Selective conversion of 5-hydroxymethylfurfural to diketone derivatives over Beta zeolite-supported Pd catalysts in water

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**Abstract**

Conversion of 5-hydroxymethylfurfural (HMF) in water to the linear diketone derivatives 1-hydroxyhexane-2,5-dione (HHD) and 2,5-hexanedione (HXD) was investigated over a series of Beta zeolite-supported transition metal catalysts (Co, Ni, Cu, Ru, Pd). Their catalytic performance was tested in a batch stirred reactor (T = 110 °C, PH2 = 20 bar) with Pd showing the highest activity and selectivity to HHD and HXD. The effects of Pd particle size, zeolite Si/Al ratio and reaction conditions (T = 80 - 155 °C, PH2 = 5 - 60 bar) were also investigated. The incorporation of Pd into Beta zeolite by the deposition-coprecipitation method produced the most efficient catalyst, affording complete HMF conversion (T = 110 °C, PH2 = 60 bar) predominantly to HHD (68% selectivity) and HXD (8% selectivity). The combination of a bifunctional acid/redox solid catalyst and water enhances the hydrolytic ring-opening and subsequent hydrogenation of the furan ring. Catalytic activity can be partially restored by a simple regeneration treatment. This work establishes a catalytic route to produce valuable diketone derivatives from renewable furanic platform sources in water.

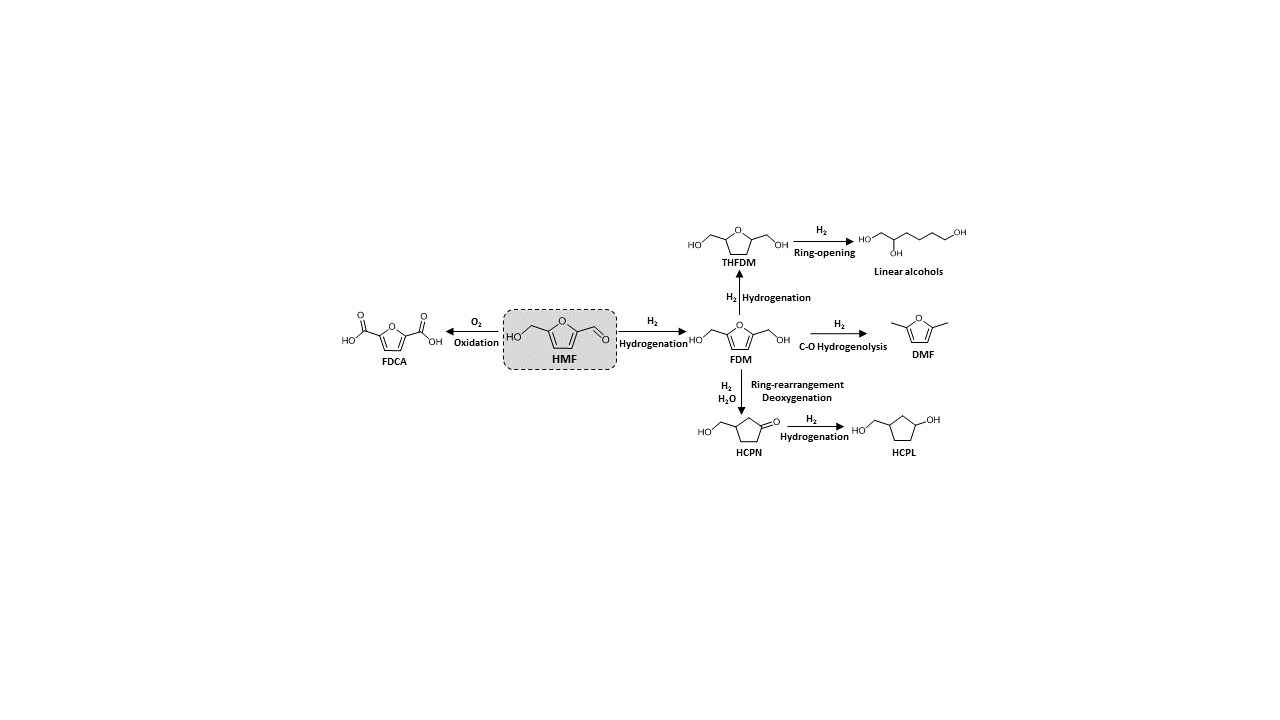
**Keywords**: 5-hydroxymethylfurfural, HMF conversion, Beta zeolite, supported Pd catalyst, hydrogenation, furan ring-opening.

**Abbreviations**: HMF: 5-hydroxymethylfurfural; HHD: 1-hydroxyhexane-2,5-dione; HXD: 2,5-hexanedione; FDM: furan-2,5-diyldimethanol; THFDM: tetrahydrofuran-2,5-diyldimethanol; DMF: 2,5-dimethylfuran; HCPN: 3-(hydroxymethyl)cyclopentanone; HHED: 1-hydroxyhex-3-ene-2,5-dione

1. Introduction

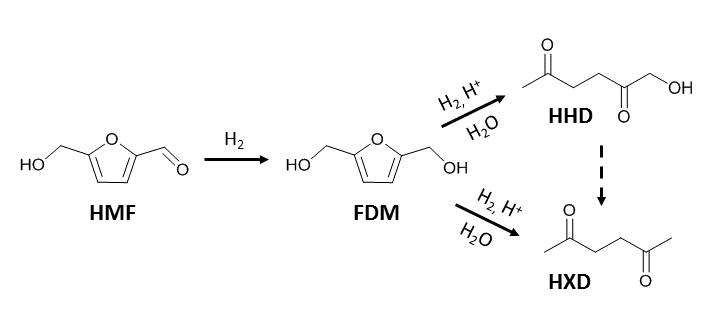
Non-edible lignocellulose is the most abundant, cheapest and fastest growing sustainable biomass resource, composed of three primary biopolymers: cellulose (a polymer of glucose), hemicellulose (a polymer mainly of pentoses) and lignin (a highly cross-linked polymer of substituted phenols) [[[1]](#endnote-1)]. In order to produce value-added bio-products which could displace petroleum feedstocks, lignocellulose must be first transformed into simpler and more easily processed platform chemicals. This approach, similar to that used in conventional petroleum refineries, would allow the simultaneous production of biofuels and biochemicals in an integrated facility, a biorefinery [[[2]](#endnote-2)].

