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Simultaneous hydrogenation and acid-catalyzed conversion of the biomass-derived furans in solvents with distinct polarities[†]

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Furfural and 5-hydroxymethylfurfural (HMF), the two typical biomass-derived furans, can be converted into biofuels and value-added chemicals *via* hydrogenation or acid catalysis or both. The potential competition between the hydrogenation and the catalyzed-conversion of HMF and furfural has been investigated with Pd/C and Amberlyst 70 as the catalysts at 170 °C in various solvents. In water, the hydrogenation of HMF or the derivatives of HMF could take place, but the acid-catalyzed conversion of HMF to the diketones (2,5-hexanedione) was the dominant reaction pathway. On the contrary, with ethanol as the solvent, the full hydrogenation of HMF to 2,5-tetrahydrofurandimethanol was the dominant route, and the acid-catalyzed routes became insignificant. The efficiency for hydrogenation of HMF was much higher in ethanol than in water. As for furfural, its hydrogenation proceeded more efficiently in the polar solvents (*i.e.* ethanol, diethyl ether) than in non-polar solvents (*i.e.* toluene): a polar solvent tended to favor the hydrogenation of the furan ring in furfural over that of the carbonyl group in the same furfural.

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Introduction

Furfural and 5-hydroxymethylfurfural (HMF) are two important furans derived from hydrolysis/pyrolysis of lignocellulosic biomass. They are the platform chemicals for manufacturing value-added chemicals or biofuels.^{1,2} The transformation of HMF and furfural usually proceeded via either acid catalysis or hydrogenation.³⁻⁷ However, hydrogenation and acid catalysis are coupled for conversion of the furans in some circumstances.8-11 One specific example is the conversion of furfural into methyltetrahydrofuran (2-MTHF), a fuel additive,12-14 which involves both acid-catalyzed dehydration reactions and hydrogenation reactions.^{15,16} From HMF to 2-MTHF also involves the acid-catalyzed degradation of HMF to levulinic acid (LA) and the subsequent dehydration/hydrogenation of LA.17,18 The acidcatalyzed reactions and the hydrogenation reactions may occur simultaneously, together determining the product distribution.

Both acid catalysis and hydrogenation are affected remarkably by the reaction environment (*i.e.* solvent and *etc.*).¹⁹⁻²³ Mediating solvent is an important strategy to control the product selectivity during the upgrading of the furans and sugars *via* either hydrogenation or acid catalysis.¹⁹⁻²³ Solvents play the roles far more than providing a reaction medium. Our previous studies have shown that the sugars and the biomassderived furans had drastically different tendencies towards the polymerization in water and in methanol.^{22,23} Upgrading of furans *via* hydrogenation coupled with acid catalysis have been investigated in a number of studies.²⁴⁻²⁸ In the co-presence of a hydrogenation catalyst and an acid catalyst, hydrogenation and acid catalysis may compete and drastically affect reaction network. Furthermore, the competition may be varied in different solvents, which, however, has not been fully understood or been purposely investigated. This is a critical knowledge gap. Understanding how acid catalysis and hydrogenation competes will provide the essential information for process optimization in biorefinery.

In this study, the hydrogenation of HMF and furfural with Pd/C only or coupled with Amberlyst 70 (A70, a commercial solid acid catalyst) were preformed in water, ethanol, methyl formate, diethyl ether, THF and toluene, respectively. The selection of Pd/C and A70 was based on the considerations that they are commercially available catalysts and were commonly employed in hydrogenation reactions or acid-catalyzed reactions. The selection of the solvents was based on the consideration of their distinct polarities. The competition between the acid catalysis and hydrogenation in the varied reaction environments was explored.

