

Efficient hydrodeoxygenation of biomass-derived ketones over bifunctional Pt-polyoxometalate catalyst

Mshari A. Alotaibi, Elena F. Kozhevnikova and Ivan V. Kozhevnikov*

*Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, United Kingdom.
Fax: +44 (0)151 794 3589; Tel: +44 (0)151 794 2938; E-mail: kozhev@liverpool.ac.uk*

Supporting information

1. Experimental

1.1. Chemicals and catalysts

MIBK (99.0%), DIBK (88.0%), copper chromite $\text{Cr}_2\text{Cu}_2\text{O}_5$ and other chemicals used for catalysts preparation were purchased from Aldrich. Commercial platinum group metal catalysts (Pt, Pd and Ru supported on active carbon) were from Johnson Matthey. Aerosil 300 silica (specific surface area $S_{\text{BET}} = 300 \text{ m}^2\text{g}^{-1}$) was from Degussa. HZSM-5 zeolite (Si/Al = 12, $S_{\text{BET}} = 403 \text{ m}^2\text{g}^{-1}$) was from Zeolyst International. H_2 and N_2 gases (>99%) were supplied by the British Oxygen Company.

$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) was prepared by adding dropwise a stoichiometric amount of aqueous Cs_2CO_3 (0.47 M) to an aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.75 M) at 40°C with continuous stirring [1]. A white precipitate was produced and aged for 48 h at room temperature and then isolated through rotary evaporation at 45°C , followed by drying under vacuum at $150^\circ\text{C}/0.1 \text{ kPa}$ for 1.5 h.

0.5%Pd/CsPW and 0.5%Pd/ SiO_2 catalysts were prepared by wet impregnation of support (CsPW or Aerosil 300) with 0.02 M benzene solution of $\text{Pd}(\text{OAc})_2$, followed by drying in a rotary evaporator at 60°C and reduction with H_2 at 250°C for 2 h. 0.5%Pt/CsPW and 0.5%Pt/ SiO_2 were prepared by the same procedure using $\text{Pt}(\text{acac})_2$ as a precursor. Ru/CsPW catalysts were prepared by wet impregnation of CsPW with 0.1 M aqueous solution of RuCl_3 , followed by drying and reduction as above. 5%Cu/CsPW and 5%Cu/ SiO_2

were prepared by wet impregnation using an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, followed by drying in a rotary evaporator, air calcination at 400°C for 2 h and final reduction with H_2 at 400°C for 2 h. Copper chromite prior to use was reduced at 400°C in an H_2 flow for 2 h. The catalysts were sieved into a powder of 45 – 180 μm particle size.

1.2. Techniques

The BET surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2010 instrument at -196°C . Before the measurement, the samples were evacuated at 250°C for 2 h. Powder X-ray diffraction (XRD) spectra of catalysts were recorded on a PANalytical Xpert diffractometer with a monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). XRD patterns were attributed using the JCPDS database. ICP-AES elemental analysis was carried out on a Spectro Ciros emission spectrometer. Thermo Flash EA 1112 series analyzer was used to determine carbon content in spent catalysts. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of catalysts were taken on a Nicolet NEXUS FTIR spectrometer using powdered catalyst mixtures with KBr. Temperature programmed reduction (H_2 -TPR) of catalysts was carried out on Micromeritics TPD/TPR 2900 apparatus equipped with a thermal conductivity detector. Catalyst samples (20-30 mg) were heated up to 800°C at a rate of $10^\circ\text{C min}^{-1}$ in a H_2 - N_2 (5:95) gas flow (60 ml min^{-1}).

