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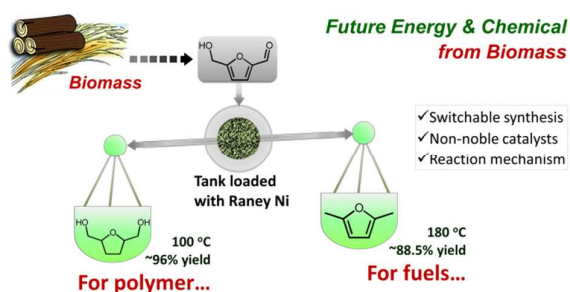
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# Switchable synthesis of 2,5-dimethylfuran and 2,5-dihydroxymethyltetrahydrofuran from 5-hydroxymethylfurfural over Raney Ni catalyst

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Switchable synthesis of 2,5-dimethylfuran and 2,5-dihydroxymethyltetrahydrofuran was achieved over Raney Ni catalyst, which has high feasibility in industry.



1    **Abstract**

2           Raney-type metals (Cu, Co and Ni) were employed to catalyze hydrogenation of  
3    5-hydroxymethylfurfural. Switchable synthesis of 2,5-dimethylfuran and  
4    2,5-dihydroxymethyltetrahydrofuran was achieved with 96% and 88.5% yield  
5    respectively over Raney Ni, demonstrating high feasibility for industrialization. The  
6    excellent yields can be explained by that Raney Ni facilitates the hydrogenation  
7    reaction but has limited deoxygenation ability at low temperature, while high  
8    temperature promotes the deoxygenation step. The reaction pathway was analyzed by  
9    time courses experiments and HMF hydrogenation over model catalysts was  
10   performed. The reaction mechanism related to the respective catalytic sites was  
11   discussed and proposed, which have great implications in design of efficient and  
12   non-noble metal catalysts.

13   **Keywords:** 5-hydroxymethylfurfural; biomass; hydrogenation; hydrogenolysis;  
14   non-noble catalysts

15

## 1 **1. Introduction:**

2 5-hydroxymethylfurfural (HMF) is a promising platform chemical for future  
3 chemical and fuel supply, as it can be obtained from abundant bio-resources<sup>1,2</sup>. The  
4 C=O, C-O and furan ring of HMF make it flexible for transformations by various  
5 methodologies (e.g., hydrogenation<sup>1</sup>, oxidation<sup>3</sup>, decarbonylation<sup>4</sup>, etherification<sup>5</sup>).  
6 Many useful products including 2,5-dimethylfuran (DMF),  
7 2,5-dimethyltetrahydrofuran (DMTHF), 2,5-dihydroxymethylfuran (DHMF),  
8 1,2,6-hexanetriol and 2,5-dihydroxymethyltetrahydrofuran (DHMTHF) could be  
9 produced by hydrogenation of HMF. Among them, DMF has been identified as a  
10 promising liquid fuel candidate with high energy density (30 kJcm<sup>-3</sup>) and octane  
11 number (RON = 119)<sup>6</sup>, and DHMTHF could be a bulk chemical in the manufacture of  
12 polyesters and a precursor for 1,6-hexanediol synthesis<sup>7-10</sup>.

13 For the potential application of both products, it would be of great convenience for  
14 switchable synthesis of both chemicals over the same reactor, because the “real-time”  
15 switching could respond more rapidly to the market demand and enhance profitability,  
16 as well as reduce the reactor downtime<sup>11</sup>. It thus would be of great importance for  
17 tunable synthesis over the same catalyst, especially over the same non-noble catalyst.  
18 To produce DMF, the hydrogenation of aldehyde group and hydrogenolysis of C-O  
19 bonds need to be proceeded efficiently. The catalysts with both C=O hydrogenation  
20 and deoxygenation ability (e.g., bifunctional/bimetallic catalysts<sup>6,12</sup>) could be good  
21 candidates. To produce DHMTHF, the furan ring and aldehyde group of HMF need to

1 be saturated without further hydrogenolysis. The catalysts with strong hydrogenation  
2 and limited deoxygenation ability could satisfy the needs. Considering the different  
3 requirements, a careful development of the catalytic system is required in order to  
4 obtain the desired products selectively.

