

# Green Chemistry

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## ARTICLE

# Cooperative catalysis of Pt/C and acid resin for the production of 2,5-dimethyltetrahydrofuran from biomass derived 2,5-hexanedione under mild condition

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Conversion of biomass into 2,5-dimethyltetrahydrofuran (DMTHF), an excellent fuel additive, solvent, and industrial intermediate, is an important reaction in green chemistry. In this work, different combinations of supported metal catalysts and solid acids were investigated for the synthesis of DMTHF from biomass derived diketone (2,5-hexanedione, 2,5-HD). Results showed that commercial Pt/C and solid acid Amberlite® IR-120H had excellent cooperative effect for the reaction. 2,5-HD could be converted into DMTHF with a yield up to 99% under milder condition. Further experiment indicated that 2,5-hexanediol (2,5-HDO) is a key intermediate in the reaction. The catalyst system could be facilely recovered due to the heterogeneity and reused for several times without notable change in the performance.

## Introduction

The rapid depletion of fossil resources and growing energy and resource demands drive the conversion of biomass into useful chemicals to become an important topic in green chemistry.<sup>1</sup> Lignocellulose and its derivatives are abundant and potential sustainable sources for bulk chemicals, fuel additives, and materials.<sup>1b-e, 2</sup> Through rational design of the catalysts or catalyst system, lignocellulose and its derivatives can be converted into value-added chemicals, such as 5-hydroxymethylfurfural (HMF),<sup>3</sup> gamma-valerolactone (GVL),<sup>4</sup> 2,5-dimethylfuran (DMF),<sup>5</sup> 2,5-bis(hydroxymethyl)furan (BHMF),<sup>5a, 6</sup> and 2,5-dimethyltetrahydrofuran (DMTHF),<sup>5a, 5c, 7</sup> indoles,<sup>8</sup> *etc.*, which have broad applications in the fields of fuel additives,<sup>5a, 5d, e, 9</sup> solvents,<sup>4c-e</sup> and industrial intermediates.<sup>3a, 5a, b, 6, 10</sup>

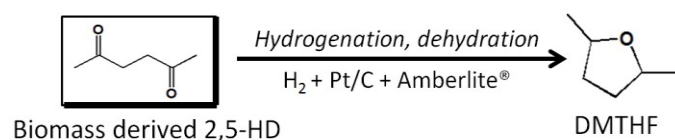
Among the biomass derived chemicals, DMTHF is an important molecule with wide applications. For example, DMTHF is an excellent candidate for gasoline replacement.<sup>11</sup> Compared with ethanol, DMTHF has higher boiling point (90–92 °C) and research octane number (119), and lower miscibility with water.<sup>5d</sup> The higher energy density of DMTHF (31 MJL<sup>-1</sup>) is comparable to gasoline (34.2MJL<sup>-1</sup>) and far superior to ethanol (23 MJL<sup>-1</sup>).<sup>11-12</sup> DMTHF is even superior to DMF as the gasoline additives. It is similar to DMF in terms of energy density (31.8 MJL<sup>-1</sup>), volatility, and solubility in water, but the saturated structure makes DMTHF have good storage

and transportation stability and become better candidate for liquid fuel.<sup>13</sup> Besides fuel additives, DMTHF can also be used as reaction solvents,<sup>14</sup> chemical intermediates,<sup>15</sup> catalyst ligands,<sup>16</sup> and battery electrolyte,<sup>17</sup> *etc.*

Different approaches have been reported to produce DMTHF. Both secondary aliphatic alcohols and diols (2,5-hexanediol) were used as starting molecules to synthesize DMTHF under the chemical or enzymatic catalysis.<sup>18</sup> However, either complex steps or unfriendly chemicals were used in these reported methods. With the development of green chemistry, synthesis of DMTHF from renewable biomass has drawn much attention.<sup>5a, 5c, 7, 13</sup> During the synthesis of DMTHF from biomass, DMF and 2,5-hexanedione (2,5-HD) are commonly used substrates or crucial intermediates,<sup>5a-d, 7, 12-13, 19</sup> and 2,5-HD could be derived from biomass.<sup>19b</sup> It was demonstrated that the DMTHF yield was higher from 2,5-HD than that from DMF, attributed to the better stability of 2,5-HD than DMF, especially under the acidic conditions.<sup>7</sup> The reaction rate of 2,5-HD to DMTHF was much higher than that of DMF to DMTHF.<sup>12</sup> Direct conversion of DMF to DMTHF also suffered from high reaction temperatures.<sup>5c</sup> Accordingly, 2,5-HD is a more suitable substrate to produce DMTHF than DMF. However, up to now, studies on the direct conversion of 2,5-HD to DMTHF is very limited, and either expensive homogeneous Ru or Ir catalysts and corrosive liquid acids or harsh reaction conditions (high temperature and H<sub>2</sub> pressure) was adopted.<sup>7, 12</sup> Therefore, it is

still highly desirable to explore efficient, robust, and readily recyclable catalyst system for the DMTHF production.

Herein, we reported an efficient catalyst system consisting of supported metal catalyst and solid acid for the production of DMTHF from biomass derived 2,5-HD (Scheme 1). Among the various combinations of metal and acid catalysts studied, the combination of commercial Pt/C and Amberlite®IR-120H was demonstrated to be the most efficient, with DMTHF yield up to 99% without using liquid acid and organic solvents, and the reaction condition was milder than those reported. Our catalytic system has some obvious advantages, such as the high efficiency and stability, milder reaction conditions, and facile recycling.



**Scheme 1.** Catalyst system for catalytic conversion of 2,5-HD into DMTHF in the presence of H<sub>2</sub>, Pt/C, and Amberlite®IR-120H.

