Hydrodeoxygenation of 2,5-dimethyltetrahydrofuran over bifunctional metal-acid catalyst Pt–Cs2.5H0.5PW12O40 in the gas phase: Kinetics and mechanism

Hanan Althikrallah,a,b Elena F. Kozhevnikova,a Ivan V. Kozhevnikova[[1]](#footnote-1)

*a University of Liverpool, Department of Chemistry, Liverpool L69 7ZD, UK*

b *Department of Chemistry, College of Science, King Faisal University, P.O Box 400, Al-Ahsa, 31982, Saudi Arabia*

**Abstract**

Hydrodeoxygenation (HDO) of 2,5-dimethyltetrahydrofuran (DMTHF) was studied at a gas-solid interface in a fixed-bed microreactor in the presence of bifunctional metal-acid catalysts comprising Pt/C and acidic heteropoly salt Cs2.5H0.5PW12O40 (CsPW). The Pt–CsPW catalyst deoxygenated DMTHF to n-hexane with >99% selectivity under mild conditions (90–100 oC, ambient pressure) and was much more efficient than monofunctional Pt/C. On the basis of kinetic studies, a mechanism for the HDO of DMTHF over Pt–CsPW was proposed, which includes a sequence of hydrogenolysis, dehydration and hydrogenation steps catalysed by Pt and proton sites of the bifunctional catalyst. The turnover rate of HDO increased with increasing Pt particle size suggesting that the hydrogenolysis of C–O bond in furanic compounds on Pt is a structure-sensitive reaction.

*Keywords:* hydrodeoxygenation, 2,5-dimethyltetrahydrofuran, platinum, heteropoly acid, kinetics, mechanism.

1. Introduction

Furanic compounds derived from biomass attract considerable interest as a renewable feedstock, which can be converted to a wide range of value-added chemicals and green fuels via catalytic hydrogenolysis, hydrogenation and hydrodeoxygenation [1–16]. Hydrodeoxygenation (HDO) of bio-furanics using heterogeneous catalysis is an effective strategy to produce green fuels ([11,12,14,16,17] and references therein). Complete deoxygenation of furanics over noble metals to produce hydrocarbons requires severe reaction conditions (200−400 oC, 7–20 MPa H2 pressure) [11,12,14]. Bifunctional metal-acid catalysis has been found more efficient than monofunctional metal catalysis for the HDO of oxygenates such as ketones, alcohols, phenols, ethers, esters, etc. [18–22]. Previously, this group has reported bifunctional catalysts comprising Pt and Keggin-type heteropoly acids for HDO of a wide range of oxygenates in the gas phase to produce alkanes under mild conditions [19,20]. Pt–CsPW comprising Pt and strongly acidic heteropoly salt Cs2.5H0.5PW12O40 (CsPW) has been reported to be a highly active catalyst for the gas-phase HDO of 2,5-dimethylfuran (DMF) to produce n-hexane with 100% yield at 90 oC and ambient pressure [21]. Among the platinum group metals, Pt is the most active catalyst for HDO of DMF due to its high activity in hydrogenolysis of furan ring. In contrast, Pd, Rh and Ru, that have high selectivity to ring-saturated tetrahydrofuran derivatives rather than furan ring hydrogenolysis [6,13,15], have low activities in HDO of DMF [21].

The HDO of DMF over Pt–CsPW can be represented by Scheme 1 including two parallel pathways: ring hydrogenolysis (1) and ring hydrogenation (2) [21]. The primary ring-opened and ring-saturated products – 2-hexanone and 2,5-dimethyltetrahydrofuran (DMTHF) – are formed in parallel on Pt sites directly from DMF [6,13,15]. Further, on Pt sites, 2-hexanone is hydrogenated and DMTHF undergoes ring opening, both giving 2-hexanol, which is dehydrated to hexene on proton sites. Finally, the hexene is hydrogenated to n-hexane on Pt sites to form n-hexane [21]. The HDO of ketones, including 2-hexanone (pathway 1), over Pt–CsPW has been studied in detail previously [19,20]. In contrast, the HDO of DMTHF (pathway 2) has not been reported yet, to the best of our knowledge. Since the HDO of furanic compounds involves tetrahydrofuran derivatives as intermediates, it would be interesting to investigate the HDO of DMTHF in the presence of bifunctional metal-acid catalysts.



