

# One-Pot Synthesis of 2,5-Diformylfuran from Fructose by Bifunctional Polyaniline-Supported Heteropolyacid Hybrid Catalysts

Shuqing Liu, Xing Fu, Jinhang Dai, Zhongbao Liu, Liangfang Zhu and Changwei Hu

**Table S1.** Preparation conditions of F<sub>y</sub>-PAN “supports” and the results resolved from the FTIR spectra of F<sub>y</sub>-PAN and 40-PMO<sub>12</sub>/F<sub>y</sub>-PAN.

Entry	Support	Formaldehyde used for modification <sup>[a]</sup>		Intensity ratio <sup>[b]</sup>	
		Concentration (wt.%)	Volume (mL)	I <sub>1675</sub> /I <sub>820</sub>	I <sub>1606</sub> /I <sub>1502</sub>
1	F <sub>1</sub> -PAN	15	10	1.094	0.435
2	F <sub>2</sub> -PAN	40	8	0.966	0.450
3	F <sub>3</sub> -PAN	40	15	0.857	0.592
4	PAN	—	—	—	0.793

[a] The PAN sulfate (0.2 g) was dissolved in aqueous formaldehyde solution (15–40 wt.%, 8–15 mL), followed by being heated to 413 K and kept stirring for 2 h. After the completion of reaction, the solid was filtrated, washed with water (20 mL \* 3), and then dried at 353 K for 10 h. [b] The data were acquired from the FTIR spectra of F<sub>y</sub>-PAN.

**Table S2.** Comparison of the production rates of several hybrid catalysts in the “one-pot” and “one-step” conversion of fructose to DFF. <sup>a</sup>

Entry	Catalyst	Number of active sites (x 10 <sup>-4</sup> mol/g) <sup>b</sup>	Production rate (mol of DFF product / mol of PMO <sub>12</sub> / h)
1	40-PMO <sub>12</sub> /PAN	1.53	49.7
2	40-PMO <sub>12</sub> /F <sub>1</sub> -PAN	0.96	55.1
3	40-PMO <sub>12</sub> /F <sub>2</sub> -PAN	1.12	71.9
4	40-PMO <sub>12</sub> /F <sub>3</sub> -PAN	1.50	56.0

<sup>a</sup> Reaction conditions: 45 mg fructose, 5 mg catalyst, 1 mL DMSO, 433 K, 4 h, in air.

<sup>b</sup> mol of PMO<sub>12</sub> HPA /weight of catalyst.

**Table S3.** The leaching of PMO<sub>12</sub> HPA during the recycled use of 40-PMO<sub>12</sub>/F<sub>3</sub>-PAN.

Catalytic run	1	2	3	4
Leaching of PMO <sub>12</sub> HPA (wt.%)	3.0	2.7	2.6	1.5
Yield of DFF (mol%) <sup>a</sup>	4.9	5.0	-	-

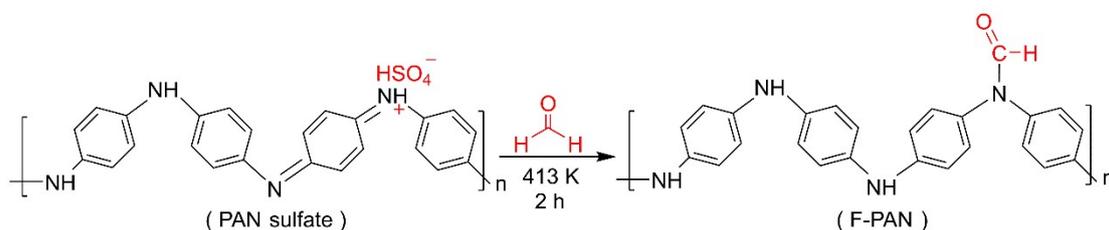
<sup>a</sup> The yield of DFF by using the leached PMO<sub>12</sub> HPA species as the catalyst for the conversion of fructose at 433 K for 4 h.

**Table S4.** Recycled use of 40-PMo<sub>12</sub>/F<sub>3</sub>-PAN catalyst in the “one-pot” and “one-step” conversion of fructose to DFF. <sup>a</sup>

