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ARTICLE

Production of 2,5-hexanedione and 3-methyl-2-cyclopenten-1-one from 5-hydroxymethylfurfural

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A novel approach for production of 2,5-hexanedione (HDN) and 3-methyl-2-cyclopenten-1-one (3-MCO) from 5-hydroxymethylfurfural (HMF) by water splitting with Zn is reported for the first time. The use of high temperature water (HTW) conditions is key for the efficient conversion of HMF to HDN and 3-MCO. Parameters regarding Zn amount, temperature and reaction time are optimized and HDN and 3-MCO are produced in 27.3% and 30.5% yields, respectively. The roles of HTW and ZnO obtained by oxidation of Zn in water for, the conversion of HMF, together with intermediates structures, are discussed to understand the mechanism of the reaction.

1. Introduction

Biomass has long been considered as a promising renewable resources, and provides an alternative to reduce the dependence on fossil fuels. The utilization of the bio-platform molecules converted from biomass to synthesize a number of fuels and chemicals is a common strategy. HMF (5-hydroxymethylfurfural) as one of promising platform chemicals selected by US Department of Energy (DOE) [1], is derived from dehydration of hexose. Researches have focused on conversion of HMF to value-added compounds, which is one of the important fields in green/energy chemistry.

Cyclopentenones including 3-MCO (3-methyl-2-cyclopenten-1-one) with α,β-unsaturated carbonyl are not only useful compounds in organic synthesis [2], but also key intermediates for the synthesis of natural products such as jasmonoids, prostanoids, cortisone, muscone, and other bioactive compounds [3, 4]. Over the past few decades, the development of synthetic methods of cyclopentenones has been reckoned as a hot topic. In the early stage, Piancatelli et al. synthesized cyclopentenones from furans, in which the reaction was catalyzed by a homogenous strong acid in acetone/water system [5]. Synthetic methods using the other starting materials such as alkynes, alkenes and carbon monoxide [3, 6], dienones [7], 1,3-dicarbonyl compounds [8], isoprene [9], mesyltriflone [10], diazo ketones [11], alkynones [12], and HDN (2,5-hexanedione) [13, 14] were also developed. It is worth mentioning that HDN can be obtained by hydrolysis of HMF-derived product, 2,5-

dimethylfuran (DMF)[15]. However, most of these synthetic processes are subject to a lot of problems. For example, high cost of catalysts, corrosiveness of liquid acid or base, toxicity of organic solvent and heavy metals, and tedious steps are problems that necessitate solutions. Furthermore, the feedstocks used in the above processes are derived from crude oil resources and related substrates. As mentioned above, utilization of bio-based material to produce cyclopentenones via green processes is a preferable choice. To the best of our knowledge, the studies about direct synthesis of cyclopentenones from bio-based materials, such as HMF have never been reported.

Diketone derivatives including HDN represent an important class of chemicals because of their wide utility. For example, they have been used for the synthesis of valuable products such as alcohols, amines, solvents, surfactants and cycloketones[16-21]. Diketone derivatives have also been utilized recently to prepare pharmaceutical ingredients such as pyrrolidine.[16, 19-21] However, little attention has been paid to the diketone derivatives, especially HDN produced from HMF. A problem for the synthesis of HDN from HMF is attributed to difficulty in precise control of a bifunctional catalytic system, which simultaneously contain acid sites for ring-opening of furan and hydrogenating sites for hydrogenation of HMF [22]. Liquids acid such as carbonic acid and solid acids such as Amberlyst-15 were investigated to provide acid site, and noble metals including Pd and Ir were used for hydrogenation of HMF [16, 22]. However, either no HDN was produced or low yields were obtained, depending on the conditions, in these reactions. In addition, H_2 has been used as hydrogen donor in these reactions, while the drawbacks of utilizing H_2 exists in safety risks for its high pressure, flammable characters and increasing the cost during transportation and handling. Recently, Tuteja et al. prepared a solid bifunctional catalyst which deposited Pd over a solid acidic zirconium phosphate to carry out conversion of HMF to HDN without support of

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hydrogen donor. The highest yield of HDN was 33.7% [23]. The authors interpreted this high yield as the acidity of the zirconium phosphate surface would effectively accelerated the cleavage of C-O bond in a furan ring. However, in the process, noble metal catalyst (Pd/ZrP, which required a quite complicated synthetic process), organic solvent (ethanol) and longer time (21 h) were used. Therefore, the development of new methods for the production of HDN is still highly desirable.

