		Not applicable	
Bio- accumulation	Not available (N/A)		Not available (N/A)		Glycerol: Not expected Others: Not Available (N/A)		Not available (N/A)	
Ecotoxicity Toxicity to daphnia LC50, otherwise stated	$\begin{array}{c} Na_2Fe(CO)_4: N/A \\ CuCl: 0.25 mg/l \\ THF: 3,485 mg/l \\ (NH_4)_2Ce(NO_3)_6: > 100 mg/l \\ Diethyl ether: 1,380 mg/l \\ Brine: N/A \end{array}$		Co(acac) ₂ : 6.68 mg/l K ₂ CO ₃ : 200 mg/l DMF: 13,100 mg/l Hantzsch ester: N/A 4CzIPN: N/A Hexane: 2.1 mg/l Ethyl acetate: 2.4 mg/l Brine: N/A		PdCl ₂ (cod): N/A Glycerol: N/A CH ₂ Cl ₂ : 27 mg/l TSC: EC50 >334 mg/l NaOH: EC50 40.4 mg/l Alanine: EC50 >100 mg/l ChoOH: EC50 >500 mg/l		PdO ^[b] : N/A TiO ₂ : 1,000 mg/l IPA: 13,299 mg/l	
Energy usage	Low		Medium-High (high-bo	oiling solvent)	Medium-High (water e	evaporation)	Low	
Eutrophication	Low		Medium (N containing	(compounds)	Medium (N containing compounds)		Low	
Flammability	High Na ₂ Fe(CO) ₄ : Catches exposed to air. CuCl: Nonflammable THF: Flash point -21.2 NH ₄) ₂ Ce(NO ₃) ₆ : Nonfla Diethyl ether: Flash po Brine: Nonflammable	fire spontaneously if 2 °C ammable pint -40 °C	High ^[c] Co(acac) ₂ : Nonflammable DMF: Flash point 57.5 Hantzsch ester: N/A 4CzIPN: N/A Hexane: Flash point - Ethyl acetate: Flash p Brine: Nonflammable	able 5°C -22 °C oint -4 °C	Low $PdCl_2(cod)$: N/A Glycerol: Flash point 199 °C $CH_2Cl_2:$ 27 mg/l TSC: Flash point 128 °C NaOH: Not applicable Alanine: Not applicable ChoOH: Not applicable		Medium PdO: Nonflammable TiO ₂ : Nonflammable IPA: Flash point 12.0	°C
Human toxicity	LC50 (rat, inhalation) CuCl: N/A Na ₂ Fe(CO) ₄ : >0.51 mg/l THF: >14.7 mg/l (NH ₄) ₂ Ce(NO ₃) ₆ : N/A Diethyl ether: 97.5 mg/l (mouse) Brine: N/A	LD50 (rat, oral) CuCl: >336 mg/kg Na ₂ Fe(CO) ₄ : N/A THF: >1,650 mg/kg (NH ₄) ₂ Ce(NO ₃) ₆ : > 300 - 2,000 mg/kg Diethyl ether: 1,211 mg/kg Brine: N/A	LC50 (rat, inhalation) Co(acac) ₂ : >5.09 mg/l K ₂ CO ₃ : >4.96 mg/l DMF: >11.1 mg/l Hantzsch ester/4CzIPN: N/A Hexane: 172 mg/l Ethyl acetate: N/A Brine: N/A	LD50 (rat, oral) Co(acac) ₂ : 300- 2,000 mg/kg K_2CO_3 : >2,000 mg/kg DMF: >3,010 mg/kg Hantzsch ester/4CzIPN: N/A Hexane: 16,000 mg/kg Ethyl acetate: 5,620 mg/kg Brine: N/A	LC50 (rat, inhalation) PdCl ₂ (cod): N/A Glycerol: > 5,850 mg/l CH ₂ Cl ₂ : 86 mg/l TSC: N/A NaOH: N/A Alanine: N/A ChoOH: N/A	LD50 (rat, oral) PdCl ₂ (cod): N/A Glycerol: 27,200 mg/kg CH ₂ Cl ₂ : > 2,000 mg/kg TSC: 4,680 mg/kg NaOH: N/A Alanine: N/A ChoOH: 11,000 mg/kg	LC50 (rat, inhalation) PdO: N/A TiO ₂ : N/A IPA: 4 h, 37.5 mg/l	LC50 (rat, oral) PdO: > 4,900 mg/kg TiO₂: > 10,000 mg/kg IPA: 5,840 mg/kg