5 Relatively few reports were conducted on the synthesis of DHMTHF, for which  
6 monometallic catalysts are usually applied (e.g., Ru, Ni, Pd) with high efficiency <sup>8,10,</sup>  
7 <sup>13-16</sup>. Nevertheless, few works were further played to investigate DMF synthesis in  
8 these systems. Moreover, dehydroxylation reaction is hard to occur in Pd/C with  
9 [BMIm]Cl/H<sub>2</sub>O system even at 200 °C <sup>10</sup>, making the switchable synthesis impossible.  
10 They considered that the protic H<sub>2</sub>O leads to the formation DHMF and DHMTHF,  
11 while the aprotic solvent tends to form DMF. For HMF hydrogenation to DMF,  
12 CuRu/C catalyst was firstly employed and exhibited a yield of ~71% <sup>6</sup>. Most following  
13 works were conducted over noble metal catalysts (e.g. Ru <sup>17, 18</sup>, Pd <sup>19-21</sup>, Au <sup>22</sup>, Pt <sup>23</sup>).  
14 Recently, a metal-acid bifunctional and non-noble Ni-W<sub>2</sub>C/AC catalyst was reported  
15 with 96% DMF yield, where W<sub>2</sub>C played a role of acid site with high deoxygenation  
16 ability <sup>12</sup>. Strong acidity of catalyst would catalyze cleavage of C-O bonds of  
17 hydroxymethyl groups <sup>24, 25</sup> and may not fit for DHMTHF synthesis. Moreover, the  
18 development of efficient and non-noble catalytic system still remains to be explored,  
19 from the aspect of large-scale industrialization.

20 **(Scheme 1)**

21 We herein employed the non-noble Raney Ni to catalyze HMF hydrogenation and

1 achieved tunable selectivity towards either DHMTHF (96.0%) or DMF (88.5%) over  
2 the same catalyst (**Scheme 1**). The catalyst saturated the C=O bonds and furan ring  
3 without broke the C-O bonds at low temperature. Instead, the high temperature  
4 compensated the limited hydrogenolysis ability of catalyst and accelerated the cleavage  
5 of C-O bonds. To our knowledge, this report possesses at least the following desirable  
6 features: 1) highly selective synthesis of DMF and DHMTHF over the same  
7 commercial non-noble catalyst, exhibiting high feasibility and profitability for industry,  
8 2) the selective synthesis only needs different reaction temperatures, of great  
9 convenience for “real-time” switching, 3) the discussion and understanding of reaction  
10 mechanism related to the catalytic sites were proposed, which were important for the  
11 rational design of efficient non-noble catalyst for HMF hydrogenation.

## 12 **2. Experimental section**

### 13 **2.1 Chemicals**

14 5-hydroxymethylfurfural (Shanghai De-Mo Pharmaceutical Science and  
15 Technology Limited Company, 98%), Raney Ni, Co and Cu catalysts (Dalian  
16 Tongyong Chemical Industry Co., Ltd.), ZSM-5 (The Catalyst Plant of Nankai  
17 University) and 1,4-dioxane (Sinopharm, AR) were purchased and used as received.  
18 5-methylfurfural, 2,5-dihydroxymethylfuran and 2,5-dihydroxymethyltetrahydrofuran  
19 were purchased from T.C.I. Corporation. The weight percentage of metal and  
20 aluminum in the Raney metals was more than 93% and less than 7%, respectively.

### 21 **2.2 Analytical method**

1 XRD patterns were recorded by a X-ray diffractometer (MiniFlex II, Rigaku) with  
2 Cu  $\alpha$  radiation operating at 40 kV, with a rate of 4 °C/min.

3 The samples after reaction were analyzed on GC-920 equipped with a  
4 DB-WAXETR capillary column and a FID detector. The products were identified by  
5 GC-MS and comparison of retention times of pure chemicals.

### 6 **2.3 Catalytic tests**

7 The tests were performed over a 100 ml tank reactor. For a typical procedure, the  
8 reactor was fed with HMF (1.5 g), Raney metals (0.5 g) and 1,4-dioxane (35 ml), then  
9 sealed and purged by H<sub>2</sub> (5 times). After that, the reactor was filled with 1.5 MPa H<sub>2</sub>  
10 and heated to object temperature within 30 minutes. After the test, the reactor was  
11 quenched in ice-water, and then the liquid and gas products were analyzed by a GC  
12 instrument with a FID detector.

## 13 **3. Results and discussion**

### 14 **3.1 Catalyst screening**

15 **(Figure 1)**

16 **(Table 1)**

17 All the Raney metals have the metal (Cu, Co and Ni) loadings higher than 93%.  
18 The fresh Raney Cu, Co and Ni catalysts were also characterized by XRD  
19 measurement (**Figure 1**). The XRD patterns of the Raney Ni and Cu catalysts are  
20 consistent with the typical crystalline Ni (PDF#04-0850) and Cu (PDF#04-0836)  
21 respectively, indicating that both metals are in a complete crystalline form. Unlike



1 Raney Ni and Cu, Raney Co exhibited the weak peaks which could be attributed to  
2 the characteristics of crystalline Co (PDF#15-0806). The result illustrated that Co has  
3 amorphous or/and microcrystalline construction and is highly dispersed. No  
4 diffraction peaks of crystalline Al were observed for all the cases.