In 2004, the U.S. Department of Energy (DOE) [[[3]](#endnote-3)] released a report, later revised by Bozell *et al.* [[[4]](#endnote-4)], identifying the top value-added platform chemicals in a future biorefinery. HMF was identified as one of the most appealing and promising building block molecules. This furan derivative can be produced from agricultural waste and forest residue such as polysaccharides (*i.e.* cellulose and hemicellulose) by acid-catalysed hydrolysis to C6 monosaccharides, followed by dehydration [[[5]](#endnote-5)]. In contrast to most petrochemical products, HMF is an oxygen-rich, functionalized compound. Its conversion to value-added chemicals usually involves several chemical transformations (*e.g.* hydrogenation, dehydration, hydrogenolysis, oxidation, etc.) which are promoted by multifunctional heterogeneous catalysts [[[6]](#endnote-6),[[7]](#endnote-7)]. The development of related catalytic heterogeneous processes has become highly topical to produce valuable bioproducts such as: tetrahydrofuran 2,5-diyldimethanol (THFDM) [[[8]](#endnote-8),[[9]](#endnote-9),[[10]](#endnote-10)], 2,5-dimethylfuran (DMF) [[[11]](#endnote-11)], 2,5-furandicarboxylic acid (FDCA) [[[12]](#endnote-12),[[13]](#endnote-13)], C6 linear alcohols [[[14]](#endnote-14),[[15]](#endnote-15)], 3-(hydroxymethyl)cyclopentan-1-one (HCPN) and 3-hydroxymethylcyclopentan-1-ol (HCPL) [[[16]](#endnote-16),[[17]](#endnote-17)] (Figure 1).



**Figure 1.** Chemical transformations of HMF to various bio-derived compounds [8 - 17].

One much less studied reaction is the conversion of HMF into the linear diketone derivatives 1-hydroxyhexane-2,5-dione (HHD) and 2,5-hexanedione (HXD). Although a large-scale synthetic route to HHD is currently not available, the presence of a hydroxymethyl functionality offers opportunities for the synthesis of valuable chemicals, as recently highlighted [[[18]](#endnote-18),[[19]](#endnote-19),[[20]](#endnote-20)]. HXD is employed as a solvent and as an intermediate for the synthesis of polymers, amines and surfactants [[[21]](#endnote-21),[[22]](#endnote-22)]. HHD can be produced from HMF in water under H2 pressure *via* the metal-catalysed selective hydrogenation of the carbonyl group to furan-2,5-diyldimethanol (FDM), followed by the acid-catalysed ring-opening of the FDM unsaturated ring [[[23]](#endnote-23)]. Notably, this pathway does not involve the formation of a more stable saturated tetrahydrofuran ring, whose ring-opening requires harsh reaction conditions (*i.e.* T> 140 °C; P> 60 bar) [[[24]](#endnote-24)]. HXD can also be produced from FDM via hydrogenolysis to DMF, followed by hydrolytic ring-opening of the latter or by HHD via scission of the hydroxyl group (Figure 2)[22,[[25]](#endnote-25)].



**Figure 2.** Catalytic reaction pathway discussed in this work for the conversion of HMF to linear diketone derivatives HHD and HXD via acid-catalysed hydrolytic ring-opening of FDM.

The formation of HHD from HMF was firstly reported in 1991 by Schiavo *et al.* using Pd/C in an aqueous solution of oxalic acid (pH = 2) at 70 bar H2 and 140 °C [23]. In 2009, Luijkx *et al.* reported a similar process using HCl [[[26]](#endnote-26)]. In 2014, Liu *et al.* developed two binary catalytic systems using Pd/C either in CO2/H2O (forming carbonic acid) [[[27]](#endnote-27)], or in THF with co-added Amberlyst-15 [[[28]](#endnote-28)], affording in both cases 77% yield of HHD (see Table SI1). Recently we reported that HHD is formed as a low yield intermediate (<7%) in the conversion of HMF to HCPN and HCPL over M-Al2O3 catalysts in H2O (M = Co, Ni, Cu). HHD was rapidly converted to HCPN via an aldol condensation reaction, catalysed by basic sites, followed by hydrogenation [17].

The requirement of hydrogenating metal phases and acidic sites for the production of HHD prompted us to investigate the deposition of various transition metals over zeolite supports to prepare easily tuneable bifunctional catalysts. Among the most investigated zeolites, Beta (with BEA topology) exhibits excellent properties to the aimed transformation due to its high hydrothermal stability, large specific surface area (>600 m2 g-1), 3D large-pore channel system (5.5 – 7.6 Å) and dual Lewis/Brønsted acidity [[[29]](#endnote-29)]. Beta zeolite-based catalysts have been used for the conversion of furfural into levulinic acid [[[30]](#endnote-30),[[31]](#endnote-31)] and for the hydrodeoxygenation of furoins into alkanes [[[32]](#endnote-32)]. However, to the best of our knowledge, there are no studies reporting the formation of linear diketone derivatives using Beta zeolite-supported catalysts.

Herein, we present the catalytic production of the diketone derivatives HHD and HXD from HMF by zeolite-supported transition metals in H2O. A series of transition metal-loaded (M) Beta zeolites were prepared (M = Co, Ni, Cu, Ru, Pd), characterised and tested in a batch stirred reactor under H2 pressure with Pd showing the highest catalytic activity. Consequently, the effects of Pd particle size, zeolite Si/Al ratio and reaction conditions were investigated, and catalyst stability and recyclability were evaluated. This work establishes Beta zeolite-supported Pd catalysts as promising candidates for the upgrading of HMF into valuable biomass-derived linear diketone derivatives by demonstrating for the first time the conversion of HMF to HHD and HXD in water by a solid state, bifunctional (no acid co-added) catalyst.

