

One-step hydrogenolysis of 5-hydroxymethylfurfural to 1,2,6-hexanetriol using Pt@MIL-53-derived Pt@Al₂O₃ catalyst and NaBH₄ in aqueous media

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1 Catalyst characterization

Transmission electron microscopy (TEM): The size distribution and dispersion of Pt nanoparticles were analyzed by JEOL JEM-2100F operating at 200 kV. In the pretreatment of samples, the powder was dispersed in methanol. The sample is sonicated for at least 30 minutes then a drop of the solution was placed on a carbon-coated copper grid. Finally, the sample was stored in the lyophilizer for drying. The elemental distributions were obtained by OXFORD X-MaxN TSR EDS connected with TEM. The elemental mapping studied with energy dispersive spectroscopy connected with TEM.

X-ray diffraction (XRD): Wide-angle X-ray diffraction patterns (XRD) were measured on Rigaku Ultima IV with Cu K α radiation ($\lambda=1.5418$ Å, 40 kV, 40 mA, 5-80°) as the X-ray source to analyze the crystal structure of particles.

N₂-sorption: The nitrogen adsorption and desorption isotherm measurements were performed on Micromeritics ASAP2020. The samples were degassed at 150 °C for 8 h under vacuum before measurement. Subsequently, the samples were kept at 77 K and the specific surface area and pore size distribution were calculated by non-linear density functional theory (NLDFT) and Brunauer-Emmett-Teller (BET) theory.

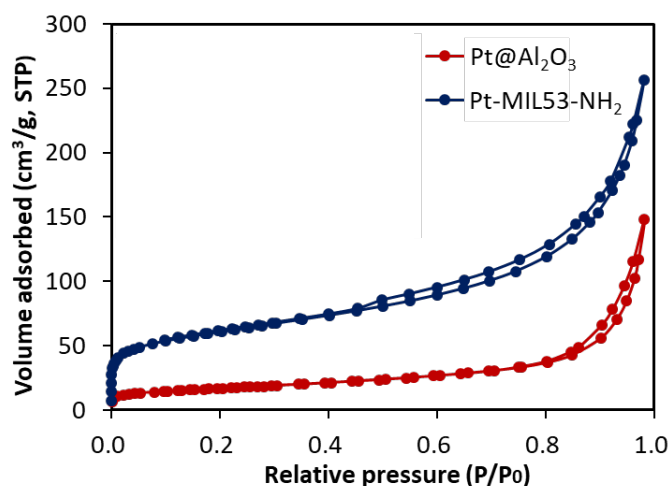


Fig. S1 N₂ adsorption-desorption isotherms for Pt/MIL-53-NH₂ and Pt@Al₂O₃

Table S1 N₂ physisorption analysis.

Entry	Sample	Pt-MIL53-NH ₂	Pt@Al ₂ O ₃
1	BET Specific surface area (m ² /g)	213.2	57.9
2*	Pore size (nm)	0.36, 1.1	1.1

*calculated by NLDFT method

X-ray photoelectron spectroscopy (XPS): XPS analysis was performed with a Thermo Scientific Al K α X-ray photoelectron spectrometer to identify the electronic states of platinum, alumina and oxygen. The reference of C 1s photoelectron peak (binding energy = 284.5 eV) was used for the binding energy calibration. The spectra were deconvoluted using peak fitting by XPSPEAK software.

²⁷Al solid-state NMR: ²⁷Al NMR experiments were performed on a BRUKER DSX 400 NMR spectrometer, operating at resonance frequencies of 104.3 MHz using a 4-mm MAS NMR probe. Sample spinning rate was ~10 kHz. The ²⁷Al NMR spectra are externally referenced to 1.0 M aqueous Al(NO₃)₃ (0 ppm).

