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Hydrodeoxygenation of HMF Over Pt/C in a Continuous Flow Reactor

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The three-phase hydrodeoxygenation reaction of 5-hydroxymethylfurfural (HMF) with H_2 was studied over a 10 wt % Pt/C catalyst using both batch and flow reactors, with ethanol, 1-propanol, and toluene solvents. The reaction is shown to be sequential, with HMF reacting first to furfuryl ethers and other partially hydrogenated products. These intermediate products then form dimethyl furan (DMF), which in turn reacts further to undesired products. Furfuryl ethers were found to react to DMF much faster than HMF, explaining the higher reactivity of HMF when alcohol solvents were used. With the optimal residence time, it was possible to achieve yields approaching 70% in the flow reactor with the Pt/C catalyst. Much higher selectivities and yields were obtained in the flow reactor than in the batch reactor because side products are formed sequentially, rather than in parallel, demonstrating the importance of choosing the correct type of reactor in catalyst screening. © 2014 American Institute of Chemical Engineers *AIChE J*, 61: 590–597, 2015
Keywords: 5-hydroxymethylfurfural, hydrodeoxygenation, dimethyl furan, continuous flow reactor, platinum catalyst

Introduction

5-Hydroxymethylfurfural (HMF) can be formed in reasonably high yields by dehydration of C-6 sugars[1–3]; however, because of its high degree of functionality, it is too reactive for many applications. To make use of it in fuels, it has been proposed to first hydrogenate the carbonyl group to an alcohol, then form a diether by reaction with simple alcohols.[4] Alternatively, HMF can undergo hydrodeoxygenation (HDO) to 2,5-dimethylfuran (DMF). DMF has a high energy density and octane rating[5] and can also be converted to p-xylene with high yields by reaction with ethylene over zeolite catalysts.[6] Because pressurized H_2 is expensive, it is usually desirable to avoid both ring opening and hydrogenation of the furan ring.

The upgrading of HMF to DMF has been studied by a large number of groups but achieving high selectivities and good catalyst stabilities remain problems. For example, Román-Leshkov et al.[7] demonstrated reasonable yields, up to 71%, for the conversion of HMF to DMF using H_2 and a carbon supported, CuRu alloy catalyst. However, that group also reported their catalysts suffered deactivation, caused in part by the presence of chloride species in their reaction system. Bell et al.[8] investigated the hydrogenation of HMF in ionic liquids using Pd/C as catalyst but observed the low DMF yields, around 15%, and difficulties with product separation. Although Thananatthanachon and Rauchfuss[9] achieved a 95% yield to DMF over Pd/C in the presence of sulfuric acid, using formic acid as the hydrogen source, the reaction required refluxing of the solvent and had the added complication of using formic acid as a reactant. In a related approach, Jae et al.[10,11] performed HDO of HMF over Ru/C using an alcohol as the hydrogen donor and achieved greater than 80% yield to DMF. Interestingly, they reported that high selectivities required the presence of both Ru and RuO_2, with the oxide presumably acting as a Lewis acid for catalyzing hydrogen transfer via the Meerwein–Ponndorf–Verley reaction.

Several very recent studies suggest that higher yields to DMF are possible, even using a H_2 source. For example, Wang et al.[12] reported yields as high as 98% using PtCo, bimetallic nanoparticles encased in hollow carbon nanospheres. They reported much lower yields with Pt-only catalysts and suggested that the high yields were possible with the PtCo@C catalysts because the carbon nanospheres maintained very small metal particle sizes and allowed for homogeneous alloying of the metal. Similarly, Nishimura et al.[13] obtained yields as high 96% for HMF to DMF with atmospheric H_2 over a PdAu, bimetallic catalyst when HCl was added to promote hydrogenolysis. In general, it seems clear that alloy catalysts are more selective for HDO reactions than their pure metal counterparts.[14–18]

However, some have also reported good yields for HDO of HMF with more conventional catalysts. For example, Hu et al. reported a 95% yield to DMF on a rather conventional Ru/C catalyst.[19] Indeed, there are often big variances in the

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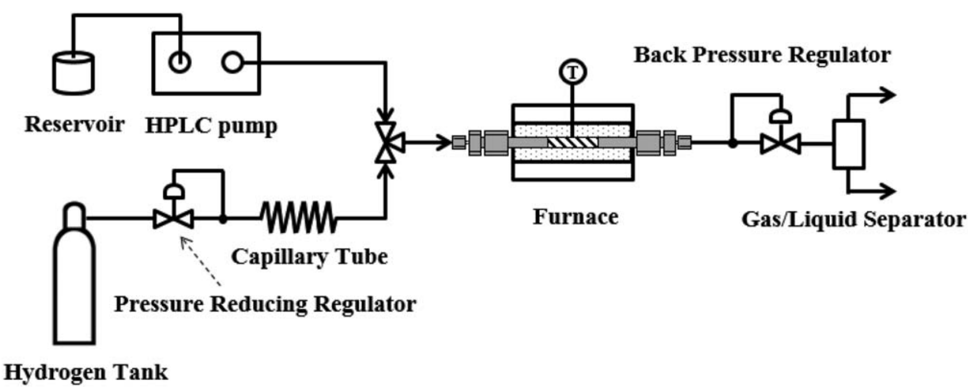