Scheme 1. Reaction network for hydrodeoxygenation of DMF over Pt–CsPW.

Here, the HDO of DMTHF is investigated at a gas-solid interface in the presence bifunctional metal-acid catalyst Pt–CsPW. The strongly acidic CsPW heteropoly salt is well documented as a solid Brønsted acid catalyst [17,23–25]. It has a large surface area, high thermal stability (~500 oC decomposition temperature) and high tolerance to water, with proton sites almost as strong as those in the parent heteropoly acid H3PW12O40 [23–25]. It is demonstrated that Pt–CsPW deoxygenates DMTHF to n-hexane with >99% selectivity under mild conditions and an insight into reaction mechanism is gained from kinetic investigation.

**2. Experimental**

*2.1. Chemicals and catalysts*

2,5-Dimethyltetrahydrofuran (*cis/trans* isomer mixture, 96%), Cs2CO3 (99%) and H3PW12O40 hydrate (99%) were purchased from Sigma-Aldrich. 1%Pt/γ-Al2O3 and carbon-supported noble metal M/C catalysts 9.6%Pt/C and 7.8%Pd/C were from Sigma-Aldrich (the metal loading in M/C catalysts determined in-house by ICP-OES analysis). Zeolite NH4+-ZSM-5 (Si/Al = 47) was from Zeolyst International. It was converted into the H+ form by air calcination at 500 oC for 6 h. Hereinafter the H+ form is designated HZSM-5-47. Commercial Aerosil 300 silica support (*S*BET ≈ 300 m2g-1) was from Degussa. H2 (>99%) was supplied by the British Oxygen Company.

Cs2.5H0.5PW12O40 (CsPW) was prepared according to the literature procedure [26] by adding drop-wise the required amount of an aqueous solution of Cs2CO3 to an aqueous solution of H3PW12O40 to afford CsPW as a white precipitate, which was isolated, dried at 150 oC/10-3 kPa for 1.5 h and ground to 45–180 μm particle size. 6.4%Pt/SiO2 catalyst was prepared by wet impregnation of Aerosil 300 silica with an aqueous solution of H2PtCl6. The mixture was stirred at 50 oC for 2 h followed by rotary evaporation to dryness and reduction with H2 flow at 250 oC for 2 h. Physically mixed metal-acid bifunctional catalysts M/C + CsPW (M = Pt and Pd) and Pt/C + zeolite were prepared by grinding a mixture of the corresponding components. Information about the catalysts prepared is presented in Table 1.

*2.2. Techniques*

The surface area and porosity of catalysts were determined by the BET (Brunauer–Emmett–Teller) method from nitrogen physisorption measured on a Micromeritics ASAP 2010 instrument at −196 oC. Before measurement, the samples were evacuated at 250 oC for 2 h. Inductively coupled plasma optical emission spectroscopy (ICP–OES) 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* = Ms/Mtotal, was determined by pulse chemisorption of CO in flow system using a Micromeritics TPD/TPR 2900 instrument as described elsewhere [19] (in He flow at 50 oC, 10–15 mg catalyst sample, 25 μl pulses of pure CO). The adsorption stoichiometry Ms/CO was assumed to be 1 for Pt [27] and 2 for Pd [28].

*2.3. Catalyst testing*

The HDO of DMTHF was carried out at the gas-solid interface in flowing H2 at ambient pressure and 60–120 oC using a Pyrex fixed-bed down-flow microreactor (9 mm internal diameter) fitted with an on-line gas chromatograph (Varian 3800 instrument with a 30 m × 0.32 mm × 0.5 μm Zebron ZB–WAX capillary column and a flame ionisation detector) described elsewhere [21]. The substrate was fed by passing H2 flow controlled by a Brooks mass flow controller through a stainless steel saturator, which held DMTHF at an appropriate temperature to maintain a chosen partial pressure of DMTHF. The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of catalyst bed. The catalyst bed (0.20 g total weight) contained a uniform physical mixture of powdered catalyst components (M/C + acid co-catalyst or SiO2). Prior to reaction, the catalysts were pre-treated in situ for 1 h at the reaction temperature in H2 flow. The downstream gas flow was analysed by the on-line GC to obtain reactant conversion and product composition. Product selectivity was defined as moles of product formed per one mole of DMTHF 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%.