Simultaneous production of HDN and 3-MCO from HMF seems to be a green strategy. However, this method has never been reported in previous studies so far. High temperature water (HTW) as reaction medium is a promising method, for the inherent characters of HTW including high ionization constant (Kw), which makes it possible to carry out acid/base catalytic reactions [24-26], and has attracted attention in energy and chemical industry. In addition, water is considered as a green hydrogen donor to participate hydrogenation and hydrogenolysis reactions [25, 27-32]. Other than that, water is one of the safest and cleanest solvents, abundant and widespread in nature.

Our group have focused on the conversion of biomass [33-35] into value-added chemicals for many years. Among some of these researches, it has been clarified that hydrogen can be generated *in situ* by oxidizing cheap metals in water [28, 30, 31, 36]. More recently, we have investigated copper-based catalysts for hydrogenation of glycolide and lactic acid into diols; and Pd/C catalyst for the conversion of glucose into diol. In both cases good results were obtained [32, 37, 38]. Excitingly, the studies by some research groups [39], who reported that ZnO can be reduced to metallic Zn by solar energy, makes our studies more meaningful.

Inspired by these findings, we here for the first time, report a novel approach for production of HDN and 3-MCO from HMF by water splitting with Zn. The main strategy is illustrated in Scheme 1.

2. Experimental

2.1 Experimental materials

Fe, Mn, Mg, Al, Zn, Ni, Cu, ZnO, Cu_2O, CuO, ZrO_2, Al/Ni alloy, HCOOH, NaOH, furfural and furfuryl alcohol were all purchased from Sinopharm Chemical Reagent (China). Pd/C and HDN

Scheme 1. The main strategy for the conversion of HMF.

were purchased from Aladdin Chemical Reagent. HMF, 3-MCO, (5-methyl-2-furyl) methanol (MFM), 5-methyfurfural (MF) and 3-methylcyclopentanone (MCPE) were purchased from Energy Chemical (China). Ni/γ-Al_2O_3, Ag/SiO_2 and porous Ni were prepared according to the previous procedures[40, 41]. All chemicals were analytical reagents.

2.2 Experimental procedure

Most of the experiments were conducted in a Teflon-lined stainless steel batch reactor whose inner volume was 30 mL. The amount of HMF was 0.20 mmol in all the experiments. Metal powder, water and feedstock were sealed into reactor after air was excluded by purged with nitrogen gas. The sealed reactor was then placed into a preheated oven. The oven temperature decreased after the reactor placed in. Hence, the reaction started when the oven temperature reached up to desired value. After the desired time, the reactor was moved out and cooled down to room temperature.

Other experiments with H_2 as hydrogen source were performed in a SUS316 stainless steel tube whose inner volume was 5.7 mL. Metal or metal oxide powder, catalyst, water and feedstock were added into this tube. After purged by H_2, it was pressured with H_2 to 3 MPa. The sealed tube was then placed into salt bath at 250 °C. After the reaction was over, the tube was cooled in water

Liquid sample was filtered with 0.45 μm syringe filter and collected into a vial for analysis. Solid sample was washed with ethanol and water for several times, and dried at 60 °C for overnight.

