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ARTICLE

Conversion of HMF to Methyl Cyclopentenolone by the Pd/Nb_2O_5 and Ca-Al Catalysts via Two-steps Procedure

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The catalytic conversion of HMF to 2-hydroxy-3-methyl-2-cyclopenten-1-one (MCP), which was a valuable edible essence traditionally obtained from adipinic acid, was achieved with 58% isolated yield. This procedure contained two steps: the hydrogenation of 5-hydroxymethylfurfural (HMF) to 1-hydroxy-2,5-hexanedione (HHD) in water on Pd/Nb_2O_5 catalysts and then the HHD isomerized to MCP in the presence of base. The Nb_2O_5 supports, possessing acidity, were characterized by FTIR, XRD and NH_3-TPD. The supported Pd/Nb_2O_5 catalysts, of highly dispersed Pd, were synthesized employing cyclohexene as reductant and characterized by XRD, TEM, ICP-AES, XPS, EDX and CO pulse chemisorption. The high conversion of HMF was attributed to high disperse of Pd and the acidity of supports led to high selectivity of HHD. The conversion of HHD to MCP was an intramolecular aldol condensation reaction and the protonic solvent was in favor of this reaction. The Ca-Al was proved to be an effective solid base for the conversion of HHD to MCP in water.

Introduciton

Production of chemicals and fuels from bio-derived furans is of great significance as the diminishing fossil resources. The furans, including furfural and HMF, could be readily obtained by the dehydration of carbohydrates and converted via various of catalytic processes.[1-8] Tetrahydrofurfuryl alcohol,[9, 10] furfuryl alcohol,[11-14] 2,5-dimethylfuran,[15, 16] tetrahydro-2,5-furandimethanol,[17, 18] furan-2,5-dicarboxylic acid[19, 20] and 2,5-diformylfuran[21, 22] are regular products from furfural and HMF.[23-26] Among these circumstances, the structure of the furan ring was kept in most of the common products from furfural and HMF. Another attractive research area is to breach the furan structure to get more categories of products which can mainly be classified as the chain compounds and aliphatic cyclic compounds. The levulinic acid was the representative chain compound through the ring-opening of the furan rings.[27-30]

HHD, another chain compound which was obtained through the hydrogenation of HMF with the homogeneous or heterogeneous catalysts, had gained many attentions recently.[31-38] Fu *et al.*[33] reported the Cp*Ir(III) half-sandwich complexes were effective catalysts for the hydrogenation of HMF in aqueous formate buffer solution and 85% yield of HHD could be achieved. The supported Pd, Pt or Au catalysts were also demonstrated to be efficient for the hydrogenation of HMF to HHD. For example, Jérôme *et al.*[31] reported a 77% yield of HHD from HMF by the combination of Pd/C and Amberlyst-15 in THF. Considering the catalysts mentioned above were mainly noble metals, how to elevate the efficiency of these catalysts involving conversion and selectivity is a key topic. Moreover, the transformation of HHD to valuable chemicals is also a significant problem due to the utility of the HHD.

Cyclopentanone (CPO), a typical aliphatic cyclic compound, obtained from furfural had been reported by Hronec *et al.* in 2012. In this procedure, the structure of the furan ring was hydrogenated then isomerized to aliphatic cyclic in water in the presence of H_2.[39] And Xu *el al.* also reported the same results and demonstrated that this process conduct through furfuryl alcohol, then 4-hydroxy-2-cyclopentenone and finally 2-cyclopentenone.[40] Then several groups had focused on this reaction and the best yield of cyclopentanone from furfural reached up to 99%. The catalysts used in these articles including Ni-Cu, Cu-Co, Au, Pd, Pt, Ru etc. and were proved to be effective for this procedure.[41-48]

Due to the same skeleton of HMF and furfural, the conversion of HMF to a cyclopentanone derivative had been gaining increasing interest recently. Different from the rearrangement of furfural to cyclopentanone, when HMF was used as feedstocks instead of furfural, a series of cyclopentanone derivatives were obtained varied on the catalysts and reaction conditions. For instance, Ohyama *et al.*[49-51] obtained 3-hydroxymethylcyclop-entanone (HCPN) from HMF by using Au/Nb_2O_5 in water and the yield of HCPN mainly depended on the acid-base properties of the support. 3-Methyl-2-cyclopenten-1-one could be acquired from HMF by water splitting with Zn at high temperature by Huo group.[52]

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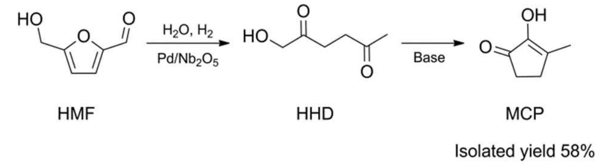
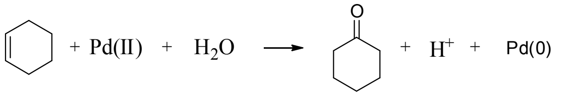


Scheme 1 The conversion of HMF to MCP.

MCP is a valuable edible essence, widely used in foods, beverages and flavors.[53] The MCP was mainly produced from adipinic acid via multistep reactions and usually employed organic solvent and toxic reagent such as Cl_2.[54] Herein, we gave a report on the catalytic conversion of HMF to MCP on Pd/Nb_2O_5 in water. The procedure contained two steps as shown in Scheme 1. The first step was the hydrogenation of HMF to HHD over Pd/Nb_2O_5 and then HHD to MCP in alkaline aqueous solution. No organic solvent and toxic reagent was used in this procedure. The niobium oxide was a water-tolerant acid and widely used as catalyst or support in the conversion of biomass.[55-60] The Pd/Nb_2O_5 was synthesized through a reduction reaction by stirring the mixture of $PdCl_2$, Nb_2O_5 and water saturated by cyclohexene which was a part of the Wacker Oxidation process as shown in eq. 1. This process was first used for the preparation of Pd/SBA-15 employing surface bonded vinyl as the reductant by our group short recently.[61] However, this procedure was complex and contained multisteps to obtain vinyl-functionalized SBA-15. In this paper, water saturated by cyclohexene was proved to be a preferable reductant for Pd catalysts given to the simple procedure and effective usage. The as-synthesized Pd/Nb_2O_5, with low Pd loading (0.61 wt%) and highly dispersed Pd, showed much higher conversion and selectivity in the hydrogenation of HMF to HHD than traditional catalysts which were obtained by H_2 or $NaBH_4$ reduction.



eq. 1

Experimental

Materials

HMF, 5-methylfuran-2-carbaldehyde, Na_3PO_4, MgO, MCP, Ru/C and Pt/C were purchased from Aladdin Chemistry Co. Ltd.. Palladium chloride ($PdCl_2$), Pd/C, (5-methylfuran-2-yl)methanol and 2,5-di(hydroxymethyl)furan were obtained from J&K Chemical Ltd.. Nb_2O_5 was purchased from Sinopharm Chemical Reagent Co., Ltd.. HF, cyclohexene, triethylamine, Na_2CO_3 and NaOH were obtained from Tianjin Kermel Chemical Reagent Development Center. Deionized water in all experiments was purified by a Milli-Q system. All other reagents were commercially available and used as received.

Preparation of catalysts

Nb_2O_5-x. The Nb_2O_5 was synthesised according to previous report.[40] Typically, Nb_2O_5 (10.00 g) was dissolved in HF aqueous solution (45 mL, 40 wt%) by stirring the mixture at 353 K for 24 h. Then ammonia water was added drop wise into the clear solution to adjust the pH 8-9 under drastic stirring. The precipitation was centrifuged and washed first with ammonia water and then water for 3 times. The solid was dried at 373 K overnight to afford niobic acid. The niobic acid was then calcined in air at different temperature to afford Nb_2O_5-x where x referred to the calcined Celsius temperature.