1. Experimental

**2.1. Catalyst preparation**

Metal-loaded zeolites were prepared by incipient wetness impregnation (IWI) of commercially available Beta (Si/Al = 12.5) and ZSM-5 (Si/Al = 11.5) zeolites purchased from Zeolyst Int. The corresponding aqueous solution of the metal precursor were prepared using: PdCl2 (Sigma-Aldrich), Pd(NO3)2·2H2O (Aldrich), RuCl3 (Aldrich), NiCl2·6H2O (Aldrich), CuCl2·2H2O (Aldrich) and CoCl2·6H2O (Fluka). Prior to the impregnation, the parent NH4-zeolites were calcined at 550 °C (heating rate of 2 °C min-1) in static air for 5 h, producing the respective H-zeolites. The deposition of the metal was carried out by adding dropwise the aqueous solution of the precursor to the zeolite support at room temperature (3 wt% for the Pd and Ru samples; 10 wt% for the Cu, Ni and Co samples). After impregnation, the catalysts were dried in a rotary evaporator at 65 °C under vacuum for 1 h. Subsequently, the dried samples were calcined in air at 500 °C for 5 h (heating rate of 2 °C min−1). The reduction treatment was performed under pure H2 flow (100 cm3 min−1) for 5 h at 200 °C (for the Pd and Ru samples), 300 °C (Cu sample) and 500 °C (Ni and Co samples) with a heating rate of 2 °C min−1. The catalysts were finally passivated under a flow of 1% v/v O2/N2 (100 cm3 min−1) for 2 h at room temperature.

Pd-loaded Beta zeolite was also prepared by deposition-coprecipitation (DP-CP) using the urea-based method developed by Geus *et al*. [[[33]](#endnote-33)]. First, 2 g of the calcined Beta zeolite were placed in a 250 ml round-bottom flask. Then, an aqueous solution (100 ml) containing PdCl2 (0.005 M) and urea (1.2 M, Sigma) was added dropwise with constant stirring (550 rpm) at room temperature. The suspension (pH = 4 - 4.5) was heated to 95 °C to initiate urea hydrolysis. After 3 h, the pH of the suspension remained stable at pH ≈ 7.5. The solution was cooled down to room temperature and the precipitate was collected by filtration, washed with deionized water, dried at 110 °C overnight and subsequently calcined in air at 500 °C for 5 h (heating rate of 2 °C min−1). The calcined sample (catalyst precursor) was then reduced under pure H2 flow (100 cm3 min−1) at 200 °C for 5 h (heating rate of 2 °C min−1). The reduced catalyst was finally passivated under a flow of 1% v/v O2/N2 (100 cm3 min−1) for 2 h at room temperature. Hereafter, the sample prepared by the DP-CP urea method will be referred as Pd(u)/Beta.

Partial dealumination of the calcined Beta zeolite (Si/Al = 12.5) was carried out by acid treatment using HNO3 aqueous solutions of different concentration (0.1, 0.5, 2 and 5 M) at room temperature for 1h (20 mL g-1 zeolite). After filtration and washing with deionized water, the resulting materials were dried overnight (110 °C) and calcined in static air at 500 °C for 5 h (heating rate of 2 °C min−1). Afterwards, the obtained dealuminated zeolites were impregnated with Pd following the DP-CP method described above. Hereafter, the four dealuminated and impregnated samples will be abbreviated as Pd(u)/Beta-dAlx (x = 1 – 4), where x = 4 refers to the sample showing the highest degree of dealumination (higher Si/Al ratio).

* 1. **Catalyst characterization**

The prepared catalysts were characterised by powder X-Ray diffraction (PXRD) on a Panalytical X’Pert Pro diffractometer with Co Kα1 radiation (λ = 1.7890 Å) in the 2θ angle range 10 - 80° (scanning speed of 0.023° s-1). Metal content of the catalysts was determined by inductively coupled plasma - optical emission spectroscopy (ICP-OES) using an Agilent 5110 SVDV instrument. The samples were digested in a strong acidic medium (10 ml HCl and 20 ml HNO3) and then diluted with water (1:10 v/v). Textural properties were evaluated through N2 adsorption–desorption isotherms at 77 K, using a Micromeritics TRISTAR II instrument. Prior to the measurement, the samples were outgassed at 120 °C under vacuum for 20 h. The BET equation was used for specific surface area calculation, whereas pore volume was determined by the BJH method.

Acidity of the catalysts was determined by temperature programmed desorption of ammonia (NH3-TPD) in a Quantachrome ChemBET 3000 unit. Firstly, the samples were outgassed under a He stream (100 cm3 min−1) heating at 10 °C min−1 up to 350 °C. Afterwards, the samples were cooled to 150 °C and saturated under an ammonia stream (100 cm3 min−1) for 10 min. Subsequently, the physically adsorbed ammonia was removed by flowing helium (100 cm3 min−1) for 30 min at 150 °C. Subsequently, the chemically adsorbed ammonia was desorbed by heating to 650 °C with a rate of 10 °C min−1 in flowing He (100 cm3 min−1). The variation of ammonia concentration was monitored continuously using a thermal conductivity detector (TCD).

Thermogravimetric analysis (TGA) was carried out on a Q600 TA Instrument; *ca*. 5 mg of sample were loaded into an alumina microcrucible and heated to 800 °C at 10 °C min-1 under a flow of air (100 cm3 min-1). Elemental analysis (C and H content) of the used catalysts was carried out on a Thermo EA1112 Flash CHNS Analyser. TEM images were obtained with a JEOL 2100 transmission electron microscope operating at 200 kV. The samples were dispersed in acetone, stirred in an ultrasonic bath and deposited on a carbon-coated Cu grid. SEM imaging and energy-dispersive X-ray (EDX) spectroscopy were run on a Hitachi S-4800 Field-Emission scanning electron microscope.

Solid state 27Al NMR experiments were performed on a 9.4 T Bruker DSX 400 MHz spectrometer using a Bruker Triple Resonance 4 mm HXY (in double resonance mode) probe under Magic Angle Spinning (MAS) at a rotational rate of 10 kHz. One-dimensional MAS NMR spectra were recorded using a rotor-synchronized (1 period) Hahn echo sequence with a radio frequency pulse of 50 kHz (π/2 pulse of 1.7 μs duration) and a quantitative recycle delay of 1 s.

