

Hydrogenation of 5-hydroxymethylfurfural in supercritical carbon dioxide–water: a tunable approach to dimethylfuran selectivity†

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The use of supercritical carbon dioxide–water on the hydrogenation of 5-hydroxymethylfurfural (HMF) was investigated over a Pd/C catalyst. It was possible to achieve a very high yield (100%) of DMF within the reaction time of 2 hours at 80 °C. A significant effect of CO₂ pressure was observed on the product distribution. Simply by tuning the CO₂ pressure it was possible to achieve various key compound, such as tetrahydro-5-methyl-2-furanmethanol (MTHFM) (<10 MPa), 2,5-dimethylfuran (DMF) (10 MPa) and 2,5-dimethyltetrahydrofuran (DMTHF) (>10 MPa) with very high selectivity. Optimization of other reaction parameters revealed that H₂ pressure, temperature, as well as the CO₂–water mole ratio, played an important role in the selectivity to the targeted DMF. It is interesting to note that a very high yield of DMF was achieved when a combination of CO₂ and water was used. For instance, in the absence of water or CO₂, the selectivity of DMF was low; similarly, an excess of water against the fixed pressure of CO₂ reduced the selectivity to DMF. Hence, an optimized amount of water was mandatory in the presence of CO₂ for the formation of DMF with high selectivity. This method was successfully extended to the hydrogenation of furfural, which could afford 100% selectivity to 2-methylfuran with complete conversion within a very short reaction time of 10 min. The studied catalyst could be recycled successfully without significant loss of catalytic activity.

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Introduction

Depletion of fossil fuel resources is a great concern for the modern world since the availability of inexpensive crude oil is diminishing and environmental pressure is escalating.¹ To meet the growing demand of energy, due to the rise of the automobile industry, sustainable and renewable sources are inevitable in the near future.² A substantial amount of research activity is currently undertaken for the development of strategies for transforming abundant lignocellulosic biomass into liquid fuel suitable for the transportation sector or platform chemicals, and to develop economically feasible processes on a commercial scale.

5-Hydroxymethylfurfural (HMF) is considered as one of the most versatile platform chemicals derived from biomass.³ The presence of two functional groups, combined with the furan

ring, makes it an appealing starting material for various chemical transformations. Comprehensive reviews of the synthetic chemistry of HMF and its derivatives have been provided by Kunz and Lewkowski.⁴ Recently, Rosatella *et al.* also reviewed the synthesis and application of HMF in different fields of importance.⁵ As mentioned before, HMF can serve as a precursor for a variety of important chemical intermediates relevant to the fuel, polymer and pharmaceutical industries.^{6–8} Among them 2,5-dimethylfuran (DMF) is one of the most attractive compounds, which can directly serve as a suitable candidate for liquid fuels. Compared to ethanol (the only sugar based liquid fuel), DMF has a low boiling point (92 °C), is stable in storage, insoluble in water, and has the highest research octane number of 119.⁹ More attractively, DMF possesses a high volumetric energy density of 31.5 MJ l⁻¹, which is 40% greater than ethanol, making it comparable to gasoline, and consumes one-third of the energy in the evaporation stage of its production in comparison to that required by the fermentation for ethanol.¹⁰ The break-through of deriving DMF from biomass derived fructose was first reported by Roman-Leshkov *et al.* using a bimetallic CuRu/C catalyst with a yield of 71% after 10 hours of reaction in 1-butanol at 120 °C and 0.68 MPa of hydrogen pressure.¹¹ On the other hand, Binder and Raines reported a DMF yield of 49% under similar

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reaction conditions.¹² In a two-step approach, Chidambaram and Bell obtained DMF with a yield of 16%, and a 47% conversion of HMF in 1 hour under a hydrogen pressure of 6.2 MPa using Pd/C catalyst in an ionic liquid (1-ethyl-3-methylimidazolium chloride) medium along with acetonitrile.¹³ They attributed the lower yield of DMF to the shorter reaction time, as well as low availability of hydrogen in ionic liquid. Furthermore, several investigators used a catalytic transfer hydrogenation (CTH) process for the conversion of HMF to DMF. Instead of molecular hydrogen, cyclohexane, secondary alcohols or supercritical methanol were used as reaction media, as well as a hydrogen source and the reported DMF yield was up to 60–80% depending on the reaction conditions used.¹⁴ However, in the CTH process, sometimes the hydrogen sources give rise to by-products or co-products, which requires basic additives and harsh reaction conditions.¹⁵ Thananathana-chon and Rauchfuss reported a high yield of 95% after refluxing a solution of HMF in THF, formic acid, H₂SO₄ and Pd/C for 15 hours at 120 °C,¹⁶ but the homogeneous acid co-catalyst is difficult to separate from the reaction mixture and leads to the formation of undesired products. In addition, other strategies were also reported to obtain high yields of DMF from the direct conversion of HMF or *via* carbohydrates.¹⁷

In this work, we attempted the hydrogenation of HMF in supercritical carbon dioxide (scCO₂) using a Pd/C catalyst under reasonably milder reaction conditions. Simple variation of the reaction conditions results in different compounds with comparatively higher selectivity.