**3. Results and discussion**

*3.1. Hydrodeoxygenation of DMTHF over bifunctional Pt–CsPW catalyst*

The HDO of DMTHF over Pt–CsPW was carried out at 60–120 oC in flowing H2 at ambient pressure. The catalyst exhibited stable performance; no deactivation was observed at least during 4 h on stream (Fig. 1). Previous H2-TPR, XRD and FTIR studies have shown that CsPW in Pt/CsPW and Pd/CsPW catalysts is resistant toward reduction by H2 below 600 oC, and the Keggin structure of CsPW is retained in CsPW-supported Pt and Pd catalysts after H2 treatment at 400 oC [29]. Therefore, the Pt–CsPW catalysts should be stable at rather mild reaction conditions applied in this work.

Table 2 shows the representative results on HDO of DMTHF. CsPW alone had a low activity to form mainly cracking products at 2.0% DMTHF conversion (entry 1). The monofunctional Pt/C catalyst in the absence of CsPW had a very low HDO activity to form 2-hexanol in 88% selectivity at 1.6–3.0% DMTHF conversion, with only 7–8% of n-hexane being formed at 90–100 oC (entries 2 and 3). Bifunctional Pt/C + CsPW catalyst had a fairly good deoxygenation activity starting from 60 oC with 74% n-hexane selectivity (entry 4). It gave >99% n-hexane selectivity at 44% DMTHF conversion at 90 oC (entry 6) and 71% conversion at 100 oC (entry 7). 100% DMTHF conversion at >99% n-hexane selectivity was obtained at 120 oC (entry 8). At such conditions no n-hexane isomerisation occurred allowing complete conversion of DMTHF to alkane without carbon chain alteration. The isomerisation of n-hexane on Pt–CsPW occurs at higher temperatures, >150 oC [30]. These results clearly show that for the efficient HDO of DMTHF both Pt and H+ sites are required, like in the case of HDO of DMF [21]. As expected, Pd–CsPW bifunctional catalyst had a much lower HDO activity compared to Pt–CsPW; Pd/C + CsPW gave only 1–5% DMTHF conversion at 90–91% n-hexane selectivity at 90–100 oC (entries 9 and 10).

While Pt is the key to the HDO of furanics, the acid co-catalyst can also have a significant effect on the performance of bifunctional metal-acid catalyst [21]. In HDO of DMTHF, the acid co-catalyst will enhance the rate of dehydration of 2-hexanol (Scheme 1), thus affecting the selectivity to hexane. It has been demonstrated that the rate of alcohol dehydration over HPA catalysts correlates with the HPA acid strength [31]. Acid co-catalysts may also enhance the rate of the preceding step of DMTHF hydrogenolysis on Pt sites through kinetic coupling (see sect. 3.2 below). Table 3 shows the effect of Brønsted acid co-catalyst by comparing CsPW with zeolite HZSM-5 at the same Pt/C amount at 80 oC under kinetic control (DMTHF conversion 2.4–11%). These acids differ significantly both in their strength and proton site density. CsPW has strong proton sites with an initial enthalpy of ammonia adsorption Δ*H* = –164 kJ mol-1 [31], but it has a low proton site density of 0.080 mmol g-1. The zeolite has weaker proton sites, Δ*H* = –130 kJ mol-1 [31], however with a much greater proton site density of 0.35 mmol g-1. The stronger acid, CsPW, despite its low proton site density, gives a higher hexane selectivity of 95.9% as compared to 87.6% for the zeolite (Table 3). Similar results have been reported for the HDO of DMF on Pt/C + CsPW [21]. This shows that the acid strength of co-catalyst has the major effect on HDO efficiency, whereas the acid site density is less important. Furthermore, the HDO reaction on Pt/C + CsPW occurs with a significantly higher rate compared to Pt/C + HZSM-5 (11 and 2.4% DMTHF conversion, respectively, Table 3). This can be explained by the kinetic coupling between DMTHF hydrogenolysis and 2-hexanol dehydration steps (see sect. 3.2 below). It may also be due to diffusion limitations in zeolite micropores.

