Selective hydrogenation of 5-hydroxymethylfurfural to 2, 5-Bis- (hydroxymethyl)-furan using Pt/MCM-41 in aqueous medium: A simple approach

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Selective hydrogenation of 5-hydroxymethylfurfural to 2, 5- Bis-(hydroxymethyl)-furan using Pt/MCM-41 in aqueous medium: A simple approach

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Abstract

The hydrogenation of HMF has been conducted in neutral aqueous medium. Without any additive, HMF was hydrogenated to 2, 5- Bis- (hydroxymethyl)-furan (BHMF) with complete conversion and selectivity (98.9 %) using Pt/MCM-41 catalyst. Very low temperature of 35 °C and 0.8 MPa of hydrogen pressure was used to accomplish the highest selectivity of BHMF within the reaction time of 2h. Different reaction parameters such as reaction time, hydrogen pressure and the amount of water was optimized to achieve highest catalytic activity. In particular, presence or absence of water and the amount of water played an important role to dictate the conversion and product distribution of the reaction. For instance, in the absence of water or large excess of water the selectivity of BHMF was decreased. In addition, instead of water the influence of three different groups of organic solvent were also explored to obtain BHMF under the studied reaction condition. It has been observed that the studied organic solvents strongly influenced the catalytic performances such as solvent with negative δ value followed a clear trend with the substrate conversion whereas no impact for solvents with positive δ value. Catalyst recycling experiments revealed that the catalyst could be recycled several times without any significant loss of catalytic activity.

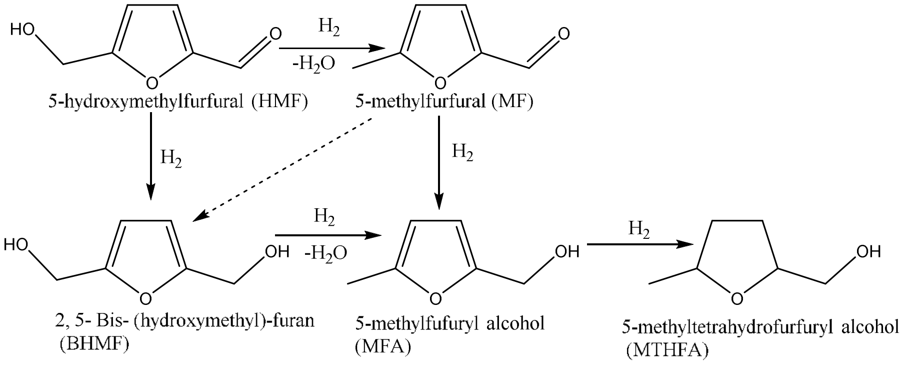
Introduction

In recent years, considerable interest was gained on the development of new pathways to obtain biomass derived platform chemicals. 5-hydroxymethylfurfural (HMF) is considered to be a versatile platform molecule can be produced by the acid-catalysed dehydrogenation of lignocellulose compounds such as glucose and fructose. A combination of furan ring, -OH and –C=O groups make it more appealing for various kind of transformations to the sustainable formation of valuable chemicals [1, 2]. In particular, selective hydrogenation of –C=O group of HMF to 2, 5- Bis- (hydroxymethyl)-furan (BHMF), has great field of application in the preparation of resin, polymer and artificial fibers [3]. It can be also used as an intermediate in the synthesis of drugs [4] as well as crown ethers [5]. In addition, further hydrogenation of BHMF results 2, 5- Bis- (hydroxymethyl) - tetrahydrofuran (BHMTHF), which is also an important compound because of its application as solvent [6], a monomer [7] and also for the production of different high-value chemicals such as 1, 6-hexanediol [8]. In this context, several catalysts were tested by different methods using sodium borohydride [9], formic acid [10] and formaldehyde [11]. In the catalytic hydrogenation, using molecular hydrogen depending on the reaction conditions and catalyst used, products distribution changed. Schiavo *et al.* investigated the reaction in an aqueous medium in the presence of Raney Ni, Cu-chromite and carbon supported metal catalysts at 140 °C and 7 MPa of hydrogen pressure. Cu or Pt catalysts yielded 80-100 % of BHMF, while BHMTHF was predominant products over Ni and Pd catalysts[12]. Furthermore, HMF was converted to BHMF with 96 % yield over Au sub-nano clusters supported on alumina at 120 °C under 6.5 MPa of H_2 for 2h[13]. Alamilo *et al.* obtained 81 % selectivity of BHMF using Ru/CeO_2

catalyst along with the formation of reduced BHMTHF [14]. Bimetallic catalyst such as Ni-Pd (Ni/Pd= 7 molar basis) was also used to hydrogenate HMF and resulted 96 % of BHMTHF at 40 °C temperature and 8 MPa of hydrogen pressure [15.]. In a recent report, Tamura *et al.* applied Ir-ReO_x catalyst for hydrogenation of HMF and obtained 99 % yield of BHMF after 6h of reaction at 30 °C and the hydrogen pressure of 0.8 MPa [16]. While preparing this manuscript another group detected 99 % yield of BHMF at 100 °C after 3h of reaction in ethanol over copper doped porous metal oxide prepared by the calcination of hydrotalcite [17]. Thus, in most of the cases, higher hydrogen pressure, longer reaction time, organic solvents or additional metal oxide additive was used to achieve a high yield of BHMF.