Metal dispersion for Pt, Pd and Ru catalysts was measured by hydrogen chemisorption on a Micromeritics TPD/TPR 2900 instrument as described previously [2]. A catalyst sample (50 mg) pre-exposed to air at room temperature was placed in a glass sample tube connected to the instrument and stabilised at 100°C under nitrogen flow. 50 μl pulses of pure H_2 were injected in the flow in 3 min intervals until the catalyst was saturated with hydrogen. Hydrogen did not adsorb on CsPW and SiO_2 under such conditions, and no reduction of CsPW in the metal-doped catalysts was observed at 100°C , as found by TPR (see below). The

metal dispersion, D , defined as the fraction of metal (M) at the surface, $D = M_s/M_{\text{total}}$, was calculated assuming the stoichiometry of H_2 adsorption: $M_sO + 1.5H_2 \rightarrow M_sH + H_2O$ [3, 4]. The average diameter of metal particles, d , was obtained from the empirical equation d (nm) = $0.9/D$ [4].

The Cu metal dispersion in 5%Cu/CsPW and 5%Cu/SiO₂ was determined using N₂O chemisorption followed by H₂-TPR [5]. Prior to N₂O chemisorption, a catalyst sample (150 mg) was reduced in a hydrogen flow (20 ml min⁻¹) at 400 °C for 0.5 h with a temperature ramp rate of 10 °C/min, then cooled down to room temperature and treated at this temperature with a gas mixture containing 1% N₂O in nitrogen at a flow rate of 60 ml/min for 15 min to convert the surface Cu atoms to Cu₂O. Finally, the amount of Cu₂O was determined by H₂-TPR, increasing the temperature up to 400°C as described above. The Cu₂O reduction peak was observed in the temperature range 140-250°C in agreement with the literature [5]. The copper metal dispersion, $D = Cu_s/Cu_{\text{total}}$, was calculated assuming a stoichiometry $Cu_s/N_2O = 2$ and $Cu_s/H = 1$ according to the equations $2Cu_s + N_2O \rightarrow (Cu_s)_2O + N_2$ and $(Cu_s)_2O + H_2 \rightarrow 2Cu_s + H_2O$ ([5] and references therein). The average diameter of Cu particles, d , was calculated from the equation d (nm) = $1.1/D$ [6]. For 5%Cu/SiO₂, the metal particle size was also determined by XRD using the Scherrer equation, with line broadening assessed as the full width at half maximum intensity (FWHM).

1.3. Catalyst testing

The hydrogenation of MIBK and DIBK was carried out in the gas phase in flowing H₂. The catalysts were tested at 100-400°C under atmospheric pressure in a Pyrex fixed-bed down-flow reactor (9 mm internal diameter) fitted with an on-line gas chromatograph (Varian Star 3400 CX instrument with a 30 m x 0.25 mm HP INNOWAX capillary column and a

flame ionisation detector). For more accurate analysis of C₁-C₅ hydrocarbon products, a 60 m x 0.32 mm GSGasPro capillary column was used, which allowed for full separation of these hydrocarbons. The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of the catalyst bed. The gas feed contained a variable amount of MIBK or DIBK in H₂ as a carrier gas. The reactants were fed by passing the carrier gas flow controlled by a Brooks mass flow controller through a stainless steel saturator, which held liquid MIBK or DIBK at appropriate temperature to maintain the chosen reactant concentration. The downstream gas lines and valves were heated to 180°C to prevent substrate and product condensation. The gas feed entered the reactor at the top at a flow rate of 20-100 ml min⁻¹. The reactor was packed with 0.2 g catalyst powder of 45-180 µm particle size. In some cases, to reduce reaction rate a smaller amount of catalyst was used as a homogeneous mixture with silica of a total weight of 0.2 g. Prior to reaction, the catalysts were pre-treated in H₂ for 1 h at the reaction temperature. Once reaction started, the downstream gas flow was analysed by the on-line GC to obtain reactant conversion and product selectivity. The selectivity was defined as moles of product formed per one mole of reactant converted and quoted in mole per cent.

2. Catalyst characterisation

The catalysts studied together with their characterisation data are shown in Table S1. The characterisation data include BET analysis of catalyst texture (surface area, pore diameter and pore volume) as well as the dispersion and particle size of supported metal.