Inductively coupled plasma (ICP): The metal loadings of catalysts were determined by ICP-mass spectrometer Agilent 7700e. For analysis of Pt element, the samples (1 mg) digested in 2 mL aqua regia (HNO₃/HCl = 1/3 v/v) and further diluted to 1 mM by 2 wt% nitric acid. The ICP calibration is showed presented in Fig. S2.

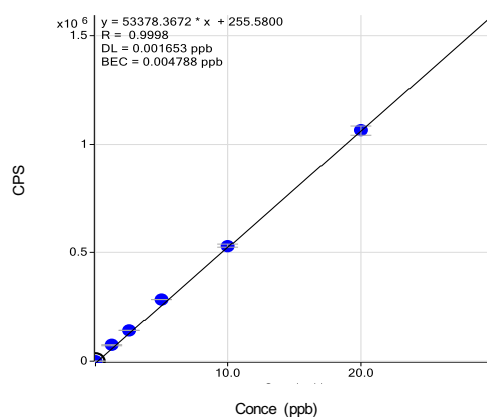


Fig. S2 ICP calibration for Pt.

Differential Scanning Calorimetry/Thermogravimetry (DSC/TGA): DSC/TGA has recorded with TA Instruments SDT 650. 5 mg of sample was placed into an alumina crucible and the temperature was linearly increased to 700 °C from room temperature with 10 °C min⁻¹ in air.

2 PtO overlayer structures on the Al³⁺_{penta} sites

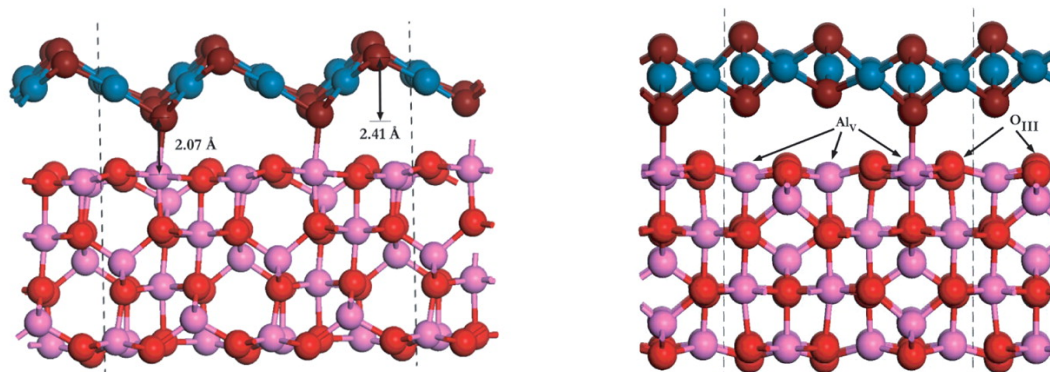


Fig. S3 illustration of PtO overlayer structures on the Al³⁺_{penta} sites¹

3 Effect of Pt loading

Fig. The results for the catalytic performance for 4 and 10wt% Pt loading is presented in Fig S7. Only 2,5-DHF formed without a catalyst. More Pt loading on the catalyst attributes to higher active sites for reaction, so the yield of 1,2,6-HT increases with the increase of Pt loading amount.