In the present work, we have attempted the hydrogenation of HMF under a mild reaction condition (temperature= 35 °C, P_{H2}= 0.8 MPa, reaction time= 2h) in an aqueous medium using Pt/MCM-41 catalyst without any additive to improve the catalytic performances.

Results and discussion



Scheme 1: Reaction path of HMF hydrogenation under studied reaction condition

A typical reaction profile of HMF hydrogenation under the working condition is shown in Scheme 1. Accordingly, HMF was hydrogenated to BHMF followed by the conversion to MFA and MTHFA. In a minor route, MF was formed from HMF via hydrogenolysis.

Table 1: Catalyst screening

Entry	Catalyst	Conv. (%)	Product selectivity (%)				
			BHMF	MF	MFA	ROP	UK
1	Ni/MCM-41	13.0	89.0	2.4	0.0	5.5	3.1
2	Pd/MCM-41	37.0	10.2	20.0	12.1	48.2	9.5
3	Pt/MCM-41	100.0	98.9	1.1	0.0	0.0	0.0
4	Au/MCM-41	16.2	73.6	0.0	11.1	13.8	1.5
5	Ru/MCM-41	> 1	-	-	-	-	-
6	Rh/MCM-41	42.1	60.7	0	3.0	32.4	3.9
7	Ir/MCM-41	9.0	43.1	27.0	0.0	29.9	0.0
8 [a]	Pt/MCM-41	75.4	0.0	0.0	73.0	0.0	0.0
9 [b]	Pt/MCM/41	2.6	-	-	85.6	-	-
10 [c]	Pt/MCM/41	15.2	-	-	90.1		
11[d]	Pt/MCM-41	96.6	99.2	0.8	0.0	0.0	0.0

Reaction condition: catalyst: substrate (wt. ratio) = 1:5; Temperature= 35 °C; reaction time= 2h; water= 2 ml; P_{H2}= 0.8 MPa; BHMF= 2, 5- Bis- (hydroxymethyl)-furan, MF= 5- methylfurfural; MFA= 5-methylfurfuryl alcohol, UK= unknown (unidentified), ROP= ring opening products are 1. 2-hexanediol, 2, 5-hexanedione and 4-hydroxypentanoic acid; a= MF as substrate; b= BHMF as substrate; c= BHMF as substrate and the reaction time 6h; d= 7th recycle

Catalyst screening

We have targeted the development of a simple method for hydrogenation of HMF to BHMF using heterogeneous catalyst. In search of the desired catalyst, the reaction was conducted over different metals such as Ni, Pt, Pd, Au, Ru, Rh and Ir supported on MCM-41. To avoid the complexity generates from the support material, neutral Si-MCM-41 was used as support. All the catalysts contain ~1 wt. % of metal. Table 1 shows the result of catalyst screening on the hydrogenation of HMF. Depending on the metal, the catalytic performance was different. Regarding the conversion of HMF, Pt gave complete conversion (Entry 3), whereas 35 % to 40 % conversion was detected over Pd and Rh catalysts (Entry 2 and 6). In other cases, the conversion was low of 13.0 % and 16.2 % for Ni and Au (Entry 1 and 4), respectively and less than 10 % for Ir catalyst (Entry 7). Among the utilized catalysts, Ru (Entry 5) was completely inactive under the studied reaction condition. The metal supported catalysts followed the conversion order of Pt > Rh> Pd ≈ Ni ≈ Au > Ir. Considering the product distribution, except Pd, BHMF was the major product detected for all the catalysts and the selectivity order was Pt> Ni> Au> Rh> Ir. BHMF, which derives from the selective hydrogenation of –C=O bond was more prominent over Ni, Pt, Au and Rh but relatively high selectivity of MF (27 %) (hydrogenolysis product of HMF) was detected in the presence of Ir. In contrast, Pd catalyst was very active, which produces 48 % of ring opening products (ROP) including 2, 5 hexanedione (hydrogenolysis and hydrolysis), and 4-hydroxypentanoic acid (hydration and reduction) (Table 1; Entry 2), highest among other catalysts used. In addition, some unidentified products (UK) were also detected using Ni, Pd and Rh catalysts. Hence, product distribution was strongly influenced by the nature of the metal used. Therefore, depending on the performances to achieve targeted highest conversion of HMF and selectivity to BHMF, Pt/MCM-41 was selected as an effective catalyst for the hydrogenation of HMF. We also optimized the different reaction parameters to obtain high catalytic activity. In the absence of catalyst no reaction was observed.