5 The performance of HMF hydrogenation over these Raney metals was compared  
6 at 180 °C (**Table 1**, entries 1, 2, 8). Raney Cu exhibited a low HMF conversion of 25.1%  
7 and a DMF selectivity of 42.0%. The main byproduct for Raney Cu was  
8 5-methylfurfural (5-MF), indicating the weak C=O hydrogenation ability of the  
9 catalyst. 2,2-methylenebis(5-methyl-furan) (OMBM) and  
10 5,5'-(oxybis(methylene))bis(2-methylfuran) (A) (2furan, formed by the condensation  
11 of 5-MF and MFA <sup>26, 27</sup>) were also observed, as a result of the insufficient  
12 hydrogenation reactivity of Cu catalyst. Raney Co catalyst exhibited a HMF  
13 conversion of 94.3% and a DMF selectivity of 78.5%, which were greatly higher than  
14 that of Raney Cu.

15 Raney Ni exhibited the HMF conversion of 100% and a higher DMF selectivity  
16 of 88.5% than other catalysts, indicating the superior reactivity of Ni catalyst. The  
17 Raney Ni catalyst was then detailed studied at different reaction temperatures. It was  
18 found that DHMTHF could be synthesized at 100 °C with a yield up to 96.0% and a  
19 DMF yield of 88.5% could be realized upon increasing temperature to 180 °C (**Table**  
20 **1**, entries 4 and 8). When further increasing temperature, C-C cracking products and  
21 DMTHF were generated and DMF selectivity was decreased. Herein, this is the first

1 report of highly selective synthesis of DHMTHF and DMF over the same non-noble  
2 catalyst, tuned simply by reaction temperatures.

### 3 **3.2 Reaction mechanism**

4 **(Figure 2)**

5 **(Scheme 2)**

6 The reaction pathways were investigated by time courses at 100 °C and 180 °C to  
7 understand the tunable synthesis of DMF and DHMTHF (**Figure 2**). Typical GC charts  
8 of the products at both 100 °C and 180 °C were shown in **Figure S1** and **S2** respectively.  
9 In both cases, HMF was totally converted within 10 h, indicating the strong  
10 hydrogenation ability of Raney Ni. The absence of 5-hydroxymethyltetrahydrofurfural  
11 and 5-methyltetrahydrofurfural for both temperatures could also indicate that  
12 hydrogenation of aldehyde group is a fast reaction among the three functional groups  
13 (C=O, C=C, C-O), which is accordance with previous reports<sup>14, 15</sup>. At 100 °C, DHMF  
14 yield reached a plateau at 5 h and then decreased, whereas DHMTHF yield increased  
15 monotonically with increase of reaction time. The results revealed a step-wise reaction  
16 sequence (**Scheme 2**, HMF → DHMF → DHMTHF). No 5-methyltetrahydrofurfuryl  
17 alcohol (MTHFA) or DMTHF was detected, indicating that hydrogenolysis of  
18 hydroxymethyl group was hard to occur. It should be noted that DHMF yield increased  
19 until HMF was fully converted, revealing that the saturation of furan ring was slow. The  
20 unconverted HMF may inhibit the DHMF conversion to DHMTHF due to the fact that  
21  $\eta^2(\text{C},\text{O})$ -type configuration endows HMF with stronger adsorption than DHMF and the

1 competitive adsorption on the active site hinders conversion of DHMF<sup>28</sup>. On the other  
2 hand, the C=C bonds on the ring are conjugated and not easily to be hydrogenated<sup>29</sup>.  
3 Thus, HMF converted to DHMF rapidly and high yield of DHMTHF could be obtained  
4 at long reaction time. At 180 °C, trace amount of DHMTHF was detected, revealing  
5 that hydrogenation of furan ring is not preferential. A series of C-O cleavage products  
6 (MFA, 5-MF, DMF, DMTHF) were obtained, indicating that hydrogenolysis reaction  
7 could be promoted at high temperature for Raney Ni catalyst, which is in accordance  
8 with previous report<sup>30</sup>. DHMF yield exhibited a similar profile to that of 100 °C,  
9 passing through the maximum at 2 h, indicating that it was a common intermediate for  
10 both cases. 5-MF was also observed at the initial stage, revealing that hydrogenolysis of  
11 alcohol group of HMF occurs in parallel to the hydrogenation of aldehyde group at high  
12 temperature. Based on the above results and previous reports<sup>29</sup>, pathways of HMF  
13 hydrogenation at high temperature are summarized (**Scheme 2**). In all, DHMF is the  
14 main intermediate for both cases due to the fast hydrogenation of aldehyde group. At  
15 100 °C, hydrogenolysis of -CH<sub>2</sub>OH was slow and little hydrogenolysis products were  
16 detected. With increase of temperature to 180 °C, the hydrogenolysis of -CH<sub>2</sub>OH is  
17 greatly promoted and 5-MF is observed. However, due to the weak deoxygenating  
18 ability of Raney Ni catalyst, DHMF is still the main intermediate. The behavior is  
19 dramatically different with Ni-W<sub>2</sub>C/AC catalyst which was designed with Lewis acid  
20 sites and strong deoxygenating ability<sup>12</sup>.