Figure 1. Diagram of the continuous flow reactor.

yields reported by different groups for materials of similar composition. A major problem in comparing rates and selectivities between groups is that the reaction conditions are almost never the same. With liquid-phase hydrogenations, contact between the solid catalyst, the liquid-phase reactant, and the gas-phase H_2 can be ineffective. When the catalyst is completely immersed in the liquid reactant–solvent mixture, diffusion of H_2 to the catalyst surface is likely to limit reaction. Mass transfer will be highly dependent on the volume and shape of the reactor and the methods used for mixing. Furthermore, in batch reactions carried out in an autoclave, reactions can occur during the heating and cooling periods.

Therefore, to determine the importance of the reactor geometry, we have examined HDO of HMF in both batch and tubular-flow reactors using the same Pt/C catalyst. In contrast to the common view that side products are formed in parallel with DMF, we will show that the formation of DMF from HMF can be viewed as a part of a sequence of reactions in which DMF is an intermediate product that goes on to form other products, so that the yields to DMF can be dramatically improved in the flow reactor with the proper residence time. Although previous work showed limited activity and selectivity with Pt/C catalysts,[12] this catalyst was found to be reasonably active and selective under flow conditions. By varying the space velocity, measurements in the flow reactor also allowed us to observe the sequence of reactions that occur during HDO of HMF and helped to explain some of the reasons for the poor selectivities in the batch experiments.

Experimental

A carbon-supported catalyst with 10 wt % Pt was prepared by impregnation of carbon black (Vulcan XC-72R) with a water/ethanol (5:1) solution of tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$, 99.99%, Alfa Aesar). The dried powders were heated in He flow at 500°C for 6 h using a heating ramp of 3°C min^{-1} and then used directly in the reactor without further pretreatment. After reduction in H_2 at 400°C, the Pt dispersion was determined to be 18% by CO chemisorption.

The batch measurements were performed in a 100 mL stainless steel Parr reactor using 0.05 g of catalyst. The reactor was charged with reactants, then sealed, purged with H_2 and pressurized with H_2 to 33 bar. The reactor was heated to 180°C with a silicon oil bath and mixing was accomplished with a magnetic stirrer. After the reaction, the reactor was quenched in ice water and the liquid products were collected, filtered, and analyzed. The liquid products were identified with a GC–MS (Shimadzu GCMS-QP2010 Plus) while the gas products were analyzed using a GC (Agilent 7890A) equipped with a flame ionization detector. To determine the effect of reaction time, the reactor was held at 180°C between 0 and 8 h; however, it took approximately 30 min to heat and cool the reactor, so that the reactant mixture was in contact with the catalyst for relatively long times in all cases. Additional details about the batch-reactor experiments can be found elsewhere.[10,11]

A schematic diagram of the flow reactor used in most of the reaction measurements is shown in Figure 1. The reactor was a stainless-steel tube, 20-cm long, with a 4.6-mm ID. In most cases, 0.05 g of catalyst was packed into the middle portion of the tube and held in place by glass wool. An inert glass tube was placed within the stainless-steel tube, downstream from the catalyst, to reduce the empty volume of the reactor and to prevent the catalyst bed from being pushed out of the heated zone by the reactant flow. The liquid feed, a mixture of 1 g HMF (99%, Sigma-Aldrich) in 100 mL of solvent (1-propanol, ethanol or toluene), was introduced into the reactor at a controllable flow rate via an HPLC pump (Series I+, Scientific Systems), which was also used to measure the total pressure in the reactor. The pressure within the reactor was controlled by a back-pressure regulator (KPB series, Swagelok) placed at the reactor exit. The H_2, UHP grade from Airgas, was supplied from gas cylinder, equipped with a regulator for high pressure delivery (Airgas). To control the H_2 flow rate, the outlet from the regulator was connected to the reactor through 8 ft of 0.002-in. ID capillary tubing (Valco Instruments). The H_2 flow rate was calibrated in separate experiments as a function of the pressure and the pressure drop across the capillary tube. The liquid flow rates could be varied from 0.02 to 0.2 mL/min while the H_2 flow rates were 2 to 20 mL/min (STP). To vary the space velocity in the reactor at fixed experimental conditions, the ratio of liquid and gas flow rates was kept constant. A bubble meter at the reactor exit was used to check continuously that the H_2 flow rates were maintained.