Effect of reaction time

To understand the temporal evaluation of products during the hydrogenation of HMF using Pt/MCM-41catalyst, the reaction was studied as a function of reaction time and the results are shown in Figure 1. As the time changes from 15 min. to 18h, the product distribution changed in a complex manner. The major product observed after 15 min, was BHMF (~ 30 %), along with the formation of minor product such as MF (~ 5 %) and MFA (~ 2%). As time progressed, the yield of MF decreased rapidly to zero. However, the yield of BHMF increased monotonically, and reached its maximum (98.9 %) after 2h of reaction. By increasing the reaction time from 2h to 6h the yield of MFA changed from 1.1 to 9.9 % followed by the formation of MTHFA. Additional experimentation with the prolonged reaction time of 18h, resulted in the decreased yield of BHMF to 69.5 %, whereas the yield of MFA and MTHFA were increased to 11.4 % and 16 %, respectively. To confirm the validity of the reaction pathway as depicted in Scheme 1, experiments were conducted separately with MF and BHMF as starting materials under similar reaction conditions and the results are shown in Table 1 (Entries 8 and 9). Results revealed that MF is more reactive and within the reaction time of 2h, the intermediate was converted mainly to MFA with the conversion of 75.4 %. On the contrary, under the similar reaction condition, the conversion of BHMF was very low of ~2 % and the main product detected was MFA (Table 1, Entry 9) and the conversion was increased to only ~ 13 % even after 6h of reaction (Table 1; Entry 10). Hence, a fast transformation of MF to MFA could be the reason behind the formation of MFA in the beginning, which was also reported previously [18] and a slow reaction of BHMF to MFA could be predicted under the working condition. To restate, HMF was hydrogenated to BHMF (major route) and the yield of BHMF was increased with time, whereas, MF, which was obtained via hydrogenolysis (minor route) was diminished to zero and the yield of MFA remain almost constant within the reaction time of 2h. This observation tempted us to suggest the conversion of MF or MFA to BHMF. However, at this stage we have no direct experimental evidence for the specific reaction path to confirm the point, thus, shown as a possible reaction pathway (dotted line) in the Scheme 1, and needs further investigation.

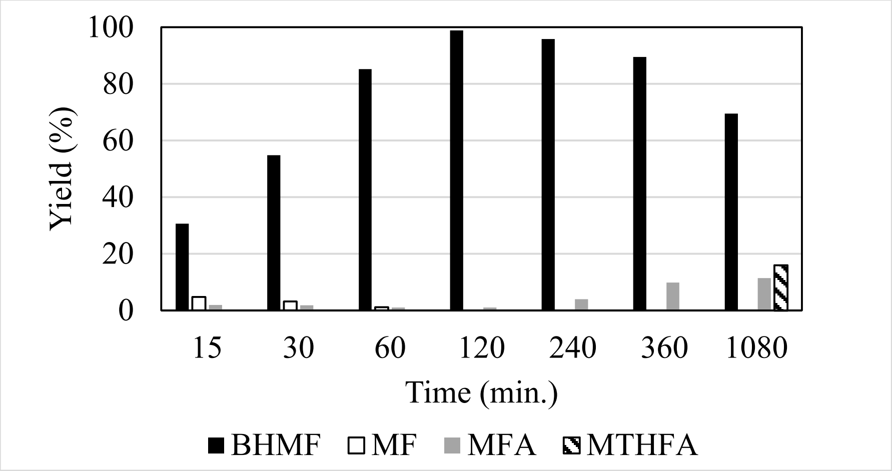


Figure 1: Evaluation of product yield as a function of reaction time. Reaction condition: P_{H2}= 0.8 MPa; catalyst: substrate (wt. ratio) = 1:5; Temp. = 35 ºC and water= 2ml

Effect of hydrogen pressure

The impact of hydrogen pressure on the conversion of HMF under the studied reaction condition is shown in Figure 2. Hydrogen pressure was varied from 0.2 to 4 MPa, while keeping other parameters constant. As expected, the conversion of HMF was increased from 67.6 % to 100 % along with the increase in pressure from 0.2 to 0.8 MPa and then remains constant. The selectivity of BHMF was slightly dropped to 86.7 % when the high pressure of 4 MPa was used. Interestingly, at higher pressure, the selectivity of MFA was enhanced from 1 % to 11 %. As mentioned before that MFA was generated by the hydrogenation of MF, hence, it might be confirmed that the reaction became faster at higher hydrogen pressure. In addition, ROP was also detected with very low selectivity of 2.1%. Therefore, to achieve higher conversion and selectivity of BHMF, lower hydrogen pressure of 0.8 MPa was chosen throughout the investigation for optimization of other parameters. No conversion of HMF was detected in the absence of hydrogen.

