Electronic Supplementary Information

Hydrogen release from liquid organic hydrogen carriers catalysed by platinum on rutile-anatase structured titania

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1 Catalysts

1.1 Preparation of catalysts

Pt catalysts on alumina and titania supports were prepared using incipient wetness impregnation procedure. Pore volumes of supports were determined, and accordingly adjusted volume of choroplatinic acid diluted with ion exchanged water was slowly added to dried support. Impregnated and dried catalysts were calcinated for two hours in air at temperature of 500 °C. Several batches of each catalyst type were prepared at University of Helsinki.

 γ - Al₂O₃ having particle size of 40µm was purchased from Alfa Aesar. TiO₂ nanopowders were purchased from Acros (anatase and rutile structures, Aeroxide) and from Sigma Aldrich (anatase only structure). Choroplatinic acid (H₂PtCl₆ · 6H₂O) precursor was purchased from Fluorochem. Pt on carbon catalyst (1wt%) was purchased from Sigma Aldrich.

1.2 Platinum concentrations

Catalysts were characterised by their Pt-contents using three methods:

- a) Microwave plasma-atomic emission spectrometer (MP-AES, Agilent Technologies SPS 3). Samples were digested in aqua regia with microwave assisted (CEM MARS) procedure at 165 °C for 20 min following by 190 °C for 10 min. University of Helsinki.
- b) SEM-EDS measurements with an INCA 350 energy dispersive X-ray spectrometer (EDS) connected with a Hitachi S-4800 field emission scanning electron microscope (FESEM). Typically, three analysis of larger areas and at least three analyses from each point were conducted. University of Helsinki.
- c) Inductively Coupled Plasma Mass Spectrometry (ICP-FSMS). Samples were treated according to standard SS EN 13656:2003 with microwave assisted procedure in mixture of HNO₃, HCl and fluoric acid (HF) at 120 °C for two hours. Service provider Measur.

Digestion with aqua regia only (method a) was applicable for alumina supported catalysts, while titania supported catalysts were not completely digested. Fluoric acid was added in method c) to digest titania catalysts. SEM EDS (method b) does not require digestion step. SEM EDS gives a view on the Pt concentrations over the catalyst surface area reaching depth of $1-2\mu m$, and thus Pt concentrations in pores of large particles are not necessarily detected. For some catalysts, Pt concentrations were not analysed, while parallel results from the same impregnation set were used. Overall, Pt concentrations of the catalysts ranged from 0.7-1.0 wt% (Table S1).

Catalyst	Batch	Pt results	Pt final
-		wt%	wt%
Pt/C		-	1e
Pt/γ - Al_2O_3	Cat 23	1.02 ^a	1.0
	Cat 61	0.69	0.7
Pt/TiO _{2 ra}	Cat 21	-	1.0 ^d
	Cat 36	0.83°	0.8
	Cat 51	0.78°	0.8
	Cat 53	0.7-1.1 ^b	0.9
	Cat 63	-	0.9 ^d
Pt/TiO _{2 ana}	Cat 64	0.86 ^c	0.9
	Cat 41	0.8-1.0 ^b ; 0.87 ^c	0.9
	Cat 42	-	0 9 ^d

Table S1	Pt concen	trations of	catalysts.
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^aMP-AES ^bSEM EDS ^cICP-FSMS ^d Based on same production sets: Cat 21 on Cat 20^a, Cat 63 on Cat 64^c and Cat 42 on Cat 41^{b,c} ^e Manufacturer's data

SEM images of Pt/TiO_{2 ra} (Cat 53) and Pt/TiO_{2 ana} (Cat 41) are shown in Fig. S1.



Figure S1. SEM image examples of a) $Pt/TiO_{2 ana}$ (Cat 41) and b) $Pt/TiO_{2 ra}$ (Cat 53).

1.3 X-ray powder diffraction (XRD)

X-ray diffractograms were measured with PANalytical X'Pert Pro MPD diffractometer in Bragg-Brentano geometry using programmable slit optics and PIXcel detector in 1D mode. XRD analyses were conducted for $Pt/TiO_{2 ra}$ and $Pt/TiO_{2 ana}$ catalysts at University of Helsinki. Quantification of weight fractions of anatase and rutile phases was based on the intensities of rutile peak at 27.355° 2 θ and anatase peak at 25.176° 2 θ . Calculation principle of quantification is described by Spurr and Myers (ref. in ¹).

The XRD results showed that the other catalyst was 100% anatase, while the other catalyst had 86% of anatase form and 14% of rutile form (Fig. S2). This confirmed that titania structures were not transformed during two hours calcination at 500 °C. Platinum was not detected by XRD analysis due to low Pt concentrations and small size of Pt particles.