Prior to rate measurements in the flow reactor, the catalyst was pretreated at 250°C in 1 bar of flowing H_2 for 30 min. Because the products left the reactor at room temperature, product analysis was carried out using a syringe to inject the liquid effluent from the reactor into a GC-MS (QP-5000, Shimadzu), equipped with a capillary column (HP-Innowax,

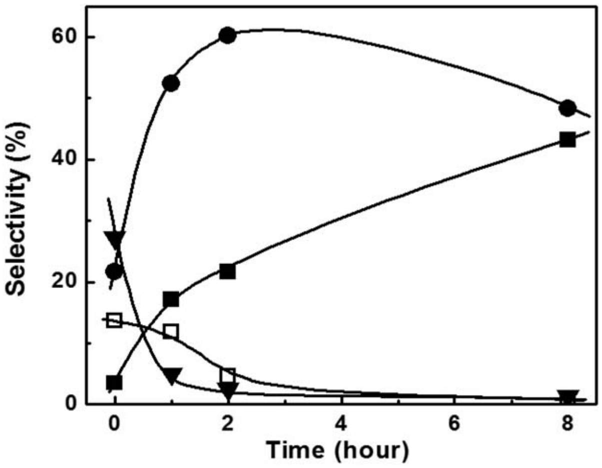


Figure 2. Product distribution for HMF hydrogenolysis in 1-propanol in the batch reactor.

Reaction conditions: 10 wt % Pt/C, 33 bar, and 180°C. (•) DMTHF, (▼) DMF, (□) 2-hexanone, (■) 2-hexanol. The HMF conversion was 100% for all conditions.

Agilent Technologies). The gas-phase products were also examined but, under the conditions of these experiments, were found to consist of only H_2 and solvent vapor in significant amounts. The conversion of HMF and the yield of the two major products, DMF and mono-ether-furfural alcohol (EFA), were quantified using standard solutions with varying concentrations. For the quantification of other products, we assumed that the GC sensitivity was the same as that for HMF. As most of these other products were produced in relatively small quantities, this assumption will not have a major impact on the conclusions of this work. Based on these measurements, the carbon balance (from the HMF) was always better than 93%. The fact that rates were stable for at least 5 h under all reaction conditions provides further evidence that minimal amounts of product were deposited onto the catalysts during the course of the reactions.

To better understand the sequence of HDO reactions, the reactivities of DMF and of furfuryl ethers were also studied. With DMF, a solution containing 0.76 g of DMF in 100 mL of 1-propanol (This is the same molar concentration as that used in the HMF experiments.) was introduced into the reactor with a flow rate of 0.2 mL/min, together with 20 mL/min (STP) H_2 flow. To study the reactivity of furfuryl ethers, the tubular reactor was packed with two beds of catalysts: 0.4 g of 15 wt % ZrO_2/SBA-15 at the front and 0.05 g of 10 wt % Pt/C at the rear. The synthesis and characterization of the ZrO_2/SBA-15 catalyst has been described in detail in the earlier study and shown to have a mixture of weak Brønsted and Lewis sites.[20] In that previous study, HMF was shown to react with 2-propanol over ZrO_2/SBA-15 to provide high yields of propyl-ether-furfuryl alcohol and di-propyl ether, 2,5-bis[(1-methylethoxy)methyl]furan, so that the presence of this catalyst at the entrance to the reactor was a way to introduce the ethers to the Pt/C catalyst.

For the conditions of this study, no reaction was observed in the absence of a catalyst in the flow reactor. Also, no products were formed in reaction measurements on the carbon support that had been washed with an NH_4NO_3 solution to simulate the conditions used in Pt impregnation.

Results

Batch reactor, HMF in 1-propanol

Results from the batch reactor measurements are summarized in Figure 2. The experiments were carried out at 180°C with 33 bar H_2 and 1 wt % HMF in 1-propanol, with varying reaction times from 0 to 8 h. The 0-h experiment was performed by immediately quenching the Parr reactor after the temperature ramp reached 180°C, which took approximately 30 min. Even in the 0-h experiment, the conversion of HMF was 100%. The yield of DMF was highest for the 0-h case (27.2%) and decreased steadily with time. Many side products were formed, including compounds with higher molecular weights, open-ring compounds, and hydrogenated-ring compounds. Significant amounts of 2,5-dimethyl tetrahydrofuran (DMTHF) were observed in all cases. 2,5-Hexanedione and hexane were also found but in yields less than 10%. These results are in good agreement with those found by Wang et al.[12] under similar reaction conditions. The fact that the highest DMF yield was achieved in the 0-h experiment implies that shorter contact times are required to maximize selectivity.