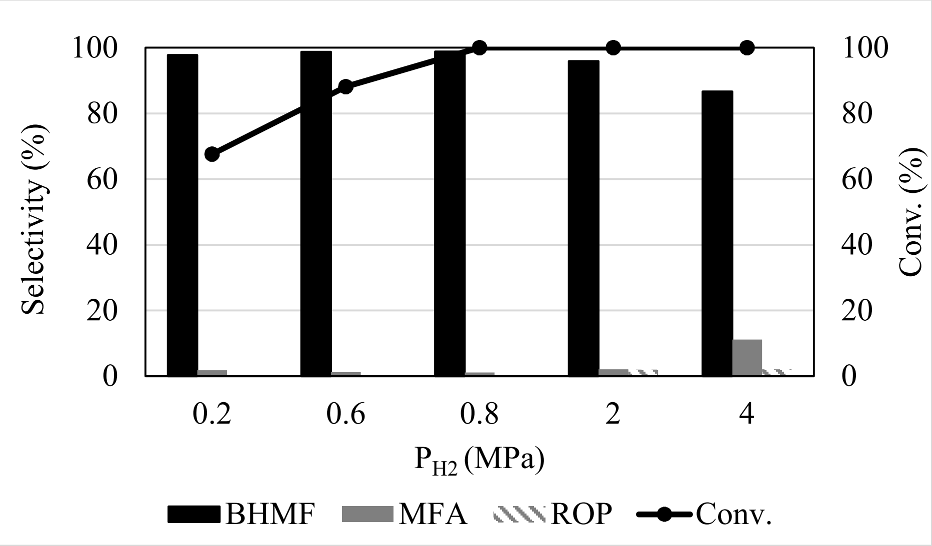


Figure 2: Effect of hydrogen pressure on the hydrogenation of HMF. Reaction condition: catalyst: substrate (wt. ratio) = 1:5; Temp. = 35 ºC, water= 2 ml and reaction time = 2h

Variation of amount of water

In this study, aqueous solution of HMF was used for hydrogenation over Pt/MCM-41. To predict the role of water as solvent, experiments were conducted in the presence and in the absence of water (Figure 3). According to the results, in the absence of water, conversion as well as the selectivity of BHMF were low of ~ 40 % and 15.3 %, respectively. On the other hand, when water was used as solvent, the conversion and the selectivity of BHMF was enhanced significantly. Hence, presence of water was required to achieve high conversion and selectivity of BHMF. For example, addition of 1 ml of water increased the conversion to 86 % and the selectivity of BHMF was improved (95.8 %). A similar result was also observed during the hydrogenation of Bisphenol-A in water using Ru/MCM-41 as catalyst [19]. They suggested that the hydroxyl groups on the silica surface could form hydrogen bonding with the water molecules. The hydrogen bonds could help the water molecules surround the catalyst surface, thus, creating a better dispersion of the catalyst, which in turn provide better catalytic activity in aqueous medium [20]. Recently, it has been also pointed out that water could accelerate chemical reactions, in which hydrogen was acted as a reactant [21].

However, the role of water is complicated and needs separate attention.

After confirming the necessity of water, the volume of water varied from 1 to 16 ml to check the effect on the catalytic activity (Figure 3). The conversion of HMF was increased from 86.5 % to 100 % with the increasing amount of water from 1 to 2 ml and then decrease to 71.4 % with further addition of water (16 ml). The decreased conversion after the addition of excess of water might be attributed to the dilution effect, which causes reduced collision between reactant and catalyst. Interestingly, the selectivity of BHMF was not affected significantly with an additional amount of water. Hence, an optimum amount of water (2 ml) was used throughout the experiment under the stated reaction condition. From the results it could be suggested that addition of proper amount of water has strong influence to accelerate the reaction.