21 At 100 °C, DHMTHF was achieved with high yield and hydrogenolysis products

1 were not detected. We ascribed the high yield to the weak acidity of Raney Ni catalyst  
2 and proved it in **Table 2** (see below). Different from reactivity at 100 °C,  
3 hydrogenolysis of hydroxymethyl group is greatly promoted at 180 °C. The slow ring  
4 hydrogenation and rapid hydrogenolysis of hydroxymethyl group contributed to the  
5 high DMF yield and trace amount of DHMTHF. It is also interesting that it was hard to  
6 stop the reaction in DHMF at 100 °C, while the ring reserved at 180 °C. According to  
7 the previous report, the polar CH<sub>2</sub>OH groups in the DHMF molecule have more  
8 affinity to the catalyst surface and can assist in the adsorption of DHMF onto the Ni  
9 metal surface<sup>28</sup>. However, the methyl group of DMF forces the aromatic ring further  
10 away from the catalytic surface, thereby reducing the probability of a reaction<sup>31</sup>.  
11 They also reported that the protective methyl group contributes to a less selectivity  
12 toward cracking in DMF hydrogenation than in 2-MF hydrogenation. Thus, DHMF is  
13 relatively more reactive than DMF and susceptible to hydrogenation. When DMF was  
14 formed, hydrogenation of furan ring became slower. Briefly, 1) the C=O bond of HMF  
15 could occupy active sites and hinder DHMF adsorption, 2) the C=C bonds are  
16 conjugated and not easily to be hydrogenated, 3) the C-O could assist in DHMF  
17 adsorption and be cleaved at high temperature. In all, the different adsorption geometry  
18 and strength of functional groups (C=O, C=C and C-O) offer a degree of flexibility to  
19 tunable DMF and DHMTHF synthesis.

20 To support the above mechanism, hydrogenation/hydrogenolysis of intermediates  
21 (DHMF and 5-MF) was performed under the working conditions (**Scheme S1, S2** and

1 **S3**). DHMF is a common intermediate for both DMF and DHMTHF synthesis  
2 (**Scheme S1** and **S2**). The reaction temperature has great effects on the reaction  
3 pathway. At low temperature, hydrogenation of furan ring occurred and DHMTHF  
4 was formed. At high temperature, hydrogenolysis of the side -CH<sub>2</sub>OH was promoted  
5 and DMF was achieved. The hydrogenation of 5-MF (**Scheme S3**) revealed that MFA  
6 can be obtained from 5-MF hydrogenation (the hydrogenation of C=O bonds) and  
7 DMF can be obtained from MFA hydrogenolysis (the hydrogenolysis of CH<sub>2</sub>OH  
8 group).

9 Pathways of HMF hydrogenation are summarized (**Scheme 2**). For Raney Cu, Co  
10 catalysts, some condensation intermediates (OMBM, A) were detected due to the slow  
11 conversion of 5-MF and MFA. For Ni catalyst with superior ability, reaction pathways  
12 were highly depended on reaction temperatures. The temperature influenced the  
13 occurrence of CH<sub>2</sub>-OH hydrogenolysis and determined the product distributions. In our  
14 case, Raney Ni catalyst plays a role in the hydrogenation step but has limited  
15 deoxygenation ability at low temperature, while high temperature promotes the  
16 deoxygenation step. Therefore, a tunable synthesis of products was achieved. The key  
17 to our success could be attributed to the nature of Raney Ni and avoidance of additional  
18 acid sites, considering that a metal catalyst with high acidity could catalyze  
19 hydrogenolysis reaction more effectively <sup>12</sup>.

20 To obtain DMF, hydrogenolysis of hydroxymethyl group is needed. It is generally  
21 concluded that metal-acid bifunctional catalysts are good candidates in hydrogenolysis

1 reaction, where acid promotes dehydration of  $\text{CH}_2\text{-OH}$  and metal acts as active phase to  
2 saturate/hydrogenate intermediates <sup>32, 33</sup>. Indeed,  $\text{W}_2\text{C}$  acts as acid to catalyze  
3 deoxygenation reaction for DMF synthesis has been reported with high efficiency <sup>12</sup>.  
4 However, the acid sites may not fit for DHMTHF synthesis, in which  $\text{C=O}$  and  $\text{C=C}$   
5 bonds are hydrogenated without further hydrogenolysis. To examine the roles of acid  
6 sites for DHMTHF synthesis, a solid acid (ZSM-5) was physically mixed with Raney  
7 Ni and employed in HMF hydrogenation (**Table 2**). HMF was fully converted in all  
8 cases. ZSM-5 could promote DHMTHF yield from 67.4 to 86.5% when the  
9 intermediate DHMF was not totally converted (15 h, **Table 2**, entry 1 and 2).  
10 However, MTHFA was formed, indicating that hydrogenolysis of hydroxymethyl  
11 group was also promoted. Besides, no obvious change was observed for the  
12 mechanical-mixed catalyst after extending the reaction time from 15 to 30 h. It might  
13 indicate the deactivation of the catalyst. This result might be also caused by the fact  
14 that acid could promote DHMF conversion to DHMTHF, but have little effect on  
15 DHMTHF conversion, considering that DHMTHF was more stable than DHMF <sup>34</sup>.  
16 The results clearly suggested that critical roles of acid sites were to promote both  
17 hydrogenation of furan ring and hydrogenolysis of  $\text{CH}_2\text{-OH}$  group. The results also  
18 suggested that DMF could be formed via dehydration of DHMF, which is similar with  
19 2-methylfuran formation from furfuryl alcohol hydrogenolysis <sup>35</sup>. Thus, when the  
20 target compound involves C-O hydrogenolysis, control of the acidity is essential. The  
21 Raney Ni system facilitated the hydrogenation reaction at low temperature and the