## Experimental

### Materials

Amberlyst® 15H (denoted as AM-1, wet, ion exchange resin, beads), Amberlite® IR-120H (denoted as AM-2, wet, ion exchange resin), Zeolite Y (hydrogen), and Pd/Al<sub>2</sub>O<sub>3</sub> (palladium, 1 wt% on alumina powder, reduced, 300 m<sup>2</sup>/g) were from Alfa Aesar®. Pt/C (1 wt% on carbon) was provided by Hubei Deli New Material Co., Ltd., China. Skeletal nickel catalyst (slurry in water) and 2,5-dimethyltetrahydrofuran (> 98.0%) were from TCI Chemicals. Silicotungstic acid (H<sub>4</sub>[SiO<sub>4</sub>(W<sub>3</sub>O<sub>9</sub>)<sub>4</sub>], AR), phosphomolybdic acid (H<sub>3</sub>Mo<sub>12</sub>O<sub>40</sub>P, AR), and tetrahydrofurfuryl alcohol (THFAL, AR) were provided by Sinopharm Chemical Reagent Co. Ltd. 2,5-Hexanedione (> 99.0%) and 2-hexanol were obtained from J&K Chemical. 2,5-Hexanediol (> 99.0%) was from Acros Organics. Nafion® SAC-13 (denoted as NS, pore diameter > 10 nm, pore volume > 0.6 mL/g) was purchased from Aldrich Chemistry. H<sub>2</sub> was provided by Beijing Analytical Instrument Company.

### Catalyst preparation

The solid acid resins, Amberlyst® 15H and Amberlite® IR-120H (denoted as AM-1 and AM-2, respectively), were washed with water and ethanol thoroughly and then dried under 100 °C overnight. Other acid catalysts were used as received. The preparation procedures of metal catalysts, including Pt/C (1 wt%), Ru/C (1 wt%), and Pt/AM-2 (1 wt%) were given in the Supporting information. The Co/AM-1 (10 wt%) was prepared by the impregnation and NaBH<sub>4</sub> reduction method according to our previous work.<sup>20</sup> The acid density of the acids used in this work was characterized according to the reported method, and the data were given in Table S1.<sup>21</sup>

### Reaction

The hydrogenation reaction was performed in a 10 mL Teflon-lined stainless steel autoclave equipped with a magnetic stirrer. In a typical experiment, 0.5 g 2,5-HD (4.4 mmol), 2 g water and certain amount of catalysts were introduced into the reactor. After removing the air via vacuum, hydrogen was charged into the reactor to a desired pressure. Then the reactor was placed in a constant temperature air bath and the stirrer was started. After reaction, the reactor was cooled in ice-water to quench the reaction and the organic phase was diluted by ethanol. The sample was analyzed by gas chromatograph (GC, HP 4890) equipped with a flame ionization detector (FID), and THFAL was used as the internal standard. Identification of the products and reactant was done using a GC-MS (SHIMADZU-QP2010) as well as by comparing the retention times to respective standards in GC traces. The yield of DMTHF was expressed in molar ratio of the added 2,5-HD and DMTHF. In the reusability experiments, the catalysts were separated via centrifugation, washed with water, and then reused for the next run directly. The virgin and used Pt/C catalysts were characterized by transmission electron microscopy (TEM, JEOL JEM-1011).

## Results and Discussion

### Selection of the metal and acid catalysts

We first studied the conditions that only metal catalyst or acid catalyst was applied as the catalyst (Entries 1, 2, Table 1). It can be seen that the DMTHF yield was very low or even no DMTHF was produced when only Pt/C or AM-1 existed. When only Pt/C was used, the product was mainly 2,5-hexanediol (2,5-HDO). But when the metal catalyst and the acid catalyst co-existed, the DMTHF yield was significantly improved (Entries 3, 4, Table 1). These results indicated that both the metal catalyst and the acid catalyst were essential and they exhibited a cooperative effect for the reaction. Therefore, we investigated different combinations of metal and acid catalyst on the reaction. The effect of different metal species, including noble metals (Ru, Pt, Pd) and transition metals (Ni, Co), was studied using commercial acid resin AM-1 as the acid catalyst (Entries 3—8, Table 1). It was found that the performance of the catalysts was significantly affected by both the metal species and the supports. The noble metal catalysts (Ru/C, Pt/C, Pd/C) generally showed higher conversion and product yield than those of transition metal catalysts (Raney Ni, Co/AM-1), and Pt/C (1 wt%) had the highest conversion and product yield (>99% and 93%, respectively), while Pd/C (1 wt%) and Ru/C (1 wt%) had a lower DMTHF yield under the same condition (Entries 3—5, 7, 8, Table 1). For Pd catalyst, Pd/C showed better performance than that of Pd/Al<sub>2</sub>O<sub>3</sub>, indicating the important role of the support (Entries 5, 6, Table 1). We also attempted to load Pt directly on AM-1 to form a bifunctional Pt/AM-1 (1 wt%) catalyst. The results showed that the conversion was moderate, but no DMTHF was formed (Entry 9, Table 1). The reasons for this are complex, and one possible reason is that the H<sub>2</sub>PtCl<sub>6</sub> precursor was not completely reduced under H<sub>2</sub> at 150 °C (adopted in this work). Further increasing the reduction temperature may destroy the -SO<sub>3</sub>H group and the skeleton structures of the acid resin. Therefore, we focused on the simple and

efficient combination of metal and acid catalysts in this work. Subsequently, we chose the Pt/C as the metal catalyst to compare the performances of different acid catalysts (Entries 10–14, Table 1). The results showed that most of the acid catalysts exhibited good to excellent activity on the reaction, including the acid resins (AM-1, AM-2, NS) (Entries 4, 10, 11, Table 1), silicotungstic acid (SA) (Entry 12, Table 1), and molecular sieve (MS) (Entry 13, Table 1), among which the AM-2 achieved the highest conversion and yield (Entry 10, Table 1). It can be seen from Table 1 that although some catalyst combinations had high conversions (for example, Entries 3, 13, and 14), some amounts of other products such as 2,5-hexanediol (2,5-HDO), 2-hexanol (2-HO), and some unknown by-products were produced. Based on the above results, the combination of Pt/C + AM-2 was chosen for further studies.