Effect of pH

According to the literature, acidic by-products or solvent phase acidity affected the product selectivity of HMF hydrogenation [12]. Thus, the reaction was performed in acidic and basic conditions and the results are shown in Figure 4, which suggested poor catalytic performance in acidic or basic condition. When the hydrogenation of HMF was conducted in acidic medium of pH ~3, this reaction proceeded with 73 % conversion and the selectivity of BHMF dropped significantly due to the formation of unidentified by-products. On the other hand, in basic aqueous solution, the transformation of HMF was slower, which resulted lower conversion and selectivity of 40 % and ~ 80 %, respectively. Hence, it might be suggested that under the studied reaction condition, neutral aqueous medium was the best choice for the hydrogenation of HMF to BHMF.

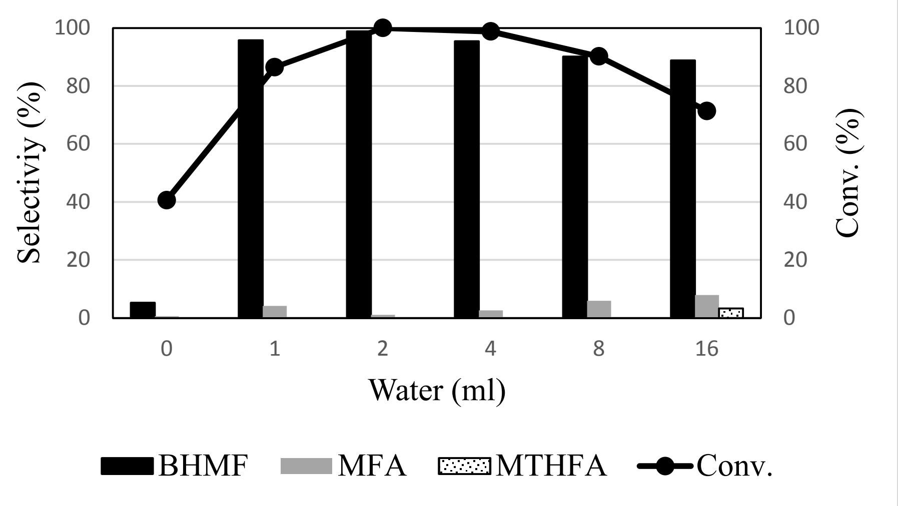


Figure 3: Variation of the amount of water. Reaction condition: catalyst: substrate (wt. ratio) = 1:5; P_{H2}= 0.8 MPa, Temp. = 35 ºC, and reaction time = 2h

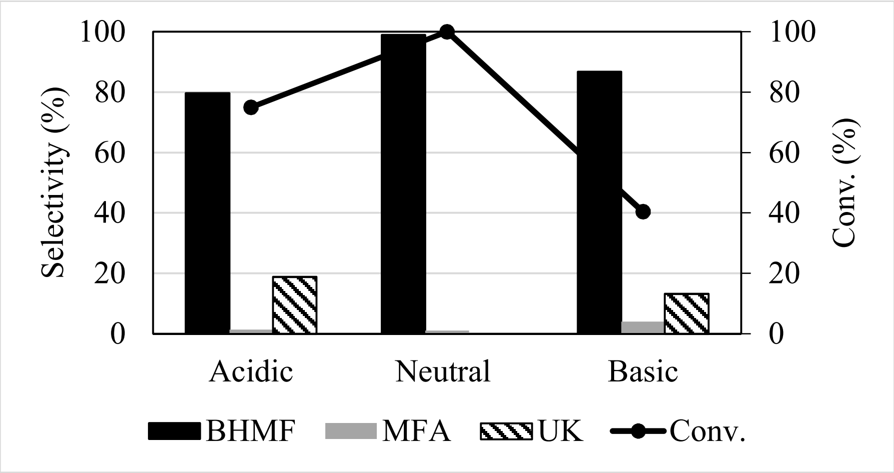


Figure 4: Effect of pH on the hydrogenation of HMF in water. Reaction condition: catalyst: substrate (wt. ratio) = 1:5; P_{H2}= 0.8 MPa, Temp. = 35 ºC, water – 2 ml and reaction time = 2h

Comparison with other solvents

Instead of water, the hydrogenation of HMF was conducted in different types of organic solvents. Three different categories of solvent including (i) polar protic, (methanol, ethanol, butanol and propanol), (ii) polar aprotic (acetone and tetrahydrofuran (THF)) and (iii) non polar (hexane) solvents were used to elucidate the solvent effect on the hydrogenation of HMF.