Next, we looked at the effect of Pt dispersion (*D*) on turnover frequency (TOF) for HDO of DMTHF over Pt–CsPW. In this study, physical mixtures of 9.6%Pt/C, 6.4%Pt/SiO2 and 1%Pt/γ-Al2O3 with CsPW were used as catalysts, in which Pt dispersion varied from 0.039 to 0.63 (Table 1). This corresponds to Pt particle size (*d*) variation from 26 to 1.6 nm as estimated from the conversion formula *d =* (1/*D*) nm [32]. The reactions were carried out at 90 oC under kinetic control (DMTHF conversion 3.6–64%); in all cases the amount of Pt in the catalyst bed was the same (0.6% per total catalyst weight). The results are shown in Table 4. With all catalysts, the selectivity to n-hexane was above 95%, which suggests the rate-limiting step being DMTHF hydrogenolysis on Pt sites (Scheme 2). From these results, TOF values per Pt site were calculated using the data on Pt dispersion (Table 1). As can be seen, the TOF values increase two orders of magnitude with increasing Pt particle size from 1.6 to 26 nm in the series of supports (s-1): γ-Al2O3 (0.0031) < SiO2 (0.12) < C (0.40). Previously, the same order of TOF has been reported for HDO of DMF on the same Pt–CsPW catalysts (s-1, at 70 oC): γ-Al2O3 (0.42) < SiO2 (2.3) < C (9.3) [21]. This suggests that the hydrogenolysis of C–O bond in furanic compounds on supported Pt catalysts is a structure-sensitive reaction occurring on active sites comprising ensembles of Pt atoms rather than single Pt atoms [32,33]. This is in agreement with Boudart’s concept of structure sensitivity [32,34] classifying the metal-catalysed reactions involving breaking or making C–C, N–N and C–O bonds as the structure-sensitive reactions. Further in-depth investigation is required to characterise the size and symmetry of active Pt ensembles for the HDO of furanic compounds.

The results above show that the turnover rate of HDO of DMTHF is much lower compared to HDO of DMF. For 9.6%Pt/C + CsPW, it is 80 times lower given the activation energy of 65 kJ mol-1 for the HDO of DMF on 9.6%Pt/C + CsPW [21]. This is not unexpected, as DMTHF hydrogenolysis on Pt/C is three orders of magnitude slower compared to DMF hydrogenolysis [15].

*3.2. Kinetics and mechanism of DMTHF hydrodeoxygenation*

Hydrodeoxygenation of DMTHF over Pt–CsPW can be represented by Scheme 2, which includes DMTHF ring opening on Pt sites to form 2-hexanol followed by 2-hexanol dehydration to hexene on proton sites and finally hexene hydrogenation to n-hexane on Pt sites [21]. Since no hexene was observed among the reaction products, the last step can be assumed to be fast and kinetically irrelevant. The rate-limiting step (first or second step in Scheme 2) is likely to be determined by the balance between metal and acid functionalities in bifunctional catalyst, i.e., by the ratio of accessible surface metal and acid sites Pts/H+.



**Scheme 2.** Hydrodeoxygenation of DMTHF over Pt–CsPW catalyst.

Fig. 2 shows the dependence of DMTHF conversion and reaction selectivity on the relative number of surface Pt and H+ sites in the catalyst mixture Pt/C + CsPW. The density of Pt surface sites was calculated from the Pt dispersion (Table 1), the density of H+ surface sites in CsPW was 0.080 mmol g-1, as calculated from the PW12O403- Keggin unit cross section of 144 Å2 [24,31] and CsPW surface area of 139 m2g-1 (Table 1). In Fig. 2A, the amount of CsPW was kept constant (0.18 g) at a sufficiently high level to effectively convert 2-hexanol to hexene. The amount of Pt/C was varied from zero to 0.06 g. As can be seen, the DMTHF conversion increases with Pts/H+ ratio and reaches a plateau (22%) at Pts/H+ ≈ 0.05. The selectivity to hexane was ~100% throughout this series. These results indicate the change of rate-limiting step from the first step (DMTHF hydrogenolysis) at low Pts/H+ to the second step (2-hexanol dehydration) at high Pts/H+, with the first step reaching equilibrium.