Pd/Nb_2O_5-x. Nb_2O_5-x (1.00 g) was added into water saturated by cyclohexene. The mixture was stirred for 30 min at room temperature. Then $PdCl_2$ (Pd: 5.0 mg) dissolved in dilute hydrochloric acid was added drop wise in the mixture under stirring. After stirring for 12 h at room temperature the mixture was centrifuged and washed first with water and then ethanol. The solid was dried at 323 K under the vacuum for 24 h to afford the Pd/Nb_2O_5-x. The Pd/Nb_2O_5-x with different content of Pd were prepared using a similar procedure with different amount of $PdCl_2$ and cyclohexene.

Pd/Nb_2O_5-400-IP. Nb_2O_5-400 (1.00 g) was added in dilute hydrochloric acid solution of $PdCl_2$ (Pd: 5.0 mg). The mixture was stirred for five minutes and kept stand for 24 h under room temperature. Then the solid was dried at 373 K overnight and reduced at 573 K by H_2.

Pd/Nb_2O_5-400-B. Nb_2O_5-400 (1.00 g) was dispersed in water containing $PdCl_2$ (Pd: 5.0 mg) dissolved in dilute hydrochloric acid. Then a solution of $NaBH_4$ (37.8 mg) was added drop wise under stirring in N_2 at 273 K. The mixture was stirred for another 30 min and washed first with water and then ethanol. The resulted solid was dried at 323 K under vacuum for 24 h.

Ca-Al. The Ca-Al was prepared according to our previous report.[10] Typically, $Al(NO_3)_3{\cdot}9H_2O$ (37.5 g) and $Ca(NO_3)_2{\cdot}4H_2O$ (23.6 g) was dissolved in the deionized water. Then ammonium carbonate aqueous solution (600 mL, 0.5 $mol{\cdot}L^{-1}$) was added dropwise under vigorous agitation. The mixture was stirred for 30 min at room temperature, and then kept stand for 24 h at the same temperature. The resulted precipitate was washed by deionized water for 3 times and then dried overnight at 373 K. After grinded and sieved and the solid was then calcinated under air to afford the Ca-Al.

Characterization of catalysts

X-ray diffraction (XRD). The crystal structures of supports and catalysts were characterized by powder X-ray diffraction (XRD) using Rigaku D/Max 2500/PC powder diffractometer with Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA in a scanning rate of 5^o/min.

Elemental analysis. The content of Pd on the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) conducted on CPS-8100, Shimadzu.

Fourier transform infrared (FT-IR). The spectra were collected on a Bruker Tensor 27 FT-IR spectrometer in KBr media. Samples were thoroughly dried before measured.

Temperature-programmed desorption of NH_3 (NH_3-TPD). The experiments were performed on a Micromeritics AutoChem II 2920 Instrument with a thermal conductivity detector (TCD) and MS detector to monitor the desorbed NH_3. Samples was first pretreated at 473 K and then NH_3 was adsorbed at 373 K in a flow of He. After the physical adsorpted NH_3 was removed,

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the temperature was increased from 373 to 1073 K in an atmosphere of He and the desorbed NH_3 was recorded by TCD and MS.

X-ray photoelectron spectroscopy (XPS). The measurements were conducted on the Thermo ESCALAB 250Xi by using Mg Kα (1253.6 eV) radiation source and a chamber pressure lower than 5×10^{-10} mbar. The binding energy (BE) was adjusted by the binding energy of C1s.

Transmission electron microscopy and Energy dispersive X-ray spectroscopy (TEM-EDX). The microstructure of the materials was examined by transmission electron microscopy (TEM) on a FEI Tecnai G2 F20 operating at 200 kV with an EDX detector.

CO pulse chemisorption. The measurements were conducted on Micromeritics AutoChem 2920 apparatus. The sample were pretreated at 393 K under flowing of He and then reduced at 373 K by H_2. After that, 1 vol.% CO/He were pulsed over the catalyst bed every 5 min at 323 K.

Catalytic reactions

Hydrogenation of HMF. The catalytic reactions were performed in a 20 mL stainless steel autoclave equipped with a magnetic stirrer, a pressure gauge and automatic temperature control apparatus. In a typical procedure, catalyst (20 mg), HMF aqueous solution (2.0 g, HMF: 1 mmol) and magnetic dipole was put in the reactor. After the reactor was sealed and purged with H_2 for 4 times to exclude air, the reactor was charged with H_2 to desire pressure. Then the autoclave was heated to the desired temperature and the reaction began by starting the stirring. After reaction, the reaction mixture was centrifugated and the liquid phase was diluted and analyzed by GC after adding the internal standard (1,2,4,5-tetramethylbenzene).

Conversion of HHD to MCP. H_2O (10.0 g), HHD (130 mg, 1mmol) and tetrahydrofurfuryl alcohol (60 mg, internal standard) was added in a 50 mL round flask. Then the bases were added and the reaction started by conducting under reflux or at 298 K. After reaction, the liquid was neutralized (not needed for MgO and Ca-Al) and diluted for GC analysis.

Conversion of HMF to MCP. The first step was the same procedure as the hydrogenation of mentioned above. After reaction, the liquid phase was divided in two parts. One part was diluted and analyzed by GC after adding the internal standard (1,2,4,5-tetramethylbenzene). The other part (1.00 g) was added into H_2O (10 mL). After base (NaOH or Ca-Al) was added the reaction started by conducting under reflux or at 298 K. After reaction, the liquid was neutralized by HAc (not needed for Ca-Al)and extracted by CH_2Cl_2. The mixture was separated by column chromatography to give the white powder final products (MCP).

Products analysis

Gas chromatography measurements were conducted on Agilent 7890A GC with autosampler and a flame ionization detector. HP-5 capillary column (30 m × 320 μm × 0.25 μm) was used for the separation of reaction mixtures. The temperature of the column was initially kept at 393 K for 3 min, and then was increased at a rate of 20 K min^{-1} to 493 K. 1,2,4,5-tetramethylbenzene (TMB) or tetrahydrofurfuryl alcohol was used as the internal standard. The products were identified by Agilent 6890N GC/5973MS as well as by comparison with the retention times of the respective standards in GC traces.

The quantification of products were determined based on GC data using internal standard method and the mass of isolated products by column chromatography method. The conversion of (%), selectivity (%) and isolated yield (%) were calculated as below.

$$\text{Conversion}(\%) = (1 - \frac{\text{Moles of substrate}}{\text{Moles of substrate loaded initially}}) \times 100\%$$

$$\text{Selectivity}\ (\%) = \frac{\text{Moles of products}}{\text{Moles of substrate converted}} \times 100\%$$

$$\text{Isolated yield}\ (\%) = \frac{\text{Moles of isolated products}}{\text{Moles of substrate}} \times 100\%$$

Results and Discussion

Characterization of catalyst

The XRD patterns of Nb_2O_5 were shown in Fig. 1. All the samples showed characteristic diffraction peaks of Nb_2O_5 according to the standard value (PDF#30-0873). The commercial Nb_2O_5 had sharp diffraction peaks due to the high degree of crystallization. The crystallization degree of as-synthesized Nb_2O_5-x increased with the calcined temperature revealed by the XRD patterns. Nb_2O_5-200 had weak broad diffraction peaks corresponding to Nb_2O_5. The intensity increased and the width reduced as the calcination temperature increased. The Nb_2O_5-x calcined at lower temperature had an additional peak at 13-14^{o}. This should be ascribed to (120) crystalline planes of the niobium hydrogen oxide (HNb_3O_8, PDF#30-083). This peak decreased as the calcination temperature increased and disappeared when the temperature was 773 K. This should be ascribed to the dehydration of niobium hydrogen oxide at evaluated temperature.

