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Direct Synthesis of 1,6-Hexanediol from HMF over a Heterogeneous Pd/ZrP Catalyst using Formic Acid as Hydrogen Source

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A new approach is developed for hydrogenolytic ring opening of biobased 5-hydroxymethylfurfural (HMF), dehydration product of hexoses, towards 1,6-hexanediol (HDO) under atmospheric pressure. The highest yield of HDO, 43 %, is achieved over reusable Pd/zirconium phosphate (ZrP) catalyst at 413 K in the presence of formic acid as hydrogen source. In comparison with various Brønsted and/or Lewis acidic supports, the specific Brønsted acidity on ZrP support effectively accelerated the cleavage of C–O bond in a furan ring.

The concept of producing materials from renewable natural sources is well-known: people have been wearing woolen clothing since many generations, and houses have been built using wood since thousands of years. In this context, lignocellulosic biomass is a promising renewable feedstock because it is abundant, cheaper, and potentially more sustainable than conventional fossil resources.^[1-3] 5-Hydroxymethylfurfural (HMF), which can be synthesized through dehydration of hexoses by using various homogeneous and heterogeneous catalysts, is one of the most promising platform chemicals in the biorefinery area and is regarded as a "sleeping giant" in the field of intermediate chemicals from renewable resources.^[4,5] HMF has been successfully transformed into various useful chemicals that may serve as building blocks in advanced polymers, such as 2,5-furandicarboxylic acid,^[6] levulinic acid,^[7] 2,5diformylfuran,^[8] succinic acid,^[9] and 2,5-dimethylfuran.^[10]

Herein, we report a new approach for the production of 1,6hexanediol (HDO; a linear diol with two primary hydroxyl groups) from inedible biomass. HDO is extensively used in the production of polyesters for polyurethane elastomers, coatings, adhesives, and polymeric plasticizers.^[11] The major route for HDO synthesis involves the hydrogenation of adipic acid or its esters by various homogeneous or heterogeneous catalysts.^[12,13] Very recently, Buntara et al. employed a novel methodology for converting HMF to HDO in a two- to five-step process under high H₂ pressure (10–80 bar) by using a ReO_x-modified rhodium-based catalyst. The five-step process has high selectivity for HDO, but a low yield (4%). Moreover, the large

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number of steps and the need to purify the product of each step render the overall process environmentally and economically undesirable. An effort towards one-step hydrogenation of HMF employing severe conditions (543 K, 150 bar H₂) afforded less than 4% yield of HDO, whereas a two-step process coupled with Nafion SAC13 gave overall yield of 86% HDO in water.^[14-16] Two other research groups, Chen et al.^[17] and Chia et al.,^[18] produced HDO by utilizing tetrahydro-2*H*-pyran-2-yl-methanol (THPM) as substrate (HMF derivative), using the same catalyst at 393 K with 34 bar H₂. High-pressure H₂, however, is difficult to handle and requires an expensive facility. Thus, an inexpensive, more practical alternative to high-pressure H₂ is needed.

Among other organic compounds such as tetrahydroquinoline, methylpyrrolidine, and cyclohexene, formic acid (FA; HCOOH) is a hydrogen donor with much potential because it is safe and cheap.^[19] It can be traditionally obtained from biomass processing and produces no waste products.^[20-22] FA has been employed by many researchers for various organic transformations.^[10a, 23-25]

The hydrogenolysis of HMF to HDO may proceed through two key reactions: (1) deoxygenation of the furan ring (C–O bond cleavage) by Brønsted-acid catalytic sites, and (2) hydrogenation of C=O and C=C bonds by the metal catalytic sites. In this study, we use zirconium phosphate (ZrP) as acidic support; ZrP has already attracted much attention as potential solid-acid catalyst^[26-28] for the dehydration of alcohols,^[29,30] isomerization of olefins,^[31,32] hydrogenation^[33] and hydrodeoxygenation reactions.^[34,35]