1 hydrogenolysis reaction at high temperature, achieving a switchable synthesis of  
2 DHMTHF and DMF.

### 3 **3.3 Catalyst stability**

4 **(Figure 3)**

5 Reusability of Raney Ni was also investigated under relatively severe condition  
6 (180 °C) (Fig. S1). After each test, the catalyst was washed with solvent (3 times) and  
7 recycled. After 5 runs, the conversion of HMF only decreased to 92.1% compared to  
8 100% conversion of the fresh catalyst, demonstrating the good hydrogenation ability of  
9 metallic Ni. Nevertheless, DMF selectivity decreased from 88.5% to 74%. The  
10 deactivated Raney Ni catalyst exhibited a similar catalytic performance with Raney  
11 Cu and Co catalysts (presence of 2furan and 5-MF), indicating a loss of  
12 hydrogenation ability. No evident growth of Ni particles was observed after 5 runs  
13 (Figure 4). The loss of DMF yield was thus probably caused by the mass loss of  
14 catalyst during washing process and the formation of high molecular weight byproducts  
15 which adsorbed on the metal sites, as confirmed in previous reports<sup>12, 18</sup>. Although the  
16 switchable synthesis of DMF and DHMTHF was achieved with high yields and a  
17 systematical reaction mechanism was proposed, the low reactivity and stability would  
18 hinder the applications. Thus, future work will be needed for exploring efficient and  
19 especially stable catalysts for selective hydrogenation of HMF.

## 20 **4. Conclusion**

21 We have demonstrated a highly efficient and selective non-noble catalyst that can

1 be used for hydrogenation of HMF. Notably, the reaction temperature offers a degree of  
2 flexibility to the process such that either DMF or DHMTHF could be obtained as the  
3 major product, due to the sufficient hydrogenation ability and weak hydrogenolysis  
4 ability of the Raney Ni catalyst. The detailed reaction mechanism and catalyst  
5 reusability were also studied. The results here demonstrated the potential of non-noble  
6 metal catalysts for HMF hydrogenation.

## 7 Acknowledgements

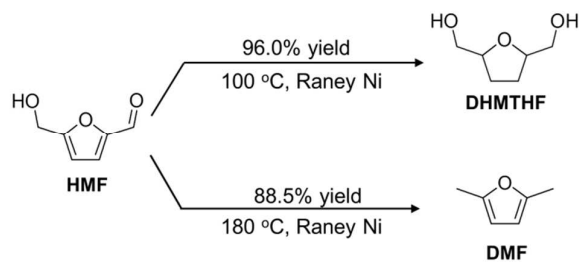
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## 10 References

- 11 1. R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de  
12 Vries, *Chem. Rev.*, 2013, **113**, 1499-1597.
- 13 2. N. Shi, Q. Liu, Q. Zhang, T. Wang and L. Ma, *Green Chem.*, 2013, **15**, 1967-1974.
- 14 3. C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana and V. Zima, *Appl. Catal. A: Gen.*, 2005,  
15 **289**, 197-204.
- 16 4. F. M. A. Geilen, T. vom Stein, B. Engendahl, S. Winterle, M. A. Liauw, J. Klankermayer and  
17 W. Leitner, *Angew. Chem. Int. Ed.*, 2011, **50**, 6831-6834.
- 18 5. P. Che, F. Lu, J. Zhang, Y. Huang, X. Nie, J. Gao and J. Xu, *Bioresour. Technol.*, 2012, **119**,  
19 433-436.
- 20 6. Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982-985.
- 21 7. F. C. A. Figueiredo, E. Jordão and W. A. Carvalho, *Appl. Catal. A: Gen.*, 2008, **351**, 259-266.
- 22 8. T. Buntara, S. Noel, P. H. Phua, I. Melián - Cabrera, J. G. de Vries and H. J. Heeres, *Angew.*  
23 *Chem. Int. Ed.*, 2011, **50**, 7083-7087.
- 24 9. T. Buntara, S. Noel, P. H. Phua, I. Melián-Cabrera, J. G. de Vries and H. J. Heeres, *Top. Catal.*,  
25 2012, **55**, 612-619.
- 26 10. H. Cai, C. Li, A. Wang and T. Zhang, *Catal. Today*, 2014, **234**, 59-65.
- 27 11. J. G. Stevens, R. A. Bourne, M. V. Twigg and M. Poliakoff, *Angew. Chem. Int. Ed.*, 2010, **49**,  
28 8856-8859.
- 29 12. Y. B. Huang, M. Y. Chen, L. Yan, Q. X. Guo and Y. Fu, *ChemSusChem*, 2014, **7**, 1068-1072.
- 30 13. T. J. Connolly, J. L. Considine, Z. Ding, B. Forsatz, M. N. Jennings, M. F. MacEwan, K. M.  
31 McCoy, D. W. Place, A. Sharma and K. Sutherland, *Org. Process Res. Dev.*, 2010, **14**, 459-465.