Table 2: Hydrogenation of HMF in different organic solvents

Entry	Solvent	Conv. (%)	Product yield (%)				
			BHMF	MF	MFA	HD	UK
1	Water	100.0	98.9	0.0	1.1	0.0	0.0
2	Methanol	72.1	89.8	5.6	1.2	0.0	3.4
3	Ethanol	55.6	87.2	3.7	0.0	0.0	9.1
4	Propanol	27.2	77.9	3.6	1.2	0.0	17.3
5	Butanol	24.4	70.5	1.8	0.0	6.2/0	21.5
6	Acetone	12.0	41.3	0.0	0.0	0.0	58.3
7	THF	18.2	32.4	5.8	0.0	54.8/0	7.0
8	Hexane	10.1	82.5	6.6	1.0	0.0	9.9

Reaction condition: catalyst: substrate (wt. ratio) = 1:5; Temperature= 35 °C; reaction time= 2h; Solvent= 2ml; P_{H2}= 0.8 MPa; BHMF= 2, 5- Bis- (hydroxymethyl)-furan, MF= 5- methylfurfural; MFA= 5-methylfurfuryl alcohol, HD= 1, 2-hexanediol, UK= unknown (unidentified products)

Table 2 summarizes the results of the hydrogenation of HMF conducted in several solvents at 35 °C under 0.8 MPa of hydrogen for 2h. From the results it is evident that the catalytic activity was strongly dependent on the solvent used. Among the solvents from first group, the conversion decreases in the following order: methanol (72.1)> ethanol (55.6)> propanol (27.2)> butanol (24.4). There are several parameters related to solvent properties are accounting for the solvent effect on the catalytic reactions. However, a simple approach is the considerations of donor and acceptor numbers of solvents, which are related to a quantitative measure of Lewis basicity and acidity, respectively. Here we plotted the conversion of HMF with the δ value of solvents (Figure 5). This δ value represents the difference between donor number and acceptor number [22]. From the results it is evident that the behaviour of the studied solvents can be divided into two groups: (i) solvents with negative δ value are capable of accepting electrons and (ii) solvents with positive δ value with the capability of donating electrons. The first group of solvents are methanol, ethanol, butanol and propanol providing a higher conversion of HMF. A clear trend was observed with the δ value and the substrate conversion. In the presence of those solvents the conversion was decreased with increased δ value attributed to a possible correlation between Lewis acidity and the substrate conversion. In addition, the selectivity of BHMF was almost same for methanol (89.8 %; Table 2, Entry 2) and ethanol (87.2 %; Table 2, Entry 3), whereas comparatively lower selectivity of ~ 78% and 77 % were detected in propanol and butanol, respectively (Table 2, Entry 4 and 5). The solvents with positive δ value has no effect on the conversion. In the presence of the second group of solvents (acetone, hexane and THF), the conversion of HMF was very poor and in the range of ~ 15 %, which provoked us to thought of a partial blocking of the metal active site by solvent adsorption. The role of solvent in a reaction is a complex matter when catalysts containing noble metals are used because of their tendency to interact with solvents containing oxygen, nitrogen and sulphur [23]. From the above results, we can suggest that water was the best choice as solvent for hydrogenation of HMF to BHMF under the studied reaction condition, but solvents with negative δ values provides better performance in comparison to the solvents with positive δ values.

Reaction pathway

It is too early to predict the reaction path of HMF hydrogenation over Pt/MCM-41 in water. However, from the accumulated experimental results it was observed that BHMF was obtained as the major product. In the present reaction condition, Pt/MCM-41 was selectively hydrogenating the –C=O group of HMF and consequently BHMF was formed. A similar trend of Pt catalyst was also observed during the hydrogenation of cinnamaldehyde over Pt catalyst [24]. Hence, primarily, it could be speculated that the adsorption of HMF takes place via –C=O and the reaction occurred through the formation of alkoxide intermediate [25]. The alkoxide formation is favoured at low temperature followed by the subsequent addition of the second hydrogen atom producing BHMF. A similar mechanism was also predicted before on the hydrogenation of furfural to furfuryl alcohol [26, 27].

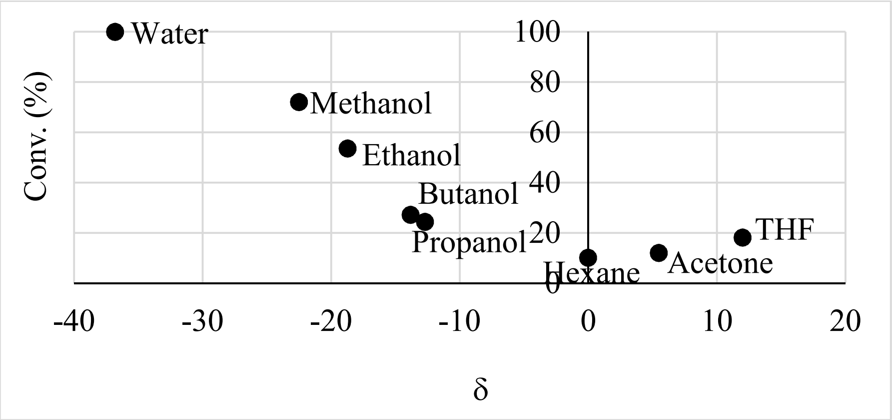


Figure 5: Relationship between conversion of HMF and δ value of solvents. Reaction condition: catalyst: substrate (wt. ratio) = 1:5; P_{H2}= 0.8 MPa, Temp. = 35 ºC, solvent = 2 ml and reaction time = 2h