Using earlier reports as basis,^[14,36] we surveyed acid-based supports for ring cleavage and palladium as metal for hydrogenation. Table 1 summarizes the results for hydrogenolysis of HMF over various Pd/support catalysts. The products obtained from the hydrogenolysis of HMF with Pd/ZrP catalyst in the presence of FA include 5-methylfurfural (MF), 2,5-hexanedione (HDN), HDO, tetrahydrofuran-2,5-dimethanol (THFDM), and 2,5dimethylfuran (DMF). The selectivity for the formation of HDO varies considerably among different acidic supports, and Pd/ ZrP exhibits the best catalytic activity for HDO in high yield (42.5%) (entries 1-10). The Brønsted/Lewis acid site ratio of different solid acid catalysts was compared by Huber et al.^[37] Among them, ZrP has the highest ratio. Accordingly, the reason for the high activity of ZrP is its high Brønsted/Lewis acid site ratio as compared to zeolites, Al₂O₃, and SiO₂-Al₂O₃, thus decreasing the carbon mass balance for these catalysts. Post-synthesis treatment of ZrP with dilute nitric acid (see Supporting Information) enhances the activity, leading to an in-

under

Table 1. Hydrogenolysis of HMF over various Pd/support catalysts. ^[a]											
	HO HMF	Pd/ZrP EtOH,FA 113 K, 21 h	HDO	он ₊ — н	T + HO	THEDM	∩он + √	0 // 0 + MF	O DMF		
Entry	Catalyst	Mean particle size [nm] ^[b]	HMF conv. [%]	HDO yield [%]	HDN yield [%]	THFDM yield [%]	MF yield [%]	DMF yield [%]	Carbon mass balance [%] ^[c]		
1	Pd/ZrP	11.9	92.5 96.9 ^[d]	37.8 42.5 ^[d]	15.2 16.2 ^[d]	12.1 15.6 ^[d]	4.6 4.8 ^[d]	2.4 2.5 ^[d]	77.9 84.2 ^[d]		
2	Pd/ZrP ^[e] Pd/HX zoolito ^[f]	4.0	72 70 4	26.9 27.4	12.7	0.0 5 1	4.3	1.6	63.2 46.2		
4	Pd/Nb ₂ O ₅	_ ^[k]	93.3	20.7	12.3	0.0	0.0	0.0	35.4		
5	Pd/ZSM-5 ^[g] Pd/SiO ₂ -ALO ₂ ^[h]	- 3 3	90.4 90.9	17.3 15.8	10.3 17 5	38.2 30.1	4.5 2 3	0.0 1 9	77.8 74 4		
7	Pd/Al ₂ O ₃	10.4	>99	13.3	25.5	30.6	0.0	16	85.5		
8	Pd/SO ₄ /ZrO ₂	3.1	39.1	5.1	0.0	0.0	0.0	0.0	13.0		
9 10	ZrP	- -	54.1 50.4	5.2 0.0	0.0	0.0	0.0	0.0	9.2 0.0		
11	Pd(NO ₃) ₂	-	61.6	trace	0.0	0.0	0.0	0.0	0.2		
12	PdO blank	-	86.2 78.7	14.3 0.0	7.5 0.0	0.0	trace 0.0	trace 0.0	25.4 0.0		
14 ^[j]	Pd/ZrP	-	84.3	7.5	33.7	0.0	0.0	0.0	48.9		
15 ¹⁰	blank	-	79.6	0.0	0.0	0.0	0.0	0.0	0.0		
[a] Reaction conditions: HMF (1 mmol), EtOH (3 mL), FA (22 mmol), $T=413$ K, $t=21$ h, 5 wt% Pd catalyst (50 mg). [b] Determined by transmission electron microscopy. [c] Determined on the basis of observed HDO, HDN, THFDM, MF, and DMF products. [d] 7 wt% Pd catalyst. [e] Without post acid treatment. [f] JRC-Z-HY5.5 (Si/AI=2.8). [g] Si/AI=12. [h] JRC-SAH-1 (Si/AI=2.1). [i] JRC-Z5-90H(1) (Si/AI=45). [j] Without FA. [k] The particles could hardly be distinguished from the support											

active (entry 11). PdO exhibits a high conversion of HMF but no yield of HDO due to the formation of levulinate ethyl ester in the presence of FA (entries 11 and 12). A control experiment without Pd catalyst affords high HMF conversion and humin formation in the presence of only FA (entry 13). In the absence of FA, the acidic proton on Pd/ZrP affords HDO in 7.5% yield. On the other hand, the absence of both catalyst and FA fails to achieve the hydrogenolysis of HMF to HDO (entries 14 and 15). These results clarify the significance of both Pd/ZrP and FA for an efficient single-step synthesis of HDO from HMF.^[40]

The course of the HMF hydrogenolysis was monitored in order to understand the reaction pathway. Figure 1 is a plot of the conversion of HMF and yields of various products as a function of time. After 3 h, an 85% conver-

crease in the carbon mass balance compared to nontreated ZrP (entries 1 and 2). This is because treating the material with dilute acid increases the number of Brønsted sites.^[38] The loss of framework SiAlOH units with increasing Si/Al ratio is attributed to a decrease of (Brønsted + Lewis) acid site density for ZSM-5 (Si/Al = 45 or 12), HY zeolite (Si/Al = 2.8), SiO₂-Al₂O₃, (Si/Al = 2.1), and it disfavors HDO formation (entries 3, 5, 6, and 9). Nb₂O₅ and sulfated ZrO₂ show lower activity for hydrogenolysis and/or hydrogenation than ZrP, therefore the carbon mass balances are very low (entries 4 and 8). On the contrary, Pd/Al₂O₃ catalyzes the ring hydrogenation reaction over ring hydrogenolysis to afford THFDM as the major product, which in turn increases the carbon mass balance (entry 7).