2.3 Products analysis

GC-FID (gas chromatography with flame ionization detector, Agilent GC7890A) and GC-MS (gas chromatography with mass spectrometer, Agilent GC7890A- MS5975C) were performed to analyze liquid samples, which equipped with HP-Innowax column (30 m × 0.25 mm × 0.25 μm). Solid samples were analyzed by XRD (X-ray diffraction, Shimadzu 6100) and the amount of oxidized Zn was also determined by XRD. The HMF conversion and product yield were defined by the following equations shown in Eqs 1 and 2.

$$Conversion_{(HMF)} (\%) = (1 - \frac{\text{mole of HMF at particular time}}{\text{initial mole of HMF}}) \times 100 \quad (1)$$

$$Yield_{(product)} (\%) = \frac{\text{mole of product at particular time}}{\text{initial mole of HMF}} \times 100 \quad (2)$$

3. Results and discussion

3.1 Active metal screening

As is well known, some active metals, such as Fe [27, 42], Mn [28, 31], Al and Mg [28, 32], can react with HTW to produce hydrogen to induce the hydrogenation reaction. A series of experiments were performed to investigate the effect of active metals for the conversion of HMF. After the reactions, the XRD analysis in Figures SI-1a, 1b and 1c showed that Fe and Al still remained unchanged and Mn and Mg were completely oxidized at 250 °C. One of the reasons for non-oxidation of Fe and Al is that
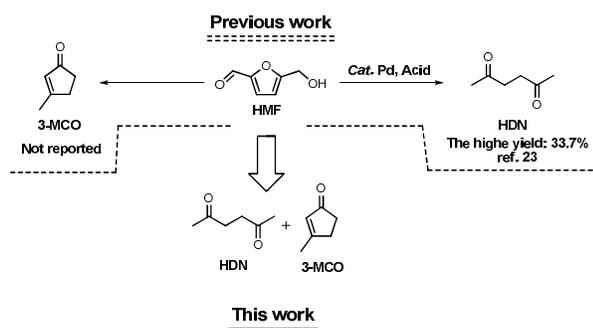
the temperature of 250 ^{o}C is too low to enable water to possess enough thermal energy for oxidation of Fe[28] and Al leading to generation of hydrogen. From Table SI-1, it is clear that no desired compounds were observed after the reaction when Fe, Mn, Al and Mg were used as reductants, although HMF was completely consumed in this process (entries 2-5). It was thought that HMF was decomposed completely under the reaction conditions to give a complex mixture of products. However, the use of Zn was effective for the conversion of HMF, and the yields of HDN of 21.3%, 3-MCO of 19.7%, MF of 4.3% and MCPE of 1.0% were obtained, respectively (entry 1).

With regard to hydrogenation and hydrogenolysis reactions, H_2 partial pressure is a vital factor for adjusting reaction rate and selectivity [16, 22]. Thus, selecting proper amount of Zn is a manner to control the H_2 pressure. Figure 1 shows the influence of the amount of Zn with corresponding theoretical partial pressure of H_2 marked below at 25 ^{o}C in HMF conversion with 7.5 mL H_2O. The HMF conversion was approximately 90% when 5 mmol Zn was used with corresponding H_2 pressure of 0.55 MPa. The HMF was completely converted when the amount of Zn was increased to exceed 15 mmol with the corresponding H_2 pressure of 1.65 MPa. The results indicate that the HMF can be easily converted by *in-situ* hydrogen even with low amounts of Zn. The yield of MF decreased with the Zn amount changed from 5 to 35 mmol, and with corresponding H_2 pressure changed from 0.55 to 3.85 MPa. The decreasing yield of MF might be owing to the decomposition of MF caused by redundant Zn. Both HDN and 3-MCO yields increased as the Zn amount increased from 5 to 25 mmol, and then decreased when amount of Zn exceeded 25 mmol, and the maximum values of 21.3% of HDN and 19.7% of 3-MCO were obtained, respectively. It means that the amount of Zn exerts influence on the HMF conversion to HDN and 3-MCO. In addition, as a product that can be generated by hydrogenation of 3-MCO, MCPE consistently maintained a low yield; indicating that *in-situ* generated hydrogen has a little effect impact on production of MCPE.
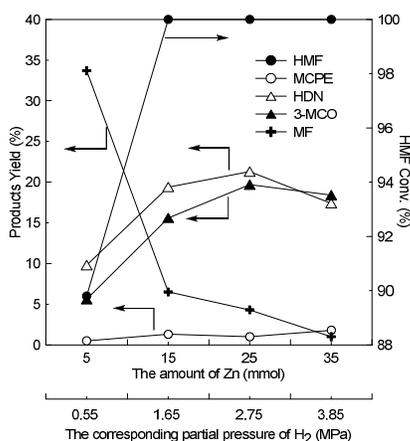
3.2 Effect of parameters