Our results demonstrated that (1): in water, the acidcatalyzed conversion of HMF was dominate, while, in ethanol, the hydrogenation of HMF was dominant; (2): the hydrogenation of furfural proceeded more efficiently in polar solvents than in non-polar solvents; (3) polarities of the solvents strongly affect the reactivities of the furan ring and the carbonyl group in

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furfural towards hydrogenation; (4): in the co-presence of Pd/C and A70 catalysts, the dominance of the hydrogenation reaction could suppress, but not terminate the polymerization of HMF or furfural; (5) synergistic effects between Pd/C and A70 was observed. A70 catalyzed the dehydration of hydroxyl groups to form carbon–carbon double bonds or π -conjugated structures, while Pd/C catalyzed the hydrogenation of these unsaturated functionalities, which worked together to eliminate the oxygen in the furans or their derivatives.

Experimental

Hydrogenation of the furans was carried out in a Hastalloy autoclave reactor (Autoclave Engineers, Division of Snap-Tite Inc. volume; 100 ml). Experimental procedures were similar to that published elsewhere.²⁹ Typically, 2 g of HMF or furfural together with 40 ml of solvent as well as 0.5 g of Pd/C catalyst and/or 0.5 g of A70 catalyst were used. Forty bar hydrogen was fed into the reactor before heating to 170 °C in *ca.* 10 min with a stirring rate of 350 rpm. Additional hydrogen was fed at 170 °C to maintain 70 bar throughout the experiment. After holding at 170 °C for 60 min, the products were quenched with a cooling coil inside the reactor vessel. The liquid products and the catalysts were collected together and were separated after the catalyst was settled down in the bottom of the sample container. The selection of 170 °C as the reaction temperature was based on the consideration that the maximum operating temperature for A70 is 190 °C. GC-MS, UV fluorescence spectrometer and FT-IR were used to analyze the products. Details for the procedures can refer to our previous work.^{20,29} Not all products can be identified with the GC-MS spectral library (NIST MS Search 2005). Thus, some products were identified by analyzing their mass spectrum. The proposed reaction pathways for dissociation of these products in the mass spectrometer were presented in the ESI.† It is difficult to obtain standards for all the products for quantification. Thus, relative proportion of the compound, which was calculated by the peak area of this compound divided by total peak area of all the products in the spectrum, was used to understand their relative abundance in the products.

Results and discussion

Conversion of HMF in water

HMF has an unsaturated furan ring and a carbonyl group, which was expected to be fully hydrogenated to form 2,5-tetrahydrofurandimethanol (TFDM) with Pd/C as the catalyst. However, the relative proportion of TFDM was quite small (Scheme 1). The main products were 2,5-hexanedione and 5hydroxy-2-hexanone. 2,5-Hexanedione was probably formed *via* the reverse of the Paal–Knorr synthesis.^{30,31} The Paal–Knorr synthesis is a reaction to synthesize furans or pyrroles from 1,4diketones, which is catalyzed by acids.^{30,31} 2,5-Hexanedione is a 1,4-diketones and opening of the furan ring *via* the reverse Paal–Knorr synthesis was a possible route for its formation.



Scheme 1 Distribution of the typical products in hydrogenation of HMF in water in the absence and presence of A70 catalyst. Reaction conditions: HMF: 2 g; Pd/C: 0.5 g; A70: 0.5 g; solvent: 40 ml; T = 170 °C; P_{H_2} at 170 °C = 70 bar; reaction time: 60 min; stirring rate: 350 rpm. Reaction conditions for those in other schemes were similar. "(x%)" is relative proportion of the product in all products. "(Yield: x%)" is the yield of the product. Conversions of HMF were >99% under the conditions specified above. GC-MS spectra for the products are presented in Fig. S1 in ESI.† 5-Hydroxy-2-hexanone was identified by manually analysing its mass spectrum (Fig. S2 and S3†). It needs to note here that the mass balances in the above experiments is less than 100%. This is because a number of unknown products could not be identified by the library of the GC-MS, as shown in Fig. S1.†

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In the absence of A70, the formation of the significant amount of 5-hexanedione and 5-hydroxy-2-hexanone in water indicates that the hydrogenation of the furan ring was not efficient. HMF has the chance to be converted *via* the reverse Paal– Knorr synthesis before the hydrogenation of the furan ring. Water might act as an acid catalyst to promote the opening of the furan ring under the subcritical conditions. The presence of the strong acid catalyst, A70, further promoted the ring opening reactions, leading to the formation of more 2,5-hexanedione and more 5-hydroxy-2-hexanone (Scheme 1). In addition, small amount of LA (yield: 4%) was also produced in the presence of A70. From the conversion of HMF to LA several intermediates with unsaturated ring structures or doubles bonds were invoved.³² These unsaturated species had the chance to make their ways to LA.

