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## **Supplementary Information**

## Can the direct conversion of biomass-derived formic acid be efficient

## for hydrogen generation?

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#### **TOF** calculation

1. TOF (h<sup>-1</sup>) calculation of FA decomposition reaction based on FA concentration in solution at low conversions (<20%):

$$TOF = \frac{C_0 * V * X}{t * n_{Pd}}$$

where  $C_0$  – initial FA concentration (M); V – reaction volume, L; X – FA conversion; t – time, h;  $n_{Pd}$  – Pd content, mole.

2. TOF (h<sup>-1</sup>) calculation of FA decomposition reaction based on volume H<sub>2</sub> released:

$$TOF = \frac{P_0 * V_{gas}}{2 * R * T * t * n_{Pd}},$$

where  $P_0$  – ambient pressure, Pa;  $V_{gas}$  – gas volume, m<sup>3</sup>; R – gas constant, m<sup>3</sup> Pa mol<sup>-1</sup> K<sup>-1</sup>, T – room temperature, K; t – time, h<sup>-1</sup>;  $n_{Pd}$  – Pd content, mole.

3. Productivity (L H<sub>2</sub>/g<sub>Pd</sub> h) of hydrogen production was estimated based on FA conversion data:

$$P = \frac{C_0 * V * X}{t * m_{Pd}},$$

where  $C_0$  – initial FA concentration (M); V – reaction volume, L; X – FA conversion; t – time, h;  $m_{Pd}$  – Pd content, g.



Fig. S1. FA conversion calculated based on the FA concentration in the solution and the volume of  $H_2$  released.



Fig. S2. XRD spectrum of 1%Pd/N-CNTs.



Fig. S3. XPS N1s spectrum of N-CNTs.

BE N 1s 398.5 eV corresponds to pyridinic nitrogen N<sub>Py</sub>, 400.0 eV – to pyrrolic nitrogen N<sub>Pyr</sub>, 401.1 eV – to graphitic nitrogen N<sub>Q</sub>, 402.5 eV – to oxidized nitrogen species N<sub>Ox</sub>, and 404.6 eV – to encapsulated molecular nitrogen N<sub>N2</sub><sup>1,2</sup>.

The ratio of nitrogen species is 32%  $N_{Py}$  : 11%  $N_{Pyr}$  : 30%  $N_Q$  : 8%  $N_{Ox}$  : 19%  $N_{N2}.$ 



**Fig. S4.** XPS Pd 3d spectrum of 1%Pd/N-CNTs catalyst after reduction in hydrogen at 300°C in the preparation chamber of the spectrometer. The sample was not exposed to ambient air.



Fig. S5. Cycling of the catalyst 1%Pd/N-CNTs. After 1<sup>st</sup> and 2<sup>nd</sup> cycles, the catalyst was dried. After 3<sup>rd</sup> cycle, the catalyst was pretreated with a mixture of 5%O<sub>2</sub>/Ar at 150°C for 30 minutes and then reduced in 15%H<sub>2</sub>/Ar at 300°C for 1 hour.



Fig. S6. FTIR spectra of  $H_4PMo_{11}VO_{40}$  and  $Cs_{3.5}H_{0.5}PMo_{11}VO_{40}$ .

In IR spectrum of H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub> the bands at 1060 cm<sup>-1</sup> ( $v_s(P-O)$ ), 960 cm<sup>-1</sup> ( $v_s(Mo=O_d)$ ), 882 cm<sup>-1</sup> ( $v_s(Mo=O_b-Mo)$ ) and 807 cm<sup>-1</sup> ( $v_s(Mo=O_c-Mo)$ ) are registered<sup>3</sup>. The incorporation of Cs into the structure resulted in the noticeable shift of some bands of HPA:  $v_s(Mo=O_d)$  (from 960 to 969 cm<sup>-1</sup>),  $v_s(Mo=O_b-Mo)$  (from 882 to 868 cm<sup>-1</sup>) and  $v_s(Mo=O_c-Mo)$  (from 807 to 790 cm<sup>-1</sup>).