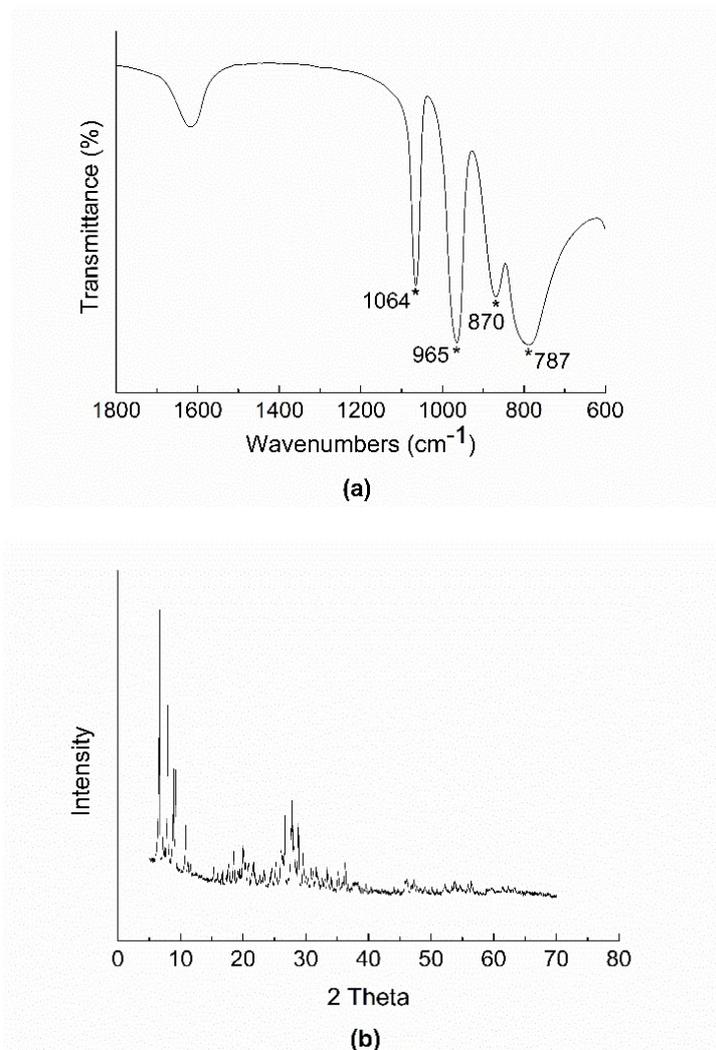
Entry	Reaction time (h)	Catalytic run	Conv. (mol%)	Y <sub>HMF</sub> (mol%)	Y <sub>DFF</sub> (mol%)	Y <sub>FA</sub> (mol%)	Carbon balance (mol%)
1 <sup>b</sup>		1	45.3	37.7	trace	-	83.2
2		1	43.5	37.0	trace	-	85.1
3	0.2	2	43.3	36.9	trace	-	85.3
4		3	41.9	37.4	trace	-	89.3
5		4	43.1	37.9	trace	-	87.9
6		1	99.6	65.9	4.5	-	70.7
7	1.0	2	99.2	67.7	5.7	-	74.0
8		3	97.9	65.5	10.1	-	77.2
9		4	98.3	64.0	10.0	-	75.3

<sup>a</sup> Reaction conditions: 45 mg fructose, 30 mg catalyst, 1 mL DMSO, 433 K, 400 rpm of stirring rate, in air. <sup>b</sup> The stirring rate was 50 rpm.

For the reaction of 0.2 h, the fructose conversions were similar (41.9 ~ 43.5 mol%) for the successive four catalytic runs with similar HMF yields ranging from 36.9 mol% to 37.9 mol% with trace amount of DFF formed, which suggested a stable catalytic performance of the 40-PMo<sub>12</sub>/F<sub>3</sub>-PAN catalyst for the fructose-to-HMF dehydration. In the meantime, the fructose conversion was performed with a smaller stirring speed of 50 rpm. Similar HMF yield (37.7 mol%) was obtained as compared with that under a faster stirring speed of 400 rpm, thereby revealing the insignificance of mass transfer limitation in the catalytic tests. The increase of the reaction time to 1.0 h resulted in the increase of the fructose conversion to approach 100 mol% with HMF as the major product while DFF as the minor product. This result indicated that the rate of fructose-to-HMF dehydration was very fast, whereas the oxidation was relatively slower. Nevertheless, the considerable total yields of HMF and DFF (70.0 ~ 75.6 mol%) in the recycling tests for shorter reaction time demonstrated the good reusability of the 40-PMo<sub>12</sub>/F<sub>3</sub>-PAN catalyst during the recycling tests.