Both LA and 2,5-hexanedione were formed *via* the acidcatalyzed reactions. These results confirm that the hydrogenation of HMF in water was not taken place effectively, and the acid-catalyzed reactions were dominant, even in the absence of A70. The presence of A70 further promoted the acid-catalyzed reactions. The characterization of the liquid products with FT-IR also proved that the hydrogenation was not efficient in water as the unsaturated carbon–carbon double bonds could still be detected (Fig. 1a).

Water has a relatively higher acidity than ethanol at the subcritical or supercritical conditions. This might be the reason for the high efficiency for the acid-catalyzed conversion of HMF in water. It was reported that the hydrolysis of biomass in organic



Fig. 1 Characterisation of the liquid products in hydrogenation of HMF in water and ethanol with FT-IR. The liquid samples were diluted with methanol/chloroform (volume/volume: 1/4) to 2 wt% before the characterisation.

solvents or the mixture of organic solvents and water are more efficient than in water.³³ The organic solvents such as γ -valerolactone could prevent the re-precipitation of by-products derived from lignin on the surface of cellulose, which helps to maintain accessibility to the reactive cellulose surface. In comparison, water itself could not effectively suppress the reprecipitation. This may be the reason for the relatively low efficiency for the hydrolysis of biomass with water as the sole solvent. However, in the conversion of the simple molecules like HMF, which does not have a complex macro polymeric structure, no such a problem (the re-precipitation) is existed. HMF could be converted efficiently in water *via* the acid-catalyzed routes.

Although water was found not to be the good solvents for the hydrogenation of HMF in this study, it was regarded as the good one for the hydrogenolysis of lignin derived phenolics^{34,35} or the oxidation of HMF.³⁶ The lignin derived phenolics have the either bonds and the benzene ring structures. Under subcritical conditions water behaves as an acid, which might help to break down the ether bond in lignin.

The furan ring in HMF, however, could not be effectively hydrogenated in water, while the benzene ring structures could. Although both the furan ring and the aromatic ring in the lignin derived compounds have aromaticity, their reactivities towards hydrogenation or acid-catalysis are probably different. The oxygen in the furan rings could facilitate the ring-opening reactions of the furans *via* acid catalysis while in water opening the aromatic ring *via* acid-catalyzed reactions is relatively difficult.

Conversion of HMF in ethanol

In ethanol, the acid-catalyzed reactions were no match with the hydrogenation reactions (Scheme 2). HMF had virtually no chance to form LA or ethyl levulinate. The fully hydrogenated products (*i.e.* TFDM) were the dominated ones. Characterization of the liquid products with FT-IR showed that the abundance of the carbon double bonds was negligible in ethanol while that in water was significant (Fig. 1). Solubility of hydrogen is much higher in ethanol than in water,³⁷ which might be a reason for the high efficiency of hydrogenation in ethanol.

Ethanol also affected the distribution of the products in a way different from water. TFDM and tetrahydro-5-methyl-2furanmethanol (TMFE) were dominant. Ethanol is less acidic than water, which might negatively affect its capability and involvement in the ring-opening reactions. However, in the presence of the strong acid catalyst, A70, the amounts of 2,5hexanedione formed were still small (0.6% versus 0.9% in the absence of A70). Thus, the low acidity of ethanol was not the main reason for the formation of the significantly less amount of 2,5-hexanedione in ethanol. The hydrogenation of the furan ring in HMF probably proceeded very quickly in ethanol, and thus the conversion of HMF to 2,5-hexanedione via the reverse Paal-Knorr synthesis was significantly suppressed. This was also confirmed by the result that HMF virtually had no chance to form levulinic acid/ethyl levulinate after the hydrogenation of the furan ring.