Supercritical carbon dioxide (scCO₂) could be introduced as a potential medium for carrying out chemical reactions. This solvent provides several advantages, including environmental

(do not contribute to increase the VOC's level in the atmosphere), health and safety (non toxic, non flammable) and process benefits, which is connected to the rare occurrence of by-products owing to side reactions, absence of solvent residue and facile product separation (cost-effective; related to the separation and purification steps). The most important advantage of using scCO₂ arises from the complete miscibility of reagents in the case of chemical reactions involving gasses. Furthermore, the yield and selectivity of a reaction can be enhanced easily by tuning of the pressure and temperature.¹⁸ Recently, scCO₂ has also been used in the conversion of biogenic substrates.¹⁹

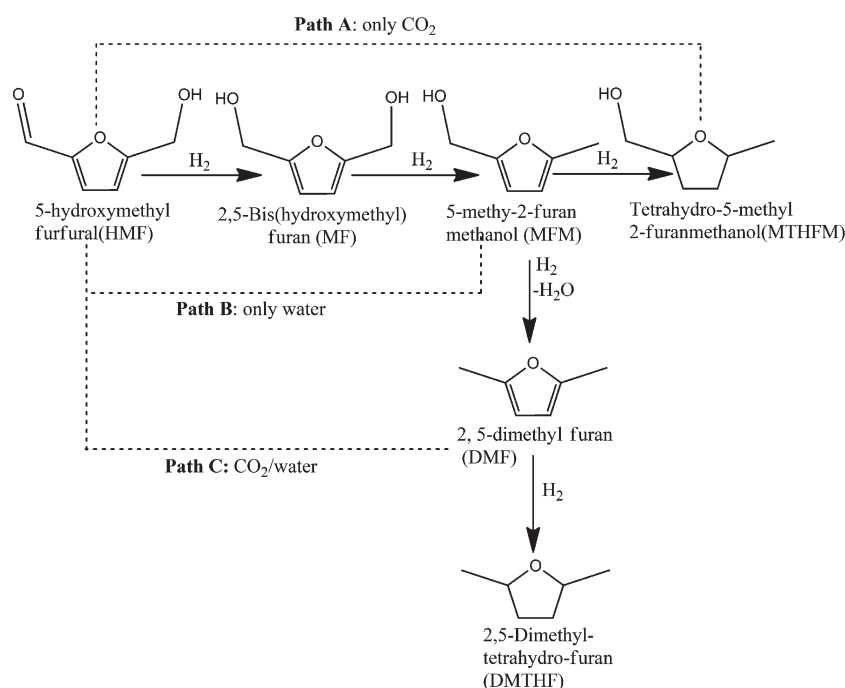
It has to be mentioned that at this stage HMF is an expensive starting material for bio-fuel production because of the difficulties related to the large scale formation of HMF. However, to design suitable hydrogenation/hydrogenolysis catalysts and to establish potential reaction conditions for achieving the highest yield of DMF, the transformation of HMF to DMF should be studied as model reaction using HMF as starting material.

Results and discussion

A possible reaction profile of HMF hydrogenation is shown in Scheme 1. All the reactions were conducted in scCO₂-water medium at 80 °C.

Catalyst screening

Different catalysts containing Pt, Pd, Rh and Ru metals on various supports, such as activated carbon (C), mesoporous



Scheme 1 Possible reaction path of HMF hydrogenation in scCO₂.

Table 1 Catalyst screening^a

Entry	Catalyst	Conv. (%)	Product selectivity (%)			
			MFM	DMF	DMTHF	MTHFM
1	Pt/C	4.6	0.0	100	0.0	0.0
2	Pd/C	100	0.0	100	0.0	0.0
3	Rh/C	23.9	0.0	65.0	2.0	9.1
4	Ru/C	1.5	0.0	86.6	0.0	13.4
5	Pt/MCM-41	0.0	0.0	0.0	0.0	0.0
6	Pd/MCM-41	41.0	100	0.0	0.0	0.0
7	Rh-MCM-41	0.0	0.0	0.0	0.0	0.0
8	Ru/MCM-41	47.0	2.6	1.7	0.0	95.7
9 ^b	Pt/Al ₂ O ₃	6.3	0.0	0.0	0.0	0.0
10	Pd/Al ₂ O ₃	2.2	92.8	5.0	2.2	0.0
11 ^b	Rh/Al ₂ O ₃	14.1	0.0	0.0	0.0	0.0
12 ^c	Ru/Al ₂ O ₃	13.0	0.0	0.0	0.0	0.0
13 ^d	Pd/C	100	63.9	26.1	2.1	6.9
14 ^e	Pd/C	94.5	0.0	100	0.0	0.0
15 ^f	Pd/C	75.8	0.0	0.0	100	0.0

^a Reaction conditions: catalyst : substrate = 1 : 5; temperature = 80 °C, reaction time = 2 hours, P_{CO_2} = 10 MPa, P_{H_2} = 1 MPa. MFM = 5-methyl-2-furanmethanol, DMF = 2,5-dimethylfuran, DMTHF = 2,5-dimethyltetrahydro-furan; MTHFM = tetrahydro-5-methyl-2-furanmethanol. ^b Unidentified products. ^c ~20% was identified as polyols. ^d In acidic condition. ^e After 4th recycle. ^f DMF as substrate, P_{CO_2} = 16 MPa.