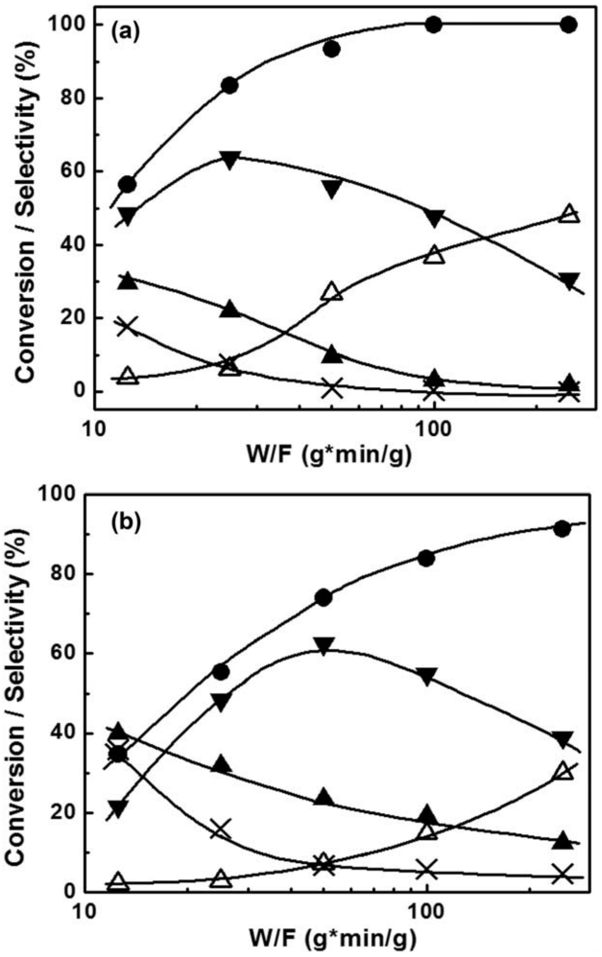
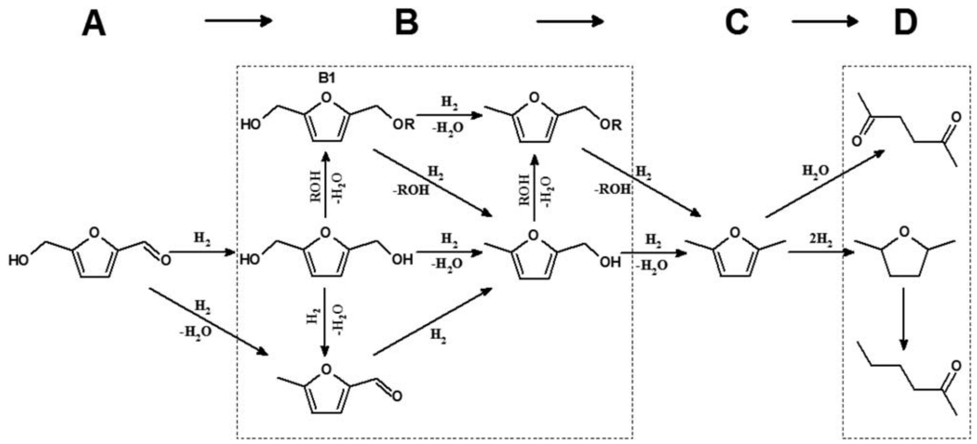


Figure 3. Product distribution for HMF hydrogenolysis in 1-propanol as a function of space time in the flow reactor.

Reaction conditions: 10 wt % Pt/C, 33 bar, and (a) 180°C, (b) 140°C. (•) HMF conversion, (▼) DMF, (▲) EFA, (×) B2, (Δ) D.



Scheme 1. Reaction network for HMF hydrodeoxygenation using alcohols as solvent.

Table 1. Product Distribution for HDO of HMF Over 10 wt % Pt/C in 1-Propanol, Under 180°C and 33 Bar

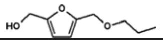
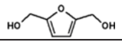
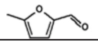
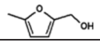
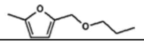
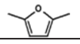
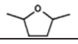
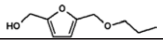
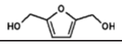
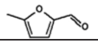
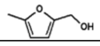
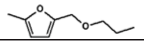
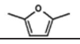
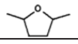
W/F (g min/g)	Conv. %	B1	B2				C	D		
									Open-Ring	Unknown
12.5	56.3	29.6	8.3	1.5	4.1	3.8	48.5	<1	3.2	<1
25	83.4	21.9	3.1	<1	2.1	1.4	63.7	1.5	4.6	<1
50	93.4	9.7	<1	–	<1	–	55.9	4.3	22.5	6.6
100	100	3.0	<1	–	–	–	47.8	7.7	29.1	12.1
250	100	1.8	–	–	–	–	30.7	10.1	37.8	19.6