### The effect of reaction temperature

The effect of reaction temperature on the conversion of 2,5-HD is shown in Table 2. 2,5-HD could be completely converted within 2 h in the temperature range of 70–120 °C. At lower temperature (70 °C), a moderate DMTHF yield of 55% was achieved. But when we prolonged the reaction time under 70 °C to 20 h, a 93% yield was obtained. The DMTHF yield could reach up to 95% at 80 °C. When the temperature was increased to 90 °C or a higher level, the DMTHF yields increased to higher than 99%, indicating that 2,5-HD could nearly be quantitatively converted into DMTHF. The final DMTHF selectivities were higher than 90% in the temperature range of 70–120 °C. These results indicated that the temperature mainly affected the reaction rate, and had no significant influence on the selectivity. Keeping in mind that the energy input should be decreased as far as possible within acceptable product yields and reaction rate, 90 °C is enough for the efficient synthesis of DMTHF from 2,5-HD.

**Table 1** Performances of different combinations of metal and acid catalysts<sup>a</sup>

Entry	Catalysts	Conv./%	Yield/%			
			DMTHF	2,5-HDO <sup>b</sup>	2-HO <sup>c</sup>	Others <sup>d</sup>
1 <sup>e</sup>	Pt/C	> 99	15	80	0	4
2 <sup>f</sup>	AM-1	23	0	0	0	23
3	Ru/C+AM-1	> 99	30	67	2	< 1
4	Pt/C+AM-1	> 99	93	0	6	< 1
5	Pd/C+AM-1	43	16	0	0	27
6	Pd/Al <sub>2</sub> O <sub>3</sub> +AM-1	38	10	0	0	28
7 <sup>g</sup>	Raney Ni+AM-1	58	23	0	0	35
8 <sup>h</sup>	Co/AM-1	30	8	0	0	22
9	Pt/AM-1	32	0	0	0	32
10	Pt/C+AM-2	> 99	> 99	0	0	< 1
11	Pt/C+NS	> 99	84	0	7	8
12	Pt/C+SA	> 99	95	0	4	< 1
13	Pt/C+MS	> 99	75	0	5	19
14	Pt/C+PA	> 99	41	20	0	38

<sup>a</sup>Typical reaction conditions were as follows until otherwise stated: 2,5-HD, 0.5 g; H<sub>2</sub>O, 2 mL; metal catalyst, 0.28 mol% of the substrate; acid catalyst, 0.05 g; reaction temperature, 120 °C; H<sub>2</sub> pressure, 3.0 MPa; reaction time, 2 h; The metal loading for Pt/C, Ru/C, Pd/C, Pd/Al<sub>2</sub>O<sub>3</sub>, and Pt/AM-1 was 1 wt%; AM-1=Amberlyst®15(H); AM-2=Amberlite®IR-120(H); NS=Nafion®SAC-13; SA=Silicotungstic acid; MS=Molecular sieve (Zeolite Y); PA=Phosphomolybdic acid. <sup>b</sup>2,5-HDO, 2,5-hexanediol. <sup>c</sup>2-HO, 2-hexanol. <sup>d</sup>Others represented the unknown by-products. <sup>e</sup>Only Pt/C was used. <sup>f</sup>Only AM-1 was used. <sup>g</sup>0.017 g Raney Ni (wet) was added. <sup>h</sup>0.05 g AM-1 supported 0.005 g Co.

**Table 2** Effect of reaction temperature on the conversion of 2,5-HD to DMTHF<sup>a</sup>

Entry	Temp./°C	Time/h	Conv./%	Yield/%	Sel./%
1	70	2	> 99	55	55
2	70	20	> 99	93	93
3	80	2	> 99	95	95
4	90	2	> 99	97	97
5	100	2	> 99	> 99	100
6	120	2	> 99	> 99	100

<sup>a</sup>Reaction conditions: 2,5-HD, 0.5 g; H<sub>2</sub>O, 2 mL; Pt/C, 0.05 g (0.28 mol% of the substrate); AM-2, 0.05 g; H<sub>2</sub> pressure, 3.0 MPa; reaction temperature and time were given in the table.

### The effect of H<sub>2</sub> pressure

The effect of H<sub>2</sub> pressure on the reaction is shown in Table 3. It can be seen that H<sub>2</sub> pressure also played an important role in the reaction. A moderate conversion (51%) with a 28% yield of DMTHF was observed within 2 h even H<sub>2</sub> pressure was as low as 1 MPa. When the reaction time was increased to 20 h, a yield of 80% was observed. Increasing the H<sub>2</sub> pressure could improve the reaction rate significantly. When the H<sub>2</sub> pressure was increased to 3 MPa or a higher level, almost total conversion of 2,5-HD was fulfilled, and DMTHF yield could reach to > 99%. The final DMTHF selectivity increased from 80% under 1 MPa to 100% under 3 MPa, indicating that H<sub>2</sub> pressure had effect on both the reaction rate and the selectivity. Therefore, 3 MPa was high enough to convert 2,5-HD into DMTHF.