silica (MCM-41) and alumina (Al₂O₃), were screened for the hydrogenation of HMF and the results are shown in Table 1. In all cases, the catalyst to substrate ratio was taken as 1 : 5 and the reaction was studied using a CO₂-water medium. Under the studied reaction conditions (temperature = 80 °C, reaction time = 2 hours, P_{CO_2} = 10 MPa and P_{H_2} = 1 MPa) mainly three quantified products 2,5-dimethylfuran (DMF), 2,5-dimethyltetrahydrofuran (DMTHF) and tetrahydro-5-methyl-2-furanmethanol (MTHFM) were observed. Notably, no evidence for the decomposition products of HMF was detected.

When activated carbon (C) was used as the support, the conversion of HMF varied from 1.5 to 100%, and followed the reactivity order of Pd > Rh > Pt > Ru. When using either Pt or Pd, the highest selectivity of DMF (100%) was obtained, (Table 1; entries 1 and 2), however, Pt/C provides only 4.6% conversion of HMF (Table 1; entry 2). On the other hand, DMF was also formed in the presence of the Rh and Ru catalysts with moderately high selectivities of 65% and 86%, respectively, but the conversion was relatively low [23.0 (Rh/C) and 1.5% (Ru/C)] for both materials (Table 1; entries 3 and 4).

By changing the catalyst support from C to MCM-41, the conversion of HMF as well as the product distribution changed significantly. For Pd/MCM-41, the conversion dropped to 41% (Table 1; entry 6) and no peak corresponding to DMF was observed in the GC-MS trace. The Pt and Rh/MCM-41 catalysts were completely inactive (Table 1; entries 5 and 7), whereas for Ru/MCM-41, a conversion of 47% and a very low selectivity to DMF (~2%) was detected (Table 1; entry 8).

As shown in Table 1 (entries 9–12), when the reaction was conducted on Al₂O₃ supported catalysts, Pt and Rh exhibited 6.3 and 14.1% conversion, respectively, and the product mixture did not reveal any significant peaks (Table 1; entries 9

and 11). Despite the very low conversion of 2.2%, the Pd catalyst results mainly in 5-methyl-2-furanmethanol (MFM) (Table 1; entry 10), whereas the majority of the HMF was converted to unidentified compounds along with polyols (~20%) when Ru supported on Al₂O₃ was used (Table 1; entry 12). From our experimental findings it could be suggested that Pd is the preferred choice for the hydrogenation of HMF under the present reaction conditions. Among the support materials studied, Al₂O₃ showed the lowest conversion in comparison to C and MCM-41 for Pd. As the reaction was conducted in the presence of water, the hydrophobic/hydrophilic nature of the support material might influence the catalytic behavior. Based on the TG/DTA of Pd/C, Pd/MCM-41 and Pd/Al₂O₃ (not shown), the hydrophobicity follows the order of C > MCM-41 > Al₂O₃, which might be a possible reason for the lowest activity of Pd/Al₂O₃, as also detected previously.²⁰ Based on the targeted high conversion of HMF, as well as the high selectivity to DMF, we have decided to continue the investigation further using Pd/C catalyst.

Effect of CO₂ pressure

The effect of CO₂ pressure on the hydrogenation of HMF was studied from 4 to 16 MPa at 80 °C and a fixed hydrogen pressure of 1 MPa (Fig. 1). Independent to the CO₂ pressure, complete conversion was achieved within the reaction time of 2 hours. However, CO₂ pressure exhibited a strong effect on the product distribution. The selectivity of DMF was increased from 42.2 to 100% as the pressure increased from 4 to 10 MPa and then remains constant until 11 MPa. At the lower pressure region (4–6 MPa), MTHFM was formed with a comparatively higher selectivity of 57.8% and then decreased with pressure. Moreover, at higher CO₂ pressures (>12 MPa), complete hydrogenation of DMF was observed and the selectivity abruptly dropped to 27%, with an increase in the selectivity of DMTHF. Therefore, for the sake of simplicity, 10 MPa was considered as the standard and the product distribution was divided into

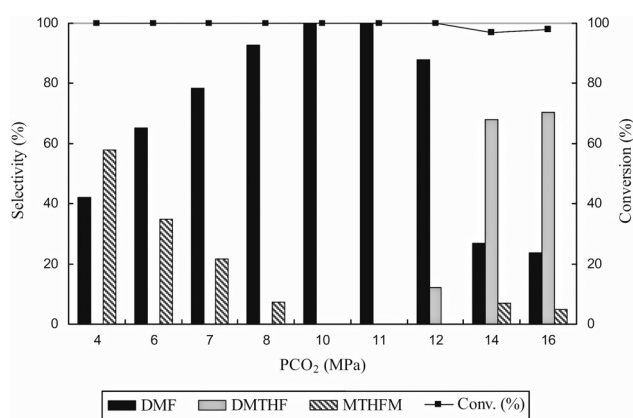


Fig. 1 Effect of CO₂ pressure on the conversion, and product profile. Reaction conditions: catalyst : substrate = 1 : 5; temperature = 80 °C, reaction time = 2 hours, P_{CO_2} = 10 MPa, P_{H_2} = 1 MPa, water = 1 ml; DMF = 2,5-dimethylfuran, DMTHF = 2,5-dimethyltetrahydro-furan; MTHFM = tetrahydro-5-methyl-2-furanmethanol.

