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Formic Acid Production via One-Pot Hydrolysis-Oxidation of Starch over Quaternary Ammonium Salts of Vanadium-Containing Keggin-Type Heteropoly Acids

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Abstract: Bifunctional solid acidic quaternary ammonium salts of Keggin-type vanadium-containing heteropoly acids, such as $R_{3.5}H_{0.5}PVMo_{11}O_{40}$ (R : $(C_2H_5)_4N$, $(C_4H_9)_4N$, $(C_6H_{13})_4N$), and $[(C_4H_9)_4N]_{4.5}H_{0.5}SiW_{11}VO_{40}$, are capable of one-pot hydrolysis-oxidation conversion (OxFA-processing) of starch to biogenic formic acid. The impact of the reaction conditions and catalyst type was revealed. The highest formic acid yield of 50% was achieved over the best $[(C_2H_5)_4N]_{3.5}H_{0.5}PVMo_{11}O_{40}$ catalyst, which was active and stable in seven reaction cycles. The kinetic computational model, which described formic acid formation well, was proposed in the presence of the most active $[(C_2H_5)_4N]_{3.5}H_{0.5}PVMo_{11}O_{40}$ catalyst.

Keywords: one-pot; hydrolysis-oxidation; OxFA-process; starch; formic acid; bifunctional catalyst; Keggin-type vanadium-containing heteropoly acids



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1. Introduction

Formic acid (FA) is widely used in pulp, leather, pharmaceutical, chemical and industries and in agriculture [1–3]. Nowadays, FA is attracting more attention as a sustainable hydrogen source [4] due to its high volumetric hydrogen density [3]. Formic acid has already been applied in the production of biofuels [2,5]. Oxidation or hydrolysis-oxidation of various plant materials with molecular oxygen (OxFA-process) seems to be the most promising method for producing biogenic FA. Significant prospects of this process have been demonstrated recently by Albert et al. [6]. The authors proposed to combine the OxFA conversion of biomass with the production of synthesis gas or hydrogen with their subsequent use in modified Fischer–Tropsch processes [6]. Formic acid can be produced via OxFA-processing of monosaccharides [2,7–9], disaccharides [7,8], cellulose [2,9–13] arabinogalactan [14], xylan [9,10,14], lignin [9,10], plant biomass of miscanthus [14], poplar [9,10], aspen [14], beech [7,8,10], pine [10], spruce [7], and agricultural waste [10,13,14]. Soluble bifunctional heteropoly acids (HPA) are most abundant catalysts for OxFA-processing of polysaccharide and biomass substrates to FA. Both advanced Brønsted acidity and oxidative potential are the main advantages of HPA catalysts which belong to green chemistry catalytic systems [15–17]. Thus, a 66–68% yield of formic acid can be reached during 2–3 h of cellulose transformation [11,13]. The pure soluble heteropoly acids demonstrated notable catalytic activity for the formic acid production from beech wood. The 60% yield of the target product was obtained in 48 h of the process [9,10].

Natural polysaccharide starch, which is an abundant commercial large scale product, can also be considered as promising feedstock for FA production [18]. However, this polysaccharide is rarely used for the synthesis of formic acid. Tang et al. demonstrated that FA can be obtained via hydrolysis-oxidation of starch in the presence of soluble vanadyl sulfate $VOSO_4$ as the catalyst to achieve a 46% yield of FA [19].

The main disadvantage of soluble vanadium-containing catalysts in general and soluble heteropoly acids, in particular, is a problematic separation of a catalyst dissolved from the reaction mixture and the target product. Recently, we demonstrated that cesium acid salts of vanadium-containing heteropoly acids can be used as high effective heterogeneous catalysts for the FA production from starch [18]. The maximum yield of FA was 51% in the presence of $\text{Cs}_{3.5}\text{H}_{0.5}\text{PMo}_{11}\text{VO}_{40}$.

This study is focused on four main issues: (a) assessment of the catalytic potential of the acidic quaternary ammonium salts of Keggin-type vanadium-containing heteropoly acids, such as $\text{R}_{3.5}\text{H}_{0.5}\text{PVMo}_{11}\text{O}_{40}$ (R: $(\text{C}_2\text{H}_5)_4\text{N}$ (Et_4N), $(\text{C}_4\text{H}_9)_4\text{N}$ (Bu_4N), $(\text{C}_6\text{H}_{13})_4\text{N}$ (Hex_4N)), and $(\text{Bu}_4\text{N})_{4.5}\text{H}_{0.5}\text{SiW}_{11}\text{VO}_{40}$ in the direct hydrolysis-oxidation of starch to FA; (b) evaluation of the effect of the alkyl group length in cation of these salts in respect of its catalytic behavior; (c) optimization of processes catalyzed by $\text{Et}_4\text{N-PMoV}$, and (d) investigation of the reaction mechanism by catalytic and computational methods.