Scheme 2 Distribution of the typical products in hydrogenation of HMF in ethanol in the absence and presence of A70 catalyst. Conversions of HMF were >99% under the conditions specified above. GC-MS spectra for the products are presented in Fig. S4 in ESI.† ETHM was identified by analyzing its mass spectrum manually (Fig. S5 and S6†).

In ethanol, A70 promoted the formation of TMFE (relative proportion: 18.1% without A70 *versus* 27.0% with A70). This indicated that the dehydration of the hydroxyl group in TFDM followed by hydrogenation was promoted by the acid catalyst. A70 also promoted the formation of tetrahydropyran-2-carbinol (THPC) (1.5% *versus* 9.7%). These ring-containing products were preserved in ethanol.

In presence of an acid-catalyst, the decomposition of HMF is always followed by polymerization.³⁸ In the absence of A70, the soluble polymer was not detected with a UV florescence spectrometer in the hydrogenation of HMF with either water or ethanol as the solvent (Fig. 2). The hydrogenation reactions helped to eliminate the polymerization reactions. However, in the presence of A70, the soluble polymers were still detected. The soluble polymer could grow bigger (longer wavelength) in water than in ethanol. However, the size of the conjugated π bond structures in the soluble polymer was smaller than that in acid-catalyzed conversion of HMF, where peak of the soluble polymer was centred at 319 nm.³⁹ The polymerization of HMF was clearly suppressed under the hydrogenation conditions, even in the presence of A70.

The above results showed that water and ethanol affected the conversion of HMF *via* the hydrogenation/acid catalysis in very different ways. This encouraged us to explore the conversion of furfural, another important biomass-derived furans, in the various solvents with Pd/C and/or A70 as the catalysts.

Conversion of furfural in ethanol

In ethanol, tetrahydrofurfuryl methanol (TFM) and 2ethoxymethyl-tetrahydrofuran (EMTF), the ring-containing products, were the major ones in the hydrogenation of furfural (Scheme 3). No significant amounts of ring-opening products were detected. The ring-containing products could be preserved in hydrogenation of furfural in ethanol, which was similar to the results in hydrogenation of HMF in ethanol. TFM



Fig. 2 Constant energy (-2800 cm^{-1}) synchronous spectra for the soluble polymer formed in hydrogenation of HMF in water and ethanol. The products were diluted in methanol to 3200 ppm before the determination.

was the main product but it was further converted into EMTF *via* the etherification even without A70, while the presence of A70 remarkably promoted the formation of EMTF.

A small amount of ethyl levulinate was also formed (yield: 2.5%) in the presence of A70 (Scheme 3). Furfuryl alcohol (FA) was the intermediate from furfural to levulinates.²³ It was produced from the partial hydrogenation of furfural. Apparently, in the presence of A70, FA had a certain chances to be further converted into ethyl levulinate before its full hydrogenation to TFM. The conversion of FA into LA proceeded very quickly even at 130 °C,²³ which was probably the reason for the

formation of ethyl levulinate from furfural here. In addition to FA, trace amount of tetrahydrofuran-2-carbaldehyde (THFC) was also detected, indicating that the hydrogenation of the furan ring and the carbonyl group in furfural might not proceed *via* a specific sequence, which will be discussed further below.

Conversion of furfural in methyl formate

In methyl formate, the yield of TFM (Scheme 4) was remarkably lower than that in ethanol. This was due to the formation of tetrahydrofurfuryl acetate *via* the esterification between TFM and the formic acid produced by the dissociation of methyl formate or the transesterification. The formation of tetrahydrofurfuryl acetate was further promoted over A70. More interestingly, methyl formate affected the hydrogenation of the furan ring and the carbonyl group of furfural in a different way.