three different regions depending on the CO_2 pressure: <10 MPa, 10 MPa and >10 MPa. As such it is difficult to explain the observed results; hence, the reaction was conducted at 4, 10 and 16 MPa of CO_2 pressure in a view cell to obtain insight into the phase behavior during reaction (Fig. 2a–c), because the reaction was performed in scCO_2 ; one factor that might contribute to the observed results is phase behavior. At 4 MPa, two phases (i) the aqueous phase containing dispersed catalyst and HMF (bottom phase) and (ii) $\text{CO}_2\text{-H}_2$ in gaseous state (upper phase) were visible (Fig. 2a). The scenario is different at 10 MPa; where one can see two immiscible liquid phases of (i) substrate–water/catalyst (bottom phase) and (ii) liquid part (middle phase) along with the (iii) $\text{CO}_2\text{-H}_2$ in gaseous state (upper phase) (Fig. 2b). Accumulated experimental results indicated that the observed situation was favorable to the formation of DMF, which is a hydrophobic product and can be separated spontaneously from water.¹¹ At the higher pressure of 16 MPa, in comparison with the substrate–catalyst/water phase (bottom phase), a large portion of the view cell was occupied by the $\text{CO}_2\text{-H}_2$ liquid phase (upper phase) (Fig. 2c), which is a favorable situation for the complete hydrogenation of DMF to DMTHF. As observed from the phase behavior of DMF, it was completely soluble in CO_2 (ESI, Fig. 1s†) at 80 °C and a CO_2 pressure of 16 MPa. From the results given above, the formation of DMTHF was observed in the single phase system where CO_2 homogenizes the mixture of DMF and hydrogen, leading to high concentrations of each reactant and hence high DMTHF selectivity. To confirm the conversion of DMF to DMTHF, a separate experiment was conducted on the hydrogenation of DMF under similar reaction conditions.

DMF was successfully converted to DMTHF (Table 1; entry 15) under the working conditions. Therefore, from the results of phase observation it might be suggested that depending on the CO_2 pressure, three completely different situations arise during the reaction and result in three different products. It has to be mentioned that the DMTHF is also an important compound with a higher carbon to hydrogen ratio, which translates into a higher energy content. In addition, it may provide additional stability on storage because of the fully hydrogenated furan ring.¹¹

Effect of hydrogen pressure

Hydrogen pressure is one of the important reaction parameters to be optimized, as the reaction was conducted in scCO_2 . Fig. 3 presents the effect of changing the hydrogen pressure from 0.2 to 2.5 MPa on the conversion and selectivity of HMF hydrogenation. The temperature and CO_2 pressure were kept constant at 80 °C and 10 MPa, respectively, in accordance with the observed highest activity and selectivity. As expected, the conversion of HMF was increased from 47.1 to 100% with the change in hydrogen pressure from 0.2 to 1 MPa, and then remained constant. The highest selectivity of the targeted DMF (100%) was maintained until 1 MPa, the selectivity then sharply decreased to 19% as the pressure was enhanced to 2.5 MPa. The increase in hydrogen pressure suppressed the selectivity of DMF due to the formation of over hydrogenated DMTHF, by-products and hexanediol. Therefore, a lower pressure of hydrogen was most suitable for the selective formation of DMF. An optimum hydrogen pressure of 1 MPa was

