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Facile gas-phase hydrodeoxygenation of 2,5-dimethylfuran over bifunctional metal-acid catalyst Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$

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Electronic Supplementary Information

Chemicals and catalysts. 2,5-Dimethylfuran (99%) was purchased from Acros Organics. 2,5-Dimethyltetrahydrofuran (*cis/trans* isomer mixture, 96%), 2-hexanol (98%), Cs_2CO_3 and $H_3PW_{12}O_{40}$ hydrate (99%) were purchased from Sigma-Aldrich. 2-Hexanone (98%) was purchased from Alfa Aesar and n-hexane (98%) from Fisher Chemicals. 1%Pt/Al_2O_3 and carbon-supported noble metal catalysts (M/C) 9.6%Pt/C, 7.8%Pd/C, 3.0%Ru/C and 4.0%Rh/C were from Sigma-Aldrich (the metal loading in M/C determined in-house by ICP-AES analysis). Zeolites NH_4^+-ZSM-5 (Si/Al = 12 and 47) were from Zeolyst International. The zeolites were converted into the H^+ forms by air calcination at 500 ^oC for 6 h; these are hereinafter designated as HZSM-5-12 and HZSM-5-47. Commercial Aerosil 300 silica support ($S_{BET} \approx 300\ m^2g^{-1}$) was from Degussa. H_2 (>99%) was supplied by the British Oxygen Company.

Cesium tungstophosphate $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) was prepared according to the literature procedure [1] by adding drop-wise the required amount of aqueous solution of Cs_2CO_3 to aqueous solution of $H_3PW_{12}O_{40}$ to afford CsPW as a white precipitate, which was isolated, vacuum dried at 150 ^oC/1 Pa for 1.5 h and ground to 45–180 μm particle size.

CsPW-supported bifunctional metal-acid catalyst, 1.0%Pt/CsPW-w, was prepared by wet impregnation of CsPW powder with an aqueous solution of H_2PtCl_6 as described previously [2]. This involved stirring the aqueous slurry at 50 ^oC for 2 h followed by rotoevaporation to dryness and reduction with H_2 flow at 250 ^oC for 2 h. Similar catalyst designated as 1.0%Pt/CsPW-b was prepared chloride-free by impregnating Pt(acac)$_2$ onto CsPW from benzene solution. This was done by stirring CsPW powder with 0.02 M Pt(acac)$_2$ solution in benzene at room temperature for 1 h, followed by rotoevaporation of benzene at room temperature and reduction by hydrogen as above. 6.4%Pt/SiO_2 was prepared by wet impregnation of Aerosil 300 silica with an aqueous solution of H_2PtCl_6 followed by rotoevaporation to dryness and reduction with H_2 flow at 250 °C for 2 h. Silica-supported $H_3PW_{12}O_{40}$ catalyst, 25%HPW/SiO_2, was prepared by wet impregnation of Aerosil 300 silica with an aqueous HPW solution as described elsewhere [3,4] and dried at 150 °C/1 Pa for 1.5 h. Physically mixed metal-acid bifunctional catalysts M/C + CsPW (M = Pt, Pd, Rh and Ru), Pt/C + zeolite and Pt/C + 25%HPW/SiO_2 were prepared by grinding a mixture of the corresponding components. Information about the catalysts prepared is presented in Table S1.

Table S1 Catalyst characterisation

Catalyst	Surface area[a] (m^2g^{-1})	Pore volume[b] (cm^3g^{-1})	Pore diameter[c] (Å)	D [d]
7.8%Pd/C	820	0.56	27	0.326±0.034
3.0%Ru/C	1108	0.94	34	0.232±0.010
4.0%Rh/C	830	0.70	34	0.513±0.032
9.6%Pt/C	713	0.56	31	0.039±0.007
1%Pt/Al_2O_3	163	0.49	121	0.63±0.042
6.4%Pt/SiO_2	266	1.06	159	0.28±0.041[f]
1.0%Pt/CsPW-w[e]	98	0.08	34	0.094±0.010[f]
1.0%Pt/CsPW-b[g]	106	0.09	32	0.13±0.01[f]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	139	0.09	27	
25%HPW/SiO_2	188	0.80	178	
HZSM-5-12	378	0.22	24	
HZSM-5-47	411	0.26	26	

[a] BET surface area. [b] Single point total pore volume. [c] Average BET pore diameter. [d] Metal dispersion from CO adsorption (average of three measurements). [e] Prepared by impregnating H_2PtCl_6 from aqueous solution. [f] Pt dispersion determined by H_2/O_2 titration (average from three measurements). [g] Prepared by impregnating $Pt(acac)_2$ from benzene solution.