- 1 14. Y. Nakagawa and K. Tomishige, *Catal. Commun.*, 2010, **12**, 154-156.
- 2 15. R. Alamillo, M. Tucker, M. Chia, Y. Pagán-Torres and J. Dumesic, *Green Chem.*, 2012, **14**,  
3 1413-1419.
- 4 16. Y. Nakagawa, K. Takada, M. Tamura and K. Tomishige, *ACS Catal.*, 2014, **4**, 2718-2726.
- 5 17. Y. Zu, P. Yang, J. Wang, X. Liu, J. Ren, G. Lu and Y. Wang, *Appl. Catal. B: Environ.*, 2014,  
6 **146**, 244-248.
- 7 18. J. Jae, W. Q. Zheng, R. F. Lobo and D. G. Vlachos, *ChemSusChem*, 2013, **6**, 1158-1162.
- 8 19. D. Scholz, C. Aellig and I. Hermans, *ChemSusChem*, 2014, **7**, 268-275.
- 9 20. T. Thananattananachon and T. B. Rauchfuss, *Angew. Chem. Int. Ed.*, 2010, **122**, 6766-6768.
- 10 21. M. Chatterjee, T. Ishizaka and H. Kawanami, *Green Chem.*, 2013, **16**, 1543-1551.
- 11 22. S. Nishimura, N. Ikeda and K. Ebitani, *Catal. Today*, 2013, **232**, 89-98.
- 12 23. G.-H. Wang, J. Hilgert, F. H. Richter, F. Wang, H.-J. Bongard, B. Spliethoff, C. Weidenthaler  
13 and F. Schüth, *Nat. Mater.*, 2014, **13**, 293-300.
- 14 24. I. Gandarias, P. Arias, J. Requies, M. Güemez and J. Fierro, *Appl. Catal. B: Environ.*, 2010, **97**,  
15 248-256.
- 16 25. M. Massa, A. Andersson, E. Finocchio and G. Busca, *J. Catal.*, 2013, **307**, 170-184.
- 17 26. M. Chidambaram and A. T. Bell, *Green Chem.*, 2010, **12**, 1253-1262.
- 18 27. M. R. Grochowski, W. Yang and A. Sen, *Chem. Eur. J.*, 2012, **18**, 12363-12371.
- 19 28. Y. Nakagawa, H. Nakazawa, H. Watanabe and K. Tomishige, *ChemCatChem*, 2012, **4**,  
20 1791-1797.
- 21 29. L. Hu, L. Lin and S. Liu, *Ind. Eng. Chem. Res.*, 2014, **53**, 9969-9978.
- 22 30. A. Perosa and P. Tundo, *Ind. Eng. Chem. Res.*, 2005, **44**, 8535-8537.
- 23 31. C. Aliaga, C.-K. Tsung, S. Alayoglu, K. Komvopoulos, P. Yang and G. A. Somorjai, *J. Phys.*  
24 *Chem. C*, 2011, **115**, 8104-8109.
- 25 32. Y. Kusunoki, T. Miyazawa, K. Kunimori and K. Tomishige, *Catal. Commun.*, 2005, **6**,  
26 645-649.
- 27 33. Y. Zhu, X. Kong, X. Li, G. Ding, Y. Zhu and Y.-W. Li, *ACS Catal.*, 2014, **4**, 3612-3620.
- 28 34. S. Yao, X. Wang, Y. Jiang, F. Wu, X. Chen and X. Mu, *ACS Sustainable Chem. Eng.*, 2013, **2**,  
29 173-180.
- 30 35. V. Vorotnikov, G. Mpourmpakis and D. G. Vlachos, *ACS Catal.*, 2012, **2**, 2496-2504.
- 31
- 32
- 33

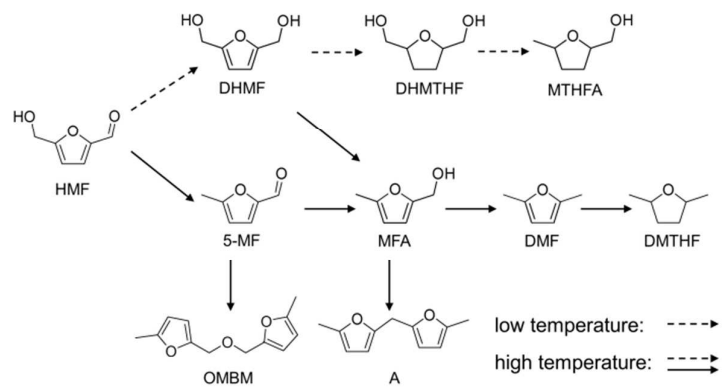


1

2 **Scheme 1** Switchable and efficient synthesis of DHMTHF and DMF from HMF

3 over Raney Ni.