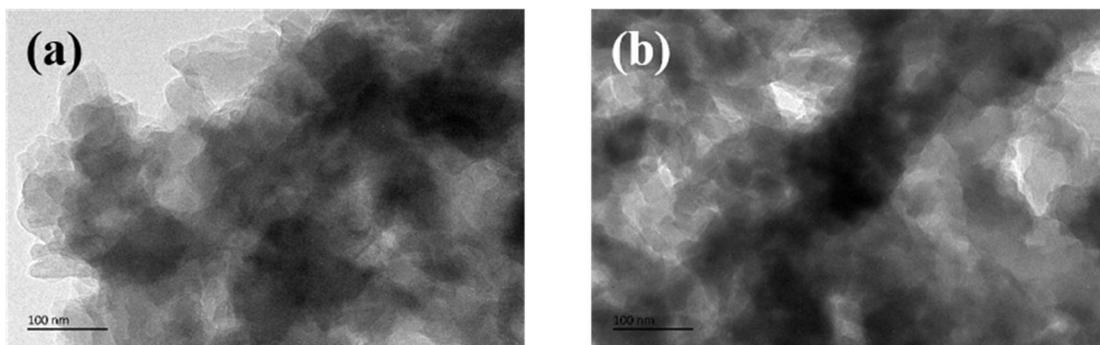
**Scheme S1.** Schematic illustration of the grafting of formyl groups on PAN.

According to our previous work,<sup>[1]</sup> the grafting of formyl groups on PAN involves the reaction of formaldehyde with the quinoid imine structure accompanying with the deprotonation of PAN sulfate and the reduction of quinoid units to benzenoid units.

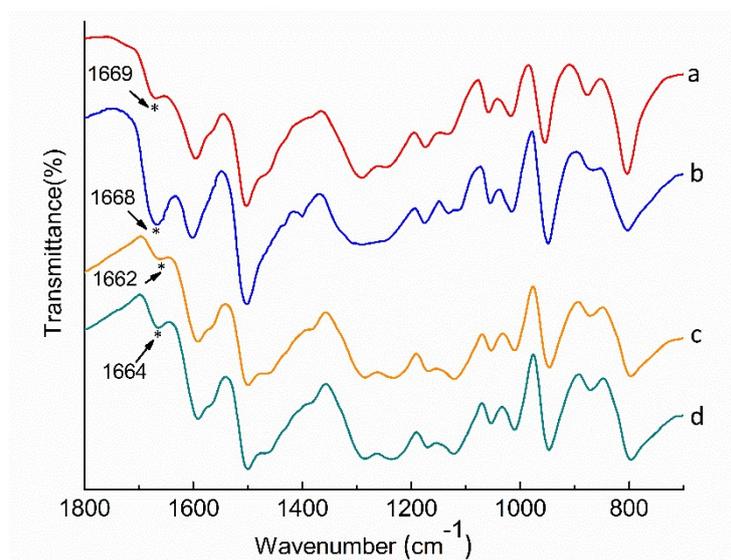


**Figure S1.** (a) FTIR spectrum and (b) XRD pattern of Keggin-type H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> HPA.

The characteristic IR bands of PMo<sub>12</sub> HPA centered at 1064 cm<sup>-1</sup>, 950 cm<sup>-1</sup>, 870 cm<sup>-1</sup> and 787 cm<sup>-1</sup>, respectively, are assigned to the P-O, M-O and M-O-M bending stretching vibrations of PMo<sub>12</sub> HPA.<sup>[2]</sup> The XRD pattern of PMo<sub>12</sub> HPA shows the typical Keggin structure with diffraction peaks centered at  $2\theta = 8.3^\circ, 8.9^\circ, 9.1^\circ, 27.9^\circ, 28.9^\circ, \text{ and } 29.9^\circ$ .<sup>[3]</sup>