* 1. **Catalytic experiments and product analysis**

The performance of the catalysts was studied in high pressure 100 ml batch stirred autoclaves (Parr Instrument Co.) A glass liner was loaded with 45 ml of an aqueous solution of HMF (0.04 M) and 0.06 g of catalyst and placed into the stainless-steel reactor. After sealing the vessel, the reactor was flushed three times with N2 and heated to the required reaction temperature (80 - 155 °C). Once the targeted temperature was reached, the vessel was pressurised with H2 to the respective value (5 - 60 bar of H2) and stirring was set to 600 rpm. After the end of the reaction (typically 6 h), the identity and distribution of the products were determined by the combination of 1H and 13C NMR spectroscopy (Bruker AVANCE III HD spectrometer), GC-MS (Agilent 6890N GC with a 5973 MSD detector) and GC (Agilent 7890A GC with an FID). GC and GC-MS were equipped with a DB-WAXetr capillary column (60 m, 0.25 mm i.d., 0.25 μm). Standard reference compounds used: HMF (Sigma), FDM (Manchester Organics), THFDM (Ambinter) and HXD (Sigma-Aldrich). Details concerning conversion, yield and selectivity calculations are given in the Supporting Information (SI).

**3. Results and discussion**

**3.1. Active metal screening for the conversion of HMF into HHD and HXD**

PXRD patterns (2θ = 10 – 80°) of the Beta-supported metal catalysts after reduction show the characteristic peaks of the corresponding metallic phase (Figure SI1). No crystalline phases of the metal oxides precursors were observed, confirming the complete reduction under the H2 treatment. Well-defined reflections associated with the zeolitic structures (Beta or ZSM-5) were identified [[[34]](#endnote-34)], verifying that crystallinity of the zeolitic support was preserved after impregnation. The composition of the prepared catalysts was determined by ICP-OES (Table 1), showing metal contents close to the corresponding nominal values (Pd, Ru = 2.7 - 2.9 wt%; Ni, Cu, Co = 8.7 - 9.3 wt%).

The comparison of the catalytic performance of several zeolite-supported metal catalysts prepared by IWI in the conversion of HMF is presented in Table 1 (110 °C, 20 bar H2). Temperature was set to 110 °C in order to minimize the extent of oligomerisation reactions which are favoured by the presence of acidic sites [24].

**Table 1**. Product distribution from the conversion of HMF over zeolite-supported metal catalysts prepared by incipient wetness impregnation.(a)

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |  |  |  |
|  |  | M(b) | Conv. | Selectivity (%) | | | | | Cmb(c) |
| Entry | Catalyst | (wt%) | (%) | FDM | THFDM | HCPN | HHD | HXD | (%) |
| 1 | Beta(d) | - | 4 | 25 | 0 | 0 | 0 | 0 | 97 |
| 2 | Beta(e) | - | 10 | N/A | 0 | 0 | 0 | 0 | 90 |
| 3 | Pd/Beta | 2.8 | 80 | 1 | 3 | 3 | 56 | 8 | 77 |
| 4 | Ru/Beta | 2.7 | 41 | 2 | 7 | 2 | 44 | 7 | 84 |
| 5 | Ni/Beta | 8.7 | 21 | 19 | 0 | 24 | 19 | 0 | 93 |
| 6 | Cu/Beta | 9 | 24 | 13 | 4 | 0 | 25 | 0 | 88 |
| 7 | Co/Beta | 9.3 | 15 | 47 | 7 | 20 | 13 | 0 | 98 |
| 8 | Pd/ZSM-5(f) | 2.9 | 74 | 1 | 1 | 1 | 41 | 14 | 74 |

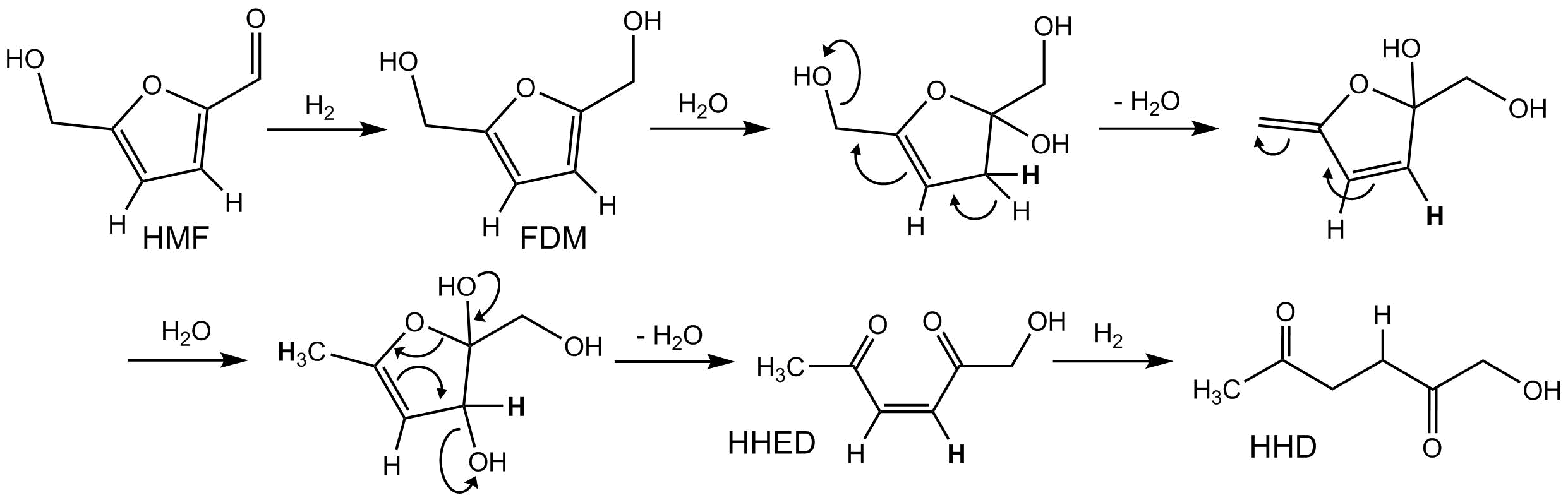
(a) Metal chloride precursors. Reaction conditions: 0.23 gHMF, 45 ml H2O, 0.06 gcat, 110 °C, 20 bar H2,600 rpm, 6 h. (b) Metal content based on ICP-OES measurements. (c) Carbon mass balance. (d) Si/Al=12.5. (e) FDM as the substrate. (f) Si/Al=11.5