2. Results and Discussion

2.1. Synthesis and Characterization of Acidic Quaternary Ammonium Salts of HPA

DRIFT spectra of the acidic quaternary ammonium salts $\text{R}_{3.5}\text{H}_{0.5}\text{PMo}_{11}\text{VO}_{40}$ (R- Et_4N , Bu_4N and Hex_4N) are shown in Figure 1A. In all spectra of salts, we can reveal bands assigned to an oxygen atom bound to three Mo atoms and to one P atom ($\nu_{\text{as}}(\text{P-O}_a\text{-Mo}_3)$, 1080–1060 cm^{-1}) (O_p -band), a terminal oxygen ($\nu_{\text{as}}(\text{Mo=O}_d)$, 990–960 cm^{-1}), a corner sharing bridging oxygen atom ($\nu_{\text{as}}(\text{Mo-O}_b\text{-Mo})$, 900–870 cm^{-1}) (O_b -band), and an edge sharing bridging oxygen atom ($\nu_{\text{s}}(\text{Mo-O}_c\text{-Mo})$, 810–760 cm^{-1}) (O_c -band) [20–23]. In spectrum of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ the band at 1065 cm^{-1} assigned to the P- O_p is splitting that point to the vanadium incorporation into the framework of heteropoly anion and formation of Mo-O-V linkages by replacing Mo substitution one of the 12 Mo atoms with V atom. Positions of bands depend on the alkyl group length in cation, i.e., n in $[\text{C}_n\text{H}_{2n-1}]_4\text{N}^+$. Thus, O_c and O_d bands at 805 and 954 cm^{-1} show a sharp red shift to 800 and 939 cm^{-1} with increasing n value from 2 to 6, respectively (Figure 1B). All these shifts can be explained by the changing of the electron density on Mo and V atoms because of the interaction of the cation with oxygen atoms of heteropoly anions via hydrogen bond formation.

The alkyl group length in cation affects the electron density of V atom that follows from DR-UV-vis spectroscopic investigation. DR-UV-vis spectra of $\text{R}_{3.5}\text{H}_{0.5}\text{PMo}_{11}\text{VO}_{40}$ salts are shown in Figure 1C. In spectra of all materials, only a single absorption edge is observed.

We can suggest that V and Mo ions are electronically dependent from nature of cation, because the edge shifts monotonically to longer wavelengths with the increase of the alkyl group length in cation. The optical band edge can be discussed in the Tauc Equation (1) related to the determination of band energy (E_g):

$$(\alpha h\nu)^{1/2} = B \cdot (h\nu - E_g) \quad (1)$$

where α is the absorbance, $h\nu$ is photon energy, B is an independent parameter of the photon's energy for the respective transitions and E_g is the band gap. The plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ are displayed in Figure S1 (Supporting Information, SI) for $\text{R}_{3.5}\text{H}_{0.5}\text{PMo}_{11}\text{VO}_{40}$ (R- Et_4N , Bu_4N and Hex_4N). The E_g values were determined from the steep absorption edge. Findings show that the E_g value for studied salts depends on the n value and decreases in the following order:

$$\text{Hex}_4\text{N-PMo}_{11}\text{V} (2.90 \text{ eV}) > \text{Bu}_4\text{N-PMo}_{11}\text{V} (2.85 \text{ eV}) > \text{Et}_4\text{N-PMo}_{11}\text{V} (2.76 \text{ eV}).$$