^[a] All information obtained from SDS sheets of the named compounds. ^[b] Data for PdO was considered as this is the suspected form of Pd in the event of metal leaching. ^[c]Partial evaluation as data is not available for some compounds. Co(acac)₂: Co(II) acetylacetonate, PdCl₂(cod): Dichloro(1,5-cyclooctadiene)palladium(II), TSC: *p*-toluene sulfonyl chloride, ChoOH: Choline Hydroxide.

Table S6. Part II. Qualitative environmental impact of this approach in comparison with other known technologies using suggestions from ref⁴.

Factor ^[a]	Homogeneous catalysis ¹	Homogeneous photocatalysis ²	Heterogeneous catalysis ³	Heterogeneous photocatalysis (this work)
Human carcinogenicity	CuCl: N/A Na ₂ Fe(CO) ₄ : N/A THF: Suspected of causing cancer NH ₄) ₂ Ce(NO ₃) ₆ : N/A Diethyl ether: N/A Brine: N/A	Co(acac) ₂ : May cause cancer by inhalation. K ₂ CO ₃ : N/A DMF: N/A Hantzsch ester: N/A 4CzIPN: ^[d] Hexane: N/A Ethyl acetate: ^[e] Brine: N/A	PdCl ₂ (cod): N/A Glycerol: N/A CH ₂ Cl ₂ : Suspected of causing cancer. TSC: N/A NaOH: N/A Alanine: N/A ChoOH: N/A	^[b] PdO: N/A TiO ₂ : N/A IPA: ^[e]
Mass of waste ^[f]	177.9 (10 mmol; 167 mM) ^{ເຊ}	663.8 (0.2 mmol; 100 mM) ^[g]	223.3 (1 mmol; 1M)	11.2 (2.5 mmol; 625 mM)
Ozone depletion	Not applicable	Not applicable	Not applicable	Not applicable
Persistence ^[h]	THF: Not readily biodegradable Diethyl ether: Not readily biodegradable	Co(acac) ₂ : Not readily biodegradable DMF: Readily biodegradable Hantzsch ester: N/A 4CzIPN: N/A but polycyclic aromatic Hexane: Readily biodegradable Ethyl acetate: Readily biodegradable	Glycerol: Readily biodegradable CH ₂ Cl ₂ : Readily biodegradable TSC: Readily biodegradable Alanine: N/A ChoOH: N/A	IPA: Readily biodegradable
Resource depletion	Low	Low	High (Pd low quantities)	Medium (Pd low quantities and reusable)
Smog formation	THF: High volatile liquid Diethyl ether: High volatile liquid	DMF: Low volatile liquid Ethyl acetate: Medium volatile liquid	CH ₂ Cl ₂ : High volatile liquid	IPA: Medium volatile liquid
Water consumption	78 g per gramme of product	> 149 g per gramme of product [c]	Unknown amount of water used for synthesis of catalyst.	None

^[a] All information obtained from SDS sheets of the named compounds. ^[b] Data for PdO was considered as this is the suspected form of Pd in the event of metal leaching. ^[c]Partial evaluation as data is not available for some compounds. ^[c] No ingredient of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC. ^[c]This product is or contains a component that is not classifiable as to its carcinogenicity based on its IARC, ACGIH, NTP, or EPA classification. IARC: International Agency for Research on Cancer. ACGIH: American Conference of Governmental Industrial Hygienists. NTP: US National Toxicology Program. EPA: US Environmental Protection Agency. ^[I]Values in brackets indicate reaction scale. ^[G]Calculations include water consumption but exclude waste generated during chromatographic separation. ^[II]Not applicable to inorganic substances.

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