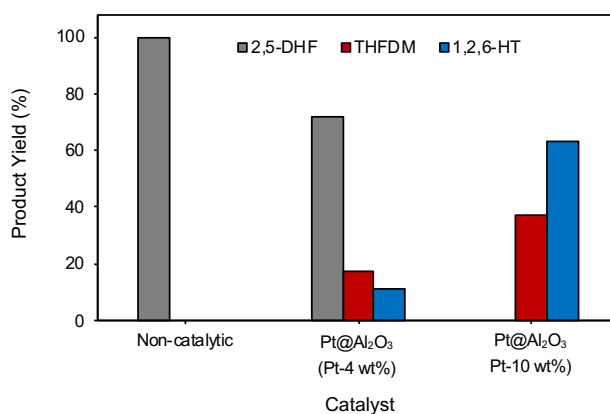
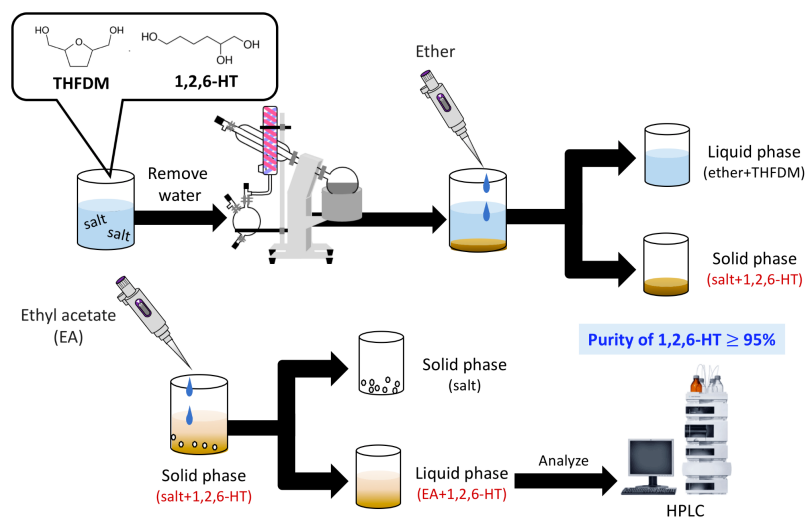


Fig. S4 Effect of Pt loading. Reaction conditions: HMF 0.5 mmol, water 10 ml, catalyst 0.05 g Pt@Al₂O₃, HMF/NaBH₄=1/4, 24 h, 35 °C.

4 Purification



Scheme S1 Procedure for the purification of 1,2,6-HT.

5 Kinetic studies

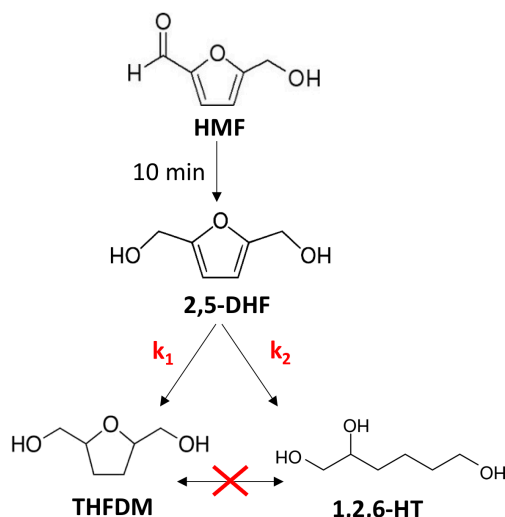


Fig. S5 Reaction pathway for the conversion of HMF into 1,2,6-HT over Pt@Al₂O₃ catalyst.

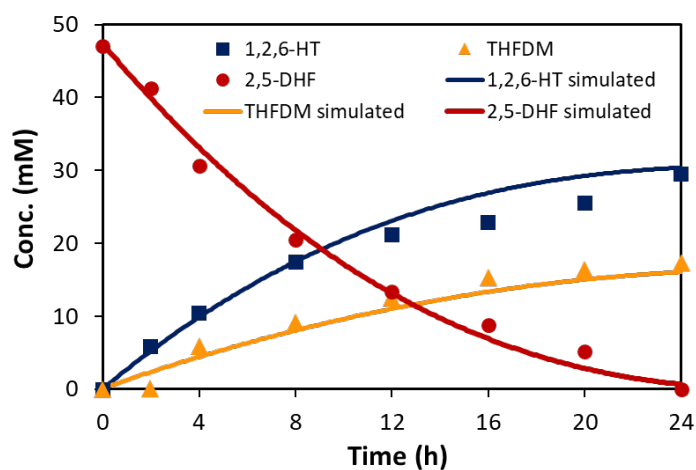


Fig. S6 Time distribution of various products at 35 °C with fitting curve

$$\frac{d}{dt} [2,5\text{-DHF}] = -k_1 [2,5\text{-DHF}]^n - k_2 [2,5\text{-DHF}]^m \quad (1)$$

