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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⁻¹) 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⁻¹) calculation of FA decomposition reaction based on volume H₂ released:

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

where P_0 – ambient pressure, Pa; V_{gas} – gas volume, m³; R – gas constant, m³ Pa mol⁻¹ K⁻¹, T – room temperature, K; t – time, h⁻¹; n_{Pd} – Pd content, mole.

3. Productivity (L H₂/g_{Pd} 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_{Py}, 400.0 eV – to pyrrolic nitrogen N_{Pyr}, 401.1 eV – to graphitic nitrogen N_Q, 402.5 eV – to oxidized nitrogen species N_{Ox}, and 404.6 eV – to encapsulated molecular nitrogen N_{N2}^{1,2}.

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 1st and 2nd cycles, the catalyst was dried. After 3rd cycle, the catalyst was pretreated with a mixture of 5%O₂/Ar at 150°C for 30 minutes and then reduced in 15%H₂/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 H₄PMo₁₁VO₄₀ the bands at 1060 cm⁻¹ ($v_s(P-O)$), 960 cm⁻¹ ($v_s(Mo=O_d)$), 882 cm⁻¹ ($v_s(Mo=O_b-Mo)$) and 807 cm⁻¹ ($v_s(Mo=O_c-Mo)$) are registered³. 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⁻¹), $v_s(Mo=O_b-Mo)$ (from 882 to 868 cm⁻¹) and $v_s(Mo=O_c-Mo)$ (from 807 to 790 cm⁻¹).

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 carbonate⁴.

Fig. S7. ³¹P and ⁵¹V 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 ³¹P and ⁵¹V NMR spectra of free HPA solution lines typical of individual heteropolyanions which contain one, two, or three vanadium atoms in the structure are registered⁵. 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 ³¹P 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 $H_5PMo_{10}V_2O_{40}$ solution⁶.

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 ₂	CO
				acid	acid		
Biogenic FA-1	Cs _{3.5} H _{0.5} PMo ₁₁ VO ₄₀	0.158	51	3	2	42	2
	(solid)						
Biogenic FA-2	Co _{0.6} H _{3.8} PMo ₁₀ V ₂ O ₄₀	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_{product} was the quantity of the reaction product (mole), m_{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⁻¹), N_{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 _{FA} , M	T, °C	FA:SF	TOF, h ⁻¹	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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