Figure S2. XRD results of a) Pt/TiO_{2 ana} and b) Pt/TiO_{2 ra} catalysts.

1.4 X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed using a Phi Quantum 2000 (Ulvac-Phi Inc.) spectrometer operating at a pass energy of 23.50 eV at Top Analytica Oy. Samples were prepared by pressing a thin powder cake on an adhesive surface. Measurements were done in a vacuum chamber with a base pressure below $1 \cdot 10^{-7}$ Pa, by illuminating the samples with monochromatized Al K α -line at a photon energy of 1486.7 eV. Binding energies were calibrated using the adsorbed carbon 1s line at 284.8 eV. The peak fitting was done using the Multipak 9.8 XPS software (Ulvac-Phi, Inc).

The Pt 4f signals are given in Fig. S3. Fittings are based on the first spectrum where least amount of changes take place. Platinum has a characteristic Pt 4f douplet, with asymmetric shape of peaks for metallic Pt⁰, while these peaks are symmetric for the platinum oxides.² Asymmetric shape with "tail" towards higher binding energies results in from high electron density at the Fermi level.³ For the Pt 4f douplet, difference in the binding energies between Pt 4f7/2 and 4f5/2 is 3.3-3.4 eV.



Figure S3. Pt 4f peaks for a) Pt/TiO_{2ana} and b) Pt/TiO_{2ra}.

Different platinum oxides cannot be distinctioned basing on XPS only.⁴ However, platinum oxides are assumedly present in our samples (summary in Table S2). For PtO and PtO₂, literature values of Pt 4f7/2 binding energies are 72.4 and 73.8 eV, respectively. Assuming increased binding energies, Pt 4f7/2 peak at 73.2 eV is potentially Pt^{II}O for samples analysed (inline with ³). Pt 4f7/2 peak at 74.5 eV (e.g. Pt^{IV}O₂ or Pt₃O₄) was observed only for Pt/TiO_{2ra} catalyst, while not for Pt/TiO_{2ana} catalyst. Small Pt nanoparticles enhance formation of oxides , e.g. PtO₂ is formed when size of Pt particles is below 1.3 nm.^{5,6}

Literature ^a	Pt/TiO _{2ana}	Pt/TiO _{2ra}
Pt 4f7/2 (eV)	Pt 4f 7/2; 4f5/2 (eV)	Pt 4f7/2; 4f5/2 (eV)
71.0-71.2	72.13 (blue);	72.01 (blue);
	75.46 (green)	75.34 (green)
72.4eV	73.23 (orange);	73.20 (orange);
	76.56 (cyan)	76.53 (cyan)
73.8eV	-	74.53 (magenta);
		77.86 (grey)

Table S2. Pt 4f	peaks in literature and	l summary of fitting	gs in Figure S3 f	or samples Pt/TiO _{2an}	and Pt/TiO _{2ra}
	1	2 2		1 24110	4 <u>21</u> 0

^a <u>http://www.lasurface.com/database/elementxps.php</u>; <u>https://xpssimplified.com/elements/platinum.php</u>; ³; ⁴

For Pt/TiO_{2ana} Pt/TiO_{2ra} samples, Pt 4f peaks in Fig. S3 indicated presence of metallic platinum, however, binding energies of Pt⁰ 4f7/2 peaks were higher (72.0-72.1 eV) than those presented for Pt⁰ in literature (71.0-71.2 eV) (Table S2). XPS showed also slightly higher atomic ratio of oxygen to titanium (2.5) than the stoichiometric atomic ratio (2). Higher binding energies of Pt⁰ when compared with that for the bulk Pt have been observed due to intercalated oxygen according to Vovk et al.³ and binding energies may be affected also by the small Pt clusters and their interaction with the support.⁷

XPS spectrum of Pt 4f for Pt/TiO_{2ra} (C36) and Pt/TiO_{2ana} (C64) were studied in one hour intervals. No change in XPS spectrum of Pt 4f was noticed for Pt/TiO_{2ana} sample (Fig. S3b), while changes were observed for Pt/TiO_{2ra} sample (Ti 2p, Pt 4f and O 1s in Figs. S4a-c). Pt 4f peaks shifted to higher energy levels indicating change of Pt towards higher oxidation state. A new peak was formed for Ti 2p (463 eV) and for O 1s. Changes in XPS spectra during analysis of Pt/TiO_{2ra} were not resolved. In literature, Ti 2p douplet for Ti⁴⁺ (Ti2p3/2 459.1 and Ti2p1/2 464.8 eV) had shoulder or asymmetry at lower binding energy in the presence of Ti⁴⁺ and Ti³⁺.⁸ For O 1s, in literature⁹ presence of e.g. OH has been close to the additional peak formed here.