Catalyst recycling

After reaction, the catalyst was separated simply by filtration and ready to recycle. Recycling experiments showed that it is possible to recycle the catalyst at least for six times. The result after 6^{th} recycle suggested moderate decrease in the activity (Table 1; entry 11; ESI Figure S3) possibly due to the slight change in the structure of the catalyst and Pt particle size (ESI; Figure S1 (b) and S2 (b)).

Conclusion

In conclusion, a simple method has been demonstrated to the hydrogenation of HMF to BHMF in aqueous medium under a mild reaction condition. The described method was highly selective to BHMF. Selectivity of the targeted compound was affected by hydrogen pressure, as well as by the presence or absence of water. In particular, a proper amount of water was necessary to obtain a high yield of the targeted compound but excess water hampered the catalytic activity. In addition, neutral medium was preferred over basic or acidic medium. A comparison with different organic solvents revealed the superiority of water as reaction medium for this reaction. Further work is necessary to understand the role of the medium. It is believed that this strategy could be extended to the other furan compounds and tuning of reaction condition might provide a scope to obtain other valuable compounds.

Experimental section

Reagents: 5-hydroxymethylfurfural, cetyltrimethylammonium bromide and H_2PtCl_6 were obtained from Aldrich. Tetraethyl orthosilicate and organic solvents (methanol, ethanol, butanol, 1-propanol, acetone, hexane, THF and chloroform) were from Wako Pure chemicals.

Catalyst synthesis

Hydrothermal synthesis of Pt/MCM-41 was based on the method as described in our previous work [28]. In brief, sodium hydroxide, cetyltrimethylammonium bromide (CTAB) were added to de-ionized water and stirred until gets dissolved. ~1 wt. % solution of Pt salt (H_2PtCl_6) was introduced in to the gel and again stirred for 2h followed by the addition of tetraethyl orthosilicate (TEOS) and stirring was continued for another 2h to reach homogeneity. Final gel composition was: 1 TEOS: 0.45 Na_2O: 0.12 CTAB: 118 H_2O. The gel was then autoclaved at 140°C for 48 h. The solid product was then filtered, washed thoroughly with de-ionized water followed by oven drying at 60°C. To remove template, the as-synthesized material was calcined at 550 °C for 8h in air. Before application, the calcined material was primarily characterized by XRD and TEM to get an insight of its structure (ESI; Figure S1 (a) and S2 (a)).

Catalytic activity

The hydrogenation of HMF was conducted in a 50 ml batch reactor. In a typical experiment, specified amount of catalyst (0.1g) was placed into the reactor containing 2 ml aqueous solution of the substrate (0.5 g). The reactor was placed in an oven with fan heater to maintain the constant temperature. After reaching the desired temperature, hydrogen of required pressure was introduced into the reactor. The reaction mixture was stirred continuously with a Teflon coated magnetic bar during the reaction. After the reaction, the liquid part was separated simply by filtration. Finally, the product mixture was identified and quantitatively analysed by GC/MS (Varian Saturn 2200). Quantification of the products was obtained by a multi-point calibration curve for each product. The selectivity to each product was calculated by the following expression $S_i = C_i / \sum Cp$, where C_i is the concentration of the product 'i' and $\sum Cp$ is the total concentration of the product.

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Supporting information

Figure S1: XRD pattern of calcined Pt/MCM-41 (a) before reaction and (b) after 7th recycle