**Table 3** Effect of H<sub>2</sub> pressure on the conversion of 2,5-HD to DMTHF<sup>a</sup>

Entry	Pressure/MPa	Time/h	Conv./%	Yield/%	Sel./%
1	1	2	51	28	55
2	1	20	> 99	80	80
3	2	2	71	49	69
4	2	20	> 99	90	90
5	3	2	> 99	> 99	100
6	4	2	> 99	> 99	100

<sup>a</sup>Reaction conditions: 2,5-HD, 0.5 g; H<sub>2</sub>O, 2 mL; Pt/C, 0.05 g (0.28 mol% of the substrate); AM-2, 0.05 g; reaction

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temperature, 90 °C; H<sub>2</sub> pressure and reaction time was given in the table.

### The effect of catalyst ratio

The effect of the ratio of two active species in our catalyst system was also investigated (Table 4). We first fixed the amounts of AM-2 (0.05 g, 10 wt % of the substrate) and varied the dosage of Pt/C (Entries 1–3, Table 4). The results showed that even under a very low dosage of Pt/C (0.02 g, corresponding to 0.02 mol% of the substrate), almost total conversion and a DMTHF yield of 86% were achieved (Entry 3, Table 4), indicating the high efficiency of the Pt catalyst. Then we fixed the amount of Pt/C at 0.05 g (corresponding to 0.05 mol% of the substrate) to study the effect of the acid catalyst dosage (Entries 2, 4, 5, Table 4). A DMTHF yield of 88% was fulfilled even under a low acid catalyst dosage of 2 wt % of the substrate (Entry 5, Table 4). When the catalyst ratio was varied by decreasing the amount of the metal catalyst to an extremely low level (0.004 g, 0.022 mol% of the substrate), the conversion of 2,5-HD was not complete (44%) within 2 h (Entry 6, Table 4), with a product selectivity of 23%. When the reaction time was prolonged to 20 h, complete conversion of the substrate was fulfilled, and the final DMTHF yield was 80% (Entry 7, Table 4). These results indicated that the metal/acid ratio affected both the reaction rate and the selectivity.

### The heterogeneity and reusability of the catalyst system

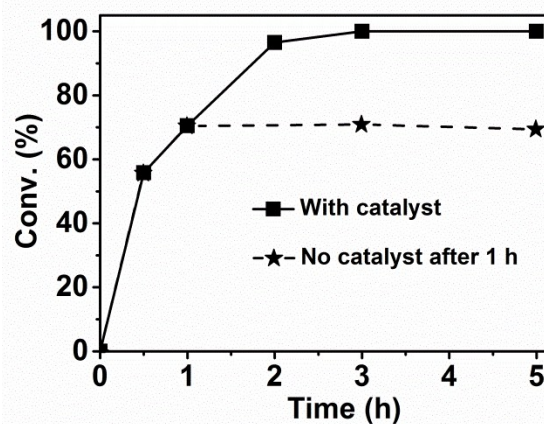
To verify the heterogeneous nature of our dual catalyst system, we removed the catalysts via hot filtration to see whether the reaction could proceed without the solid catalysts. In the experiments, a less amount of the catalysts was used to slow down the reaction rate and detect the change of the conversion. It can be known from Fig. 1 that the conversion of 2,5-HD was not changed with the reaction time after the removal of the catalysts. We also detected the yield change of DMTHF and found that no more DMTHF was produced after the removal of the catalysts. These results proved the heterogeneous property of the catalyst system.

Then we studied the reusability of the catalyst system with product yield controlled at ca. 35% by using a less amount of catalysts (Fig. 2). After reaction, the catalysts were separated by centrifugation, washed with water, and then directly used for the next run. The results showed that the catalyst system could be used for at least 5 times without considerable change in the yields of DMTHF. TEM images of the virgin and the recycled catalysts were shown in Fig.3. It can be shown from the images that the change of the catalyst morphologies and size distributions of Pt particles were not considerable, and the average size of Pt particles in the recycled catalyst was similar to that of the virgin catalyst (ca. 2.0 nm), indicating the excellent stability of Pt/C catalyst in the system.

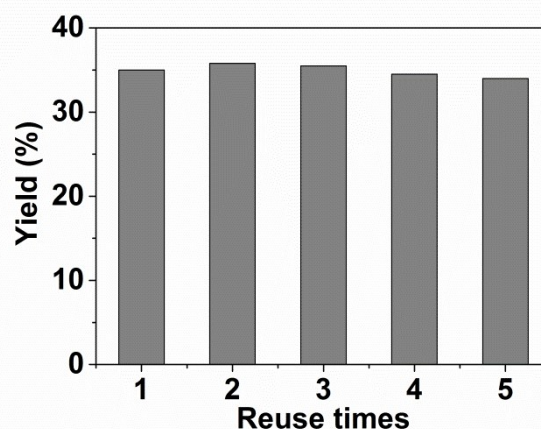
**Table 4** Influence of the catalyst ratio on the conversion of 2,5-HD to DMTHF<sup>a</sup>

Entry	Catalysts	Conv./%	Yield/%	Sel./%
	$m_{\text{Pt/C}}/m_{\text{AM-2}}(\text{g/g})$			
1	0.10/0.05	>99	>99	100
2	0.05/0.05	>99	>99	100
3	0.02/0.05	>99	86	86
4	0.05/0.03	>99	96	96
5	0.05/0.01	>99	88	88
6	0.004/0.05	44	10	23
7 <sup>b</sup>	0.004/0.05	>99	80	80

<sup>a</sup>Typical reaction conditions were as follows until otherwise stated in the table: 2,5-HD, 0.5 g; H<sub>2</sub>O, 2 mL; Pt/C and AM-2 were added as stated in the table; reaction temperature, 90 °C; H<sub>2</sub> pressure, 3.0 MPa; reaction time, 2 h. <sup>b</sup>The reaction time was prolonged to 20 h.