Table 2. Product Distribution for HDO of HMF Over 10 wt % Pt/C in 1-Propanol, Under 140°C and 33 Bar

W/F (g min/g)	Conv. %	B1	B2				C	D		
									Open-Ring	Unknown
12.5	34.8	40.0	21.2	2.3	8.4	4.0	21.6	<1	1.8	<1
25	55.3	31.9	8.4	1.1	3.7	2.9	48.3	<1	2.3	<1
50	74.0	23.5	3.7	<1	1.4	1.3	62.5	1.2	4.5	1.5
100	83.9	19.2	3.5	<1	1.2	1.0	54.9	2.8	12.1	5.1
250	91.2	12.5	2.8	<1	1.0	<1	39.0	6.2	23.8	13.8

Flow reactor, HMF in 1-propanol

The analogous results for the flow-reactor experiments, measured in 33 bar H_2 using 1 wt % HMF in 1-propanol, showed product distributions that were noticeably simpler. All major products were easily identified by GC/MS and DMF selectivities were reasonably high. The conversions and product selectivities are shown in Figure 3 for reactions at 140 and 180°C as a function of the reactor space time (W/F = weight of the catalyst/mass flow rate) and the overall reaction network can be understood from Scheme 1. To simplify understanding of the reaction results, some of the products are summed together in Figure 3 but a more complete listing of the products is given in Tables 1 and 2. What the data show is that the reaction can be viewed as a sequential reaction, with the HMF (A in Scheme 1) first forming a group of partially hydrogenated compounds and ethers (B in Scheme 1) that then go on to form DMF (C). With longer residence times, DMF is further converted to several undesired products (D). Because the reaction is sequential, the DMF selectivity goes through a maximum at intermediate residence times.

Among the intermediate B compounds, the largest fraction is 5-propoxymethyl-2-furanmethanol (EFA). We considered the possibility that the ethers formed on acid sites associated with the carbon support; however, as there were no products formed on the carbon support in the absence of Pt, the Pt

Table 3. Furfuryl Ether Feed Experiment in 1-Propanol, 180°C, 33 Bar, 25 g min/g W/F

Catalyst Bed	Conv.%	DMF	EF	EFA	BEF	DMTHF	Open-Ring	Unidentified
Carbon Support	0	–	–	–	–	–	–	–
ZrO_2/SBA-15	73.5	–	20.0	2.4	67.1	–	–	10.5
ZrO_2/SBA-15 + Pt/C	100	77.6	<1	1.7	<1	2.3	9.2	11.1

Table 4. DMF Feed Experiment in 1-Propanol, 180°C, 33 Bar, 25 g min/g W/F

Catalyst Bed	Conv.%	2-Hexanone	2-Hexanol	DMTHF
10 wt % Pt/C	26.1	68.9	11.8	10.2

must also be capable of forming the ether with relatively high efficiency. Other intermediate products were observed in lesser amounts and included 5-propoxymethyl-2-methylfuran (ether-methyl furan), 5-methyl furfural (MF), 5-methyl-2-furanmethanol (methyl furfuryl alcohol), 2,5-bis(hydroxymethyl)furan (BHMF). The presence of small amounts of MF (always less than 1%) indicates that HDO of the alcohol group can occur in parallel with hydrogenation of the carbonyl group.

Since DMF selectivity goes through a maximum with increasing space time, DMF must undergo further reactions. With longer space times, DMF was converted to DMTHF and several ring-opened products, 2-hexanone and 2,5-hexanedione. At the longest space times at 180°C, additional products were formed that could not be identified. No decarbonylation products, such as furan or methyl furan, were observed. The differences between results for reactions carried out 140 and 180°C were modest. As expected, the conversions at a given space time were higher at 180°C but the products formed were the same.

Reaction of DMF and furfuryl ethers

To further characterize the reaction network in Scheme 1, we investigated the reactions of furfuryl ethers and DMF. To form high concentrations of ethers, the 15 wt % ZrO_2/SBA-15 catalyst was placed in the tubular reactor, before the Pt/C catalyst. Reaction was carried with 1 wt % HMF in 1-propanol at 180°C, with 33 bar H_2, and W/F of 25 g min/g. Table 3 shows the product distributions when only the ZrO_2/SBA-15 catalyst was present and when both ZrO_2/SBA-15 and Pt/C were present. With only the ZrO_2/SBA-15 in the reactor, the conversion of HMF was greater than 70% and the primary products were furfuryl ethers. No DMF was detected but approximately 10% of the products could not be identified and should likely be classified as humins. For reaction over the dual bed, almost all the furfuryl ethers were converted to DMF and only 2% of these compounds remained. The unidentified products appear to pass over the Pt/C catalyst unaffected. Interestingly, even with humin formation over ZrO_2/SBA-15, the yield to DMF, 77.6%, was significantly higher with the dual bed than with the single bed. The explanation for this appears to be that the ethers react to DMF more rapidly than does HMF. Because of the sequential nature of the reaction, increasing the rate at which DMF is formed without changing the rate at which DMF is converted to other products leads to the higher yield. Our results indicate the rate-determining step is probably the initial hydrogenation of HMF to BHMF and various ethers and propose a strategy using staggered catalysts, whereby an inexpensive catalyst (e.g., ZrO_2/SBA-15) is used upstream to produce ethers followed by a second catalyst (Pt/C) that more readily converts the ethers into DMF.