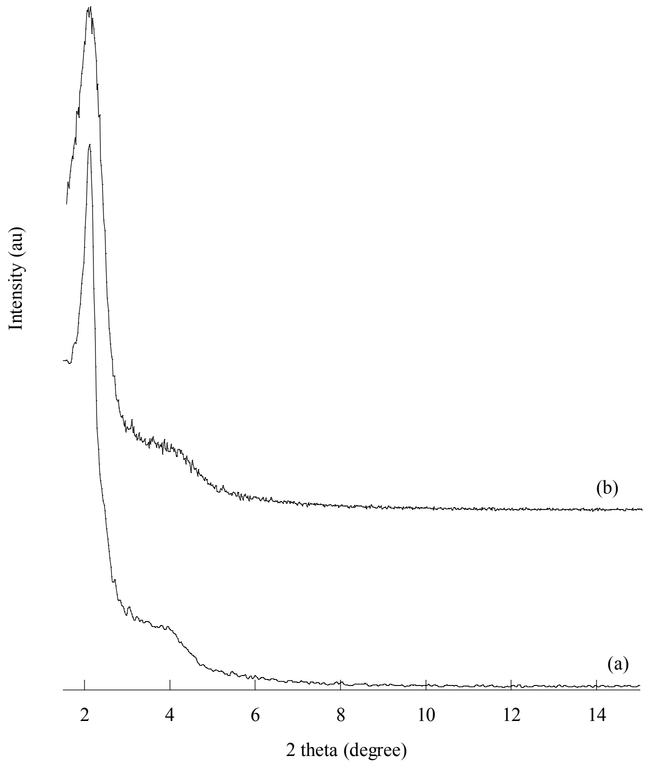


Figure S2: TEM image of Pt/MCM-41 (a) calcined and (b) after 7th recycle

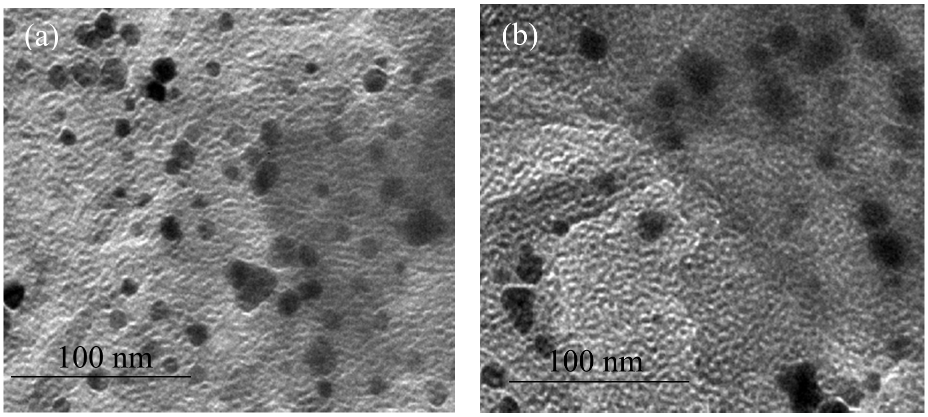
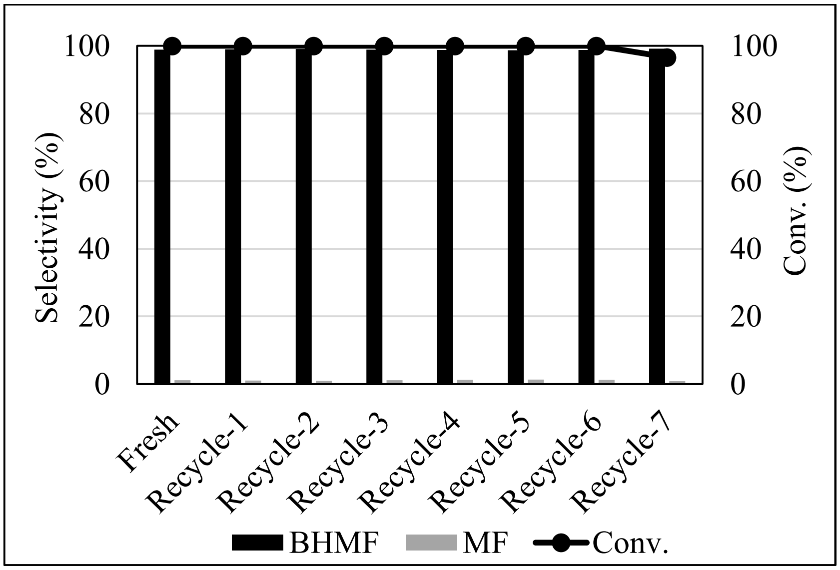


Figure S3: Catalyst recycling



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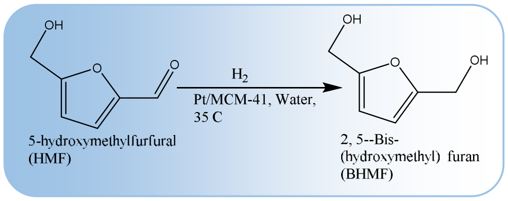
Selective hydrogenation of 5-hydroxymethylfurfural to 2, 5- Bis- (hydroxymethyl)-furan using Pt/MCM-41 in aqueous medium: A simple approach

Maya Chatterjee*, Takayuki Ishizaka and Hajime Kawanami*



An effective method was developed to obtain very high yield of BHMF (98 %) via hydrogenation of HMF in water.