A preliminary control reaction with non-impregnated Beta zeolite (entry 1) showed negligible HMF conversion (4%) to FDM (1% yield), verifying that a reduced metal phase is essential for the productive conversion of HMF to the targeted diketone derivatives. An additional control experiment using the more reactive FDM intermediate as the substrate over Beta zeolite (entry 2) resulted in 10% FDM conversion with a concomitant colour change of the reaction mixture from pale to dark yellow. However, no products were detected by GC and carbon mass balance (Cmb) was only 90%. The decrease in Cmb suggests that the highly reactive unsaturated intermediates formed by FDM hydrolytic ring opening, such as 1-hydroxyhex-3-ene-2,5-dione (HHED) [27,28], can form heavier ill-defined products, such as humins [[[35]](#endnote-35),[[36]](#endnote-36)]. This undesired oligomerisation reaction always takes place in parallel with productive FDM conversion. It should be noted that decarboxylation of HHED to levulinic and formic acid [[[37]](#endnote-37)] was not observed due to the highly reducing conditions employed.

Among the screened active metal phases, the Pd/Beta catalyst (entry 3) afforded the highest HMF conversion (80%) and selectivity to HHD (56%), whereas HXD was also detected as a minor product (8% selectivity). However, Cmb was only 77%, consistent with the formation of undetectable oligomers. The Ru/Beta catalyst (entry 4) showed lower HMF conversion (41%) and HHD selectivity (44%). The non-noble metal based catalysts (*i.e.* Ni, Cu and Co, entries 5-7) showed even lower HMF conversion (15-24%) despite having considerably higher metal loadings. Moreover, selectivity to HHD was rather poor (13-25%), whereas HXD was not detected. It should be noted that the higher Cmb observed for the Ru, Ni, Cu and Co supported catalysts (84-98%) is a direct consequence of the lower HMF conversion. The superior catalytic activity of Pd relative to other transition metals has also been demonstrated for the hydrogenation of HMF to THFDM in water, using Pd/C carbon [[[38]](#endnote-38)] or Pd@MIL-101(Al)-NH2 MOF [[[39]](#endnote-39)].

The effect of the zeolitic support was also explored by using ZSM-5 (Si/Al = 11.5) instead of Beta (Si/Al = 12.5) and preparing Pd/ZSM-5 (entry 8). The latter showed a high HMF conversion (74%) and HHD selectivity (41%), albeit slightly lower than Pd/Beta. Importantly, Pd/ZSM-5 also afforded the highest selectivity to HXD (14%) which can be attributed to the higher concentration of Brønsted acid sites in ZSM-5 [[[40]](#endnote-40)] and the different structural frameworks (MFI in ZSM-5 *vs.* BEA in Beta) which affect the shape selectivity by either mass transfer or transition state effects [[[41]](#endnote-41),[[42]](#endnote-42)]. Overall, both zeolite-supported Pd catalysts gave the highest HMF conversion and HHD selectivity but also showed the lowest Cmb due to the formation of heavier undetectable oligomers [27,28].

In order to clarify the role of water in the reaction mechanism, an isotopic labelling experiment was performed using D2O as the solvent under the same reaction conditions (110 °C, 20 bar H2). GC-MS revealed the formation of [D3]-HHD and [D4]-HXD as the main products, as well as traces of [D4]-HCPN. FDM was also detected but it was not deuterated (Figure SI2). Specifically, higher m/z values were observed in the mass spectra of the products when D2O was employed as the solvent instead of H2O: *m/z* = 118 ([D4]-HCPN), 133 ([D3]-HHD) and 118 ([D4]-HXD) compared to *m/z* = 114 (HCPN), 130 (HHD) and 114 (HXD). This in turn suggests that two D2O molecules participate in the catalytic mechanism, specifically in the ring-opening of FDM via consecutive hydration-dehydration steps (Figure 3), as originally proposed by Horvat *et al.* [37]. Notably, none of the above compounds is formed in water-free reaction mixtures [7]. Therefore, H2O not only serves as an environmentally benign solvent but is also necessary for FDM ring opening [[[43]](#endnote-43)].



**Figure 3.** Proposed mechanism for formation of HHD via double hydration/dehydration of the FDM intermediate [37], based on experiments carried out in D2O.

**3.2. Influence of Pd particle size**

The effect of the Pd particles size in the Beta zeolite-supported catalysts was also investigated. In addition to the catalyst prepared by IWI and PdCl2 (Pd/Beta), two more catalysts were prepared by either (i) IWI and Pd(NO3)2 as the precursor (Pd(n)/Beta) or (ii) DP-CP with urea and PdCl2 (Pd(u)/Beta). Samples were then calcined and reduced as before. The different preparation methods led to different morphologies of the supported Pd nanoparticles (NPs), as deduced by TEM imaging (Figures 4 and SI3) and PXRD patterns (Figure SI4).

The Pd/Beta catalyst (Figure 4a) resulted in intermediate Pd NPs (average diameter of 5.2 ± 3.4 nm). Employment of Pd(NO3)2 as the precursor (Figure 4b) led to much larger Pd NPs with a significantly less uniform particle size distribution (average diameter of 16.2 ± 10.4 nm). The higher dispersion of Pd catalysts with PdCl2 as the precursor has been ascribed to the formation of complex PdxOyClz species on alumina/aluminosilicate surfaces [[[44]](#endnote-44),[[45]](#endnote-45)]. The DP-CP method (Figure 4c) resulted in the smallest Pd NPs and the most uniform size distribution (average diameter of 3.5 ± 1.5 nm). The smaller and uniform particle size observed for Pd(u)/Beta can be associated with the slow and homogenous generation of hydroxide ions through the hydrolysis of urea at 95 °C which hinders the uneven precipitation of PdII species due to a sudden, local increase of pH [[[46]](#endnote-46),[[47]](#endnote-47)].