Particle size distributions, determined from transmission electron microscopy (TEM) images (see Figure S6), show that only a few different supports, such as HY zeolite, ZSM-5, SiO₂– Al_2O_3 , and sulfated ZrO_2 , lead to catalysts with small-sized (mean diameter 3.1–3.3 nm); however, the activities of these catalysts are not so high. Accordingly, we find that the activity has no correlation with the size of the palladium nanoparticles. It is well-known that hydrogenation reactions do not depend on the size of the metal particles.^[39]

The hydrogenolytic ring opening of HMF demands a high Brønsted/Lewis acid ratio, whereas the role of palladium is to dissociate formic acid, leading to the hydrogenation. The activity of the Pd/ZrP catalyst was studied in more detail. Almost half of the HMF could be converted with no yield of HDO in the presence of only support (ZrP; Table 1, entry 10), probably due to adsorption of the substrate onto the support. Pd(NO₃)₂, the metal source used to prepare the active catalyst, itself is insion of HMF is achieved and the primary products (HDO and HDN) are formed. Competitive products such as MF and THFDM are produced after 6 h, whereas DMF is obtained in the reaction mixture after 9 h. The yield of HDO reaches a maximum of 42.5% (HMF conv. 96.9%) after 21 h.^[41] Scheme 1 shows a proposed reaction pathway for hydrogenolysis of HMF over the Pd/ZrP, based on the time course displayed in Figure 1 that clearly shows the simultaneous conversion of HMF into HDO, THFDM, and HDN.

Moreover, even after longer reaction times, no significant change in product distribution is observed, indicating that ring



Figure 1. Time course for hydrogenolysis of HMF over Pd/ZrP. Conditions: HMF (1 mmol), FA (22 mmol), EtOH (3 mL), 7 wt % Pd/ZrP (50 mg), 413 K. HMF Conv. (\Box), Yields of HDO (Δ), HDN (\odot), THFDM (\blacktriangle), MF (\blacksquare) and DMF (\bullet).

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Scheme 1. Various possible reaction pathways from HMF.

hydrogenolysis to HDO (Scheme 1, step A) or HDN (steps C, D, and E), or ring hydrogenation to THFDM (step B) progress as competitive reactions. MF and DMF are formed in small amounts from HMF as hydrogenation products (steps D and E). This proposed reaction scheme is in agreement with the observed trends for THFDM, MF, DMF, and HDN as substrates under similar reaction conditions (see Supporting Information, Table S1); HDO formation is not noticed from the hydrogenolysis of MF, DMF, and THFDM.

To certify the formation route of HDO is from hydrogenolysis of the HMF ring or THFDM ring, the hydrogenolysis of THFDM on Pd/ZrP was investigated under the same reaction conditions. No HDO or HDN was detected (Table S1, entry 5). This finding indicates that the reaction route from THFDM to HDO can be practically neglected. These results are in correlation with previous studies showing that the hydrogenolysis of a tetrahydrofuran ring is not possible under conditions in which furan ring hydrogenolysis occurs.^[42,43] The results of MF and DMF as a substrate (Table S1, entries 2 and 3) suggest that MF is hydrogenated to DMF and successively to HDN. Under the present conditions, the rate of ring cleavage of DMF to HDN is faster than the side chain hydrogenation of HMF to MF and then to DMF. This is the reason why MF and DMF appears late in the reaction progress.