Various conventional catalysts were investigated to improve the yields of products, and the results shown in Table SI-2 indicated that extra added catalysts did not improve the conversion of HMF into HDN and 3-MCO.

To investigate the effect of reaction time for HMF conversion, a series of experiments were performed by changing reaction time at 250 ^{o}C. The yields/conversions of products confirmed by GC-MS were plotted in Figure 2. HMF could be rapidly consumed at the first 40 min and HMF conversion was 97.3%. The yield of HDN with the average growth rate of 25.2%/h increased rapidly, and then the average rate slowed down to 5.1%/h from 40 to 140 min. The highest HDN yield of 27.3% was achieved at 140 min, and then decreased slowly with the average decrease rate of 1.2%/h. Similarly, the average growth rate of 3-MCO was 15.8%/h at first 100 min, and then decreased to 0.9%/h from 100 to 480 min. The highest yield of 3-MCO was up to 30.5%. The yield of MFM was 9.4% at first 10 min, and exhausted quickly. Also the yield of MF increased at first, and then gradually decreased. The yield of MCPE kept at a low level during the reaction.
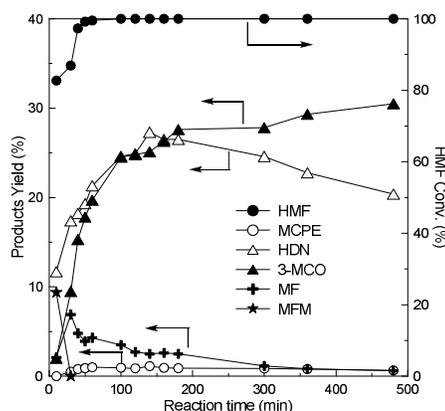

Figure 2. Effect of time for the conversion of HMF (0.20 mmol HMF, 25 mmol Zn, 7.5 mL H_2O, 250 ^{o}C)

Figure 1. Effect of the amount of Zn (0.20 mmol HMF, 7.5 mL H_2O, 250 ^{o}C, 60 min)
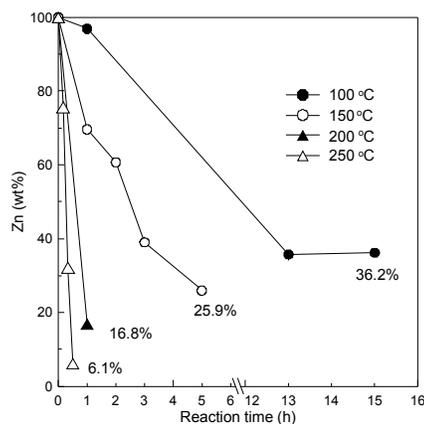

Figure 3. The change of the amount of Zn during the reaction at different temperature (25 mmol Zn, 7.5 mL H_2O)

Reaction temperature is also an important factor for water possessing acid/base catalytic activity [25], which is closely connected in furan ring-opening/rearrangement process. HMF conversion was monitored at 100 ^{o}C (see Figures SI-2 and SI-3) and 150 ^{o}C (see Figures SI-4 and SI-5). Although the oxidation of Zn at 100 and 150 ^{o}C was much slower than at 250 ^{o}C (Figure 3), HMF was completely converted in a short time.