4



1

2 **Scheme 2** Proposed reaction pathway for HMF hydrogenation/hydrogenolysis

3 (MTHFA was presented only when ZSM-5 was added.).

4

1 **Table 1.** Hydrogenation of HMF over Raney metal catalysts.<sup>a</sup>

Entry	Catalyst	T/°C	Conv. /%	Selectivity /%						
				DMF	5-MF	MFA	DHMF	DHMTHF	2furan	Others
1	Raney Cu	180	25.1	42.0	34.5	4.5	0	3.0	11.4	4.6
2	Raney Co	180	94.3	78.5	1.8	2.7	0	2.7	5.9	8.4
3	Raney Ni	100	100	1.4	0	2.0	27	67.4	0	2.2
4 <sup>b</sup>	Raney Ni	100	100	1.9	0	0	0	96.0	0	2.1
5	Raney Ni	120	100	6.0	0	5.1	18.1	65.4	0	5.4
6	Raney Ni	140	100	10.2	0	8.3	13.8	60.7	0	7.0
7	Raney Ni	160	100	46.3	0	8.6	6.1	32.6	0	6.4
8	Raney Ni	180	100	88.5	0	0	0	3.0	0	8.5
9	Raney Ni	200	100	79.8	0	0	0	3.0	0	17.2
10	Raney Ni	220	100	69.3	0	0	0	0	0	30.7

2 <sup>a</sup> Reaction conditions: HMF 1.5 g, catalyst 0.5 g, 1,4-dioxane 35 ml, 1.5 MPa H<sub>2</sub>, and reaction time 15 h at the  
3 defined temperatures. 2furan means OMBM and A. Others mainly include 2,5-DMTHF, 2-MF, 2-hexanol and C-C  
4 cracking products. <sup>b</sup> 30 h was used to optimize the DHMTHF yield.

5

1 **Table 2.** Hydrogenation of HMF over model catalysts.<sup>a</sup>

Entry	Catalyst	Yield /%					
		DMF	DMTHF	DHMTFH	MTHFA	DHMF	Others
1	RaneyNi	1.4	0	67.4	0	27	4.2
2	RaneyNi+ ZSM-5	1.6	0.8	86.5	5.1	2.4	3.6
3	RaneyNi <sup>b</sup>	1.9	0	96.0	0	0	2.1
4	RaneyNi+ ZSM-5 <sup>b</sup>	0.8	2.9	85.9	4.5	0	5.9

2 <sup>a</sup> Reaction conditions: Raney Ni: Raney Ni (0.5 g); Raney Ni+ZSM-5: Raney Ni (0.5 g) and  
3 ZSM-5 (0.1 g), HMF 1.5 g, 1,4-dioxane 35 ml, 100 °C 1.5 MPa H<sub>2</sub>, reaction time = 15 h. <sup>b</sup>  
4 reaction time = 30 h.

5

1 **Figure captions**

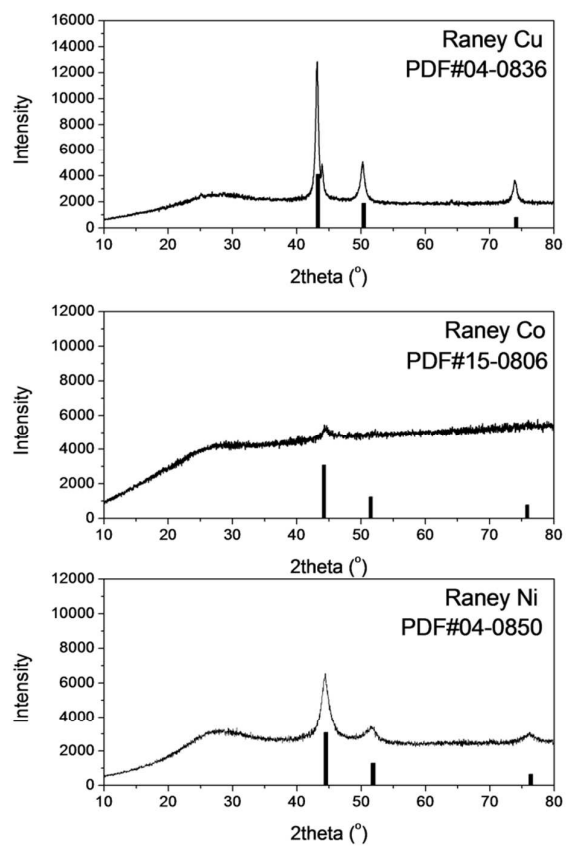
2 **Figure 1.** XRD patterns of fresh Raney Cu, Co and Ni catalysts.