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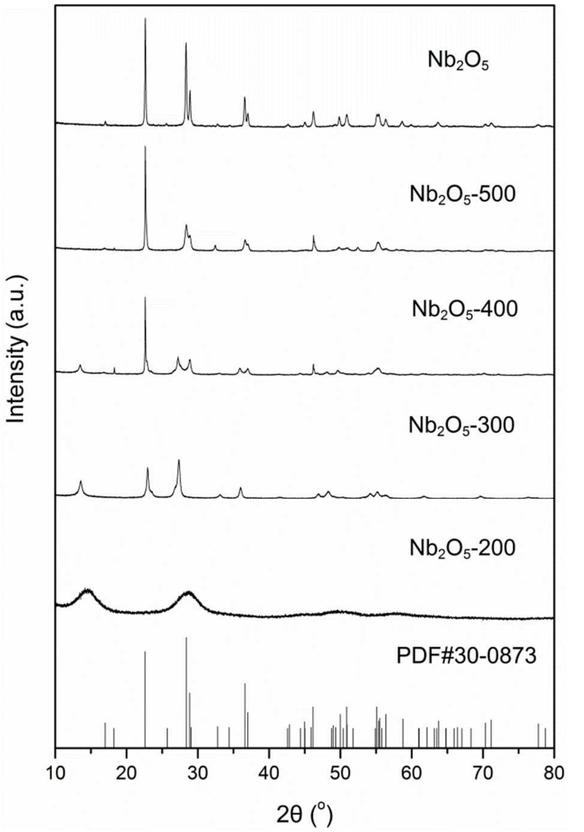
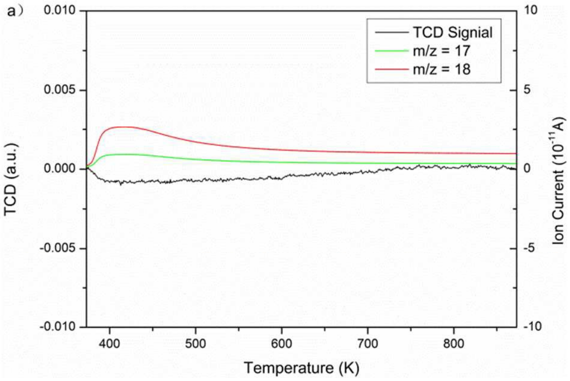


Fig. 1 The XRD patterns of Nb_2O_5.

The surface acidity of the commercial Nb_2O_5 and as-synthesized Nb_2O_5-400 was detected by the NH_3-TPD (Fig. 2). Both the TCD signal and the mass spectrum signal were collected. No desorption of NH_3 was observed during the whole temperature range for the commercial Nb_2O_5 (Fig. 2a). This result indicated that the commercial Nb_2O_5 did not have acidity. In contrast, the Nb_2O_5-400 had a desorption peak around 630 K (Fig. 2b) and the MS detector showed the main desorption substance was NH_3 (m/z = 17) as well as a little H_2O (m/z = 18). These results indicated that the Nb_2O_5-400 had strong acidity which was introduced during the preparation process.



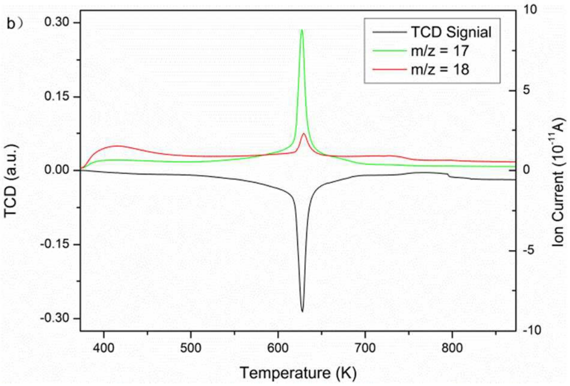


Fig. 2 The NH_3-TPD profiles of Nb_2O_5 (a) and Nb_2O_5-400 (b).

The Nb_2O_5 supported Pd catalysts were prepared through the reduction of $PdCl_2$ by cyclohexene saturated water. The surface bonded vinyl had been proved to be an effective reductant for the reduction of $PdCl_2$ in our earlier work.[61] Herein, the surface bonded vinyl was replaced by cyclohexene saturated water. For comparison, Pd/Nb_2O_5-400-IP and Pd/Nb_2O_5-400-B were also prepared by H_2 and $NaBH_4$ reduction method respectively. The XRD patterns of the Pd catalysts were shown in Fig. 3. No obvious changes were observed on the supports after the introduction of Pd by the comparison of Pd catalysts (Fig. 3) and the supports (Fig. 1). The crystal structure of the supports was well kept after the introduction of palladium. All the catalysts showed no characteristic diffraction peaks of palladium. These could be attributed to the low Pd loading (Table S2) and well dispersed Pd on the surface of the supports.

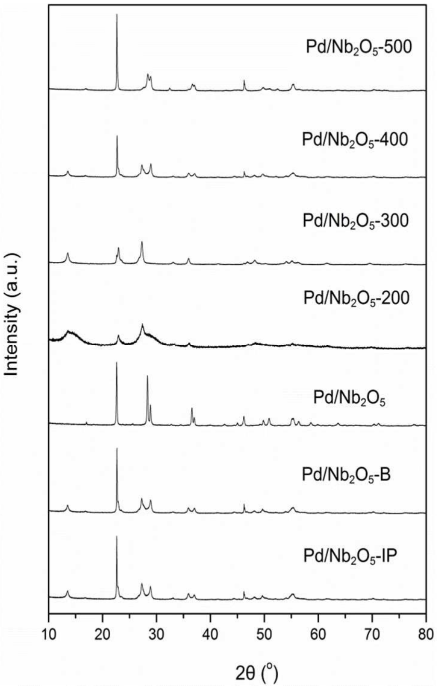


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Fig. 3 The XRD patterns of Pd catalysts.

The presence of palladium species as well as the oxidation state of palladium on the supports could be testified by the X-ray photoelectron spectroscopy (XPS). The 3*d* spectra of Pd had been collected and analyzed and the results were summarized in Fig. 4 and Table S1. All the samples showed binding energy peaks at 335 eV and 340 eV, which are the characteristic peaks of Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively. Curve fitting analysis showed that the main binding energy peaks appeared at 334.7 eV and 339.9 eV for Pd/Nb_2O_5-400. and these peaks should be attributed to Pd(0) according to the literature reports.[61, 62] Additionally, two weak binding energy peaks at 336.7 eV and 341.8 eV were observed, with the ownership of $3d_{5/2}$ and $3d_{3/2}$ of Pd(II). The results indicated that the palladium species for Pd/Nb_2O_5-400 was primarily Pd(0) while the Pd(II) should be ascribed to the oxidation of Pd(0) in the air atmosphere. Similar results could be observed on the Pd/Nb_2O_5-B and Pd/Nb_2O_5-IP.