According to stoichiometry, 8 hydrogen atoms are required for the conversion of HMF to HDO. To meet the requirement, experiments with different amounts of FA were performed and compiled (see Supporting Information, Table S2). In fact, 22 mmol of FA produces HDO in highest yield over 7 wt% Pd/ ZrP, whereas 8.2 mmol of FA is consumed. The highest efficiency of FA is observed when using 11 mmol of FA with high metal content that is, 10 wt% Pd/ZrP, to achieve the highest yield of HDO (43.6%). A high-metal-content catalyst can break the FA more efficiently than a low-metal-content catalyst. However, the same yield of HDO can also be obtained by using a low-metal-content (7 wt%) catalyst and a high amount of FA. Therefore, we discourage the use of a catalyst with high metal content. In the absence of FA, HDN is formed in large amounts while HDO is also detected in small quantities due to the acidity of the ZrP surface. On addition of FA, HDO formation is enhanced with a decrease of HDN. A large amount of acid favors a ring hydrogenation to THFDM, which can not be cleaved further into HDO because tetrahydrofuran rings are rather stable. This is why the reaction conditions, favoring step B, diminish the progress of reaction step A. On the other hand, it is known that HDN formation is favored in acidic environments,^[37] but a high FA content lowers the yield of HDN because of competitive THFDM formation.

The present hydrogenolysis of HMF to HDO is proposed to consist of 6 major steps, marked as steps 1-6 in Figure 2. In step 1, HMF is adsorbed onto the catalyst surface by electrostatic interactions with both metal as well as the acidic ZrP support. Step 2 is proposed based on previous literature,^[37,38] in which ZrP is held responsible for the furan ring opening with the loss of ring oxygen. In this case, scissoring of the furan ring would most probably form hex-1,3,5-triene-1,6-diol (steps 2 and 3). This expected intermediate (hex-1,3,5-triene-1,6-diol) is not commercially available but is assumed to appear at a retention time of 6.96 min in the GC chromatogram. The same peak, with a high intensity, is observed in reactions performed without FA. The dissociation of FA (step 4) may occur at the initial stages of the reaction, however, in order to maintain a reaction cascade it is shown as step 4. The product generated in step 3 can undergo keto-enol tautomerism (step 5). The enol form is expected to dominate in polar protic solvent (ethanol). The ratio of the intensity of the peak at 6.96 min to that of an internal standard (naphthalene) to decreased with increasing metal loading on the catalyst. The highest ratio occurs in the absence of FA, which is possibly due to the absence of hydrogen source for hydrogenation of double bonds. The reason for the appearance of the peak for low metal loading could be explained by the inefficient dissociation of FA with low metal content on the catalyst surface. The final step was the hydrogenation of the double bonds to form HDO using Pd/ZrP with FA as the hydrogen source (Figure 2, step 6).

Recyclability is an important property of heterogeneous catalyst, so the reusability of the catalyst Pd/ZrP was investigated. The catalyst was simply recovered by centrifugation, through washing with ethanol, and drying in vacuum overnight, followed by calcination at 773 K for 6 h. The catalyst could be recycled without any significant loss of activity even after 5 cycles (see Supporting Information, Figure S3). Furthermore, the product was isolated by using silica gel column chromatography, eluted with hexane–ethyl acetate solvent system (8:2–2:8) to yield HDO in 39.6% yield (0.467 g from 10 mmol of HMF, in a set of 5 batch reactions of 2 mmol each) as a white to pale-yellow solid. Analysis by ¹H- and ¹³C NMR confirmed the HDO structure (see Supporting Information, Figures S4 and S5).

In summary, we report a new, safe, economical, and environmentally benign pathway for the formation of HDO from HMF; a renewable source that can be obtained from hexoses. Using the one-step direct reaction, we convert HMF to yield 43% HDO over reusable Pd/ZrP catalyst and HCOOH as hydrogen source at 413 K for 21 h under an atmospheric pressure. To the

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Figure 2. Proposed mechanistic steps demonstrating the role of Pd/ZrP and FA in hydrogenolysis of HMF to HDO in the presence of FA.

best of our knowledge, such a high yield of HDO from HMF is reported for the first time without using high-pressure H_2 gas. Experimental data shows that both the catalyst and HCOOH are indispensable for the formation of HDO. It is suggested that the acidity of the surface, for ring cleavage; the presence of a transition metal, for FA dissociation; and thereby utilization of in situ generated hydrogen for hydrogenation are the important aspects governing HDO formation from HMF.

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- [40] The use of excess water instead of EtOH is not favorable for the present HDO production (Supporting Information, Table S3).
- [41] These phenomena were also observed in recycling runs. A conversion of 45% was observed even at 0.5 h of reaction progress, demonstrating the facile adsorption of HMF onto the catalyst surface. Subsequently, adsorbed HMF is converted into products. A significant effect on conversion rate of HMF and HDO was noticed with additional experiments. The rates of consumption of both HMF and HDO were suppressed in the presence of one another, which may explain the maxima for HDO yield (for a detailed explanation, see Supporting Information, Figure S5). A detailed product analysis by GC-MS revealed that HDO is slowly converted into oxepane at longer reaction times.
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