3 **Figure 2.** HMF conversion and product yield versus reaction time at 100 °C (a) and 180  
4 °C (b). Reaction conditions: HMF 1.5 g, Raney Ni 0.5 g, 1,4-dioxane 35 ml, 1.5 MPa  
5 H<sub>2</sub>.

6 **Figure 3.** Recycle experiments of the Raney Ni catalyst. Conditions: HMF 1.5 g, Raney  
7 Ni 0.5 g, 1,4-dioxane 35 ml, 1.5 MPa H<sub>2</sub>, 180 °C, 15 h.

8 **Figure 4.** XRD patterns of fresh and used Raney Ni catalyst.

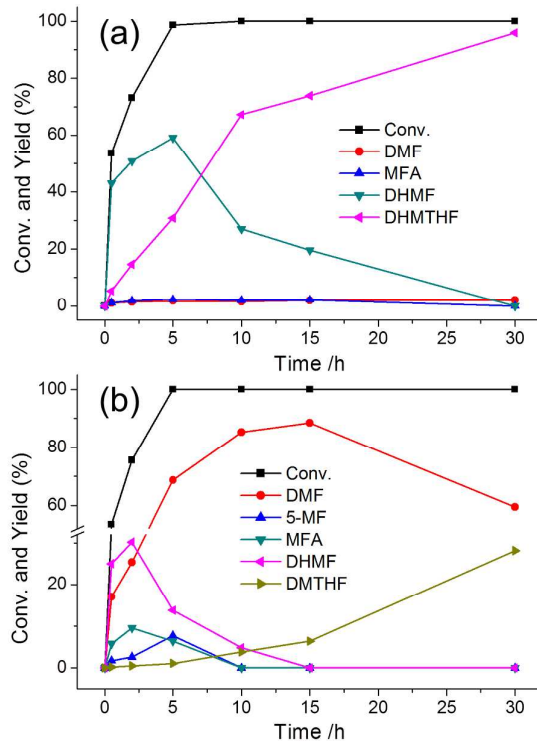
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2 **Figure 1.** XRD patterns of fresh Raney Cu, Co and Ni catalysts.

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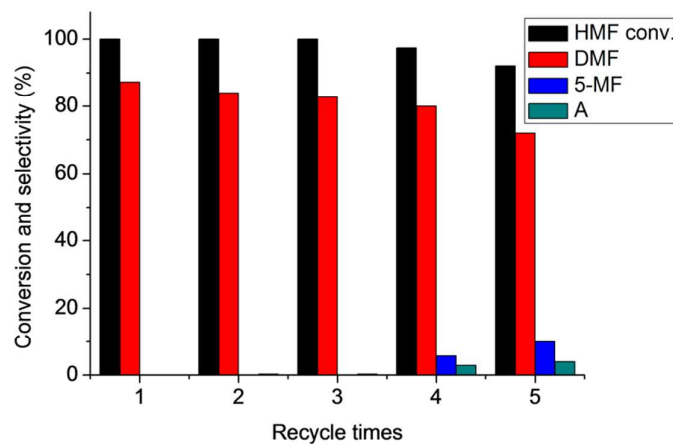
2 **Figure 2.** HMF conversion and product yield versus reaction time at 100 °C (a) and 180

3 °C (b). Reaction conditions: HMF 1.5 g, Raney Ni 0.5 g, 1,4-dioxane 35 ml, 1.5 MPa

4 H<sub>2</sub>.

5

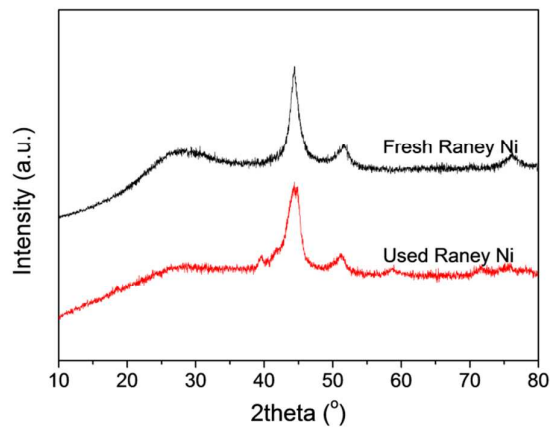




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2 **Figure 3.** Recycle experiments of the Raney Ni catalyst. Conditions: HMF 1.5 g,3 Raney Ni 0.5 g, 1,4-dioxane 35 ml, 1.5 MPa H<sub>2</sub>, 180 °C, 15 h.

4



1

2 **Figure 4.** XRD patterns of fresh and used Raney Ni catalyst.

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