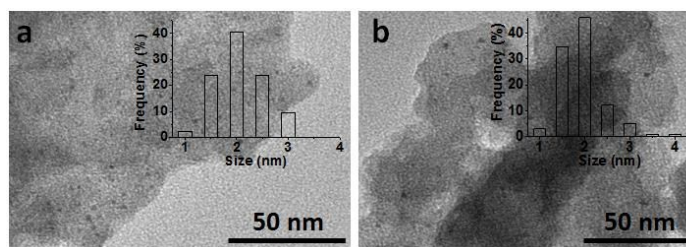
**Fig. 1** Heterogeneous nature of the dual catalyst system. Reaction conditions: 2,5-HD, 0.5 g; H<sub>2</sub>O, 2 mL; Pt/C, 0.02 g; AM-2, 0.02 g; reaction temperature, 90 °C; H<sub>2</sub> pressure, 3.0 MPa.



**Fig. 2** Reusability of the dual catalyst system. The product yields were controlled at ca. 35% by using a smaller amount of catalysts. Reaction conditions: 2,5-HD, 0.5 g; H<sub>2</sub>O, 2 mL; Pt/C,

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0.02 g; AM-2, 0.02 g; reaction temperature, 90 °C; H<sub>2</sub> pressure, 3.0 MPa; reaction time, 1 h.

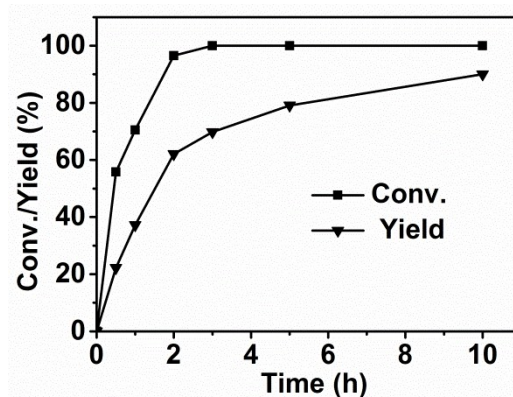


**Fig. 3** TEM images of the virgin (a) and the recycled Pt/C catalyst (b) after being reused for 5 times. The insets were the size distributions of Pt particles in the virgin and used catalysts.

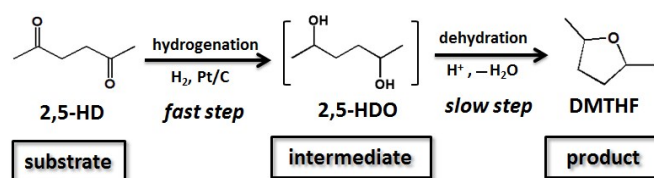
### Mechanism analysis

To give an insight into the reaction mechanism, we studied the concentration change of the substrate and products with reaction time and analysed the intermediates. A less amount of catalysts was used in order to slow down the reaction rate and detect the concentration change of the reactant and product with reaction time in detail. As can be seen from Fig. 4, more than 50% of the reactant was converted within the first 30 min. Nearly total conversion was finished within 2 h, indicating the conversion of 2,5-HD was a fast step. However, the rate for the formation of DMTHF was much slower. These results indicated that the reactant was converted first to certain intermediates, and the conversion rate of the intermediates was relatively slow. A new chemical identified as 2,5-hexanediol (2,5-HDO) was detected in our GC and GC-MS analysis (Table 1). Thus it was reasonable to deduce that 2,5-HDO was the intermediate for conversion of 2,5-HD to DMTHF. Shirai *et al.* reported that 2,5-HDO could indeed be converted to DMTHF under acid catalysis via intramolecular dehydration.<sup>22</sup> In our experiments, we also used 2,5-HDO as the direct substrate using AM-2 as the acid catalyst under the same conditions as 2,5-HD conversion. It was found that almost quantitative DMTHF was produced, while nearly no DMTHF was produced without acid catalyst. From these results, we deduced that 2,5-HDO was an intermediate during the conversion of 2,5-HD into DMTHF and acid catalysts promoted the conversion of 2,5-HDO into DMTHF.

Based on the above experimental results and previous report,<sup>7, 18c, 22-23</sup> a plausible pathway was proposed (Scheme 2). Firstly, the carbonyl groups in 2,5-HD were hydrogenated to hydroxyl groups under the catalysis of Pt, which was a fast step. Secondly, the formed diol intermediate was converted to cyclic ether structures via intramolecular dehydration under the catalysis of acid catalyst. The second step proceeded smoothly at a slower rate compared with the first step under the present condition in this work.



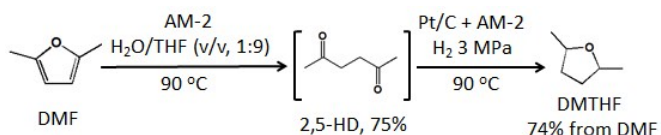
**Fig. 4** Conversion and product yield as a function of reaction time. Reaction conditions: 2,5-HD, 0.5 g; H<sub>2</sub>O, 2 mL; Pt/C, 0.02 g; AM-2, 0.02 g; reaction temperature, 90 °C; H<sub>2</sub> pressure, 3.0 MPa.