Figure S4. XPS spectrum for Pt/TiO_{2ana} sample in one hour intervals a) Ti 2p and b) Pt 4f.



Figure S5. XPS spectrum for Pt/TiO_{2ra} sample in one hour intervals a) Ti 2p and b) Pt 4f c) O 1s.

1.5 Transmission electron microscopy (TEM)

Particle sizes of support and Pt particles of titania nanopowders, and general view on alumina support were characterized by transmission electron microscopy (TEM). A FEI Technai F20 TEM at 200 kV was used for determination at University of Helsinki. Samples having approximately 1 wt% Pt were as follows:

- Pt on TiO₂ nanopowder formed of rutile and anatase (Fig. S6a, Cat 53)
- Pt on TiO₂ anatase nanopowder (Fig. S6b, Cat 41)
- Pt on Al_2O_3 (Fig. S6c, Cat 23)

Support characteristics. Pt catalysts supported on titania nanopowders had agglomerated structure, however, not sintered. Titania particles were more uniform in Cat 53 (from 16nm to 20nm) than in Cat 41 (from 12nm to 26nm). Interference of 3.64 Å observed in regions of Cat 53 indicated anatase lattice planes. Particle size of alumina support was nominally 40 µm with fine structure of pores in a size class of 10nm.

Pt characteristics. Pt particles on titania were extremely small for Cat 53 and Cat 41 (see next section). EDS analysis of Cat 53 TEM grid confirmed presence of Pt.





c) Cat 23

Figure S6. TEM images of Pt 1wt% on a) TiO_{2ra} (Cat 53) b) TiO_{2ana} (Cat 41) c) Al₂O₃ (Cat 23).

1.6 Scanning transmission electron microscopy (STEM) with EDS

Pt particles were very small and not clearly visible in the images shown in previous Section. Further analysis was conducted for the active Pt/TiO_{2ra} catalyst (Cat 36) using high resolution scanning transmission electron microscope STEM TALOS F200X, equipped with EDS, analysed at VTT.

Pt particle sizes were small, 1-2 nm or even lower (Figs. S7, S8). High-angle annular dark-field (HAADF)-STEM images and EDS elemental maps (Fig. S8) confirmed presence of unevenly distributed Pt particles in small size classes. Taira et al.¹⁰ found that Pt was concentrated on rutile when titania support consisted of anatase and rutile forms. In our measurements, this aspect was not studied, but in images presented lattice spacing of anatase was observed (0.362nm).



Figure S7. Images for Pt 1wt% on TiO_{2ra} (Cat 36) a-c) high resolution TEM d-e)





Figure S8. High-angle annular dark-field (HAADF)-STEM images and EDS elemental maps for Pt 1wt% on TiO_{2ra} (Cat 36). The EDS spectra correspond to integrated counts from area #1 and area #2 indicated in HAADF image (left). Copper and carbon in EDS spectra arise from the sample support (holey carbon film on 400 mesh copper TEM grid).

2 Dehydrogenation procedure and dehydrogenation degree

2.1 Dehydrogenation procedure

A mixture of H18-DBT (purchased from Hydrogeniuous GmbH, hydrogenation degree of 95%) and catalyst was heated in a round bottom flask while stirring with a magnetic stirrer at 300 min⁻¹. Molar ratio of substrate and Pt was targeted 400:1 (0.25 mol%), however, molar ratios varied depending on the Pt concentration of catalyst used in calculations (see Table S3). Dehydrogenation tests were carried out at University of Helsinki.

2.2 Volumetric determination of dehydrogenation degree

Formed hydrogen was collected in the measuring glass and readings were recorded periodically to obtain time series of released hydrogen. Volumetric measurement of hydrogen release is addressed with uncertainties related e.g. to the effect of temperature on hydrogen density. Additionally, hydrogen leaks of system are difficult to detect. Therefore, NMR analyses were conducted to determine dehydrogenation degree quantitatively (Section S2.3). Dehydrogenation degree at 45 minutes reaction time was achieved by interpolating the time series of released hydrogen obtained from NMR corrected results of volumetric measurements.

2.3 NMR determination of dehydrogenation degree

Quantitative NMR determination of the dehydrogenation degree of H18-DBT was carried out by Varian 300 MHz and Broker 400 MHz at University of Helsinki. Samples were diluted with dichloromethane-d2 and filtered before NMR analysis.