However, the yields of HDN and 3-MCO at 100 ^{o}C were only around 14% and 5%, respectively, even when the reaction time was prolonged to 10 h. The strong signal of MFM was found at 15 h, which seemed to be an intermediate. It seems that the lower temperature leads to low acid catalytic ability and low thermal energy of water, although both of which should be high enough to promote the MFM ring opening process. The HDN yield of 20.1% and the 3-MCO yield of 9.9% were obtained at 150 ^{o}C, which were still much lower than those at 250 ^{o}C. These results indicate that higher temperatures contributed to the efficient conversion of HMF.

In general, hydrogen production depends on the temperature of oxidation of Zn in water. To better understand the hydrogen production during the reaction, the remaining percentage of Zn in solid residue after the reaction was investigated by XRD at different temperatures as shown in Figure 3. When the temperature was 100 ^{o}C, the amount of Zn decreased slowly to 36.2% between 0 and 13 h, and kept unchanged after 13 h. Perhaps, an oxide film would be formed on the surface of Zn which would inhibit further oxidation of Zn, leading to a low hydrogen production. When the temperature was at 150 ^{o}C, the reaction between Zn and HTW was accelerated and the rest of Zn was 25.9% after 5 h. The higher temperatures such as 200 and 250 ^{o}C showed the faster oxidation of Zn, and the rest of Zn was 16.8% after 1 h and 6.1% after 0.5 h, respectively. It is obvious that hotter water results in faster oxidation of Zn to efficiently produce hydrogen for the conversion of HMF. In addition, XRD patterns in Figure 4 agree with these results. It can be seen that the oxidation of Zn to ZnO is very quick at 250 ^{o}C; peaks of ZnO can be observed after 10 min. The peaks of ZnO increase with the time increased from 10 to 30 min, and the peaks of Zn decrease and vanish at the end.
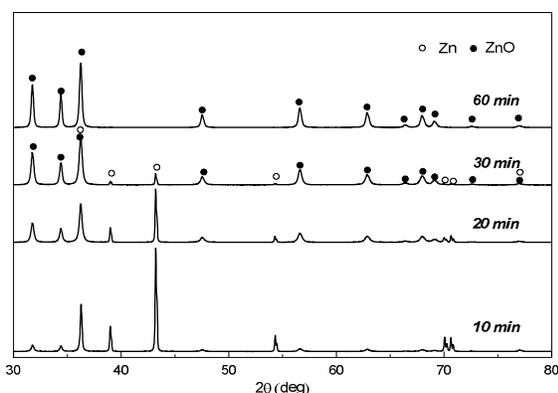

Figure 4. XRD patterns for the oxidation of Zn into ZnO in water (25 mmol Zn, 7.5 mL H$_2$O, 250 ^{o}C)

3.3 Possible catalytic activity of ZnO formed *in situ*

To investigate the effect of ZnO formed during the reaction, two comparative experiments were conducted for the conversion of HMF by the addition of 3 MPa gaseous hydrogen with two kinds of ZnO; one was formed by Zn oxidation in water and another commercial one. As shown in Table SI-3, only a low yield of MF was obtained and no other products were detected, although the conversion of HMF was approximately 60% (entries 1-2). It indicates that the gaseous hydrogen is ineffective and *in-situ* hydrogen generated by oxidation of Zn in water plays an important role for the conversion of HMF. Furthermore, when ZnO was not added, no desired products but black humins were obtained (entry 3). It might be thought that hydrogen generated in situ from Zn oxidation is active for the hydrogenation/hydrogenolysis reactions, while the externally supplied hydrogen is not[30, 36, 43, 44]. As mentioned later, self-aldol condensation of HDN to 3-MCO are catalyzed by ZnO. Hence, we suggested that obtained ZnO exhibited catalytic performance to promote the conversion of HMF or formed intermediates in the process.