**Scheme 2.** Plausible mechanism for the conversion of 2,5-HD to DMTHF under the catalysis of Pt/C-AM-2 system.

### Conversion of DMF to DMTHF

Finally, we attempted to apply the present catalyst system to the conversion of another biomass derived molecule DMF into DMTHF via 2,5-HD (Scheme 3). It has been reported that CO<sub>2</sub>/H<sub>2</sub>O system was efficient for the conversion of DMF to 2,5-HD at 150 °C and CO<sub>2</sub> pressure of 4 MPa.<sup>19b</sup> In our experiments, we found that AM-2 was also efficient for this reaction in a H<sub>2</sub>O/THF (v/v, 1:9) system. A moderate 2,5-HD yield (75%) was obtained, and the reaction condition was much milder with lower temperature at ambient pressure. Nearly quantitative conversion of the produced 2,5-HD into DMTHF was achieved with a final yield of 74% under the catalysis of Pt/C + AM-2 without the separation of 2,5-HD (Scheme 3). Therefore, the catalyst system for the synthesis of DMTHF from biomass derived 2,5-HD and DMF are greener and more efficient than those via chemical synthetic route,<sup>18</sup> and has potential application for DMTHF production.



**Scheme 3.** Conversion of DMF into DMTHF via 2,5-HD under the catalysis of Pt/C and AM-2 system.

### Conclusion

In this work, a simple and efficient catalyst combination consisting of commercial Pt/C and AM-2 was applied for the conversion of biomass derived 2,5-HD to DMTHF. Almost quantitative conversion of 2,5-HD to DMTHF could be fulfilled with high yield up to 99% under 90 °C and 3 MPa H<sub>2</sub> within 3 h, which was a milder condition than those reported for this reaction with satisfactory efficiency. The Pt/C+AM-2 catalyst system can be easily recovered and reused for at least five times without decreasing the activity and selectivity. In the reaction process, the reactant (2,5-HD) is first converted into the intermediate 2,5-HDO by hydrogenation, which is further dehydrated to the desired product DMTHF. Pt/C and AM-2 promote the reaction cooperatively. We believe that the highly efficient, greener, facilely prepared, and easily recoverable catalytic system has great potential application for the reaction.