Fig. S1 shows H₂-TPR profiles for the H₃PW₁₂O₄₀ (HPW) and CsPW catalysts. The TPR profile of HPW peaked at 530°C, with a reduction onset at ~400 °C. For CsPW these temperatures were 750 and ~650 °C. These results are in agreement with previous reports [7, 8]. The TPR profiles for Pd/CsPW and Pt/CsPW peaked at 710 and 730 °C, respectively, both

with a reduction onset at ~600 °C. Since Pd and Pt are already reduced in these catalysts and Cs⁺ will not be reduced under these conditions, it leaves W(VI) reduction as the source of the H₂-TPR signals. Therefore, all these catalysts should be resistant to reduction with H₂ upon MIBK and DIBK hydrogenation at the chosen reaction temperatures (100-400°C).

Table S1 Catalyst characterisation^a

Catalyst	S_{BET}^b [m ² g ⁻¹]	Pore volume ^c [cm ³ g ⁻¹]	Pore size ^d [Å]	D^e
CsPW	111	0.07	26	
5%Cu/CsPW	75	0.06	30	0.11
5%Cu/SiO ₂	251	0.74	118	0.05
0.5% Pd/CsPW	87	0.06	29	0.37
0.5% Pd/SiO ₂	255	0.68	106	0.62
0.5% Pt/ CsPW	100 (67)	0.07 (0.05)	28 (28)	0.36 (0.36)
0.5% Pt/SiO ₂	287	0.52	74	0.27
0.25%Pt/CsPW	101 (80)	0.06 (0.05)	26 (26)	0.80 (0.80)
1%Pt/CsPW	106 (90)	0.07 (0.05)	25 (26)	0.18 (0.18)
0.5%Ru/CsPW	118	0.09	30	0.24
5%Ru/CsPW	105	0.10	36	0.11
10%Pt/C	801	0.58	29	
5%Ru/C	792	0.64	32	
5%Pd/C	924	0.58	25	
10%Pd/C	823	0.57	28	
Cr ₂ Cu ₂ O ₅ ^f	55	0.13	93	

^a In brackets are the values for spent catalysts after MIBK hydrogenation at 100°C. ^b BET surface area. ^c Single point total pore volume. ^d Average BET pore diameter. ^e Metal dispersion in fresh catalysts. ^f After reduction at 400°C in H₂ for 2 h.

Fig. S2 displays the DRIFT spectra for fresh and spent catalysts in the range of 750–1150 cm⁻¹ characteristic of the Keggin structure. All spent catalysts based on CsPW after reaction at 400 °C in H₂ exhibited the well-known spectrum of the Keggin anion [PW₁₂O₄₀]³⁻ with strong bands of stretching vibrations at 1080 (P-O), 987 (terminal W=O group), 890 and 800 cm⁻¹ (edge- and corner-sharing W-O-W groups), matching exactly the spectrum of fresh CsPW [9, 10]. This shows that bulk CsPW and CsPW-supported Pd, Pt and Cu catalysts

retained their primary structure (the Keggin structure of heteropoly anion) intact after reaction at 400 °C in H₂. Moreover, all these catalysts, fresh and spent, show the same XRD pattern of crystalline CsPW (Fig. S3). Therefore, the CsPW catalysts also retained their secondary structure (crystal structure) after reaction.