Table 2 shows the conversion of HMF and the obtained product distribution for the three Beta zeolite-supported Pd catalysts after 6 h under 20 bar of H2 at 110 °C. All the catalysts have similar Pd contents varying between 2.6 and 2.8 wt% (based on ICP-OES). A direct correlation between higher HMF conversion and smaller Pd particle size was identified. Thus, the Pd(n)/Beta catalyst (dM = 16.2 ± 10.4 nm) showed the lowest HMF conversion (56%). Moreover, the lower hydrogenation activity of Pd(n)/Beta resulted in the lowest selectivity to HHD (39%) due to a higher degree of oligomerisation of the unsaturated intermediates formed *via* FDM ring-opening. On the other hand, the Pd(u)/Beta catalyst (dM = 3.5 ± 1.5 nm) afforded almost complete HMF conversion (96%) and the highest selectivity to HHD (56%).



Figure 4. TEM images and histograms of Pd particle size distribution (after counting >200 particles) of (a) Pd/Beta, (b) Pd(n)/Beta and (c) Pd(u)/Beta catalysts.

**Table 2**. Product distribution from the conversion of HMF over Beta zeolite-supported Pd catalysts with different metal particle size.(a)

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | M(e)  (wt%) | dM(f)  (nm) | Conv.  (%) | Selectivity (%) | | | | | Cmb  (%) |
| FDM | THFDM | HCPN | HHD | HXD |
| Pd/Beta(b) | 2.8 | 5.2 | 80 | 1 | 3 | 3 | 56 | 8 | 77 |
| Pd(n)/Beta(c) | 2.8 | 16.2 | 56 | 2 | 2 | 2 | 39 | 7 | 74 |
| Pd(u)/Beta(d) | 2.6 | 3.5 | 96 | 0 | 1 | 1 | 56 | 9 | 71 |

(a) Reaction conditions: 0.23 gHMF, 45 ml H2O, 0.06 gcat, 110 °C, 20 bar H2,600 rpm, 6 h. (b) IWI and PdCl2. (c) IWI and Pd(NO3)2. (d) DP-CP with urea and PdCl2. (e) Metal content based on ICP-OES. (f) Mean metal particle diameter based on TEM images.

The N2 adsorption-desorption isotherm of the Pd(u)/Beta catalyst was similar to the parent Beta zeolite (Figure SI5), presenting features of Type I isotherms. The resulting textural properties showed a slight decrease in specific surface area and pore volume after the incorporation of Pd (621 m2 g-1 and 0.297 cm3 g-1 *vs.* 574 m2 g-1 and 0.286 cm3 g-1) due to partial blockage of the zeolite pores by Pd NPs, characteristic of a highly dispersed metal phase [[[48]](#endnote-48)]. Thus, the enhanced hydrogenation activity with the decrease of Pd particle size can be attributed to the corresponding higher metal dispersion (higher metal active surface) [[[49]](#endnote-49)] and to the higher uniformity in Pd particle size which favours the adsorption and hydrogenation of furanic compounds [38,39]. Additionally, well dispersed and uniform Pd NPs enhance catalytic lifetime by hindering leaching and sintering of particles [[[50]](#endnote-50)]. In this sense, SEM-EDX analysis of the Pd(u)/beta catalyst (Figure SI6) confirmed the absence of residual chlorine (from the PdCl2 precursor) which is known to increase metal atom mobility and cause sintering.

The product distribution obtained over the Pd(u)/Beta catalyst (Table 2) revealed that at 96% HMF conversion no product exceeded 1% selectivity apart from the targeted diketone derivatives HHD and HXD. Notably, full conversion was achieved in 24 h and only two well-defined peaks corresponding to HXD and HHD were observed in the respective GC chromatogram of the product mixture (Figure SI7). However, Cmb was found lower than 80% for all runs. Taken together, these observations suggest that an undetectable by GC fraction of products is produced *via* an acid-catalysed oligomerisation of unsaturated intermediates, formed *via* FDM ring-opening [24,27]. The formation of oligomers could be potentially suppressed by co-addition of organic solvents [[[51]](#endnote-51)]. Alternatively, techniques like biphasic reactive extraction, adsorbent-based separation or reactive distillation could be applied to separate the oligomer fraction from the targeted compounds [[[52]](#endnote-52),[[53]](#endnote-53)].

**3.3. Time evolution of HMF conversion**

The time evolution of HMF conversion, product distribution and Cmb over the Pd(u)/Beta catalyst are depicted in Figure 5. HMF was swiftly consumed, reaching 87% conversion in 120 min and 96% in 360 min. FDM was detected at early reaction times, with a maximum yield of 4% at 20 min but was fully consumed in 240 min. HHD and HXD yields rapidly increased during the first 120 min (47% and 7%, respectively) but did not significantly change afterwards, achieving final values of 54% (HHD) and 9% (HXD). Notably, exposing a mixture of HHD and HXD to a fresh batch of Pd(u)/Beta with or without H2 (T = 110 °C, 3 h) showed no interconversion between HHD and HXD. A selectivity *vs*. conversion plot (Figure SI8) is consistent with HHD and HXD being formed via two separate pathways (Figure 2). Previous works have shown that hydrogenolysis of FDM to DMF and hydrolysis of the latter can lead to HXD [21,25]. However, we did not detect any trace of DMF, indicating that HXD is formed through a currently unidentified mechanism.

The observed time profile supports the reaction mechanism for the conversion of HMF into HHD (Figure 2) which begins via the hydrogenation of the carbonyl group of HMF to form FDM, followed by the hydrolytic furan ring-opening and hydrogenation to form HHD [10,17,20,28]. The intermediate nature of FDM was confirmed by a separate experiment using a lower amount of catalyst (40 mg instead of 60 mg, Figure SI9) with FDM yield reaching a maximum of 23% and then gradually decreasing as HHD is formed. The time evolution of the Cmb showed a pronounced decrease within the first 120 min (from 100% to 73%), remaining practically constant afterwards (71% in 360 min). This is consistent with the formation of undetected heavier oligomers, catalysed by the zeolite acid sites.