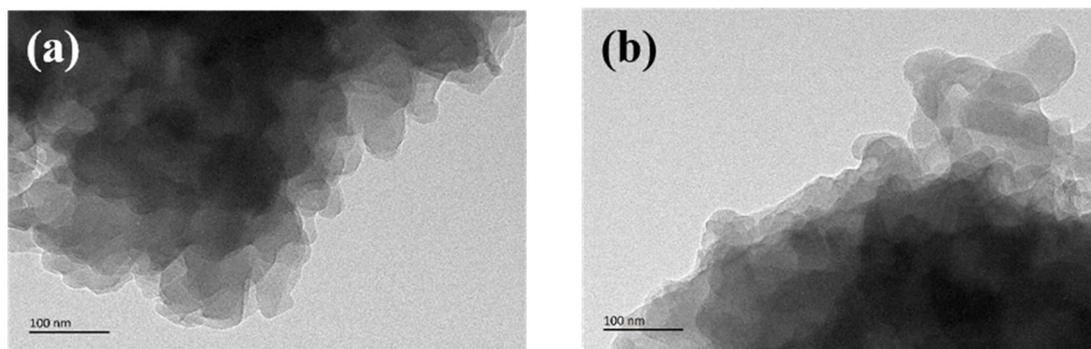


**Figure S2.** TEM images of (a) PAN, and (b) 40-PMO<sub>12</sub>/PAN.

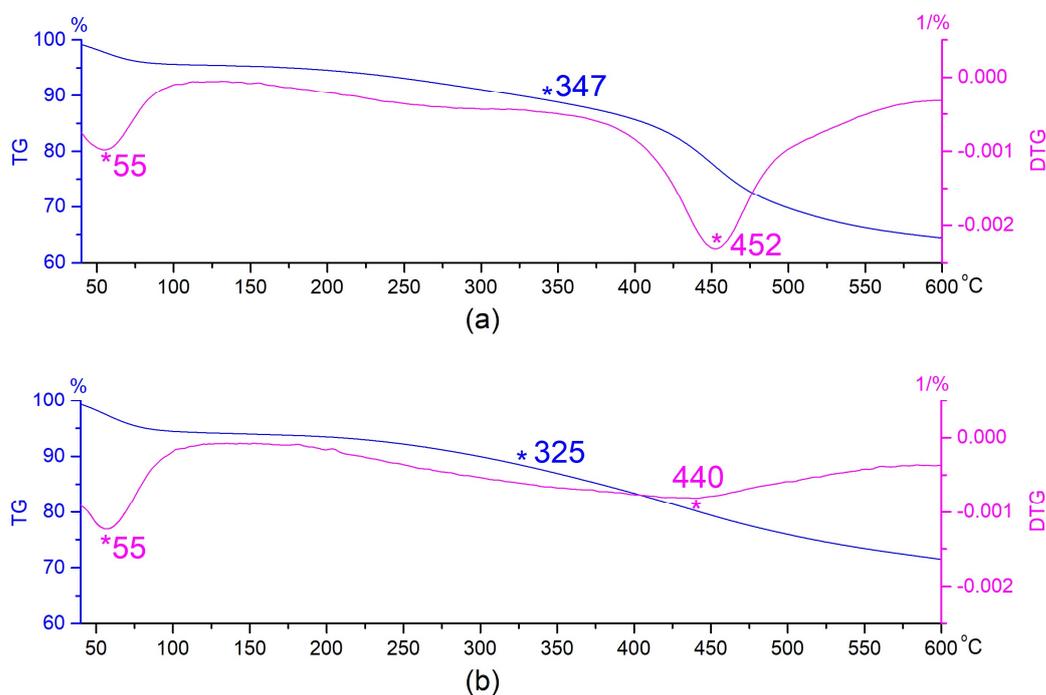


**Figure S3.** FTIR spectra of 40-PMO<sub>12</sub>/PAN catalysts after reacting with different substances. a) fructose; b) formaldehyde; c) HMF; d) DFF.

The IR band assigning to the stretching vibration of aldehyde group varies from 1662 to 1669 cm<sup>-1</sup> on the FTIR spectra of 40-PMO<sub>12</sub>/PAN catalysts after reacting with different substances. The similarity of curve a and b indicates that the 40-PMO<sub>12</sub>/PAN catalyst might undergo formyl grafting during the fructose-to-DFF transformation. Besides, the possible absorption of HMF and DFF was excluded because the IR bands belonging to the aldehyde group in HMF (1662 cm<sup>-1</sup>) and DFF (1664 cm<sup>-1</sup>) are lower in wavenumber than that in the used catalyst (1669 cm<sup>-1</sup>).



**Figure S4.** TEM images of (a) F<sub>3</sub>-PAN, and (b) 40-PMo<sub>12</sub>/F<sub>3</sub>-PAN.



**Figure S5.** TG and DTG profiles of (a) fresh and (b) spent 40-PMo<sub>12</sub>/F<sub>3</sub>-PAN catalysts.

For the fresh 40-PMo<sub>12</sub>/F<sub>3</sub>-PAN catalyst, it began to lose moisture at 55 °C, and decomposed (defined as  $\geq 10\%$  weight loss) starting at about 347 °C (majority weight loss at 452 °C); For the spent 40-PMo<sub>12</sub>/F<sub>3</sub>-PAN catalyst, it began to lose moisture at 55 °C, and decomposed (defined as  $\geq 10\%$  weight loss) starting at about 325 °C (majority weight loss at 440 °C).

#### References:

- [1] L. Zhu, J. Dai, M. Liu, D. Tang, S. Liu, and C. Hu, *ChemSusChem*, **2016**, 9, 2174-2181.
- [2] L. R. Pizzio, P. G. Vázquez, C. V. Cáceres, and M. N. Blanco, *Appl. Catal. A: Gen.* **2003**, 256, 125-139.

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- [3] C. Rocchiccioli-Deltcheff, R. Thouvenot, and R. Franck, *Spectrochim. Acta, Part A*, **1976**, 32(3), 587-597.