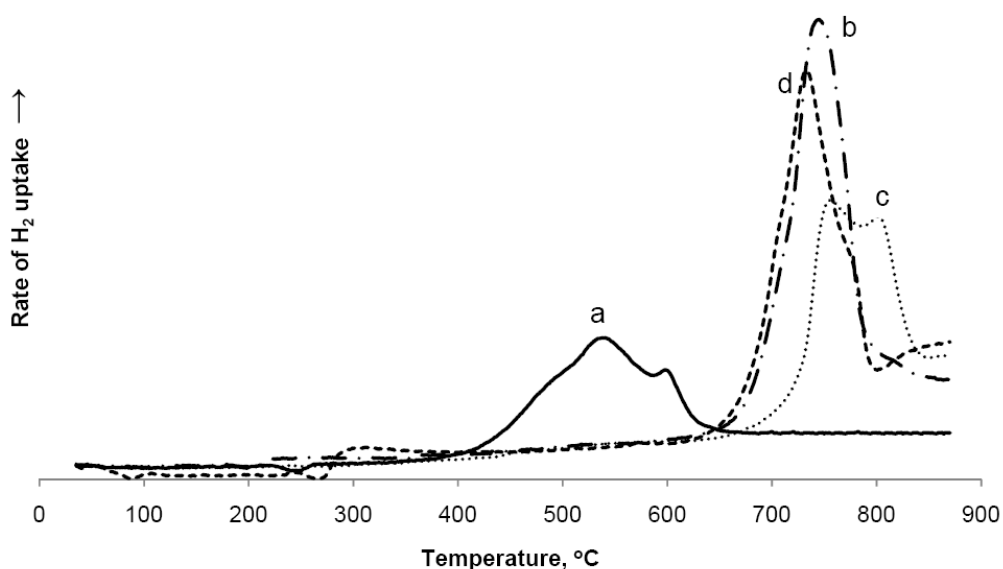


Fig. S1 H₂-TPR for HPW (a), 0.5%Pt/CsPW (b), CsPW (c) and 0.5%Pd/CsPW (d). The catalysts were pretreated at 300 °C/1 h in N₂, 10 °C min⁻¹ temperature ramp rate.

Powder XRD analysis of our Pt, Pd and Ru catalysts did not reveal any metal phase on CsPW and SiO₂, indicating that the metals were finely dispersed. Table S1 shows metal dispersion in fresh and some spent catalysts determined from H₂ chemisorption. Pt dispersion did not change after MIBK hydrogenation at 100°C, which shows high stability of Pt nanoparticles under reaction conditions. 5%Cu/SiO₂ exhibited sharp XRD pattern of Cu metal (Fig. S3), with (111) and (200) reflections at 43.4 and 50.5°, respectively, which is in agreement with the standard values 43.3 and 50.4° (JCPDS, copper 04-0836). From these, a mean diameter of 45±10 nm for Cu particles was obtained using the Scherrer equation. This corresponds to a Cu dispersion of $D = 0.024$ (Table S1). From N₂O uptake, a higher Cu

dispersion for this catalyst, $D = 0.055$, was obtained. This corresponds to a Cu metal particle size of 20 nm, which is in reasonable agreement with the XRD value. 5%Cu/CsPW possessed smaller Cu particles. It clearly displayed the XRD pattern of crystalline CsPW, but only traces of Cu metal phase can be seen (111 reflection at 43.4°) (Fig. S3, a and b). From N_2O chemisorption, this catalyst had a Cu metal dispersion of 0.11 corresponding to a metal particle size of 10 nm (Table S1). Fresh and spent Cu catalysts had about the same metal dispersion within the accuracy of measurement. The higher Cu dispersion in Cu/CsPW compared to Cu/SiO₂ may be due to ion exchange of Cu²⁺ with strong proton sites in CsPW upon impregnation of CsPW with Cu(NO₃)₂ aqueous solution. For Pd and Pt catalysts, no significant difference in metal dispersion on CsPW and SiO₂ was observed (Table S1). This may be explained by different preparation of these catalysts, namely, using non-ionic metal precursors and non-polar solvent (benzene) for the impregnation. Copper chromite reduced at 400°C in H₂ exhibited sharp XRD pattern of Cu metal (Fig. S4),