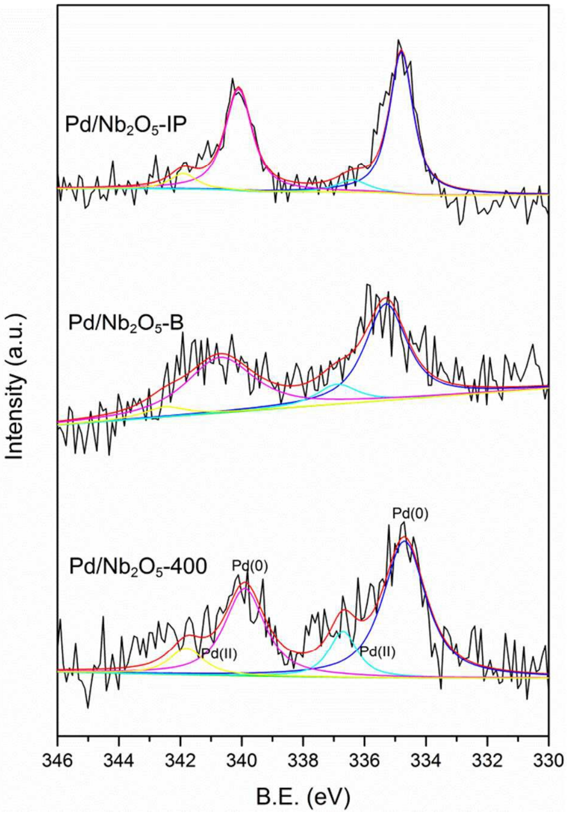

Fig. 4 The XPS spectra of Pd/Nb_2O_5-400,Pd/Nb_2O_5-B and Pd/Nb_2O_5-IP.

The morphology of Pd/Nb_2O_5-400, Pd/Nb_2O_5-B and Pd/Nb_2O_5-IP was characterized by the TEM images as well as HRTEM. As the results of XPS showed the presence of Pd, it is surprising that no Pd nanoparticle was observed after 50 TEM or HRTEM images were checked for Pd/Nb_2O_5-400 (Fig. 5a, 5d). The HRTEM images only exhibited the lattice for Nb_2O_5. The EDX spectra also gave the clue for the existence of Pd. This should be due to the high disperse of Pd on the support. The high disperse of Pd was also supported by the CO pulse chemisorption experiments (Fig. S3). The calculated Pd dispersion was 34% based on the CO chemisorption on the catalysts. The The employing of cyclohexene as reductant was responded for this high disperse. Firstly, the cyclohexene had weaker reducing power comparing to other reductant such as $NaBH_4$. And the solubility of cyclohexene in water was very low. As a result, the reduction reaction conducted too slow to form TEM observable Pd nanoparticles. In contrast, the Pd/Nb_2O_5-B and Pd/Nb_2O_5-IP which had similar Pd loading to Pd/Nb_2O_5-400 (Table S2) showed clear Pd nanoparticles (Fig. 5b and 5c). In addition, the HRTEM inset and the EDX spectra also verified the Pd nanoparticles on the Pd/Nb_2O_5-B and Pd/Nb_2O_5-IP.

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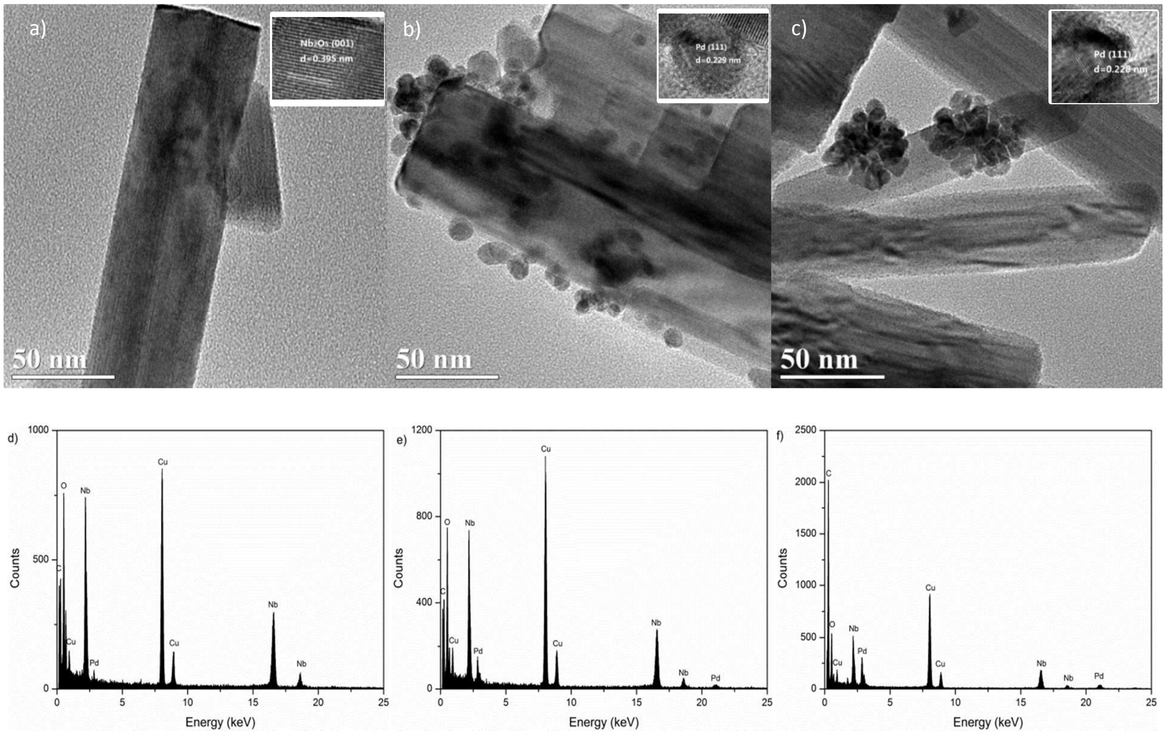

Fig. 5 The TEM images and EDX spetra of Pd/Nb_2O_5-400 (a, d), Pd/Nb_2O_5-B (b, e) and Pd/Nb_2O_5-IP(c, f). Insets showed HRTEM images for the corresponding samples.

The Hydrogenation of HMF to HHD

The hydrogenation of HMF to HHD was conducted on the catalyst prepared above in water in the presence of H_2 and the results were summarized in Table 1. When the commercial Nb_2O_5 was used as support, both the conversion of HMF and the selectivity of HHD were very low (Table 1, Entry 1). The by-products were chiefly 2,5-hexanedione, 2,5-di(hydroxymethyl)furan (DHMF) and tetrahydro-2,5-furandimethanol (THFDM). When Nb_2O_5-x were used as supports, the selectivity of HHD increased from 31% to 61-85% (Table 1, Entries 2-5). The enhanced selectivity should be ascribed to the acidity of the Nb_2O_5-x. The addition of acid was necessary for the reported homogeneous or heterogeneous catalytic system for this reaction. It is widely accepted that the acid facilitates the ring-opening procedure during the reaction.[38] The NH_3-TPD results (Fig. 2) showed that the Nb_2O_5-x had acidity after the prepared procedure. As a result, the Nb_2O_5-x worked both as support for Pd and as the acid catalyst. And no additional acid was needed for the high selectivity of HHD when Pd/Nb_2O_5-x was used as the catalyst. To verify the importance of acid site, the reaction was performed employing Pd/C as the catalyst by the addition of acid or base additives. After 1 mmol of HAc was introduced, the selectivity of HHD increased from 30% to 61%. On the contrary, no HHD was detected after 1 mmol NaOH was added at the same reaction conditions.

For comparison, the Pd/Nb_2O_5-B, Pd/Nb_2O_5-IP and Pd/C, Ru/C, Pt/C catalysts were also tested for this reaction. The Pd/Nb_2O_5-B and Pd/Nb_2O_5-IP gained 67% and 65% selectivity of HHD respectively while the Pd/C gave 30% selectivity (Table 1, Entries 6-8). These results revealed the advantage of Nb_2O_5-x as support for the hydrogenation of HMF to HHD. However, the conversion of HMF was 19% and 18% for Pd/Nb_2O_5-B and Pd/Nb_2O_5-IP respectively which were much lower than that of Pd/Nb_2O_5-400 (56%) (Table 1, Entries 6 and 7 vs Entry 4). As the Pd loading determined by ICP-AES was similar for the three catalysts (Table S2), the main reason for this difference in conversion was the high disperse of Pd on the Pd/Nb_2O_5-400 prepared by the cyclohexene reduction method. The Ru/C and Pt/C did not give good results for this reaction with the selectivity of 13% and 10% respectively.