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### Notes and references

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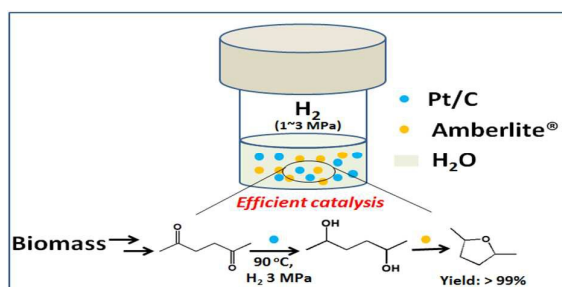
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- a) M. Y. He, Y. H. Sun and B. X. Han, *Angew. Chem. Int. Ed.*, 2013, **52**, 9620;b) G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044;c) C. H. Zhou, X. Xia, C. X. Lin, D. S. Tong and J. Beltramini, *Chem. Soc. Rev.*, 2011, **40**, 5588;d) M. Besson, P. Gallezot and C. Pinel, *Chem. Rev.*, 2014, **114**, 1827;e) J. L. Song, H. L. Fan, J. Ma and B. X. Han, *Green Chem.*, 2013, **15**, 2619.
- a) A. Q. Wang and T. Zhang, *Acc. Chem. Res.*, 2013, **46**, 1377;b) B. B. Zhang, J. L. Song, G. Y. Yang and B. X. Han, *Chem. Sci.*, 2014, **5**, 4656.
- a) J. B. Binder and R. T. Raines, *J. Am. Chem. Soc.*, 2009, **131**, 1979;b) H. B. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597.
- a) X. L. Du, L. He, S. Zhao, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *Angew. Chem. Int. Ed.*, 2011, **50**, 7815;b) Z. Yang, Y. B. Huang, Q. X. Guo and Y. Fu, *Chem. Commun.*, 2013, **49**, 5328;c) D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Green Chem.*, 2013, **15**, 584;d) J. L. Song, L. Q. Wu, B. W. Zhou, H. C. Zhou, H. L. Fan, Y. Y. Yang, Q. L. Meng and B. X. Han, *Green Chem.*, 2015, **17**, 1626;e) H. C. Zhou, J. L. Song, H. L. Fan, B. B. Zhang, Y. Y. Yang, J. Y. Hu, Q. G. Zhu and B. X. Han, *Green Chem.*, 2014, **16**, 3870.
- a) G. Bottari, A. J. Kumalapati, K. K. Krawczyk, B. L. Feringa, H. J. Heeres and K. Barta, *ChemSusChem*, 2015, **8**, 1323;b) M. Chatterjee, T. Ishizaka and H. Kawanami, *Green Chem.*, 2014, **16**, 1543;c) X. Kong, R. X. Zheng, Y. F. Zhu, G. Q. Ding, Y. L. Zhu and Y. W. Li, *Green Chem.*, 2015, **17**, 2504;d) B. Saha, C. M. Bohn and M. M. Abu-Omar, *ChemSusChem*, 2014, **7**, 3095;e) Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982.
- a) J. Mitra, X. Zhou and T. Rauchfuss, *Green Chem.*, 2015, **17**, 307;b) A. J. Kumalapati, G. Bottari, P. M. Erne, H. J. Heeres and K. Barta, *ChemSusChem*, 2014, **7**, 2266.
- R. J. Sullivan, E. Latifi, B. K. M. Chung, D. V. Soldatov and M. Schlaf, *ACS Catal.*, 2014, **4**, 4116.
- L. J. Xu, Y. Y. Jiang, Q. Yao, Z. Han, Y. Zhang, Y. Fu, Q. X. Guo and G. W. Huber, *Green Chem.*, 2015, **17**, 1281.
- a) Q. N. Xia, Q. Cuan, X. H. Liu, X. Q. Gong, G. Z. Lu and Y. Q. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 9755;b) M. Mascal, S. Dutta and I. Gandarias, *Angew. Chem. Int. Ed.*, 2014, **53**, 1854;c) X. Y. Li, R. Shang, M. C. Fu and Y. Fu, *Green Chem.*, 2015, **17**, 2790.
- a) Y. H. Xiu, A. J. Chen, X. R. Liu, C. Chen, J. Z. Chen, L. Guo, R. Zhang and Z. S. Hou, *RSC Adv.*, 2015, **5**, 28233;b) W. W. Zhu, H. M. Yang, J. Z. Chen, C. Chen, L. Guo, H. M. Gan, X. G. Zhao and Z. S. Hou, *Green Chem.*, 2014, **16**, 1534.
- H. K. Chakravarty and R. X. Fernandes, *J. Phys. Chem. A*, 2013, **117**, 5028.
- M. R. Grochowski, W. R. Yang and A. Sen, *Chem. Eur. J.*, 2012, **18**, 12363.
- W. R. Yang and A. Sen, *ChemSusChem*, 2010, **3**, 597.
- a) T. L. Church, Y. D. Y. L. Getzler and G. W. Coates, *J. Am. Chem. Soc.*, 2006, **128**, 10125;b) M. Hansson, P. I. Arvidsson, S. O. N. Lill and P. Ahlberg, *J. Chem. Soc., Perkin Trans. 2*, 2002, 763.
- a) Á. Molnár, I. Ledneczki, I. Bucsi and M. Barták, *Catal. Lett.*, 2003, **89**, 1;b) J. F. Costello, W. N. Draffin and S. P. Paver, *Tetrahedron*, 2005, **61**, 6715;c) L. Vilcoq, A. Cabiac, C. Especel, S. Lacombe and D. Duprez, *J. Catal.*, 2014, **320**, 16.
- a) F. Marchetti, G. Pampaloni and S. Zacchini, *Inorg. Chem.*, 2008, **47**, 365;b) R. Krishnan and R. H. Schultz, *Organometallics*, 2001, **20**, 3314;c) C. Su, J. Guang and P. G. Williard, *J. Org. Chem.*, 2014, **79**, 1032.
- Y. Sasaki, M. Handa, S. Sekiya, K. Kurashima and K. Usami, *J. Power Sources*, 2001, **97-98**, 561.
- a) M.-J. Kim and I. S. Lee, *J. Org. Chem.*, 1993, **58**, 6483;b) M. L. Mihailović, S. Gojković and S. Konstantinović, *Tetrahedron*, 1973, **29**, 3675;c) Á. Molnár, K. Felföldi and M. Barták, *Tetrahedron*, 1981, **37**, 2149.
- a) W. R. Yang and A. Sen, *ChemSusChem*, 2011, **4**, 349;b) F. Liu, M. Audemar, K. D. O. Vigier, J.-M. Clacens, F. D. Campo and F. Jérôme, *ChemSusChem*, 2014, **7**, 2089.
- H. C. Zhou, J. L. Song, X. C. Kang, J. Y. Hu, Y. Y. Yang, H. L. Fan, Q. L. Meng and B. X. Han, *RSC Adv.*, 2015, **5**, 15267.
- a) Z. H. He, Z. S. Hou, Y. P. Luo, Y. Dilixiati and W. M. J. Eli, *Catal. Sci. Technol.*, 2014, **4**, 1092;b) G. Morales, M. Paniagua, J. A. Melero, G. Vicente and C. Ochoa, *Ind. Eng. Chem. Res.*, 2011, **50**, 5898;c) Q. L. Meng, H. L. Fan, H. Z. Liu, H. C. Zhou, Z. H. He, Z. W. Jiang, T. B. Wu and B. X. Han, *ChemCatchem*, 2015, DOI: 10.1002/cctc.201500479;d) B. B. Bardin, S. V. Bordawekar, M. Neurock and R. J. Davis, *J. Phys. Chem. B*, 1998, **102**, 10817.
- A. Yamaguchi, N. Hiyoshi, O. Sato and M. Shirai, *ACS Catal.*, 2011, **1**, 67.
- M. L. Mihailović, S. Gojković and Ž. Čeković, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2460.

## Graphical abstract

Biomass derived 2,5-hexanedione can be converted to 2,5-dimethyltetrahydrofuran with 99% yield by Pt/C and Amberlite® 120H system under mild conditions.





## Supporting Information for

### Cooperative catalysis of Pt/C and acid resin for the production of 2,5-dimethyltetrahydrofuran from biomass derived 2,5-hexanedione under mild condition

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## 1. Experimental Section

### 1.1 Catalyst preparation

The supports, activated charcoal and Amberlyst<sup>®</sup> 15H, were thoroughly washed with water and ethanol, and then dried under 100 °C overnight before use. The preparation process of Pd/C (1 wt%) was as following: 4.33 mL of 0.01 g/mL Pd(NO<sub>3</sub>)<sub>2</sub> stock solution was dropped onto 2 g activated charcoal under stirring, and the slurry was continually stirred under 60 °C to remove extra water. The obtained powder was dried under 110 °C overnight, and then reduced by H<sub>2</sub> under 300 °C, 5 °C/min for 2 h. Ru/C (1 wt%) was prepared by a similar process with RuCl<sub>3</sub> as the precursor. Pt/AM-1 was prepared as following: 2.1 mL 0.01 g/mL H<sub>2</sub>PtCl<sub>6</sub> was dropped onto 1 g dried AM-1, and the mixture was stirred overnight. Water was evaporated via continually stirring under 60 °C. The obtained catalyst precursor was dried under 110 °C overnight, and then reduced under H<sub>2</sub> atmosphere, 150 °C, 5 °C/min, 1 h. The metal loadings on the supports were analyzed on ICP-AES (VISTA-MPX).