**Figure 5.** Time evolution of HMF conversion to HHD over the Pd(u)/Beta catalysts. Reaction conditions: 0.23 gHMF, 45 ml H2O, 0.06 gcat, 110 °C, 20 bar H2,600 rpm

**3.4. Influence of support Si/Al ratio**

Since the catalytic properties of the Pd(u)/Beta catalysts are directly related to the acidity of the zeolite framework, it was expected that the removal of Al atoms would affect catalyst activity and selectivity [[[54]](#endnote-54)]. In order to understand the influence of the Si/Al ratio on the two competitive acid-catalysed reaction pathways, *i.e.* FDM ring-opening and oligomerisation of unsaturated intermediates, four Beta zeolite-supported Pd catalysts with different Si/Al ratio were prepared (Pd(u)/Beta-dAlx, x = 1-4) *via* dealumination (acid treatment) and subsequent Pd impregnation (DP-CP with PdCl2). The parent Beta zeolite (Si/Al=12.5) was partially dealuminated by using gradually more concentrated HNO3 aqueous solutions of 0.1, 0.5, 2 and 5 M which led to increasingly higher Si/Al atomic ratios in the range of 17.8 - 34.5 (Table 3).

**Table 3**. Catalytic conversion of HMF to HHD and HXD over dealuminated Beta zeolite-supported Pd catalysts.(a)

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Si/Al(b) | dM(c)  (nm) | Conv.  (%) | Selectivity (%) | | | | | Cmb (%) |
| FDM | THFDM | HCPN | HHD | HXD |
| Pd(u)/Beta | 12.5 | 11 | 96 | 0 | 1 | 1 | 56 | 9 | 71 |
| Pd(u)/Beta-dAl1 | 17.8 | 11 | 70 | 1 | 1 | 1 | 53 | 11 | 79 |
| Pd(u)/Beta-dAl2 | 20.6 | 12 | 64 | 2 | 2 | 1 | 47 | 16 | 81 |
| Pd(u)/Beta-dAl3 | 27.0 | 14 | 52 | 2 | 2 | 0 | 42 | 12 | 80 |
| Pd(u)/Beta-dAl4 | 34.5 | 15 | 49 | 4 | 2 | 2 | 39 | 12 | 82 |

1. Reaction conditions: 0.23 gHMF, 45 ml H2O, 0.06 gcat, 110 °C, 20 bar H2,600 rpm, 6 h.
2. Based on SEM-EDX measurements.
3. Mean metal particle diameter based on PXRD patterns and Scherrer equation.

Crystallinity and microporosity of the zeolitic support were preserved after the dealumination treatment based on the respective PXRD patterns and N2 isotherm profiles (Figure SI10). Removal of Al resulted in a progressive decrease of acid sites according to NH3-TPD measurements (Figure SI11 and Table SI2), due to removal of: (i) extra-framework aluminium, associated to Lewis acidity and (ii) tetrahedrally coordinated aluminium, associated to Brønsted acidity [[[55]](#endnote-55),[[56]](#endnote-56)]. Important differences were observed in the catalytic performance of the Pd(u)/Beta-dAlx catalysts (Table 3). A non-negligible increase of Cmb was observed over the dealuminated supports (from 71% for Pd(u)/Beta to 79-82% for Pd(u)/Beta-dAlx). However, a gradual decrease in HMF conversion and selectivity to HHD was also observed as the Si/Al ratio was increased due to the lower extent of the acid-catalysed hydrolytic ring-opening reaction.

**3.5. Influence of temperature and H2 pressure on HHD production**

The effect of reaction temperature (80-155 °C) and H2 pressure (5-60 bar) on the production of diketone derivatives from HMF over the Pd(u)/Beta catalyst was also investigated (Table 4). Comparison with the original run (entry 1) revealed that lowering the temperature below 110 °C resulted in lower HMF conversion (entries 2-3). Raising the temperature to 125 °C or 140 °C (entries 4-5) restored HMF conversion (≥95%). Notably, HCPN was also detected as a minor product as the temperature increased (4-5% selectivity), resulting in a slight improvement of Cmb (from 71% at 110 °C to 78% at 140 °C). However, the combined selectivity of targeted HHD and HXD was practically not affected (65±1%), although a marginal shift towards HXD was observed (56% HHD and 9% HXD at 110 °C *vs.* 53% HHD and 13% HXD at 140 °C). Further increasing the temperature to 155 °C (entry 6) led to a significant decrease of HHD selectivity, mainly due to oligomerisation (Cmb = 65%).

Having established that T = 110 °C is the optimal temperature for the production of the targeted compounds, the effect of H2 pressure was explored. Running the reaction under 40 bar of H2 afforded again 96% HMF conversion, albeit with a slightly higher Cmb (77%, entry 9). Increasing the H2 pressure to 60 bar resulted in 98% HMF conversion with 66% HHD selectivity in 6 h and 100% conversion with 68% HHD selectivity in 24 h (entries 10-11). Cmb increased to 82%, consistent with a faster hydrogenation rate of the unsaturated intermediates (*vs.* oligomerisation) to form HHD.

**Table 4**. Product distribution from the conversion of HMF over the Pd(u)/Beta catalyst.(a)

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Entry | T  (°C) | P  (bar) | T  (h) | Conv.  (%) | Selectivity (%) | | | | | Cmb (%) |
| FDM | THFDM | HCPN | HHD | HXD |
| 1 | 110 | 20 | 6 | 96 | 0 | 1 | 1 | 56 | 9 | 71 |
| 2 | 80 | 20 | 6 | 67 | 3 | 1 | 0 | 39 | 3 | 68 |
| 3 | 95 | 20 | 6 | 88 | 1 | 1 | 0 | 57 | 6 | 71 |
| 4 | 125 | 20 | 6 | 96 | 0 | 1 | 4 | 54 | 10 | 75 |
| 5 | 140 | 20 | 6 | 95 | 0 | 1 | 5 | 53 | 13 | 78 |
| 6 | 155 | 20 | 6 | 99 | 1 | 2 | 7 | 37 | 14 | 65 |
| 7 | 110 | 5 | 6 | 69 | 0 | 0 | 1 | 48 | 9 | 73 |
| 8 | 110 | 10 | 6 | 90 | 0 | 1 | 1 | 59 | 8 | 75 |
| 9 | 110 | 40 | 6 | 96 | 1 | 1 | 2 | 61 | 7 | 77 |
| 10 | 110 | 60 | 6 | 98 | 1 | 1 | 1 | 66 | 7 | 82 |
| 11 | 110 | 60 | 24 | 100 | 0 | 2 | 2 | 68 | 8 | 82 |

1. Reaction conditions: 0.23 gHMF, 45 ml H2O, 0.06 gcat, 600 rpm.

**3.6. Stability and reusability studies**

The stability of the Pd(u)/Beta catalyst was examined by testing the catalytic activity of the supernatant after physically separating the catalyst from the reaction mixture. HMF conversion did not increase any further (≈50% conversion at 110 °C and 20 bar H2) and product distribution did not change once the catalyst was filtered off after 40 min (Figure SI12). Likewise, Pd concentration in the supernatant was less than 0.2 ppm (<0.5% of the total Pd content), according to ICP-OES. Both results verify that Pd does not leach into the solution phase and confirm the heterogeneous nature of the catalytic system.