Techniques. The surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2010 instrument at −196 °C. Before measurement, the samples were evacuated at 250 °C. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) elemental analysis was carried out on a Spectro Ciros optical emission spectrometer.

Metal dispersion, D, defined as the metal fraction at the surface of metal particles, $D = M_s/M_{total}$, was determined by pulse chemisorption of CO or H_2/O_2 titration in flow system using a Micromeritics TPD/TPR 2900 instrument as described elsewhere [5]. For carbon supported catalysts and 1%Pt/Al_2O_3, the metal dispersion was determined by CO chemisorption in He flow at 50 °C (10-15 mg catalyst sample, 25 μl pulses of pure CO). The adsorption stoichiometry M_s/CO was assumed to be 1 for Pt, Rh, Ru and 2 for Pd [6]. Platinum dispersion in Pt/CsPW and Pt/SiO_2 catalysts was measured by the H_2/O_2 titration at room temperature [6] and calculated assuming the stoichiometry of H_2 adsorption: $Pt_sO + 1.5\ H_2 \rightarrow Pt_sH + H_2O$ [7,8]. For the Pt catalysts on inorganic supports CO chemisorption and H_2/O_2 titration gave concordant results.

Catalyst testing. The HDO of DMF was carried out at the gas-solid interface in flowing H_2 at ambient pressure and 70–100 °C using a fixed-bed microreactor (9 mm internal diameter) fitted with an on-line GC analysis as described elsewhere [9]. DMF was fed by passing H_2 flow controlled by a Brooks mass flow controller through a saturator, which held the liquid substrate at an appropriate temperature to maintain the chosen reactant partial pressure. The gas feed entered the reactor at a flow rate of 20 ml min^{-1} unless stated otherwise. The catalyst bed (0.20 g total weight) contained a uniform physical mixture of powdered catalyst components (M/C + acid co-catalyst or SiO_2). Prior to reaction, the catalysts were pre-treated in situ for 1 h at the reaction temperature in H_2 flow. Reactions were carried for 4 h time on stream (TOS) unless stated otherwise; each run was reproduced at least twice. Product selectivity was defined on the carbon basis as moles of product formed per one mole of substrate converted and quoted in mole per cent. The mean absolute percentage error in conversion and selectivity was ≤ 5% and the carbon balance was maintained within 95%.

Effect of acid co-catalyst. The acid strength (initial enthalpy of ammonia adsorption, ΔH) and proton site density of the acid co-catalysts studied are given in Table S2. The proton site density was calculated as follows: for zeolites from their Si/Al ratio, for 25%HPW/SiO_2 assuming that all HPW protons were accessible [3,4] and for CsPW assuming the Keggin unit cross section of 144 Å^2 [3,10] and using the CsPW surface area of 139 m^2g^{-1} (Table S1).

Table S2 Acid properties of acid co-catalysts

Catalyst	CsPW	25%HPW/SiO_2	HZSM-5-12	HZSM-5-47
H^+ density, mmol g^{-1}	0.080	0.26	1.28	0.35
$-\Delta H$, kJ mol^{-1} (at 150 °C)^a	164 [3]	167 [4]	~130 [3]	~130 [4]

Kinetics. Accurate measurement of reaction rates of the gas-phase HDO of DMF over Pt/C + CsPW was difficult due to very high catalyst activity. Kinetics was examined at 80 °C and short contact times (at high flow rates and small amounts of Pt/C catalyst), which allowed to reduce DMF conversion to 15–70%. At such conditions the rates were reproducible within 10–15% accuracy. The rates (R) based on Pt/C were determined as $R = XF/W$, where X is the DMF conversion (average conversion for 3 h TOS), F is the inlet molar flow rate of DMF and W is the weight of Pt/C catalyst. The reaction was found to be zero order in DMF within the range of DMF partial pressure of 1.6–6.8 kPa (Fig. S1), which indicates that catalyst active sites were saturated with DMF molecules. For a zero-order reaction, the rate does not depend on substrate conversion and is equal to the rate constant, which simplifies kinetic studies. The reaction was first order in Pt/C catalyst as can be seen from the plot of reaction rate per Pt/C weight versus the amount of Pt/C (Fig. S2).