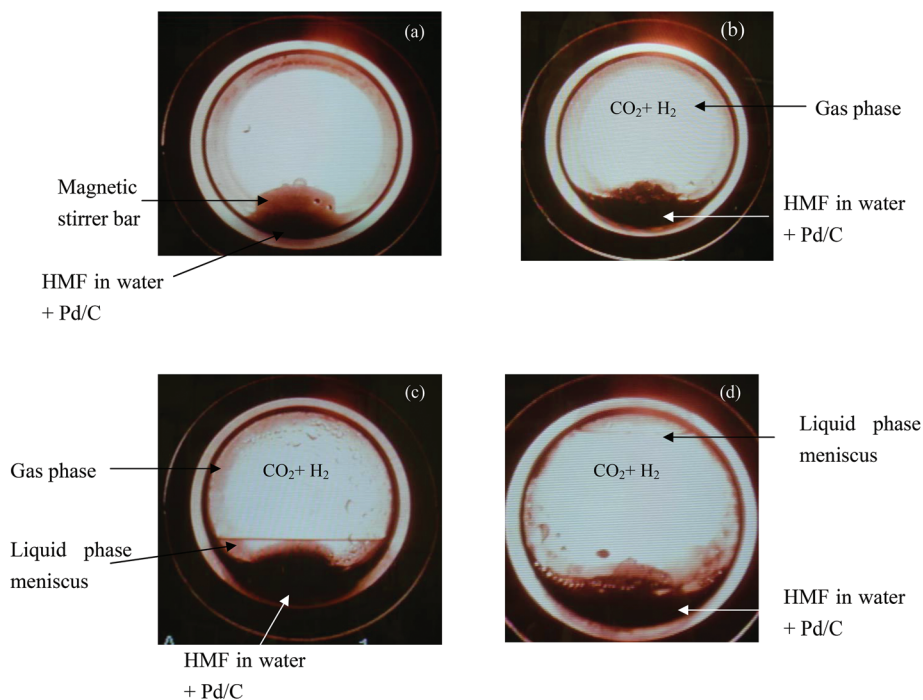


Fig. 2 Phase observation through the view cell during reaction (a) initial (b) 4 MPa, (c) 10 MPa and (d) 16 MPa. Reaction conditions: temperature = 80 °C, reaction time = 2 hours, P_{H_2} = 1 MPa.

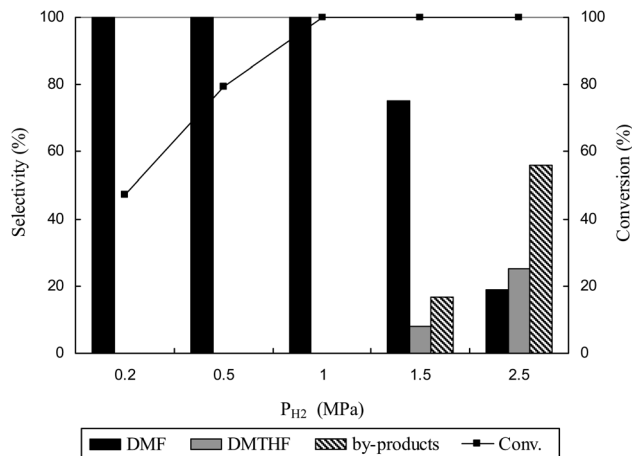


Fig. 3 Variation of hydrogen pressure. Reaction conditions: catalyst : substrate = 1 : 5; P_{CO_2} = 10 MPa, temperature = 80 °C, reaction time = 2 hours, water = 1 ml; DMF = 2,5-dimethylfuran, DMTHF = 2,5-dimethyl-tetrahydro-furan; MTHFM = tetrahydro-5-methyl-2-furan-methanol.

chosen to achieve a high yield of the desired DMF in order to optimize the other reaction parameters.

Variation of reaction time

To understand the reaction path of HMF hydrogenation it is necessary to evaluate the intermediate product/products formed during the reaction. The hydrogenation of HMF was studied as a function of time and the results are shown in Fig. 4. Under the investigated conditions, a very short reaction time of 5 min provided low conversion of <10% and then gradually improved to 100% as the reaction time progressed to 2 hours. Surprisingly, independent to the reaction time, DMF was the sole product detected, even in the shortest reaction time of 5 min, which might be attributed to the rapid hydrogenation/hydrogenolysis of HMF, possibly because of the easy availability of hydrogen in the reaction system. Thus, to slow down the reaction rate, the reaction was conducted at a very low pressure of hydrogen (0.1 MPa) within the shortest reaction time of 5 min and the results are described in Table 1s

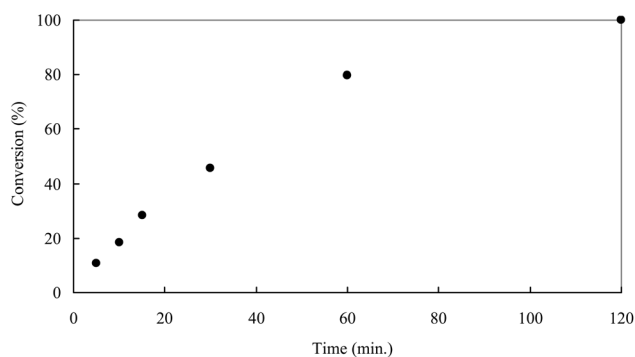


Fig. 4 Time dependent conversion of HMF hydrogenation in $scCO_2$ -water. Reaction conditions: catalyst : substrate = 1 : 5; P_{CO_2} = 10 MPa, temperature = 80 °C, reaction time = 2 hours, water = 1 ml.

(ESI†). The GC-MS traces of the product mixture displayed a few signals, allowing the detection of 2,5-bis(hydroxymethyl)-furan (MF) as the main intermediate. In addition to that, some other compounds (<10%) were also identified in the GC-MS traces (Table 1s, ESI†). Thus, it could be suggested that when a 1 MPa hydrogen pressure was used, HMF was directly converted to DMF, but the presence of an intermediate (MF) was evident at a very low pressure of hydrogen. Based on this observation, we hypothesized that the reaction proceeds by rapid reduction of the -CHO group in HMF, followed by hydrogenolysis of the hydroxyl functionalities in $scCO_2$ -water. However, additional research is necessary to determine the exact reaction path of HMF hydrogenation in the studied reaction conditions.

In addition, DMF was fully converted to DMTHF due to the reduction of the furan ring after a reaction time of 6 hours. With further extension of the reaction time to 18 hours, DMTHF along with 1,2-hexandiol was formed.