Table 1 Hydrogenation of HMF to HHD over different catalysts.[a]

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Entry	catalysts	Conversion (%)	Selectivity of Products (%)				
			HHD	HD	DHMF	THFDM	Others [b]
1	Pd/Nb_2O_5	35	31	12	13	17	27
2	Pd/Nb_2O_5-200	14	71	13	3	5	8
3	Pd/Nb_2O_5-300	39	67	6	8	2	17
4	Pd/Nb_2O_5-400	56	85	4	1	<1	9
5	Pd/Nb_2O_5-500	45	71	9	4	2	14
6	Pd/Nb_2O_5-400-IP	18	65	12	4	3	16
7	Pd/Nb_2O_5-400-B	19	67	11	2	2	18
8	Pt/C	43	10	7	44	1	38
9	Ru/C	80	13	2	2	60	23
10	Pd/C	98	30	5	6	20	39
11	Pd/C + HAc [c]	98	61	12	<1	6	20
12	Pd/C + NaOH [c]	99	*N.D.*	*N.D.*	7	33	60

[a] Reaction conditions: catalyst (20 mg), 2.00 g HMF aqueous solution (HMF: 1 mmol), 413 K, 4 MPa H_2, 2 h. [b] The others referred to 2,5-hexanedione, 2,5-dimethyltetrahydrofuran and unidentified products, [c] 1 mmol, *N.D.* not detected.

Effect of H_2 pressure

The effect of H_2 pressure on the hydrogenation of HMF to HHD in water was shown in Fig. 6. The selectivity of HHD were between 77% and 90% when the pressure varied from 1 MPa to 5 MPa. It is noteworthy that 90% selectivity of HHD could be obtained when the H_2 pressure was 1 MPa. This indicated that the H_2 pressure did not influence the selectivity of HHD in the pressure range. However, the conversion of HMF were promoted from 21% to 57% when the H_2 pressure increased from 1 MPa to 5 MPa.

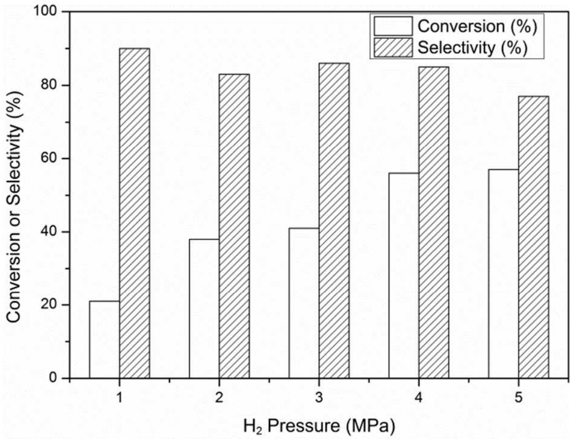

Fig. 6 Hydrogenation of HMF to HHD at different H_2 pressure. Reaction conditions: Pd/Nb_2O_5-400 (20 mg), 2.00 g HMF aqueous solution (1 mmol) 413 K, 2 h.

Effect of Temperature

The effect of temperature on the hydrogenation of HMF in water was also investigated and the results were shown in Table 2. The reaction could conduct at a temperature as low as 393 K, and 37% conversion as well as 82% selectivity of HHD were obtained after 2 h at 4 MPa (Table 2, Entry 1). The conversion increased with the temperature increased which was accordance to our expectations. The selectivity of HHD decreased when the temperature was higher than 413 K. This should be attributed to the more side reaction at higher temperature.

Table 2 Hydrogenation of HMF to HHD under different temperature.[a]

Entry	Temperature (K)	Conv. (%)	Selectivity of products (%)	
			HHD	Others
1	393	37	82	18
2	403	42	75	25
3	413	56	85	15
4	423	71	54	46
5	433	82	61	39

[a] Reaction conditions: Pd/Nb_2O_5-400 (20 mg), 2.00 g HMF aqueous solution (1 mmol), 4 MPa H_2, 2 h.

Effect of reaction time

The influence of time on the hydrogenation reaction was studied by conducting the reaction for a specified time. The results were shown in Fig. 7. It is logical that the conversion of HMF increased as the time prolonged. The conversion of HMF was 28% when the reaction time was 1 h. The conversion

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increased steadily as the reaction time prolonged. The conversion of HMF reached 93% when the reaction lasted for 6 h. However, the selectivity of HHD remained stable around 80% as the reaction time changed from 1 h to 6 h. The selectivity of HHD was 83% at low conversion of 28%. When the conversion of HMF reached 93% the selectivity of HHD was still as high as 73%.

Based on the study of the effect of H_2 pressure, temperature and the reaction time, it had been found that the reaction could conduct at mild condition on Pd/Nb_2O_5-400. And the selectivity of HHD kept high even at the conversion of HMF over 90%.

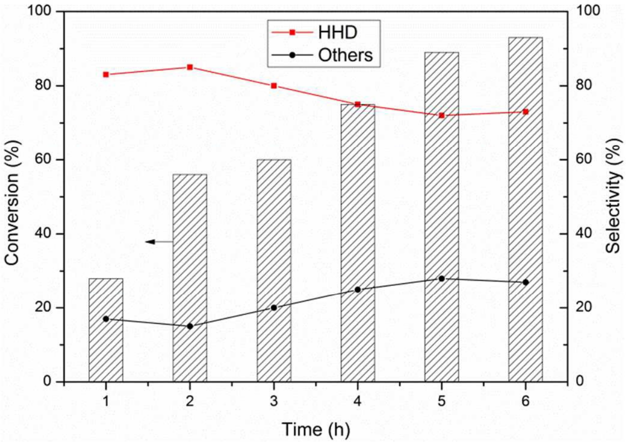

Fig. 7 Time-course of HMF hydrogenation to HHD. Reaction conditions: Pd/Nb_2O_5-400 (20 mg), 2.00 g HMF aqueous solution (1 mmol) 413 K, 4 Mpa H_2.

Effect of Pd contents

The catalysts with different contents of Pd could be obtained by changing the amount of water saturated by cyclohexene and $PdCl_2$. The actual contents of Pd were determined by ICP-AES and the results were shown in Table 3. The Pd contents could be varied from 0.61 wt% to 4.62 wt%. The catalysts were used for the hydrogenation of HMF. The conversion of HMF increased from 56% to 99% as the contents of Pd increased. This phenomenon should be ascribed to the increase of active sites in catalysts with the increase of Pd-loading amount. As the catalyst with 4.62 wt% contents of Pd had the highest Pd loading, this catalyst could convert HMF to HHD at a very low H_2 pressure (Table 3, Entry 6). The Pd contents did not affect the selectivity to HHD obviously. All the catalysts had high selectivity to HHD, and the catalyst with 0.61 wt% Pd contents had the best selectivity to HHD (Table 3, Entry 1).

Table 3 Hydrogenation of HMF on Pd/Nb_2O_5-400 with different Pd contents.[a]

Entry	Pd contents (wt%)[b]	Conv. (%)	Selectivity of products (%)	
			HHD	Others
1	0.61	56	85	15
2	0.74	78	74	26
3	1.94	84	77	23
4	2.48	97	73	27
5	4.62	>99	69	31
6[c]	4.62	91	71	29

[a] Reaction conditions: Pd/Nb_2O_5-400 (20 mg), 2.00 g HMF aqueous solution (1 mmol), 4 MPa H_2, 2 h, [b] determined by ICP-AES, [c] 0.5 MPa H_2, 8 h.