In Fig. 2B, the experiment was carried out the other way around. The amount of Pt/C was kept constant at a typical level of 0.020 g, whereas the amount of CsPW was varied from zero to 0.22 g. As seen, the DMTHF conversion increases with the H+/Pts ratio to reach a plateau (18%) at H+/Pts ≈ 30 or Pts/H+ ≈ 0.03. At such conditions the first step is not equilibrated, being the rate-limiting step throughout this series. The levelling off trend of DMTHF conversion can be explained by kinetic coupling [35] between the first and the second step in Scheme 2. As the H+/Pts ratio increases, the rate of the second (dehydration) step in the forward direction becomes greater than the rate of the first step in reverse direction, which drives the HDO reaction forward. An important outcome of the kinetic coupling is a dramatic increase in reaction selectivity (Fig. 2B). In the absence of CsPW, the reaction over Pt/C gave 85% of 2-hexanol and 15% of hexane at ~1% DMTHF conversion. Increasing the amount of CsPW greatly affected the selectivity, with hexane becoming the main and then the only product at the expense of 2-hexanol. The acid-catalysed dehydration of secondary alcohol intermediate, 2-hexanol, is known to occur readily in the presence of CsPW [19], which greatly enhances the HDO process.

Kinetics of the gas-phase HDO of DMTHF was examined at 60–100 oC and DMTHF conversion *X* < 20%. The HDO reaction was carried out at Pts/H+ = 0.026 with the catalyst mixture 9.6%Pt/C + CsPW (1:9 w/w), which was diluted with SiO2 whenever required to keep the conversion low. In this system, the HDO reaction was under impact of kinetic coupling, with the first (hydrogenolysis) step being rate-limiting (see above) and hexane selectivity >90%. The kinetic parameters obtained at such conditions are therefore attributable to the first step. The rate based on Pt/C was determined as *R = XF/W*, where *X* is the DMTHF conversion, *F* is the inlet molar flow rate of DMTHF and *W* is the weight of Pt/C catalyst. In most cases, catalyst performance was stable, practically no deactivation was observed (Fig. 1).

The reaction order in DMTHF was close to zero (0.11) (Fig. 3), which indicates saturation of catalyst surface sites by the substrate. To measure the reaction order in H2, the partial pressure of H2 was varied by changing the composition of H2 + N2 gas mixture at ambient pressure. This did not affect the selectivity to hexane, which was 92–93% throughout the measurement. The order in H2 was found to be negative, –0.45 (Fig. 4), which indicates competitive adsorption of DMTHF and H2 on the Pt sites. The order in Pt–CsPW catalyst was close to 1 (Fig. 5), which confirms that the DMTHF ring opening is the rate-limiting step.

The reaction was found to have an activation energy *E* = 78.5 kJ mol-1 (the Arrhenius plot is shown in Fig. 6). Given zero order in DMTHF, this is the true value *E*. The high *E* value and zero reaction order in DMTHF indicate no diffusion limitations in this reaction. As specified above, the *E* value can be attributed to the DMTHF hydrogenolysis step. The activation energy for the dehydration step is expected to be higher. This is indicated by the increase in hexane selectivity with reaction temperature (64% at 60 oC, 94% at 80 oC and >99% at 100 oC). The gas-phase dehydration of a similar secondary alcohol, 2-methyl-4-pentanol, over CsPW has been reported to have *E* = 130 kJ mol-1 at 60–80 oC [19].

The rate equation (eq 1) was derived for the HDO reaction (see Supporting Information) assuming that the reaction proceeds through equilibrated competitive adsorption of DMTHF (equilibrium constant *K*1) and dissociative adsorption of H2 (*K*2) on Pt sites, followed by the rate-limiting hydrogenolysis of the adsorbed DMTHF by addition of the first hydrogen atom (rate constant *k*). Then the second H atom adds to form 2-hexanol. The latter step and subsequent steps of 2-hexanol dehydration to hexene on acid sites and hexene hydrogenation to hexane on Pt sites were assumed to be fast, hence kinetically irrelevant. Rate equation (1) thus derived is consistent with the kinetics observed for hydrodeoxygenation of DMTHF. It accounts for zero order in DMTHF pressure (*PDMTHF*) at sufficiently high *PDMTHF* and –0.45 order in H2 pressure (*PH2*). It also accounts for the first order in Pt/C catalyst since the rate constant *k* is proportional to the density of Pt sites.