$$\frac{d}{dt} [\text{THFDM}] = k_1 [2,5\text{-DHF}]^n \quad (2)$$

$$\frac{d}{dt} [1,2,6\text{-HT}] = k_2 [2,5\text{-DHF}]^m \quad (3)$$

$$\text{Selectivity of 1,2,6-HT} = \frac{\text{reaction rate of 2,5-DHF to 1,2,6-HT}}{\text{reaction rate of 2,5-DHF to THFDM}} = \frac{k_2 [2,5\text{-DHF}]^m}{k_1 [2,5\text{-DHF}]^n}$$

$$= \frac{A_2 \exp\left(-\frac{E_{a_{1,2,6\text{-HT}}}}{RT}\right) [2,5\text{-DHF}]^{0.45}}{A_1 \exp\left(-\frac{E_{a_{\text{THFDM}}}}{RT}\right) [2,5\text{-DHF}]^{0.67}}$$

$$= A \exp\left(\frac{E_{a_{\text{THFDM}}} - E_{a_{1,2,6\text{-HT}}}}{RT}\right) [2,5\text{-DHF}]^{-0.22} \quad (4)$$

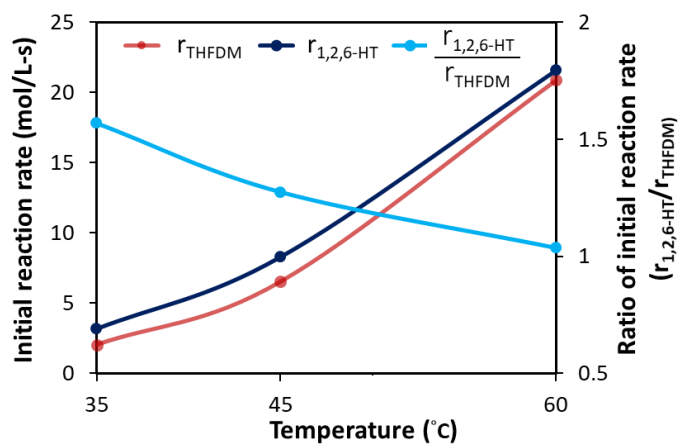


Fig. S7 Relationship between reaction rate and temperature.

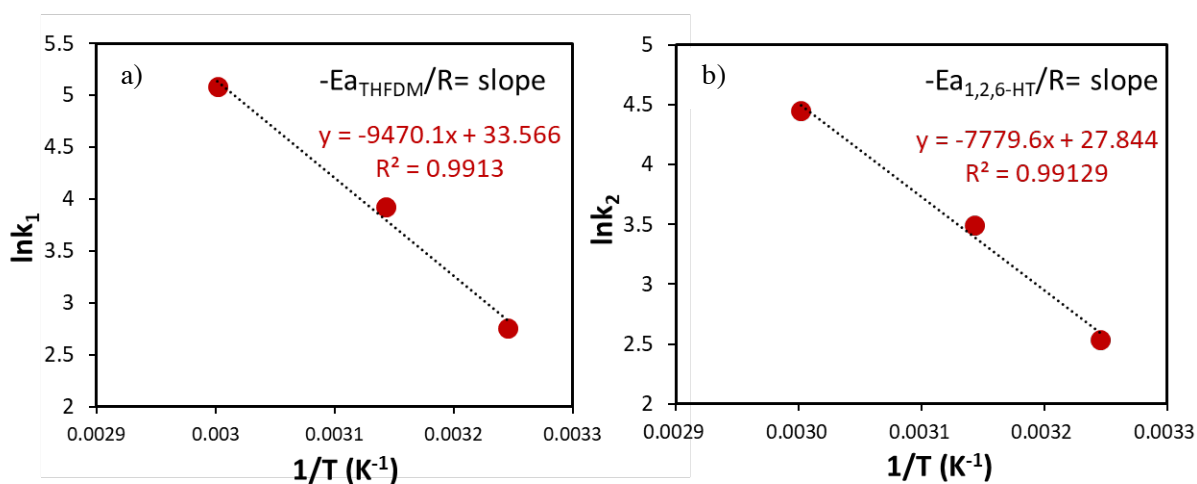


Fig. S8 Arrhenius plots for the conversion of (a) 2,5-DHF to THFDM and (b) 2,5-DHF to 1,2,6-HT