Catalyst recycling

The recyclability of the Pd/Nb_2O_5-400 was elucidated in Fig. 8 and the reaction time was fixed at 6 h to achieve the high conversion of HMF over 90%. The catalyst was reused for 4 times. The catalyst was centrifuged and fully washed after each cycle. And then the catalyst was dried at 323 K under vacuum and used for the next run. It was found that the conversion of HMF and selectivity of HHD kept stable in all the four cycles from Fig. 8. The selectivity of HHD was 71% even in the fourth cycle with 89% conversion. This examination illustrated the high stability of the catalyst under the reaction conditions.

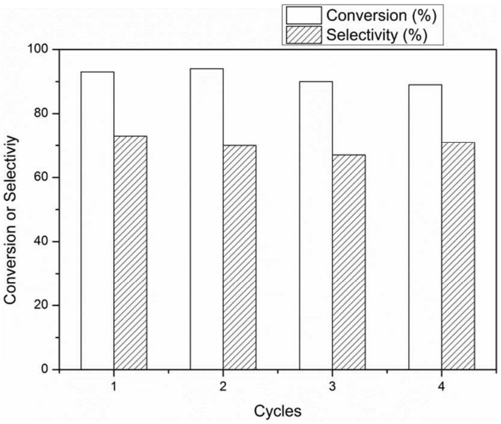

Fig. 8 Cycle experiments for the hydrogenation of HMF in water. Reaction conditions: Pd/Nb_2O_5-400 (20 mg), HMF aqueous solution (2.00 g, 1 mmol) 413 K, 4 MPa H_2, 6 h.

Possible reaction pathway

Different substrates were used instead of HMF to find the possible reaction pathway and the results were shown in Table 4. 54% selectivity of HHD was achieved when DHMF was used as the substrates (Table 4, Entry 2). The DHMF should be one of the intermediates from HMF to HHD. When 5-methylfuran-2-carbaldehyde (MFA), (5-methylfuran-2-yl)methanol (MFOL) and 2,5-dimethylfuran (DMF) was used as substrates respectively, no HHD was detected after 2 h reaction. Instead, HD was found to be the main products in these cases (Table 4,

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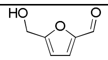
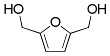
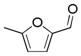
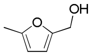
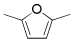
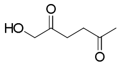
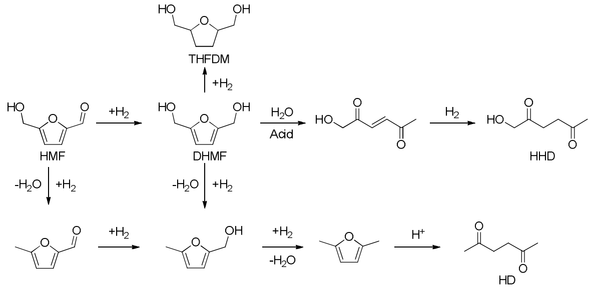
Entries 3-5). The MFOL and DMF gave much lower selectivity to HD than the MFA. This should be caused by the increased side reactions at high concentration of MFOL or DMF. 5,5'-(oxybis(methylene))bis(2-methylfuran), the dimer of MFOL, was easy to be produced when MFOL was used as the substrate.[63, 64] The 2,5-dimethyltetrahydrofuran emerged as the by-product when DMF was the substrate. At the standard reaction conditions, the HHD kept stable and almost no HHD was transformed after 2 h reaction at 413 K (Table 4, Entry 6).

Table 4 Hydrogenation of different substrates on Pd/Nb_2O_5-400.[a]

Entry	Substrates	Conv. (%)	Selectivity of products (%)		
			HHD	HD	Others
1		56	85	4	15
2		78	54	2	44
3		78	*N.D.*	72	28
4		>99	*N.D.*	26	74
5		>99	*N.D.*	35	65
6		2	97	*N.D.*	3

[a] Reaction conditions: Pd/Nb_2O_5-400 (20 mg), 2.00 g aqueous solution of substrate (1 mmol), 4 MPa H_2, 2 h, 413 K. *N.D.*: not detected.

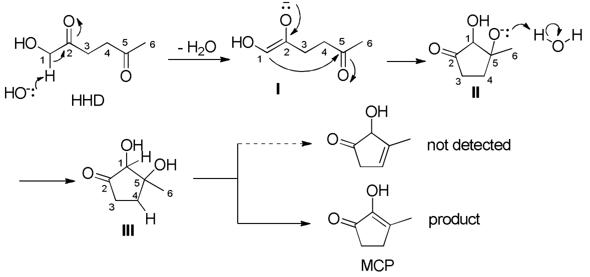
Based on the results mentioned above and the literatures[33, 35, 38], we proposed the possible reaction pathway for the hydrogenation of HMF to HHD as shown in Scheme 2. Firstly, the HMF was hydrogenated to DHMF on the Pd catalyst in the presence of H_2. And then the DHMF was converted to HHD by the cooperation of Pd catalysts and acid sites. The acid sites were responsible for the opening of the furan rings of DHMF and the most likely product was 1-hydroxyhex-3-ene-2,5-dione while the Pd catalysts behaved as hydrogenation catalysts. One of the by-products was THFDM which was produced through the hydrogenation of THFDM. Another by-product detected was HD which should be produced by the hydrolysis of 2,5-dimethylfuran.



Scheme 2 The proposed reaction pathway for the hydrogenation of HMF to HHD.

Conversion of HHD to MCP

The conversion of HHD to MCP is an aldol condensation reaction as illustrated in Scheme 3. Due to the more acidity of C1-H, C1 could attack C5 to accomplish a five-memebered ring **II** with the assistance of base. As the C5 of the intermediate **III** had no H atom, the dehydroxylation should conduct at C1. Then, the dehydration took place to give more stable product MCP and another dehydration product was not detected. These must be the reasons for the high selectivity to MCP.



Scheme 3 The conversion of HHD to MCP.

Effect of bases

The effect of different bases was studied by performing the aldol condensation reaction in water employing different bases as catalysts and the results were summarized in Table 5. Most of the alkaline substance was effective for this aldol condensation reaction. The reaction could conduct smoothly even at 298 K when the 0.15 mol L^{-1} NaOH was used with full conversion and 90% selectivity (Table 5, Entry 1). When weaker base was empolyed for this reaction, higher temperature or/and longer time should be adopted. Satisfying results were achieved in the case of Na_2CO_3 and Na_3PO_4 with 87% and 91% yields under reflux (Table 5, Entries 3 and 4). The organic bases such as triethylamine were also effective for this reaction with 89% selectivity of HHD and 83% conversion of HHD (Table 5, Enter 5). Solid bases should be a good options for the reaction. 74% selectivity of MCP was obtained with 47% conversion of HHD when MgO was used (Table 5, Enter 6). To our delight, 87% selectivity of MCP with full conversion of HHD was achieved when the Ca-Al was used as catalyst (Table 5, Enter 2). As a solid base, Ca-Al meets the green principle better and could give a comparable good results. What is more, the pH value of the reaction liquid was almost 7 after 2 h reaction when Ca-Al was used. Therefore, no additional acids were needed to neutralize the reaction mixture. These can be accout for the Ca-Al to be chosen as the best candidate of base.