(1)

Conclusions

Catalytic hydrodeoxygenation (HDO) of biomass-derived furanic compounds attracts interest for sustainable production of chemicals and green fuels. In this work, we demonstrate the high effectiveness of metal-acid bifunctional heterogeneous catalysis for the gas-phase HDO of a saturated furan derivative 2,5-dimethyltetrahydrofuran (DMTHF). The Pt–CsPW bifunctional catalyst comprising a mixture of Pt/C and strongly acidic heteropoly salt CsPW deoxygenates DMTHF to n-hexane with >99% selectivity under mild conditions (90–100 oC, ambient pressure) and is much more efficient than monofunctional Pt/C. At such conditions no n-hexane isomerisation takes place allowing complete conversion of DMTHF to alkane without carbon chain alteration. The proposed reaction mechanism includes a sequence of hydrogenolysis, dehydration and hydrogenation steps catalysed by Pt and proton sites in the bifunctional catalyst. The results suggest that the HDO of furanic compounds on Pt–CsPW is a structure-sensitive reaction occurring on active sites that are complex ensembles of Pt atoms. Synergistic action of the metal and acid sites is essential for the effectiveness of the HDO process. Easy dehydration of secondary alcohol intermediate, 2-hexanol, on strong proton sites of CsPW is an effective driving force of the HDO process by bifunctional metal-acid catalysis through kinetic coupling between DMTHF hydrogenolysis and 2-hexanol dehydration steps.

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**Table 1**

Catalyst characterisation.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalyst | Surface areaa  m2g-1 | Pore volumeb  cm3g-1 | Pore diameterc  Å | *D* d |
| 7.8%Pd/C | 820 | 0.56 | 27 | 0.33±0.03 |
| 9.6%Pt/C | 713 | 0.56 | 31 | 0.039±0.007 |
| 1%Pt/Al2O3 | 163 | 0.49 | 121 | 0.63±0.04 |
| 6.4%Pt/SiO2 | 266 | 1.06 | 159 | 0.28±0.04 |
| Cs2.5H0.5PW12O40 (CsPW) | 139 | 0.09 | 27 |  |
| HZSM-5 (Si/Al = 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).

**Table 2**

Hydrodeoxygenation of DMTHF.a

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No | Catalyst | Temp.  oC | Conv.b  % | Product selectivityb (% mol) | | | | | | | |
|  |  | Hexane | | 2-Hexanone | | 2-Hexanol | Other | |
| 1 | CsPW | 90 | 2.0 |  | |  |  | |  | | |
| 2 | 9.6%Pt/C+SiO2 (1:9 w/w) | 90 | 1.6 | | 8.1 | 1.4 | | 87.6 | | 2.9 | | |
| 3 | 9.6%Pt/C+SiO2 (1:9 w/w) | 100 | 3.0 | | 7.4 | 2.7 | | 88.3 | | 1.7 | | |
| 4 | 9.6%Pt/C+CsPW (1:9 w/w) | 60 | 4.0 | | 73.7 | 0.0 | | 25.7 | | 0.0 | | |
| 5 | 9.6%Pt/C+CsPW (1:9 w/w) | 80 | 29 | | 96.4 | 0.0 | | 3.4 | | 0.0 | | |
| 6 | 9.6%Pt/C+CsPW (1:9 w/w) | 90 | 44 | 99.6 | | 0.0 | 0.4 | | 0.0 | | |
| 7 | 9.6%Pt/C+CsPW (1:9 w/w) | 100 | 71 | 99.9 | | 0.0 | 0.1 | | 0.0 | | |
| 8 | 9.6%Pt/C+CsPW (1:9 w/w) | 120 | >99 | 100 | | 0.0 | 0.0 | | 0.0 | | |
| 9 | 7.8%Pd/C+CsPW (1:7 w/w) | 80 | 0.9 | 89.9 | | 3.0 | 2.0 | | 5.5 | | |
| 10 | 7.8%Pd/C+CsPW (1:7 w/w) | 100 | 5.1 | 91.0 | | 3.8 | 0.2 | | 5.0 | | |

a 0.20 g catalyst (1% metal loading per total catalyst weight, 20 mg Pt/C or 30 mg Pd/C), 2.3 kPa DMTHF, 20 ml min-1 H2 flow, 4 h TOS. b Average conversion and product selectivity over 4 h TOS.