Effect of temperature

The effect of temperature on the hydrogenation of HMF was studied at 35, 50, 80, 100 and 130 °C at constant pressures of CO_2 and H_2 , 10 and 1 MPa, respectively (Fig. 5). When the reaction was performed at a temperature of 35 °C the conversion was low (28.2%), but with an increase in temperature the conversion increased and reached a maxima of 100% at 80 °C. Regarding the product selectivity, at the lower temperature of 35 °C, the main product was MTHFM (68%) and the selectivity of the targeted DMF was substantially low (11%), which was improved significantly with an increase in temperature, where the highest selectivity of 100% was achieved at 80 °C. Interestingly, when the temperature was further increased to 130 °C, a ring hydrogenated product (DMTHF) constitutes up to 80% of the total products and consequently the selectivity to DMF

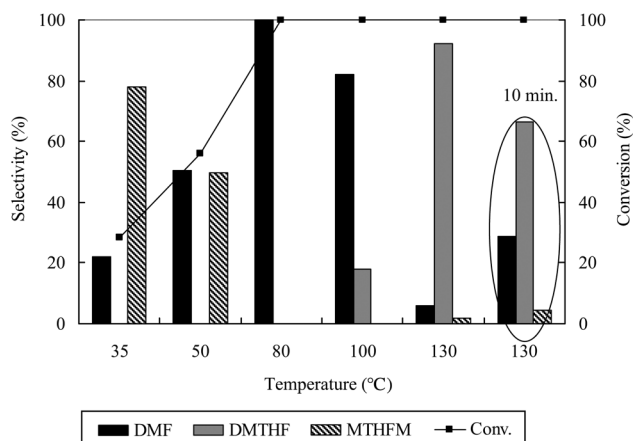


Fig. 5 Effect of temperature on the conversion and product selectivity. Reaction conditions: catalyst : substrate = 1 : 5; P_{CO_2} = 10 MPa, P_{H_2} = 1 MPa, reaction time = 2 hours, water = 1 ml; DMF = 2,5-dimethylfuran, DMTHF = 2,5-dimethyl-tetrahydro-furan; MTHFM = tetrahydro-5-methyl-2-furanmethanol. The circled section shows the results of 10 min reaction time.

dropped. This result might be attributed to the increase in the reaction rate, facilitated by the formation of DMF and consequently DMTHF, which is in good agreement with the results of the previous section on the hydrogen pressure effect. To explain this observation, the reaction time was shortened from 2 hours to 10 min at 130 °C and the results are shown in Fig. 5 (circled). The reaction rate (turnover frequency; TOF) was compared at 80 and 130 °C under a fixed CO₂ pressure of 10 MPa and reaction time of 10 min. As expected, the TOF was very high (3167 h⁻¹) at 130 °C, in comparison with 351 h⁻¹ at 80 °C. The acceleration of the reaction rate with increased temperature at a given CO₂ pressure was also observed for the hydrogenation that occurred in water–CO₂ biphasic media.²¹ Regarding the product profile, the selectivity of DMF and DMTHF was changed from 100 to 28.9% and 0 to 66%, respectively (Fig. 5, circled) within the reaction time of 10 min, as the temperature increased from 80 to 130 °C. From the results it seems that very low temperatures were clearly unsuitable for the generation of DMF, and a higher temperature of 130 °C boosted the reaction rate and consequently the selectivity of DMTHF. Therefore, a mild temperature of 80 °C, which provides complete conversion of HMF to DMF, was used throughout the rest of the optimization process.

Variation of the water to CO₂ mole ratio

Fig. 6 presents the results of the hydrogenation of HMF in CO₂–water, only water and only CO₂ systems under similar reaction conditions. Complete conversion of HMF was achieved within the reaction time of 2 hours in each case. However, the product distribution was different, depending on the presence or absence of the either of CO₂ or water. In the absence of water (only CO₂), the major product was MTHFM, which was obtained with a selectivity of 95.3% (Scheme 1: Path A). On the other hand, when only water was used, the reaction ended with the formation of MFM (95.8%) and DMF (4.2%)

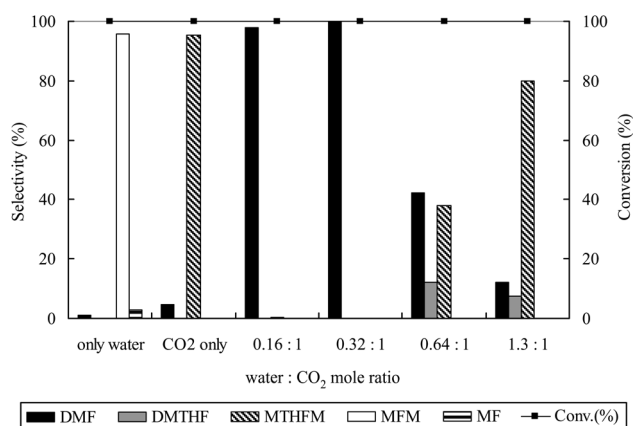


Fig. 6 Variation of the water–CO₂ mole ratio. Reaction conditions: catalyst : substrate = 1 : 5; P_{CO_2} = 10 MPa, P_{H_2} = 1 MPa, reaction time = 2 hours, temperature = 80 °C; DMF = 2,5-dimethylfuran, DMTHF = 2,5-dimethyl-tetrahydro-furan; MTHFM = tetrahydro-5-methyl-2-furan-methanol, MF = 2,5-bis(hydroxymethyl)furan (MF), MFM = 5-methylfuran-yl methanol.