Solid salt  $Cs_{3.5}H_{0.5}PMo_{11}VO_{40}$  was prepared by a two-step route. First, the HPA was synthesized, and second, the aqueous-alcoholic solution of  $H_4PMo_{11}VO_{40}$  was partially neutralized by a stoichiometric quantity of cesium carbonate<sup>4</sup>.



Fig. S7. <sup>31</sup>P and <sup>51</sup>V NMR spectra of 0.4M  $H_5PMo_{10}V_2O_{40}$  (A) and 0.4M  $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$  (B). 1-3 corresponds to individual heteropolyanions which contain 1, 2 or 3 vanadium atoms in the structure.

In the <sup>31</sup>P and <sup>51</sup>V NMR spectra of free HPA solution lines typical of individual heteropolyanions which contain one, two, or three vanadium atoms in the structure are registered<sup>5</sup>. The average equilibrium composition corresponds to the  $H_5PMo_{10}V_2O_{40}$  anion. The spectra of  $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$ are similar to those of the free acid, indicating a similar qualitative composition. Meantime, the <sup>31</sup>P NMR lines are noticeably shifted to the low-field region and broadened caused of the paramagnetism of Co(II) and its interaction with the internal coordination sphere of heteropolyanions.

Soluble salt  $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$  was prepared by a two-step route. First, the HPA solution was synthesized, and second, the stoichiometric quantity of cobalt carbonates was added to the  $H_5PMo_{10}V_2O_{40}$  solution<sup>6</sup>.



**Fig. S8.** Gas chromatograms of the released gas after decomposition of distilled biogenic FA-1 and reference gases.



**Fig. S9.** Pd 3d region of XPS spectra for 1%Pd/N-CNTs catalyst after using in catalytic runs 1, 4 and and 5 in Figure 4b and catalytic run 3 in Figure 4a, followed by drying in open air.



Fig. S10. The XPS Mo 3d spectrum of 1%Pd/N-CNTs catalyst after decomposition of biogenic FA-1 in run 4 in Fig. 4b.

FA sample	HPA catalyst	FA (M)	FA	Other product yield, %			
			Yield,				
			%	Acetic	Glycolic	CO <sub>2</sub>	CO
				acid	acid		
Biogenic FA-1	Cs <sub>3.5</sub> H <sub>0.5</sub> PMo <sub>11</sub> VO <sub>40</sub>	0.158	51	3	2	42	2
	(solid)						
Biogenic FA-2	Co <sub>0.6</sub> H <sub>3.8</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub>	0.187	60	2	0	36	2
	(soluble)						

**Table S1.** Mass balance of FA solutions derived via hydrolysis-oxidation of starch.

The yields of the reaction products were calculated according to the equation:

$$Y = \frac{\frac{V_{\text{product}}}{N_{\text{C}}} \cdot 100\%}{\frac{M_{\text{starch}}}{M_{\text{glucan unit}}}}$$

where Y was the product yield (mole %),  $v_{\text{product}}$  was the quantity of the reaction product (mole),  $m_{\text{starch}}$  was the weight of pure starch with allowance for moisture and impurities in the sample (g),  $M_{\text{glucan unit}}$  was the molar weight of glucan unit in a starch molecule (g·mole<sup>-1</sup>),  $N_{\text{C}}$  was the factor of molar ratio between glucose unit in a starch molecule and a product.

**Table S2.** Literature data on decomposition of biogenic formic acid.

Catalyst	FA	C <sub>FA</sub> , M	T, °C	FA:SF	TOF, h <sup>-1</sup>	Reference
Ir complex	biogenic	0.04-0.18	90	not added	9796-21943	7
homogeneous					(TON)	
9%Pd/NH2-KIE-6	biogenic	0.15	25	1:5	69	8
9%Pd/NH2-KIE-6	biogenic, distilled	0.28	25	1:2	279	9
1%Pd/N-CNTs	biogenic	0.04	50	not added	155 100% FA conversion- > 3 h	This work
1%Pd/N-CNTs	Biogenic, filtered and distilled	0.04	50	not added	281 100% FA conversion – 2 h	This work

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