**Table 3**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalyst | H+ b | Conversionc  % | Product selectivityc (%) | |
| mmol g-1 | Hexane | 2-Hexanol |
| Pt/C+CsPW | 0.080 | 11 | 95.9 | 3.6 |
| Pt/C+HZSM-5-47 | 0.35 | 2.4 | 87.6 | 12.4 |

Effect of acid co-catalyst on HDO of DMTHF in the gas phase.a

a 80 oC, 2.3 kPa DMTHF, 20 ml min-1 H2 flow rate, 1 h TOS, 0.10 g catalyst 9.6%Pt/C + solid acid (1:9 w/w, 10 mg Pt/C, 1% Pt loading) diluted with SiO2 (0.10 g). b Proton site density per gram of acid co-catalyst; for CsPW calculated from the Keggin unit cross section of 144 Å2 and CsPW surface area of 139 cm2g-1 (Table 1); for zeolite calculated from Si/Al ratio. c Average conversion and product selectivity over 1 h TOS.

**Table 4**

Effect of support on HDO of DMTHF over Pt–CsPW.a

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | *D*b | *d­*c  nm | Conversion  (%) | TOF  (s-1) | Product selectivity (%) | |
| Hexane | 2-Hexanol |
| 9.6%Pt/C+CsPW | 0.039 | 26 | 31 | 0.40 | 99.5 | 0.5 |
| 6.4%Pt/SiO2+CsPW | 0.28 | 3.6 | 64 | 0.12 | 99.4 | 0.5 |
| 1%Pt-Al2O3+CsPW | 0.63 | 1.6 | 3.6 | 0.0031 | 95.8 | 1.1 |

a 0.2 g total catalyst weight, 0.6% Pt loading, 90 °C, 2.3 kPa DMTHF, 20 ml min-1 H2 flow rate, 3 h TOS. b Pt dispersion (from Table 1). c Pt particle size (*d* = 1/*D* nm).

**Fig. 1.** Time course for HDO of DMTHF: 9.6%Pt/C+CsPW (1:9 w/w, 0.10 g, 10 mg Pt/C, diluted by 0.10 g SiO2), 90 oC, 2.3 kPa DMTHF partial pressure, 40 ml min-1 H2 flow rate.

**Fig. 2.** Effect of molar ratio of surface Pt and H+ sites on DMTHF conversion and reaction selectivity at 80 oC, 2.3 kPa DMTHF partial pressure, 20 ml min-1 H2 flow rate: (A) 9.6%Pt/C (varied from 0 to 0.060 g), CsPW (0.18 g), catalyst diluted by 0.10 g SiO2; (B) 9.6%Pt/C (0.020 g), CsPW (varied from 0 to 0.22 g), catalyst diluted by 0.10 g SiO2.

**Fig. 3.** Effect of DMTHF partial pressure on reaction rate (based on Pt/C): 9.6%Pt/C+CsPW (1:9 w/w, 0.10 g, 10 mg Pt/C, diluted by 0.10 g SiO2), 80 oC, 40 ml min-1 H2 flow rate; reaction order in DMTHF 0.11.

**Fig. 4.** Effect of hydrogen partial pressure (*P*H2, kPa) on reaction rate (mol g-1h-1 based on Pt/C): 9.6%Pt/C+CsPW (1:9 w/w, 0.10 g, 10 mg Pt/C, diluted by 0.10 g SiO2), 80 oC, 2.3 kPa DMTHF partial pressure, 40 ml min-1 H2 + N2 flow rate; reaction order in H2 –0.45.

**Fig. 5.** Effect of catalyst amount on DMTHF conversion: 9.6%Pt/C+CsPW (1:9 w/w, 1% Pt loading, varied amount, diluted by 0.10 g SiO2), 80 oC, 2.3 kPa DMTHF partial pressure, 20 ml min-1 H2 flow rate.

**Fig. 6.** Arrhenius plot for HDO of DMTHF: 9.6%Pt/C+CsPW (1:9 w/w, 0.10 g, 10 mg Pt/C, diluted by 0.10 g SiO2), 2.3 kPa DMTHF partial pressure, 40 ml min-1 H2 flow rate; *R* is the reaction rate (mol h-1g-1) per Pt/C weight; *E* = 78.5 kJ mol-1.

1. Corresponding author. Tel.: +44(0)1517942938

   *E-mail address:* *kozhev@liverpool.ac.uk* (I. V. Kozhevnikov) [↑](#footnote-ref-1)