Both the furan ring and the carbonyl group in furfural could be hydrogenated, but it was more difficult to hydrogenate the carbonyl group than the furan ring of furfural in methyl formate, as evidenced by the higher relative proportion of THFC than that of FA (Scheme 4). Methyl formate has an ester group with a relatively polar C–H bond (H–COOCH₃) as the carbon is connected to the oxygen with a high electron-withdrawing capability. Thus, the carbonyl group in furfural might form hydrogen bonds with methyl formate, increasing the difficulty for its hydrogenation. The conjugated π bonds in furfural, however, could not form the hydrogen bonds, which might be the reason for its higher reactivity towards hydrogenation.

Conversion of furfural in diethyl ether

The solvents with ether group (diethyl ether) and hydroxyl group (ethanol) had very different impacts on the hydrogenation reactions. As can be seen from Scheme 5, the yields of TFM were significantly higher in diethyl ether than in ethanol. Diethyl ether did not react with TFM to form EMTF in the absence of A70. More importantly, the acid-catalyzed reactions could not compete with the hydrogenation reactions in diethyl ether. No FA was detected while the amount of LA formed was quite small.



Scheme 3 Distribution of the typical products in hydrogenation of furfural in ethanol in the absence and presence of A70 catalyst. Conversions of furfural were >99% under the conditions specified above. GC-MS spectra for the products are presented in Fig. S7 in ESI.† EMTF (Fig. S8 and S9†) and THFC (Fig. S10 and S11†) were identified by analyzing its mass spectrum manually.



Scheme 4 Distribution of the typical products in hydrogenation of furfural in methyl formate in the absence and presence of A70 catalyst. Conversions of furfural were >99% under the conditions specified above. GC-MS spectra for the products are presented in Fig. S12 in ESI.†



Scheme 5 Distribution of the typical products in hydrogenation of furfural in diethyl ether in the absence and presence of A70 catalyst. Conversions of furfural were >99% under the conditions specified above. GC-MS spectra for the products are presented in Fig. S13 in ESI.†

Hydrogenation of the furan ring possibly proceeded more efficiently in diethyl ether than in ethanol or in methyl formate. Consequently, furfural had little chance to go to FA or LA. Similar to that in methyl formate, the formation of THFC was favoured in diethyl ether. The hydrogenation of the furan ring was very quick, leaving little chance for the formation of LA from FA.

Conversion of furfural in THF

THF is a cyclic ether, and it behaved quite differently from diethyl ether as the solvent for the hydrogenation of furfural (Scheme 6). Hydrogenation of the furan ring was not efficient in THF, and furfural had the chance to be converted into FA and then into LA, especially in the presence of A70. In addition, there were also some interesting products formed with THF as the solvent. For example, gamma-valerolactone (GVL) is a product from the hydrogenation/dehydration of LA.^{40,41} It was detected only when THF was used as solvent. Clearly, LA could be hydrogenated and then dehydrated to form GVL in THF.

Di-tetrahydrofuran methyl ether formed from the intermolecular etherification of TFM was also detected. Some even much bigger compounds, the soluble polymers, were formed in not only THF but also in other solvents (Fig. 3). Furfural has a very high tendency towards polymerization at the elevated temperatures.⁴² It polymerizes in the presence of Pd/C catalyst to a small extent, but to a more pronounced extent with the copresence of A70 (Fig. 3). The size of the π -conjugated structures were smaller than that in acid-treatment of furfural with only A70 as the catalyst, where a intensified peak centered at 379 nm



Scheme 6 Distribution of the typical products in hydrogenation of furfural in THF in the absence and presence of A70 catalyst. Conversions of furfural were >99% under the conditions specified above. GC-MS spectra for the products are presented in Fig. S14 in ESI.† Di-tetrahydrofuran methyl ether was identified by analyzing its mass spectrum manually (Fig. S15 and S16†).