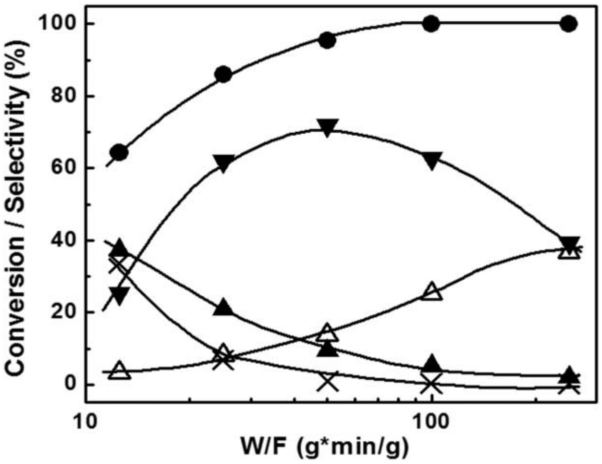


Figure 4. Product distribution for HMF hydrogenolysis in ethanol as a function of space time in the flow reactor.

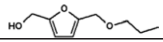
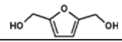
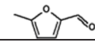
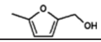
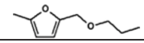
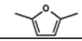
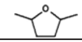
Reaction conditions: 10 wt % Pt/C, 33 bar, and 180°C. (•) HMF conversion, (▼) DMF, (▲) EFA, (×) B2, (Δ) D.

The conversion of 0.76 wt % DMF in 1-propanol (the same molar concentration as 1.0 wt % HMF in 1-propanol) was also carried out at 180°C, with 33 bar H_2, and W/F of 25 g min/g, over the Pt/C catalyst, with the products formed shown in Table 4. The conversion of DMF was only 26.1%, showing that DMF is much less reactive than either HMF or the furfuryl ethers. DMTHF, 2-hexanone, and 2-hexanol were found to be the major products. Unlike the case when HMF was fed to the reactor, no 2,5-hexandione was observed in the products. This difference may due to the presence of small amounts of water formed during the reaction with HMF, as the DMF requires a H_2O molecule to form 2,5-hexandione via hydrolysis.[6,21]

Effect of solvent

Because the furfuryl ethers formed by reaction of HMF with 1-propanol appear to be converted to DMF more rapidly than HMF, we also examined the effect of solvents on the reaction. Figure 4 and Table 5 present results for the HDO reaction using ethanol as solvent at 180°C and 33 bar. The observed products and product distributions are similar to that observed with reaction in 1-propanol. DMF and EFA (5-ethanoxymethyl-2-furanmethanol) were found to be the major initial products. With increasing residence times, the

Table 5. Space Time Study of HMF Hydrogenolysis Over 10 wt % Pt/C in Ethanol, Under 180°C and 33 Bar

W/F (g min/g)	Conv. %	B1	B2				C	D		Unknown
									Open-Ring	
12.5	64.3	37.3	14.0	1.5	12.8	5.3	25.2	<1	3.0	<1
25	85.9	20.9	3.1	<1	2.1	1.4	62.0	1.6	6.6	2.1
50	95.3	9.4	<1	–	<1	<1	71.9	2.4	11.4	3.9
100	100	5.2	<1	–	–	<1	62.7	3.8	21.5	6.5
250	100	2.0	<1	–	–	<1	39.3	6.1	30.6	21.8

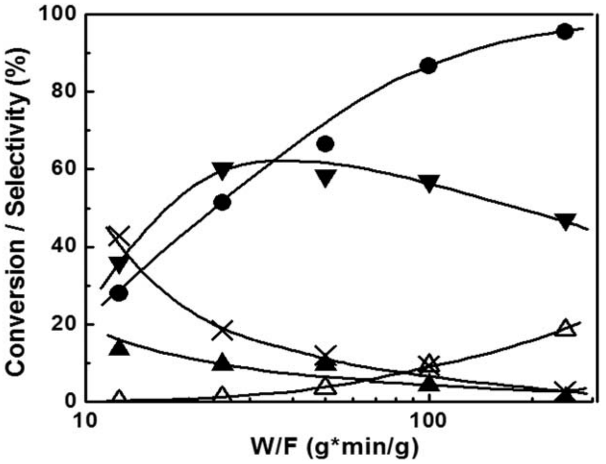


Figure 5. Product distribution for HMF hydrogenolysis in toluene as a function of space time in the flow reactor.