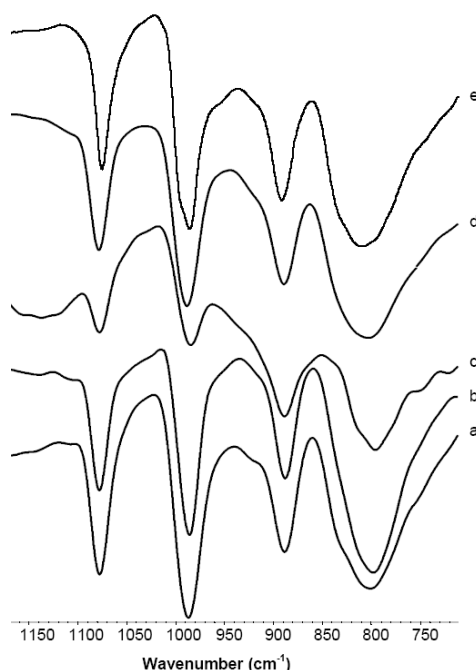


Fig. S2 DRIFT spectra for spent catalysts after reaction at 400 °C in H₂: 0.5%Pt/CsPW (a), Cs₃PW₁₂O₄₀ (b), CsPW (c), 0.5%Pd/CsPW (d) and 5%Cu/CsPW (e). The four peaks at 800, 890, 987 and 1080 cm⁻¹ match the corresponding peaks of fresh CsPW.

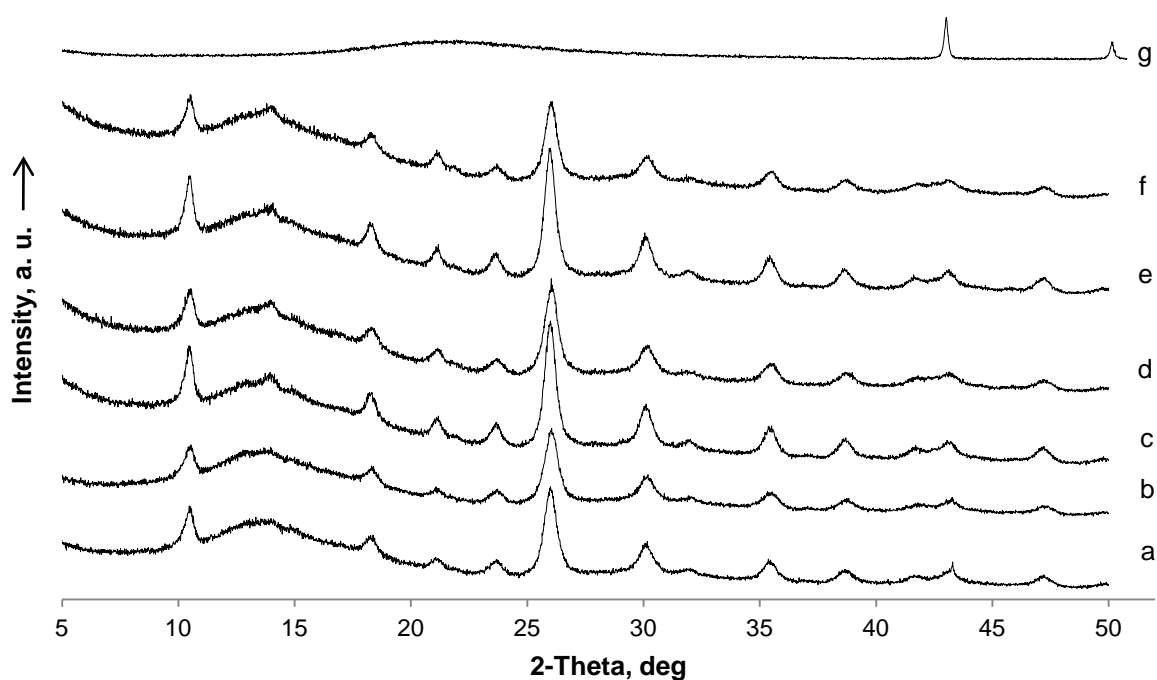


Fig. S3 XRD patterns for fresh and spent catalysts after reaction at 400 °C in H₂: (a) spent 5% Cu/CsPW, (b) fresh 5% Cu/CsPW, (c) spent 0.5% Pd/CsPW, (d) fresh 0.5% Pd/CsPW, (e) spent 0.5% Pt/CsPW, (f) fresh 0.5% Pt/CsPW, (g) fresh 5% Cu/SiO₂.