Fig. 3 Constant energy (-2800 cm^{-1}) synchronous spectra for the soluble polymer formed in hydrogenation of furfural in the various solvents. The products were diluted in methanol to 3200 ppm before the determination.

were observed.³⁹ The presence of hydrogen and Pd/C catalyst could limit the growth of the soluble polymer, but could not completely prevent the polymerization of furfural.

Conversion of furfural in toluene

The product distribution during the hydrogenation of furfural in toluene (Scheme 7) was very different from that in other solvents. In the presence of A70, TFM formation was decreased in ethanol, methyl formate, diethyl ether and THF, due to the competition between hydrogenation and acid catalysis. However, in toluene, TFM formation was even increased to a small extent in the co-presence of Pd/C catalyst and A70 catalyst, which was opposite to that in other solvents.

A70 is a solid acidic resin catalyst bearing the polar acidic sites $(-SO_3H)$ on its local surface. It cannot swell effectively in

toluene and hence majority of the acidic sites on the inner surface are not accessible.⁴³⁻⁴⁵ Thus, TFM formation in toluene was not affected much by A70 catalyst. The methyl-cyclohexane formed from the hydrogenation of toluene was also not affected much by the presence of A70 (2.3% without A70 *versus* 2.4% with A70). This result further confirmed the negligible effect of A70 on the hydrogenation reactions in toluene.

The relative proportion of THFC and the yields of FA were remarkably higher in toluene than in other solvents (Scheme 7). Further to this, even in the presence of A70, the abundance of THFC did not decrease significantly. Both THFC and FA have the unsaturated double bonds, but they could not be effectively hydrogenated in toluene. In addition, trace amount of furfural still could be detected at the end of the test in toluene but not in other solvents. This indicated the relatively low hydrogenation



Scheme 7 Distribution of the typical products in hydrogenation of furfural in toluene in the absence and presence of A70 catalyst. Conversions of furfural were >99% under the conditions specified above. GC-MS spectra for the products are presented in Fig. S17 in ESI.†

efficiency in toluene. Both toluene and furfural have the conjugated π bonds and toluene is a very good solvent to extract furfural. It was possible that the interaction between furfural and toluene had a shielding effect, negatively affecting the hydrogenation of the furan ring and the carbonyl group in furfural.

In the relatively polar solvents such as methyl formate, diethyl ether and THF, the hydrogenation of the furan ring in furfural proceeded more efficiently than the hydrogenation of the carbonyl group, as evidenced by the presence of the relatively higher abundance of THFC. In toluene, no such effect was observed. Hydrogenation of the furan ring and the carbonyl group in furfural proceeded in parallel, producing THFC and FA with the similar relative proportions (9.8% *versus* 8.7%). This result, from an opposite angel, confirmed that the hydrogenation of the furan ring in furfural was more favorable in the polar solvent.

Solvent dielectric constant versus TFM formation

In the absence or presence of A70, the difference in terms of TFM yields was significant in the solvents investigated but except that in toluene. The solvents affected the competition between the hydrogenation and the acid catalysis in different ways. TFM was the main product from furfural in the various solvents *via* either hydrogenation or hydrogenation coupled with acid catalysis. The ratio of its yields in the absence and the presence of A70 could roughly indicate the effect of A70 on the hydrogenation of furfural.



Fig. 4 (a) Ratio of TFM yields in the presence of Pd/C and A70 to the TFM yields in the presence of Pd/C in the various solvents. (b) Dielectric constants of the solvents. ^aThe ratio calculated in methyl formate also included that of tetrahydrofurfuryl acetate. The ratio calculated based on only TFM yields was presented in Fig. S18.[†]

As can be seen in Fig. 4a, in toluene, the ratio between the TFM yield in the presence of A70 and in the absence of A70 was above 1. The effect of A70 on the formation of TFM was not remarkable. In comparison, the yields of TFM varied significantly in ethanol in the presence and the absence of A70 with the ratio of *ca.* 0.5. One important difference between toluene and ethanol is their distinct polarities. This inspired us to correlate dielectric constants of the solvents with their effects on TFM formation. It was found that the ratio of TFM yields without A70 to that with A70 (Fig. 4a) followed an opposite trend to the dielectric constants from ethanol to toluene (Fig. 4b). Clearly, the effect of A70 on the hydrogenation reactions was more pronounced in the polar solvent than in the non-polar solvent.