Reaction conditions: 10 wt % Pt/C, 33 bar, and 180°C. (•) HMF conversion, (▼) DMF, (▲) EFA, (×) B2, (Δ) D.

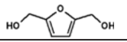
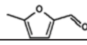
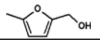
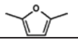
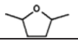
sequential nature of the reaction, A → B → C → D, presented in Scheme 1, is still apparent. The selectivity of DMF reached a maximum of 71.9% at W/F of 50 g min/g, with an HMF conversion 95.3%, which gives a yield that is slightly better than the 63.7% obtained in 1-propanol.

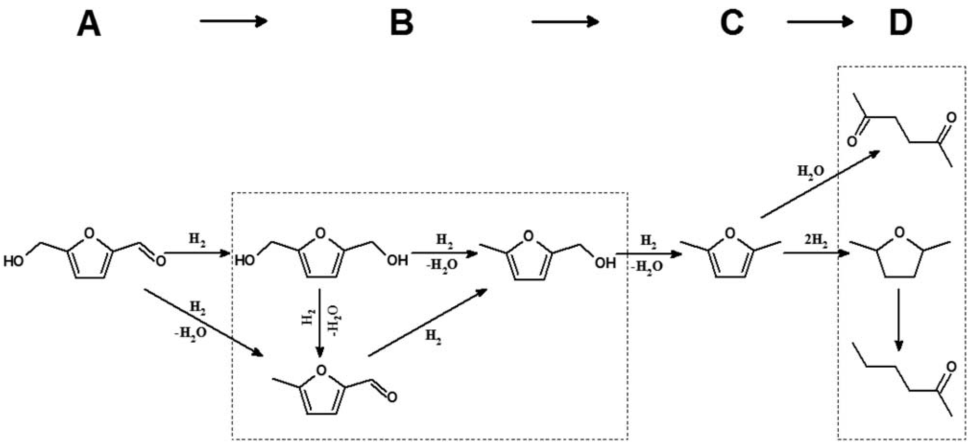
The HDO of HMF in toluene at 180°C and 33 bar was also investigated, with results given in Figure 5 and Table 6. For this solvent, ether formation is not a possibility. The rates of HMF conversion were noticeably slower with toluene and complete conversions were approached only at the highest W/F. However, in other ways, the products and reaction pathways are similar and a modified network is shown in Scheme 2. Although the maximum selectivity to DMF was similar to that obtained when using alcohol solvents, the maximum yield with toluene was much lower as this selectivity was achieved at relatively low HMF conversions. Aside from typical mechanisms via which solvents affect reaction, a possible explanation for these results is that turning off the ether pathway decreases the rate of DMF formation without changing the rate at which DMF is further converted to other products. It is also worth noting that the formation of unknown products, mostly humins, was much more severe with toluene as solvent than with alcohols, especially with long residence times. Some hydrogenation of toluene (methylcyclohexane, 4% conversion) and decarbonylation products (mainly furfural alcohol, <2% selectivity) were also observed.

Kinetic models

To further quantify the reaction network for HDO of HMF, the reactions in Schemes 1 and 2 were modeled as a series of first-order reactions, with rate constants k_1 for the reaction A → B, k_2 for B → C, and k_3 for C → D. The data in Figures 2 through 5 were then fitted to give the values shown in Table 7. It should be noted that B and D represent groups of compounds and that the rate constants reported here should be used for comparison purposes only because the reaction in the complex, three-phase environment will likely lead to very different rates for different reactor geometries. In agreement with our earlier qualitative conclusions that rates to DMF in 1-propanol and ethanol are higher than in toluene, we observe roughly threefold higher values for k_1 and a twofold higher values for k_2 in the alcohol solvents. That reaction of DMF to undesired products is solvent independent is shown by the fact that k_3 was nearly the same for

Table 6. Space Time Study of HMF Hydrogenolysis Over 10 wt % Pt/C in Toluene, Under 180°C and 33 Bar

W/F (g min/g)	Conv. %	B		C	D		Open-Ring	Unknown	Decarbonylation
									
12.5	30.1	42.8	0.2	13.6	36.0	0.1	0.2	4.9	2.2
25	51.3	18.5	0.2	9.7	60.2	0.1	1.1	7.8	2.4
50	66.4	12	0.2	9.6	58.3	0.7	3.0	12.2	4
100	86.7	9.3	0.2	4.4	56.9	1.9	7.5	22.3	0.5
250	95.4	2.7	0.2	1.1	47.1	3.1	15.5	29.8	0.5



Scheme 2. Reaction scheme of HMF hydrodeoxygenation in toluene.