### 1.2 Acid strength of the acid catalyst

The acid strength of the acid resin, including Amberlyst<sup>®</sup>15(H) (AM-1), Amberlite<sup>®</sup>IR-120(H) (AM-2), and Nafion<sup>®</sup>SAC-13 (NS) was measured by the titration method according to the reported literature.<sup>1</sup> Typically, 0.5 g acid resin was thoroughly washed with water, dried under 100 °C, and then suspended into 20 mL of 0.01 M NaOH solution. The mixture was stirred overnight. Then the particles were separated out by filtration, and the filtrate was titrated with 0.01 M HCl using methyl orange as indicator. The acid strength was calculated according to the amounts of consumed NaOH. The results were

expressed in the form of acid density (mmol H<sup>+</sup>/g catalyst). The acid properties of the molecular sieve, Zeolite Y (hydrogen, the framework Si/Al ratio=35), were studied by Pyridine Adsorbed Fourier Transformed Infrared method in the recent work of our group and the data were used directly.<sup>2</sup> For the heteropoly acids, silicotungstic acid and phosphomolybdic acid, due to their special structures, the acid density was calculated according to the structure in the reported literatures.<sup>3</sup>

### 1.3 Conversion of 2,5-HDO

0.5 g 2,5-HDO, 2 g water and 0.05 g AM-2 were introduced into a 10 mL Teflon-lined stainless steel autoclave equipped with a magnetic stirrer. After removing the air via vacuum, nitrogen was charged into the reactor. The reaction was conducted under 90 °C for 2 h. After reaction, the reactor was cooled in ice-water to quench the reaction and the organic phase was diluted by ethanol. The sample was analyzed by gas chromatograph (GC, HP 4890) equipped with a flame ionization detector (FID), and THFAL was used as the internal standard. Identification of the products and reactant was done using a GC-MS (SHIMADZU-QP2010) as well as by comparing the retention times to respective standards in GC traces.

### 1.4 Conversion of DMF to DMTHF via 2,5-HD

0.43 g DMF and 0.1 g AM-2 were added into the mixture of 0.2 ml H<sub>2</sub>O and 2 ml THF, and the reaction was conducted under 90 °C for 24 h. After reaction and cooling down, 0.05 g Pt/C and 3.0 MPa H<sub>2</sub> were charged into the reaction solution directly. The mixture was maintained under 90 °C for 10 h. The product was analysed by gas chromatograph (GC, HP 4890) equipped with a flame ionization detector (FID), and THFAL was used as the internal standard.

## 2. Results and Discussion

### 2.1 Acid strength of the acid catalyst

**Table S1.** The acid density of acid catalysts used in this work<sup>d</sup>

Entry	Catalyst	Acid density mmol H <sup>+</sup> /g
1 <sup>b</sup>	Am-1	4.2
2 <sup>b</sup>	Am-2	2.5
3 <sup>b</sup>	NS	0.13
4 <sup>c</sup>	MS	0.22
5 <sup>d</sup>	SA	1.3
6 <sup>d</sup>	PA	1.5

<sup>a</sup>AM-1=Amberlyst<sup>®</sup>15(H); AM-2=Amberlite<sup>®</sup>IR-120(H); NS=Nafion<sup>®</sup>SAC-13; MS=Molecular sieve (Zeolite Y); SA=Silicotungstic acid; PA=Phosphomolybdic acid. <sup>b</sup>The acid density was measured by the titration method. <sup>c</sup>The acid property was detected in our recent work, and the value was the sum of the amounts of Brønsted acid and Lewis acid sites.<sup>2</sup> <sup>d</sup>The acid densities were calculated according to the reported literature.<sup>3</sup> The amounts of protons in one structure unit (Keggin unit) for SA and PA were 3.6 and 2.8, respectively. The composition of one Keggin unit for SA and PA was H<sub>4</sub>W<sub>12</sub>O<sub>40</sub>Si and H<sub>3</sub>Mo<sub>12</sub>O<sub>40</sub>P, corresponding to the acid density of 1.3 and 1.5, respectively.

#### References:

1. a) Z. H. He, Z. S. Hou, Y. P. Luo, Y. Dilixiati, and W. Eli, *Catal. Sci. Technol.*, 2014, **4**, 1092; b) G. Morales, M. Paniagua, J. A. Melero, G. Vicente, and C. Ochoa, *Ind. Eng. Chem. Res.*, 2011, **50**, 5898.
2. Q. L. Meng, H. L. Fan, H. Z. Liu, H. C. Zhou, Z. H. He, Z. W. Jiang, T. B. Wu, and B. X. Han, *ChemCatChem*, 2015, DOI: 10.1002/cctc.201500479.
3. a) B. B. Bardin, S. V. Bordawekar, M. Neurock, and R. J. Davis, *J. Phys. Chem. B*, 1998, **102**, 10817; b) N. D. Feng, A. M. Zheng, S-J Huang, H. L. Zhang, N. Y. Yu, C-Y Yang, S-B Liu, and F. Deng, *J. Phys. Chem. C*, 2010, **114**, 15464.