In addition, in toluene, the ratio of the THFC abundance in the absence and the presence of A70 were also much higher in toluene (0.8) than in methyl formate (0.3) or THF (0.4). This further confirmed the insignificant effect of A70 on the hydrogenation reactions in toluene. Solvent polarity has been known to significantly affect behaviors of the solid acid catalysts.⁴⁴⁻⁴⁶ The solid acidic resin catalyst cannot swell effectively in the non-polar solvent such as toluene. Therefore, the effect of the acid catalyst on the hydrogenation reactions was compromised in toluene.

Roles of the solvents in the conversion of the furans

According to the above results, it was found that the solvents used for the acid-catalyzed conversion and hydrogenation of the furans was not just a reaction medium, but affected the conversion of the furans in many ways. Firstly, solvent remarkably affected the reaction pathways of the furans. For example, in water the acid-catalyzed conversion of HMF to 1,4diketones was dominant while in ethanol the hydrogenation of HMF was dominant (Scheme 1 and 2). Secondly, solvents can be the reactants and could modify the reaction network. For example, ethanol or methyl formate reacts with the furans or the reaction intermediates (Scheme 2 and 4), which significantly changed the product distributions. Thirdly, solvents can affect the catalytic behaviors of the acid catalysts. A70 catalyst used in this study could swell effectively in the polar solvents like alcohols but not in the less polar solvents like toluene,44 which affected the competition of the acid-catalyzed reactions and the hydrogenation reactions. Fourthly, solvents affected the solubility of hydrogen, which might further affect the hydrogenation reactions. The solubility of hydrogen is much higher in ethanol than in water,33 which might be the reason for the relatively high efficiency of hydrogenation of HMF in ethanol. Fifthly, the properties of the solvents also affected the conversion of the furans. For example, the polar solvent tended to favor the hydrogenation of the furan ring over the carbonyl groups of furfural (Fig. 4). In the less polar solvents like toluene, the furan ring and the carbonyl groups had almost the equal chance to be hydrogenated. The competitive absorption between the solvents and hydrogen is also one factor that might affect the conversion of furans, which needs further investigation.

Conclusions

Potential competition of the acid-catalyzed conversion and the hydrogenation of HMF and furfural were investigated in the solvents with distinct polarities with A70 and Pd/C as the catalysts. Our results showed that the solvents significantly affected the reaction pathways of the furans and the dominance of the hydrogenation or the acid-catalyzed reactions in the solvents. In the co-presence of A70 catalyst and Pd/C catalyst, the acid-catalyzed conversion of HMF was dominant in water while the hydrogenation of HMF was dominant in ethanol. The hydrogenation reactions were the preferred routes in ethanol while the acid-catalyzed reactions were effectively suppressed even in the presence of A70. In water, it is *vice versa*. The distinct reactivities of HMF towards hydrogenation and acid catalysis in water and in alcohols need to be considered during the upgrading of HMF to other value-added chemicals.

The competitive conversions of furfural *via* the acidcatalyzed routes or the hydrogenation routes were affected significantly by polarities of the solvents. The hydrogenation of furfural proceeded more effectively in the polar solvents than in the non-polar solvents. In addition, in polar solvents the furan ring in furfural was more reactive towards hydrogenation than the carbonyl group in furfural. In the non-polar solvents, their reactivities towards hydrogenation were similar. During upgrading of the furans, the competition between acid catalysis and hydrogenation in the varied solvents should be taken into consideration and be controlled to facilitate the production of the targeted products.

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