With optimized conditions in hand, two substrates, furfural and furfuryl alcohol, with similar structure as MF and MFM to synthesize cyclopentenone was also proved to be feasible. The results of Table SI-4 and Figure SI-6 indicated that furfuryl alcohol provided higher yield of cyclopentenone than that of furfural.

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4. Mechanistic Studies

HTW, as we know, possesses good acid/base catalytic abilities, and the concentration of H$^+$ and OH$^-$ which can be determined by *Kw* value is an important factor for acid and base catalytic performance. Table SI-5 shows the theoretical values of p*Kw* under different temperatures[24]. The highest p*Kw* is 11.2 when the temperature is at 250 ^{o}C. Therefore, HTW at 250 ^{o}C was desirable for acid/base catalysed HMF conversion.

Table 1 and Figure 5 show some results in which the reactions of formed intermediates were investigated. As shown in Figure 2, the yield of HDN decreased slowly after 140 min while the yield of 3-MCO kept increasing during the reaction, suggesting that HDN can be slowly converted to 3-MCO. As evident from Table 1, 20.9% of HDN was converted to give 3-MCO in 10.1% yield (entry 1). But the base supplied by HTW could not catalyze the conversion of HDN into 3-MCO without any additives (entry 2). When ZnO was added, the base catalyzed aldol condensation happened (entry 3). However, the conversion of HDN and the yield of 3-MCO were low. The previous results, shown in Figure 2, indicated that 3-MCO production was quick at the beginning of the reaction. Therefore, it is possible that 3-MCO was generated not only from HDN, but also from other intermediates. The yield of MF increased at first and then gradually decreased, suggesting that MF might be an intermediate (Figure 2). The reaction of MF gave HDN in 60.2% and 3-MCO in 7.1% yield, respectively,

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Table 1. The investigation of possible intermediates conversion.[a]

Entry	Feedstock	Conv (%)	Yield (%)					
			HDN	3-MCO	MF	MFM	DMF	MCPE
1	HDN	20.9	-	10.1	0	0	0	0
2[b]	HDN	17.2	-	0	0	0	0	0
3[c]	HDN	23.2	-	6.4	0	0	0	0
4	MF	100	60.2	7.1	-	0	0	0
5[d]	MF	100	21.2	1.3	-	0	0	0
6[d]	MFM	100	25.9	19.6	0	-	0	0
7	DMF	100	8.9	2.6	0	0	-	0
8	3-MCO	0.5	0	-	0	0	0	0

[a]Reaction condition: Feedstock (0.17 mmol HDN, 0.19 mmol DMF, 0.20 mmol MF, 0.20 mmol MFM, 0.20 mmol 3-MCO), 25 mmol Zn, 7.5 mL H_2O, 250 °C, 140 min; [b] no Zn was added; [c] 25 mmol ZnO was added; [d] The reaction time was 10 min.
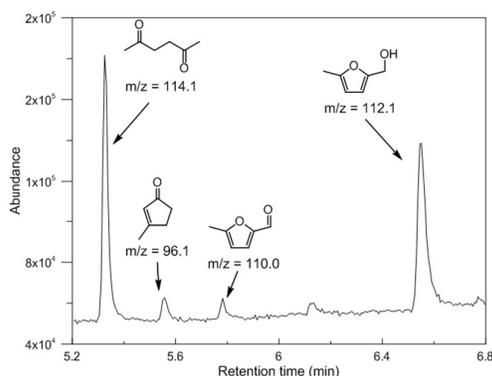

Figure 5. GC-MS chromatogram of main products after the HMF conversion (0.20 mmol HMF, 25 mmol Zn, 7.5 mL H_2O, 250 °C)

at 140 min with 100% conversion of MF, while lower yields were obtained after the first 10 min (entries 4 and 5). The conversion of MFM as a starting material gave the yield of 25.9% for HDN and 19.6% for 3-MCO (entry 6). The interesting thing is that MF was converted completely after 140 min, but in the previous HMF conversion MF could still be detected after 480 min (Figure 2). This might be due to the fact that the *in-situ* hydrogen first reacted with HMF to produce MF and then quickly desorbed on the surface of ZnO. After 40 min, Zn had been almost exhausted and the amount of Zn remained was only 6.1 wt% at 30 min as mentioned in Figure 3. Thus not enough *in-situ* hydrogen was generated to convert MF.