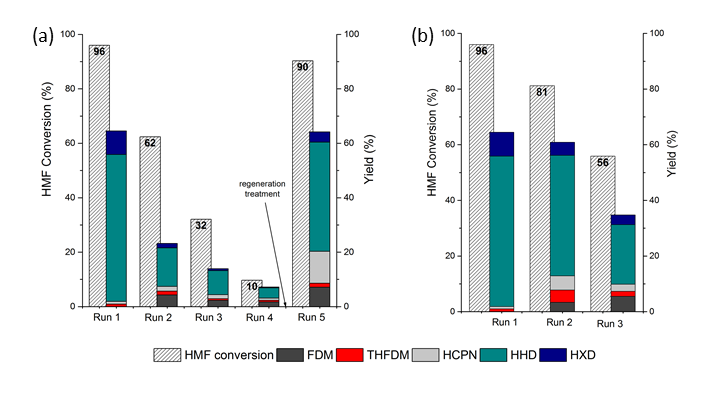


**Figure 6.** (a) TGA curves (air, 100 cm3 min-1) and C and H elemental microanalysis (inset), (b) PXRD pattern, (c) TEM image and (d) histogram of Pd particle size distribution (after counting >200 particles) of the used Pd(u)/Beta catalyst.

The reusability of the Pd(u)/Beta catalyst was investigated by evaluating its catalytic activity upon consecutive runs (110 °C, 20 bar H2). The used catalyst was recovered after each run by filtration at room temperature, washed with distilled water and dried at 25 °C overnight. Figure 6a depicts the TGA curves of the fresh and the used Pd(u)/Beta catalysts, showing a noticeable increase in the total weight loss for the used catalyst (28% *vs.* 7%). Furthermore, the elemental microanalysis of the used catalyst (Figure 6a inset) revealed a significant carbon content (9.32 % weight), consistent with deposition of organic compounds on the catalyst’s surface during turnover. This result compensates to a certain extent (5-6%) for the lower Cmb observed. The PXRD pattern of the used Pd(u)/Beta catalyst (Figure 6b) showed the expected reflections of the Pd metallic phase, indicating that Pd remains reduced after turnover. However, TEM images of the used catalyst (Figure 6c and SI12) revealed an increase in Pd particle size (dM = 7.6 ± 2.3 nm, Figure 6d) compared to the fresh catalyst (dM = 3.5 ± 1.5 nm, Figure 4c), indicative of aggregation and formation of larger Pd particles [[[57]](#endnote-57)].

Recycling tests were conducted after recovering the Pd(u)/Beta catalyst (figure 7a). HMF conversion gradually decreased from 96% (1st run) to 10% (4th run) due to deposition of organic compounds and aggregation of Pd NPs (Figure 6 and Figure SI13). In order to restore the catalytic activity, the used Pd(u)/Beta catalyst (after 4 consecutive runs) was subjected to a regular regeneration treatment: calcination (air/500 °C/5 h) and reduction (H2/200 °C/5 h). Catalytic activity was partially restored (5th run), affording 90% HMF conversion to HHD (40% yield) and HXD (4% yield). A non-negligible amount of FDM (7% yield) and HCPN (12% yield) was also detected in the products mixture.

In order to investigate this selectivity change, a separate set of experiments was conducted during which the catalyst was regenerated after each run (Figure 7b). HMF conversion gradually decreased from 96% (run 1) to 56% (run 3) with a concomitant increase in FDM yield (6% for run 3), as also observed for the dealuminated samples (Table 3). Measurement of the 27Al MAS NMR spectra of the fresh and the regenerated Pd(u)/Beta catalyst (Figure SI14) revealed a decrease in the fraction of tetrahedrally coordinated Al after turnover and regeneration. This in turn suggests a lower number of Brønsted acid sites [[[58]](#endnote-58)] which promote the ring-opening of FDM. Moreover, PXRD verified an increase in Pd particle size (Figure SI15) after regeneration, consistent with a lower hydrogenation activity. Therefore, the observed differences in activity and selectivity during recycling can be ascribed to aggregation of Pd NPs and partial loss of Brønsted acidity [58,[[59]](#endnote-59),[[60]](#endnote-60),[[61]](#endnote-61),[[62]](#endnote-62)].



**Figure 7.** HMF conversion (black, left column) and yield of FDM (dark grey), THFDM (red), HCPN (grey), HHD (cyan) and HXD (blue) over the Pd(u)/Beta catalyst (6 h, 110 °C, 20 bar H2): (a) consecutive runs before (runs 1-4) and after regeneration (run 5) ; (b) consecutive runs after regeneration at the end of each run. Cmb is less than 100% due to formation of heavier oligomers.

Conclusions

Diketone derivatives such as HHD and HXD are produced from HMF over a bifunctional Beta zeolite-supported Pd catalyst in water under relatively mild reaction conditions. The DP-CP method afforded the most active catalyst, compared to IWI, due to smaller and more uniformly dispersed Pd particles among the zeolitic support. Complete conversion of HMF was achieved at 110 °C and 60 bar of H2 with 68% selectivity to HHD. Leaching of Pd was not observed and catalytic activity can be partially restored after a simple regeneration step. Selectivity to HHD is mostly limited by the formation of heavier ill-defined oligomers. The key distinguishing feature of this study is the synergic effect of the zeolite acid sites and the highly active hydrogenating Pd metallic phase which promotes the hydrolytic ring-opening and subsequent hydrogenation of the FDM intermediate without necessitating co-addition of an acid or use of an organic solvent.

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