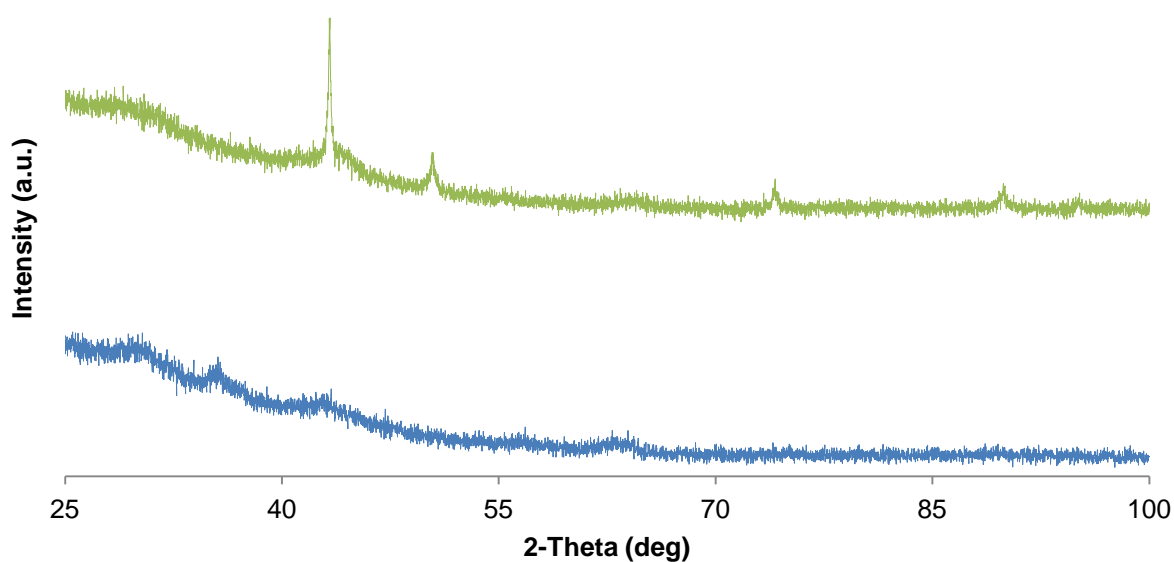


Fig. S4 XRD patterns for copper chromite catalysts: 2CuO-Cr₂O₃ unreduced (bottom) and reduced at 400 °C in H₂ for 2 h (top).

References

- 1 Y. Izumi, M. Ono, M. Kitagawa, M. Yoshida and K. Urabe, *Microporous Mater.* 5 (1995) 255.
- 2 F. Al-Wadaani, E.F. Kozhevnikova and I.V. Kozhevnikov, *J. Catal.* 257 (2008) 199.
- 3 J. E. Benson and M. Boudart, *J. Catal.* 4 (1965) 704.
- 4 J. E. Benson, H.S. Hwang and M. Boudart, *J. Catal.* 30 (1973) 146.
- 5 A. Gervasini and S. Bennici, *Appl. Catal. A* 281 (2005) 199.
- 6 A. Dandekar and M.A. Vannice, *J. Catal.* 178 (1998) 621.
- 7 S. Yoshida, H. Niiyama and E. Echigoya, *J. Phys. Chem.* 86 (1982) 3150.
- 8 K.M. Parida, S. Rana, S. Mallick and D. Rath, *J. Colloid. Interface Sci.* 350 (2010) 132.
- 9 T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.* 41 (1996) 113.
- 10 J.B. Moffat, *Metal-Oxygen Clusters. The Surface and Catalytic Properties of Heteropoly Oxometalates*, Kluwer, N. Y., 2001.