6 Effect of substrate concentration

The use of higher substrate concentration is crucial to make an economically viable 1,2,6-HT synthesis method. Hence the effect of substrate concentration was studied to optimize the reaction condition with higher substrate concentration. The HMF concentration in the reaction solution changed by changing the amount of water solvent. The high yield of 1,2,6-HT can be obtained with 0.6 wt% HMF solution, as illustrated in Fig. S8. Higher HMF concentration triggers competitive reaction (e.g. hydrogenolysis and hydrogenation of 2,5-DHF), and the formation of unwanted products (5-MTHFA), results in a decrease in 1,2,6-HT yield.

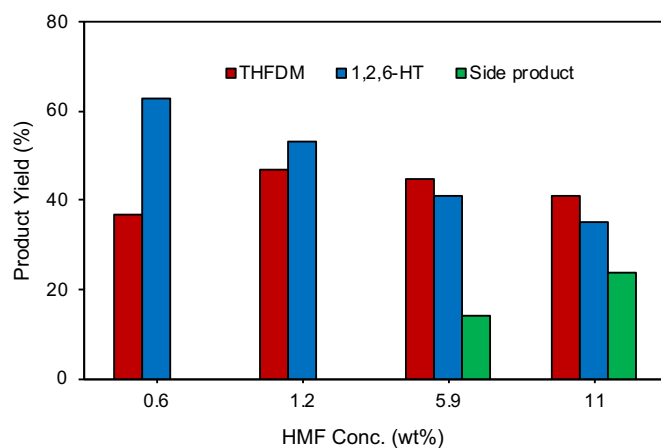


Fig. S9 Effect of HMF concentration. Reaction conditions: HMF 0.5 mmol, catalyst 0.05 g Pt@Al₂O₃, HMF/NaBH₄=1/4, 24 h, 35 °C.

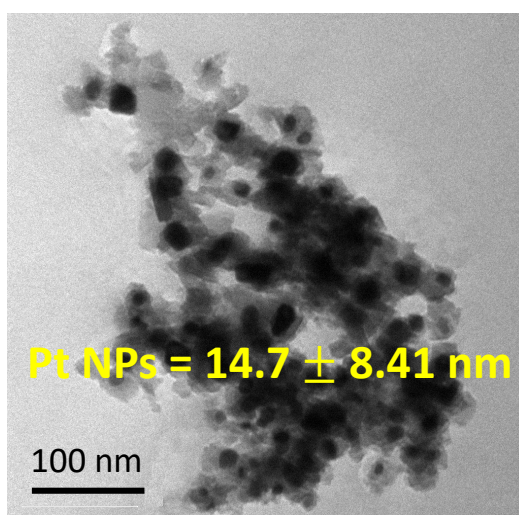


Fig. S10 TEM image of Pt@Al₂O₃-800

Table S2 Elemental analysis of Pt@Al₂O₃-500 and PtAl₂O₃-600

Sample	Elemental composition (%)		
	N	C	H
Pt@Al ₂ O ₃ -500	0.16	1.44	1.62
Pt@Al ₂ O ₃ -600	0.16	0.57	0.93

References:

1. J. H. Kwak, J. Z. Hu, D. Mei, C. W. Yi, D. H. Kim, C. H. F. Peden, L. F. Allard and J. Szanyi, *Science*, 2009, **325**, 1670-1673.