(Scheme 1: Path B). From the accumulated results one can understand that in the absence of water or CO₂, the reaction proceeds through the path of HMF → MFM → MTHFM. A combined effect of CO₂ and water forced the reaction to move in the direction of HMF → DMF (Scheme 1: Path C). We hypothesized that the acidity of the CO₂–water system might be one of the responsible factors.²² A truly biphasic system consisting of CO₂–H₂ and the aqueous solution of HMF exists during the course of the reaction (neglecting the solid catalyst phase) (Fig. 2s, ESI†). In the presence of CO₂, water cannot expand; therefore, the properties of the water remain intact, except the acidity.²³ Thus, when CO₂ was introduced into the reaction system, the reaction medium became acidic. According to the literature, the pH value of 3 MPa CO₂ in water at 50 °C was reported to be about 3.4, and there was no significant change observed upon increasing the CO₂ pressure.²⁰ Namely, the weak acidic conditions might be one of the factors behind the hydrogenation of HMF to DMF. To confirm this observation, the reaction was conducted separately at pH 3.0 using acetic acid and without addition of any CO₂. Interestingly, the selectivity of DMF was increased to 26.1% in comparison with only water or the CO₂ system (Table 1; entry 13), but considerably lower than for the CO₂–water combined system, which emphasizes the beneficial effect of CO₂ for achieving excellent catalytic activity. Previously, a similar effect was also detected during the hydrogenation/hydrogenolysis of diphenylether in scCO₂–water medium.²⁴

To optimize the amount of water, the hydrogenation of HMF was also studied with the variation of CO₂ to water mole ratio (Fig. 6). Independent to the amount of water used, the conversion remain constant, however the product distribution was strongly affected. It can be seen that when the water–CO₂ ratio was changed from 0.16 : 1 to 1.3 : 1 the hydrogenation of HMF followed a different reaction path of HMF to MTHFM and the selectivity of DMF was dropped significantly. For instance, the selectivity of DMF changes from 100 to 32% as the water–CO₂ ratio changes from 0.17 : 1 to 1.3 : 1. Based on our observations, we might conclude that the formation of DMF prefers low water–CO₂ ratio. When the amount of water increased at the fixed concentration of CO₂, the system behaves like an only water system and shifts the reaction towards the formation of MTHFM except that DMF was formed with very low selectivity because of the presence of CO₂. This result agreed well with the observation of the reaction at lower CO₂ pressure (4 MPa), where MTHFM was detected with comparatively higher selectivity due to the water–CO₂ ratio of 0.64 : 1. Depending on the highest conversion and selectivity an optimum ratio of water–CO₂ = 0.32 : 1 was used throughout the experiment.

Instead of CO₂, different organic solvents such as hexane, 1-butanol and tetrahydrofuran (THF) were used along with the water (Fig. 7). According to the results, highest and lowest conversion of HMF was detected in 1-butanol (69.2%) and hexane (23.3%), respectively. In hexane, no DMF was detected, whereas THF shows highest selectivity of 38.3%. The selectivity of DMF follows the order of THF > 1-butanol > hexane. It has

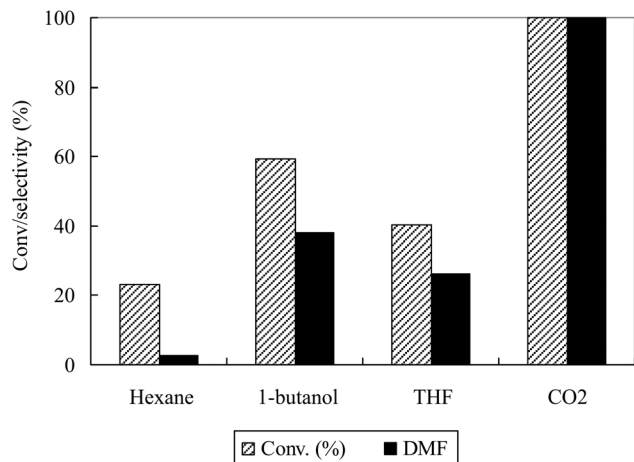


Fig. 7 Different organic solvents along with water; Reaction conditions: catalyst : substrate = 1 : 5; P_{CO_2} = 10 MPa, P_{H_2} = 1 MPa, reaction time = 2 hours, temperature = 80 °C, water = 1 ml; DMF = 2,5-dimethylfuran.

to be mentioned that although scCO_2 is considered as a non-polar solvents, it is superior to similar organic solvents (hexane) as it possesses substantially different characteristics, which can direct the activity and selectivity of a reaction.