Dehydrogenation of H18-DBT produces mixture of various molecules. DBT having three aromatic rings (ArArAr) per molecule represents 100% hydrogen release degree from H18-DBT having three hydrogenated rings (SatSatSat). H6-DBT has hydrogenated outer (ArArSat) or middle ring (ArSatAr). H12-DBT has hydrogenated outer and middle ring (ArSatSat) or two outer rings (SatArSat). Furthermore, all these structures have regioisomers with varying positions of the benzyl groups relative to the methyl at the middle ring as shown for DBT in Fig. S9.



Figure S9. Regioisomers of DBT. Six regioisomers with different locatons of the benzyl groups relative to the methyl at the middle ring.



Fig. S10 shows the NMR spectra of DBT (from Sasol), H18-DBT and an example of partially dehydrogenated product in these measurements.

Figure S10. NMR spectra of a) H18-DBT, b) partially dehydrogenated product of H18-DBT (with Cat 16) and c) DBT. Analysed by NMR Varian 300 MHz.

Interpretation of the NMR results for dehydrogenated H18-DBT is described by Do et al.¹¹ and Shi et al.¹². Depending on dehydrogenation degree of H18-DBT, chemical shifts (CS) are moving from aliphatic to the aromatic regime over the mixed regimes. Integrals of these regimes can be used for quantitative determination of hydrogen release rate from H18-DBT (Table S3).

Chemical shift (ppm)	Structure
0.84-1.58	Sat H R R R R
2.00-2.45	$R \xrightarrow{H}_{H} \xrightarrow{R}_{H} \xrightarrow{R}_{H} \xrightarrow{H}_{H} \xrightarrow{R}_{H} \xrightarrow{R}_{H}$
3.80-4.15	
6.75-7.35	

Table S3. Chemical shifts for protons of dehydrogenated forms of H18DBT ^{11,12}.

Number or aromatic protons vary depending on the positions of aromatic rings as shown in Table S4. For example, ArArSat structure has 8 aromatic protons and ArSatAr structure has 10 aromatic protons, although dehydrogenation degree for both structures is 66.7%.

Table S4. Dependence on share of aromatic	protons and hydrogen released for different DBT structures.
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	ArArAr	ArArSat	ArSatAr	ArSatSat	SatArSat	SatSatSat
	$C_{21}H_{20}$	$C_{21}H_{26}$	$C_{21}H_{26}$	$C_{21}H_{32}$	$C_{21}H_{32}$	$C_{21}H_{38}$
Protons, number	20	26	26	32	32	38
Aromatic protons, number	13	8	10	5	3	0
Fraction of aromatic [CS 7]	0.65	0.31	0.38	0.16	0.09	0
Fraction of [CS 4]	0.20	0.08	0.00	0.00	0.00	0.00
Fraction of [CS 0.8-2.5]	0.15	0.61	0.62	0.84	0.91	1.00
Hydrogen released (%)	100	66.7	66.7	33.3	33.3	0

Fractions of protons in regime of CS [7] and respective degree of dehydrogenation was used to determine fitting curve (Fig. S11) for calculating the dehydrogenation degree of products from dehydrogenation of H18-DBT.



Figure S11. Relationship between hydrogen release rate and fractions of protons in the NMR regimes of CS [7].

3 Hydrogen release results

Hydrogen release rates were calculated as shares of the theoretical maximum, interpolated to 45 minutes for equal comparison of different catalysts. Interpolation was based on volumetric measurements corrected by the NMR results. Substrate to Pt ratio of respective tests were calculated based on the analysed Pt concentrations. Results are shown in Table S5.

Catalyst	Batch	Substrate to Pt (molar ratio)	Hydrogen release in 45 min (% of theor. max.)	average ± SD (% of theor. max.)
Pt/C		400;400;400	77; 62; 66	68±5.8
Pt/Al_2O_3	Cat 23	400;400;450	58; 51; 51	55±4.0
	Cat 61	500;600;550	59; 51; 60	
Pt/TiO _{2 ra}	Cat 21	400;400	68; 64	65±4.6
	Cat 36	450;450;400	64; 67; 72	
	Cat 51	500;500	69; 68	
	Cat 53	450;400	57; 60	
	Cat 63	500;500	57; 63	
Pt/TiO2 ana	Cat 41	450;450	29; 42	32±5.3
	Cat 42	400;350	28; 35	
	Cat 64	450	28	

Table S5. Hydrogen release results from individual tests.

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