Table 5 The conversion of HHD to MCP by different bases .[a]

Entry	Catalsyts	Concentration (mol L^{-1})	Temperature (K)	Conv. (%)	Select. (%)
1	NaOH	0.15	298	>99	90
2	Ca-Al[b]	200[c]	reflux	>99	87
3	Na_2CO_3	0.10	reflux	>99	87
4	Na_3PO_4	0.10	reflux	>99	91
5	Et_3N	0.10	reflux	83	89
6	MgO	200[c]	reflux	47	74

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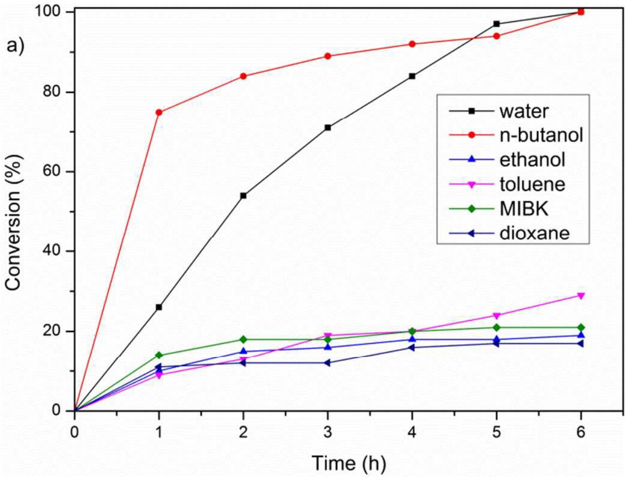
[a] Reaction conditions: HHD (130 mg), H_2O (10.0 g), 1 atm air, 298 K or reflux, 2 h , [b] 6 h, [c] 200 mg.

Effect of solvent and reaction time

We also evaluated the reaction time for the conversion of HHD to MCP in several solvents and the results were shown in Fig. 9a. The HHD was completely transformed after 6 h when the reaction was performed in water and in n-butanol. As the reaction was performed under reflux condition, the low conversion of HHD for ethanol might be attributed to the low boiling point of ethanol (351 K). Though toluene and methyl isobutyl ketone (MIBK) had similar boiling point to n-butanol, the conversion was very low for both solvents (toluene and MIBK) after 6 h. Similarly, the dioxane, though had a boiling point close to water, gave very low conversion of HHD. As a result, the protonic solvent should be a favour for this aldol condensation reaction. However, the selectivity of MCP was not affected sharply by the time and the nature of the solvent. The selectivity of MCP kept between 80-90% in different solvent as the time prolonged (Fig. 9b).



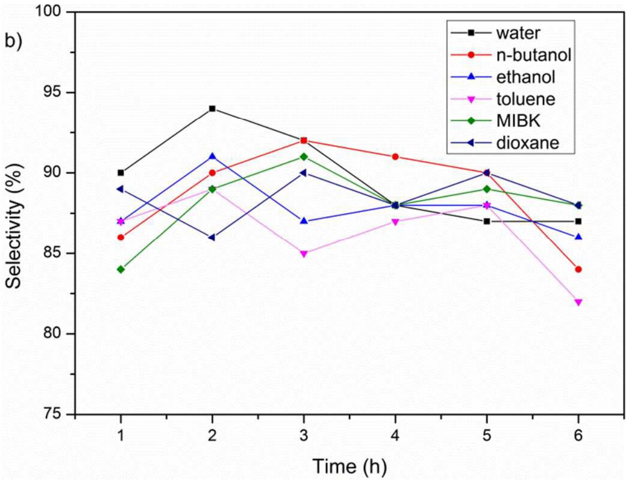


Fig. 9 Conversions (a) and selectivity (b) at different reaction time for the conversion of HHD to MCP in different solvents.

Conversion of HMF to MCP

The conversion of HMF to MCP undergoes through two steps as expatiated in the experimental section and in Scheme 1. And the results were summarized in Table 6. The first step was the hydrogenation of HMF to HHD on Pd/Nb_2O_5-400 and the next step was the conversion of HHD to MCP through aldol condensation catalyzed by base in water. The conversion of HMF varied from 90% to 93% while the selectivity changed from 68% to 73% for the Step 1 showing the satisfying repeatability (Table 6, Entries 1-5). It had been discussed above that the selectivity of MCP from HHD was usually very high. As a result, the isolated yield of MCP most depended on the results of the Step 1. The isolated yield of MCP varied from 49% to 58% according to the base. The best isolated yield of MCP was 58% when Ca-Al was used (Table 6, Entry 1).

Table 6 The Conversion of HMF to methyl cyclopentenolone via a two-steps peocedure.[a]

Entry	Step 1		Step 2			
	Conv. (%)	Selectivity of HHD (%)[b]	catalysts	Concentration (mol L^{-1})	Temperature (K)	Isolated yield of MCP (%)[c]
1	93	73	Ca-Al[d]	200[e]	reflux	58
2	92	71	Ca-Al[d]	200[e]	reflux	55
3	91	70	NaOH	0.15	298	57
4	90	71	Na_2CO_3	0.10	reflux	53
5	93	68	Et_3N	0.10	reflux	49

[a] Reaction conditions: Pd/Nb_2O_5-400 (20 mg), 2.00 g HMF aqueous solution (1 mmol), 413 K, 4 MPa H_2, 6 h for HMF hydrogenation and H_2O (10.0 g), reflux or 298 K for the conversion of HHD to MCP , [b] The selectivity of HHD, [c] The isolated yield of MCP based on HMF, [d] 6 h, [e] 200 mg.

Conclusions

In summary, a series of Nb_2O_5-x possessing acidity was synthesized and used as support for the preparation of Pd catalysts. The Pd catalysts, synthesized through the cyclohexene reduction method with high disperse of Pd, were used for the hydrogenation of HMF to HHD in water. The high disperse of Pd was responsible for the high conversion of HMF and the acidity of Nb_2O_5-x leads to the high selectivity of HHD. Finally, the HHD was converted to MCP, a kind of valuable edible essence, catalyzed by a solid base Ca-Al in water with

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58% isolated yield based on HMF. This work provides a new method for the preparation of Pd catalysts and presents a good example for the conversion of HMF to valuable chemicals.