The change of gas chromatogram during the reaction was shown in Figure SI-7. Peak 7, MFM, appeared after 10 min and almost disappeared after 20 min. According to its structure and previous research [45], MFM might be an important intermediate for 3-MCO production. Other peaks such as 9, 11, 12 also looked like intermediates, but their structure could not be confirmed by GC-MS. 2,5-Dimethylfuran (DMF) was also a

possible intermediate according to previous report [23], however, when it was used as starting material, the yields of target products HDN and 3-MCO were very low (entry 7). However, no DMF was detected in HMF conversion. Therefore, DMF was not an intermediate in the process. The experiment of 3-MCO conversion indicated that 3-MCO did not undergo further conversion under the reaction conditions (entry 8).

Based on the above finding and discussion[5, 16, 45-48], the possible reaction pathways of HMF conversion are illustrated in Scheme 2. HMF is first converted into MF and then to MFM by the reaction of *in-situ* hydrogen generated by oxidation of Zn in water. Under HTW condition, acid-catalyzed formation of HDN from MFM is as follows: (1) rehydration of MFM, followed by (2) a ring opening, and (3) a subsequent conversion of *in-situ* produced C=C bond to HND with *in-situ* formed hydrogen. Meanwhile, acid-catalyzed rearrangement to transform MFM into 3-MCO takes place, which involves the formation of a carbocation driven by a protonation-dehydration sequence of the 2-furylcarbinol, and then
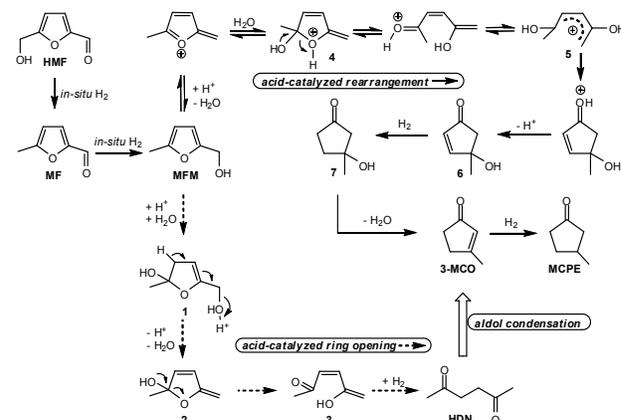
Scheme 2. The proposed pathways for the conversion of HMF.

attack of water as a nucleophile leads to intermediate **4** which undergoes ring opening. 1,4-Dihydroxypentadienyl cation **5** gives compound **6** through a 4p-conrotatory cyclization. The hydrogenation-dehydration of compound **6** produces 3-MCO. Hydrogenation of 3-MCO produces MCPE. Finally, aldol condensation of HDN catalyzed by ZnO gradually occurred to give 3-MCO.

Conclusions

In summary, we first developed an efficient method for direct production of 3-MCO and HDN from bio-based HMF by water splitting with Zn. *In-situ* generated hydrogen by oxidation of Zn in water was effective for the conversion of HMF. The results indicated that HTW showed good catalytic performance while the addition of catalysts did not improve the selectivity and yield in the process. The highest yield of 3-MCO was 30.5% and that of HDN was 27.3% at 250 $^{\circ}$C. The roles of HTW and ZnO for the conversion of HMF were clarified and intermediates of the reactions were also discussed.

Acknowledgements

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Production of 2,5-hexanedione and 3-methyl-2-cyclopenten-1-one

from 5-hydroxymethylfurfural

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Graphic abstract