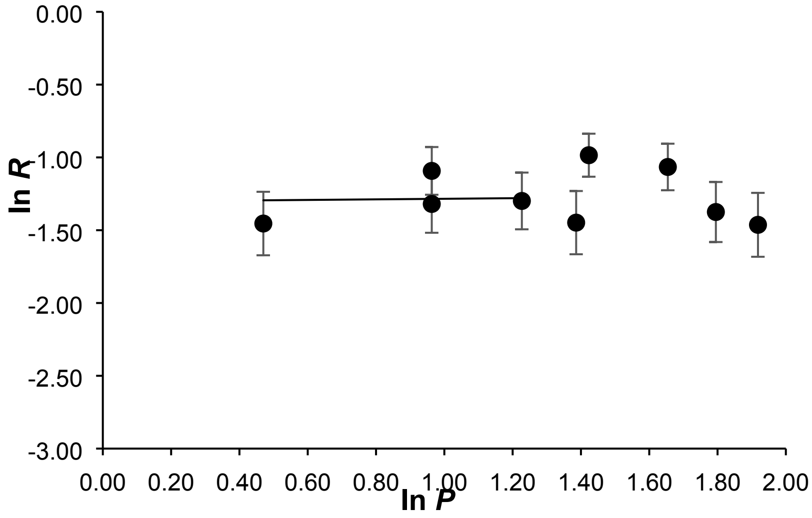

Fig. S1 Effect of DMF partial pressure (*P* in kPa) on reaction rate (based on Pt/C, in mol $g^{-1}h^{-1}$): 9.6%Pt/C (5.0 mg), CsPW (0.20 g), 80 ^{o}C, 40 ml min^{-1} H_2 flow rate.

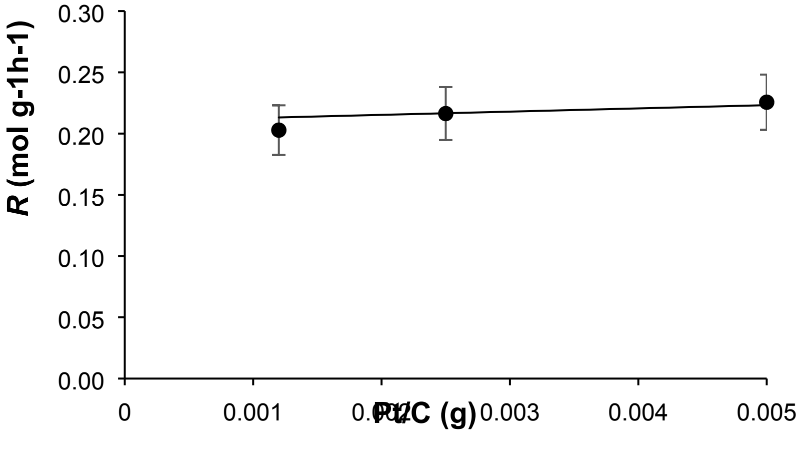

Fig. S2 Effect of Pt/C amount on the reaction rate per Pt/C weight: 9.6%Pt/C (1.2 – 5.0 mg), CsPW (0.20 g), 80 ^{o}C, 1.6 kPa DMF partial pressure, 40 mL min^{-1} H_2 flow rate.

Table S3 Liquid-phase hydrodeoxygenation of DMF in the presence of bifunctional Pt–CsPW catalyst[a]

Temperature (°C)	Conversion (%)	Product selectivity (% mol)				
		Hexane	DMTHF	2-Hexanone	2-Hexanol	Other
90	98	5.0	20.0	45.0	20.0	10.0
100	>99	12.9	19.3	49.2	12.5	6.1
120	>99	40.2	13.3	42.7	0.1	3.7
140	>99	48.4	11.0	32.0	0.0	8.6

[a] In 120-ml stainless steel autoclave, 9.6%Pt/C+CsPW (1:9 w/w) catalyst (0.20 g, 20 mg Pt/C, 1% Pt loading per total catalyst weight), DMF (5.2 mmol), dodecane (GC standard, 5.0 mmol), decane (solvent, 3.0 ml), 20 bar H_2 pressure (at room temperature), 600 rpm stirring speed, 2 h reaction time.

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