Table 7. Rate Constant of HMF Hydrogenolysis Over 10 wt % Pt/C

Entry	Solvent	Temperature(°C)	k_1 (s^{-1})	k_2 (s^{-1})	k_3 (s^{-1})
1	1-Propanol	140	0.023	0.037	0.004
2	1-Propanol	180	0.058	0.092	0.008
3	Ethanol	180	0.065	0.091	0.006
4	Toluene	180	0.021	0.047	0.005

each of the solvents. With 1-propanol as solvent, all of the rate constants approximately doubled when the temperature was increased from 140°C to 180°C.

Discussion

The first important lesson from this work is that reactor configuration has an enormous effect on the selectivities for HMF conversion. Previous reports have suggested that the selectivity of Pt catalyst is typically less than 10% due to formation of over-hydrogenated products[12,22] and our own work with the batch reactor using the very same catalyst confirmed this result. However, in a flow system, yields above 60% could be achieved easily. This has very important implications for catalyst characterization. Some catalysts that are not under consideration for this reaction could simply have been tested under conditions that are poor for that catalyst. Clearly, catalyst screening must take into account what kind of reactor is going to be used in the final process.

The poor selectivity of Pt in previous studies is at least partially explained by the sequential nature of the reaction. As the desired DMF product goes on to form undesired products, the use of a flow reactor allows the reaction to be stopped at the optimal time by the choice of residence time. It is interesting to consider that, in our flow experiments, the estimated contact time for a typical W/F of 25 g min/g is only 0.5 min, whereas the residence time in most batch experiments is over an hour. The long times required to heat the Parr reactor to our chosen conditions renders the realization of a short contact times in the batch system very challenging. The batch reactor data with 0-h reaction time showed relatively better DMF yields, up to 27.2%. However, it is apparent that the DMF yield had already passed through the maximum at this point and that over-hydrogenation reactions had already become severe.

In addition to allowing very short contact times, the catalyst-reactant contacting is very different for the batch and flow reactors. In the batch reactor, the catalyst is effectively immersed in a much larger body of fluid, whereas the catalyst surface is much more accessible to the gas-phase H_2 with the flow reactor. A hydrogen-covered Pt surface is expected to be less prone to forming humins by dehydrogenation of adsorbed species. Furthermore, even though ideal batch and plug-flow reactors show identical performance with space time for homogeneous reactions, there can be significant mixing problems with batch reactors when the volume of the catalyst is small compared to the reactor volume. This can be a serious problem for sequential reactions in which the desired product is an intermediate.

It is worth noting that our three phase, flow reactor has some similarities to a trickle-bed reactor. Reaction rates are dependent on catalyst wetting by the liquid phase, as well as mass transfer of HMF, H_2, and products within the liquid phase and within the solid catalyst. This makes the quantitative analysis of rates difficult and highly dependent on the flow configuration. The purpose of this study was primarily to demonstrate the importance of recognizing the role these factors play in choosing an experimental configuration for catalyst screening. Understanding the nature of the reaction network for HMF also provides important clues for improving catalysts for DMF formation. The formation of side products has often been viewed as being due to reactions that occur in parallel with the desired reaction, so that the goal is to turn off these side reactions. However, in a sequential reaction, $A \rightarrow B \rightarrow C$, in which B is the desired product, the maximum selectivity can be achieved by either increasing the rate at which A is converted to B or by decreasing the rate at which B reacts to C. The key to increasing yield, then, is to optimize these relative rates, which are likely affected by H_2 pressure and temperature, as well as choice of catalytic materials. Also of interest is the higher reactivity of furfuryl ethers compared to HDO. The possibility of forming intermediates by reaction with the solvent adds an additional tool for optimizing yield.

It is well established in the literature that alloy catalysts can greatly increase the yield for the reaction of HMF to DMF.[14–18] As it is likely that a similar reaction network is operational for these catalysts as for Pt, it is interesting to ask how alloying affects the rates of the various reactions. Given that alloy catalysts appear to be selective even with the long residence times found in batch systems, it would appear that the rate of DMF conversion must be significantly decreased on alloy catalysts. Studying this reaction network over highly selective catalysts will be enlightening.

Clearly, a better understanding of the reaction network for HMF leading to DMF is important for understanding how a given catalytic material will perform. Knowing how this varies with material properties should lead to improved catalytic materials and better catalytic processes.

Conclusions

This study demonstrates that HDO of HMF to DMF over Pt/C is a sequential reaction in which DMF is an intermediate and reasonably high yields can be achieved by controlling the contact time in a flow reactor. Because of this, previous catalyst screening in batch reactors did not properly reflect the effectiveness of Pt for this reaction. Consideration of the sequential nature of this reaction should also be used in future catalyst-development strategies.

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