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references

1. C. Chatterjee, F. Pong and A. Sen, *Green Chem.*, 2015, **17**, 40-71.
2. Z. Zhang, J. Song and B. Han, *Chem. Rev.*, 2017, **117**, 6834–6880.
3. P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538-1558.
4. A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754-793.
5. R. J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499-1597.
6. A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411-2502.
7. X. Li, P. Jia and T. Wang, *ACS Catal.*, 2016, **6**, 7621-7640.
8. P. Zhou and Z. Zhang, *Catal. Sci. Technol.*, 2016, **6**, 3694-3712.
9. Y. Nakagawa, H. Nakazawa, H. Watanabe and K. Tomishige, *ChemCatChem*, 2012, **4**, 1791-1797.
10. Y. Yang, J. Ma, X. Jia, Z. Du, Y. Duan and J. Xu, *RSC Adv.*, 2016, **6**, 51221-51228.
11. M. J. Taylor, L. J. Durndell, M. A. Isaacs, C. M. A. Parlett, K. Wilson, A. F. Lee and G. Kyriakou, *Appl. Catal. B*, 2016, **180**, 580-585.
12. A. B. Merlo, V. Vetere, J. F. Ruggera and M. L. Casella, *Catal. Commun.*, 2009, **10**, 1665-1669.
13. F. Wang and Z. Zhang, *ACS Sustain. Chem. Eng.*, 2017, **5**, 942-947.
14. O. F. Aldosari, S. Iqbal, P. J. Miedziak, G. L. Brett, D. R. Jones, X. Liu, J. K. Edwards, D. J. Morgan, D. K. Knight and G. J. Hutchings, *Catal. Sci. Technol.*, 2016, **6**, 234-242.
15. Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982-985.
16. A. J. Kumalaputri, G. Bottari, P. M. Erne, H. J. Heeres and K. Barta, *ChemSusChem*, 2014, **7**, 2266-2275.
17. R. Alamillo, M. Tucker, M. Chia, Y. Pagán-Torres and J. Dumesic, *Green Chem.*, 2012, **14**, 1413-1419.
18. J. Chen, R. Liu, Y. Guo, L. Chen and H. Gao, *ACS Catal.*, 2015, **5**, 722-733.
19. G. Yi, S. P. Teong and Y. Zhang, *Green Chem.*, 2016, **18**, 979-983.
20. J. Cai, H. Ma, J. Zhang, Q. Song, Z. Du, Y. Huang and J. Xu, *Chem. Eur. J.*, 2013, **19**, 14215-14223.
21. J. Ma, Z. Du, J. Xu, Q. Chu and Y. Pang, *ChemSusChem*, 2011, **4**, 51-54.
22. J. Nie, J. Xie and H. Liu, *J. Catal.*, 2013, **301**, 83-91.
23. K. Yan, G. Wu, T. Lafleur and C. Jarvis, *Renew. Sust. Energ. Rev.*, 2014, **38**, 663-676.
24. M. Besson, P. Gallezot and C. Pinel, *Chem. Rev.*, 2014, **114**, 1827-1870.
25. Y. Nakagawa, M. Tamura and K. Tomishige, *ACS Catal.*, 2013, **3**, 2655-2668.
26. K. Zeitsch, *The chemistry and technology of furfural and its many by-products [M]*, 2000.
27. L. Wu, J. Song, B. Zhou, T. Wu, T. Jiang and B. Han, *Chem. Asian. J.*, 2016, **11**, 2792-2796.
28. D. W. Rackemann and W. O. S. Doherty, *Biofuel. Bioprod. Bior.*, 2011, **5**, 198-214.
29. A. Mukherjee, M.-J. Dumont and V. Raghavan, *Biomass Bioenerg.*, 2015, **72**, 143-183.
30. J. Zhang, S. Wu, B. Li and H. Zhang, *ChemCatChem*, 2012, **4**, 1230-1237.
31. F. liu, M. Audemar, K. De Oliveira Vigier, J.-M. Clacens, F. De Campo and F. Jérôme, *Green Chem.*, 2014, **16**, 4110-4114.
32. F. Liu, M. Audemar, K. De Oliveira Vigier, J. M. Clacens, F. De Campo and F. Jerome, *ChemSusChem*, 2014, **7**, 2089-2093.
33. W. P. Wu, Y. J. Xu, R. Zhu, M. S. Cui, X. L. Li, J. Deng and Y. Fu, *ChemSusChem*, 2016, **9**, 1209-1215.
34. T. Buntara, S. Noel, P. H. Phua, I. Melian-Cabrera, J. G. de Vries and H. J. Heeres, *Angew. Chem. Int. Ed.*, 2011, **50**, 7083-7087.
35. Z. Xu, P. Yan, W. Xu, X. Liu, Z. Xia, B. Chung, S. Jia and Z. C. Zhang, *ACS Catal.*, 2015, **5**, 788-792.
36. Y. Yang, Z. Du, J. Ma, F. Lu, J. Zhang and J. Xu, *ChemSusChem*, 2014, **7**, 1352-1356.
37. K. Gupta, D. Tyagi, A. D. Dwivedi, S. M. Mobin and S. K. Singh, *Green Chem.*, 2015, **17**, 4618-4627.
38. Z. Xu, P. Yan and Z. C. Zhang, *Chin. J. Org. Chem.*, 2016, **37**, 40-46.
39. M. Hronec and K. Fulajtarová, *Catal. Commun.*, 2012, **24**, 100-104.
40. Y. Yang, Z. Du, Y. Huang, F. Lu, F. Wang, J. Gao and J. Xu, *Green Chem.*, 2013, **15**, 1932-1940.
41. G.-S. Zhang, M.-M. Zhu, Q. Zhang, Y.-M. Liu, H.-Y. He and Y. Cao, *Green Chem.*, 2015, **18**, 2155-2164.
42. X.-L. Li, J. Deng, J. Shi, T. Pan, C.-G. Yu, H.-J. Xu and Y. Fu, *Green chem.*, 2015, **17**, 1038-1046.
43. R. Fang, H. Liu, R. Luque and Y. Li, *Green Chem.*, 2015, **17**, 4183-4188.
44. M. Hronec, K. Fulajtárova and T. Soták, *Appl. Catal. B*, 2014, **154-155**, 294-300.
45. M. Hronec, K. Fulajtárová, I. Vávra, T. Soták, E. Dobročka and M. Mičušík, *Appl. Catal. B*, 2016, **181**, 210-219.
46. J. Guo, G. Xu, Z. Han, Y. Zhang, Y. Fu and Q. Guo, *ACS Sustain. Chem. Eng.*, 2014, **2**, 2259-2266.
47. Y. Liu, Z. Chen, X. Wang, Y. Liang, X. Yang and Z. Wang, *ACS Sustain. Chem. Eng.*, 2017, **5**, 744-751.
48. M. Zhou, J. Li, K. Wang, H. Xia, J. Xu and J. Jiang, *Fuel*, 2017, **202**, 1-11.
49. J. Ohyama, R. Kanao, A. Esaki and A. Satsuma, *Chem. Commun.* , 2014, **50**, 5633-5636.
50. J. Ohyama, R. Kanao, Y. Ohira and A. Satsuma, *Green Chem.*, 2015, **18**, 676-680.
51. J. Ohyama, Y. Ohira and A. Satsuma, *Catal. Sci. Technol.*, 2017, **7**, 2947-2953.
52. D. Ren, Z. Song, L. Li, Y. Liu, F. Jin and Z. Huo, *Green Chem.*, 2016, **18**, 3075-3081.
53. G. M. Strunz, *J. Agr. Food. Chem.*, 1983, **31**, 185-190.
54. C. M. Leir, *J. Org. Chem.*, 1970, **35**, 3203-3205.
55. C. Yue, G. Li, E. A. Pidko, J. J. Wiesfeld, M. Rigutto and E. J. Hensen, *ChemSusChem*, 2016, **9**, 2421-2429.
56. Y. Zhang, J. Wang, X. Li, X. Liu, Y. Xia, B. Hu, G. Lu and Y. Wang, *Fuel*, 2015, **139**, 301-307.
57. Q. N. Xia, Q. Cuan, X. H. Liu, X. Q. Gong, G. Z. Lu and Y. Q. Wang, *Angew. Chem. Int. Ed.* , 2014, **53**, 9755-9760.
58. E. L. S. Ngee, Y. Gao, X. Chen, T. M. Lee, Z. Hu, D. Zhao and N. Yan, *Ind. Eng. Chem. Res.*, 2014, **53**, 14225-14233.
59. I. Nowak and M. Ziolek, *Chem. Rev.*, 1999, **99**, 3603-3624.
60. K. Tanabe, *Catal. Today*, 1990, **8**, 1-11.
61. Y. Duan, M. Zheng, D. Li, D. Deng, C. Wu and Y. Yang, *RSC Adv.*, 2017, **7**, 3443-3449.
62. M. Brun, A. Berthet and J. C. Bertolini, *J. Electron. Spectrosc. Relat. Phenom.*, 1999, **104**, 55-60.
63. Y. Zu, P. Yang, J. Wang, X. Liu, J. Ren, G. Lu and Y. Wang, *Appl. Catal. B*, 2014, **146**, 244-248.

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DOI: 10.1039/C7GC02310C

64 A. S. Nagpure, A. Venugopal, N. Lucas, M. Manikandan, R. Thirumalaiswamy and S. Chilukuri, *Catal. Sci. Technol.,* 2015, **5**, 1463–1472.