Recycling of catalyst

After reaction, the catalyst was separated simply by filtration, washed with acetone and then ready to recycle. Recycling experiments showed that it is possible to recycle the catalyst four times. The result after the 4th recycle suggested a moderate decrease in the activity (Table 1; entry 14). The TEM image before and after the 4th recycle indicated a slight increase in the Pd particle size, which might be the probable reason behind the decrease in the catalytic activity (ESI, Fig. 3s†).

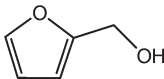
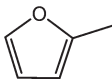
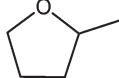
Hydrogenation of furfural

This method was also been extended to the hydrogenation of furfural and the results are shown in Table 2. Under similar reaction conditions, furfural was completely hydrogenated to 2-methyltetrahydrofuran (Table 2; entry 1) within the reaction time of 2 hours. However, when the reaction time was changed from 2 hours to 10 min, furfural was completely converted to 2-methylfuran (Table 2; entry 3). Similarly, tuning of the different reaction parameters, such as hydrogen pressure, changes the product profile and a mixture of products was obtained (Table 2; entries 4–6).

Conclusion

In conclusion, it has been demonstrated that scCO_2 -water is a potential medium for facilitating the hydrogenation/hydrogenolysis of HMF to DMF. The activity of Pt, Pd, Rh and Ru supported on C, MCM-41 and Al_2O_3 was compared. Complete conversion of HMF to DMF was achieved under mild reaction conditions within the reaction time of 2 hours using Pd/C catalyst at 80 °C. The product distribution was found to be dependent on the different reaction parameters, such as CO_2 and H_2 pressure, temperature, and the amount of water used. A combined effect of CO_2 and water played a critical role in the formation of DMF with highest selectivity. A promotional effect of the CO_2 -water system was discovered when different organic solvents were used along with water. Tuning of the reaction conditions offers the ability to achieve either DMF, DMTHF or MTHFM with very high selectivity. This study suggested that it is possible to obtain a very high yield of DMF by the hydrogenation/hydrogenolysis of HMF under reasonably mild reaction conditions, which is an example of a green and sustainable process. Further studies are necessary to improve the

Table 2 Hydrogenation of furfural^a

Entry	P_{H_2} (MPa)	Time (min)	Conv. (%)	Product selectivity (%)		
						
1	1	120	100	0.0	0.0	100.0
2	1	20	100	0.0	74.9	25.1
3	1	10	100	0.0	100	0.0
4	0.2	15	65.5	0.0	59.9	40.1
5	0.2	10	21.1	0.0	100	0.0
6	0.2	5	13.0	91.9	8.1	0.0

^a Reaction conditions: catalyst : substrate = 1 : 5; temperature = 80 °C and P_{CO_2} = 10 MPa.

reusability of the catalyst and also to understand the reaction path in the CO₂-water system.

Experimental

Materials

5-Hydroxymethylfurfural (HMF) (Aldrich) was used as received. Carbon dioxide (>99.99%) was supplied by Nippon Sanso Co. Ltd. Pd/C, Pd/Al₂O₃, Pt/C, Pt/Al₂O₃, Rh/C, Ru/C and Ru/Al₂O₃ were from Aldrich, except Rh/Al₂O₃, which was from Wako Pure Chemicals. In each case, the metal content was 5%. Metal catalysts supported on MCM-41 were synthesized in our laboratory using a modified method.²⁵

Catalytic activity

The HMF hydrogenation studies were carried out in a 50 ml batch reactor placed in a hot air circulating oven, full details are given elsewhere.²⁶ In a typical experiment, a specified amount of catalyst and substrate dissolved in water was introduced into the reactor. The reactor was heated for a specified amount of time. After the required temperature of 80 °C was attained; hydrogen, followed by CO₂, was charged into the reactor using a high-pressure liquid pump and then compressed to the desired pressure. The content of the reactor was stirred with a magnetic stirrer bar during the reaction. After the reaction was complete, the reactor was quenched using an ice bath followed by the separation of solid catalyst from the liquid product by filtration. The products were identified by GC-MS against a standard, which was also used for qualitative analysis. For all results reported, the selectivity is follows:

$$\% \text{ selectivity} = \frac{\text{concentration of the product}}{\text{total concentration of products}} \times 100$$

Phase observation

To determine the phase behavior of the hydrogenation/hydrogenolysis of HMF during the reaction, an aqueous solution of HMF and DMF was studied separately in a 10 ml high pressure view cell fitted with a sapphire window. The cell was placed over a magnetic stirrer for stirring of the contents and was connected to a pressure controller in order to regulate the pressure inside the view cell. In addition, a temperature controller was also used to maintain the desired temperature of 80 °C. Required materials were introduced into the view cell at a constant hydrogen pressure of 1 MPa, while the CO₂ pressure was varied and the phase was observed. For phase observation during the reaction, the catalyst dispersed in an aqueous solution of HMF was introduced into the view cell and the content was stirred continuously. The image was recorded after stopping the stirrer. The phase behavior of HMF and DMF was also checked separately. Independent to the CO₂ pressure, an aqueous solution of HMF and CO₂ always existed as a biphasic system and shown in Fig. 2s,[†] whereas the solubility of DMF was increased with increasing CO₂ pressure. A homogeneous phase was observed at 12 MPa of CO₂ (Fig. 1s-d[†]).

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