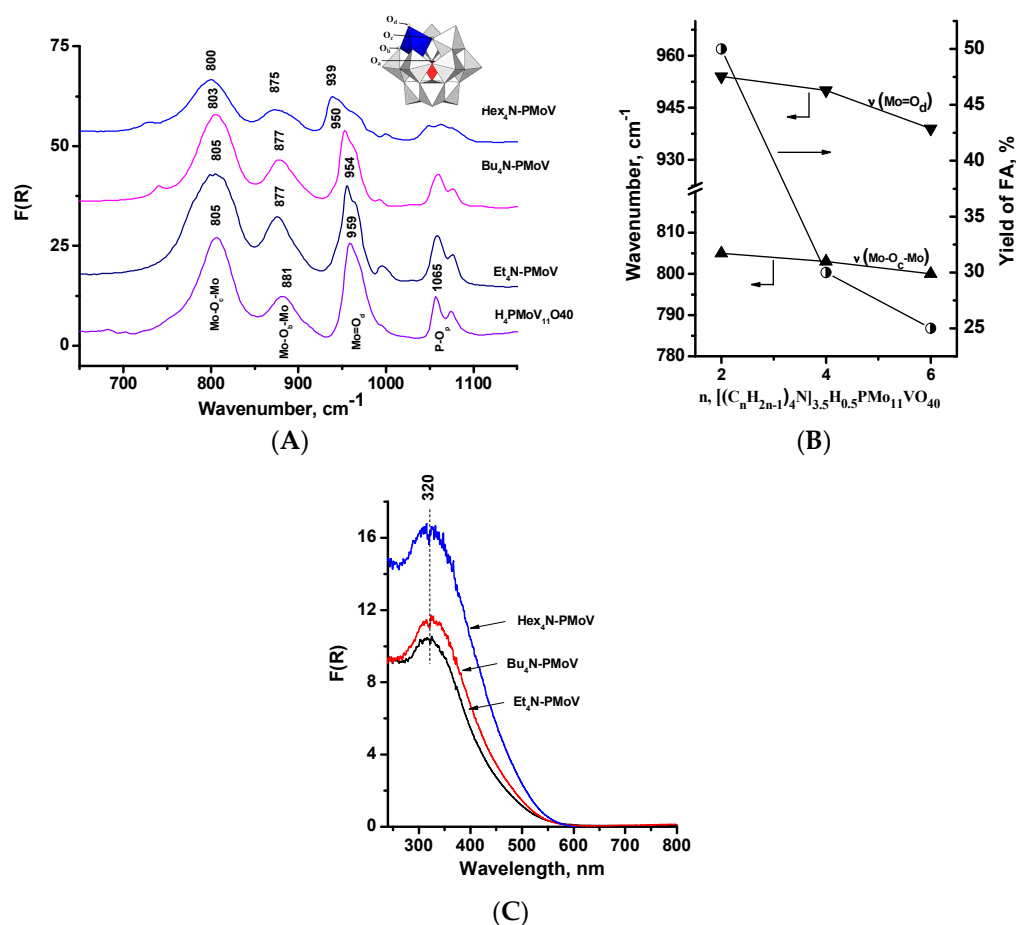


Figure 1. (A) IR spectra of H₄PMo₁₁VO₄₀, R_{3.5}H_{0.5}PMo₁₁VO₄₀ (R-Et₄N, Bu₄N and Hex₄N); (B) Effect of the alkyl group length in cation of R_{3.5}H_{0.5}PMo₁₁VO₄₀ on $\nu_{as}(\text{Mo}=\text{O}_d)$, $\nu_s(\text{Mo}-\text{O}_c-\text{Mo})$ and yield of FA; (C) DR-UV-vis spectra of R_{3.5}H_{0.5}PMo₁₁VO₄₀ salts.

This trend agrees with changing of positions of O_c and O_d bands (Figure 1B).

The alkyl group length in cation also affects the surface acidity of R_{3.5}H_{0.5}PMo₁₁VO₄₀. According to the method of mass titration in aqueous solution [24], these samples possess acid sites (Table 1, Figure S2, SI).

Table 1. Textural and acidic properties of solid HPA catalysts.

	Textural Properties			pH _{PZC}
	S _{BET} (m ² /g)	V _μ (cm ³ /g)	D (nm)	
Et ₄ N-PMoV	2	0.001	13	3.5
Bu ₄ N-PMoV	9	0.002	32	5.0
Hex ₄ N-PMoV	8	n.d.	n.d.	5.2
Bu ₄ N-SiWV	9	0.001	34	4.5

V_μ is the total pore volume, cm³/g. D is the pore diameter, nm.

The values of pH_{PZC} (zero point of charge of the surface) are in the range of 3.5–5.2 and decreased as follows: Et₄N-PMoV (3.5) < Bu₄N-PMoV (5.0) < Hex₄N-PMoV (5.2).

Therefore, we can suggest that the catalytic properties of these salts can depend on their surface acidity and different charge states of the vanadium atom.

2.2. Catalytic Properties of Acidic Quaternary Ammonium Salts of HPA

2.2.1. Catalytic Properties of Et₄N-PMoV

Catalytic properties of acidic quaternary ammonium salts of V-HPAs were investigated in hydrolysis-oxidation of potato starch in a high-pressure autoclave (Autoclave Engineers, Erie, PA, USA) under vigorous stirring 1500 rpm, 2 MPa of air mixture (O₂/N₂ 20/80 vol./vol.), 120–170 °C and (8–1)/1 of weight ratio of starch/catalyst. Detailed information about catalytic tests is shown in SI. Both gaseous and liquid phases of the reaction mixture were analyzed by HPLC, GC, ¹H and ¹³C NMR, TOC according to the techniques described briefly in Section S3.5 and in the Supporting Information in detail. According to a blank experiment at 140 °C, the yield of glucose was 8 mol%, while only a 2 mol% yield of formic acid was achieved in 7 h (Table 2, line 1). In the presence of Et₄N-PMoV yield of FA rose (Table 2). Glucose and FA (1/1 mol/mol) were found to be the target reaction products for the first 0.5 h (Figure S3, SI). Then glucose was converted to FA via two possible pathways (Scheme 1).

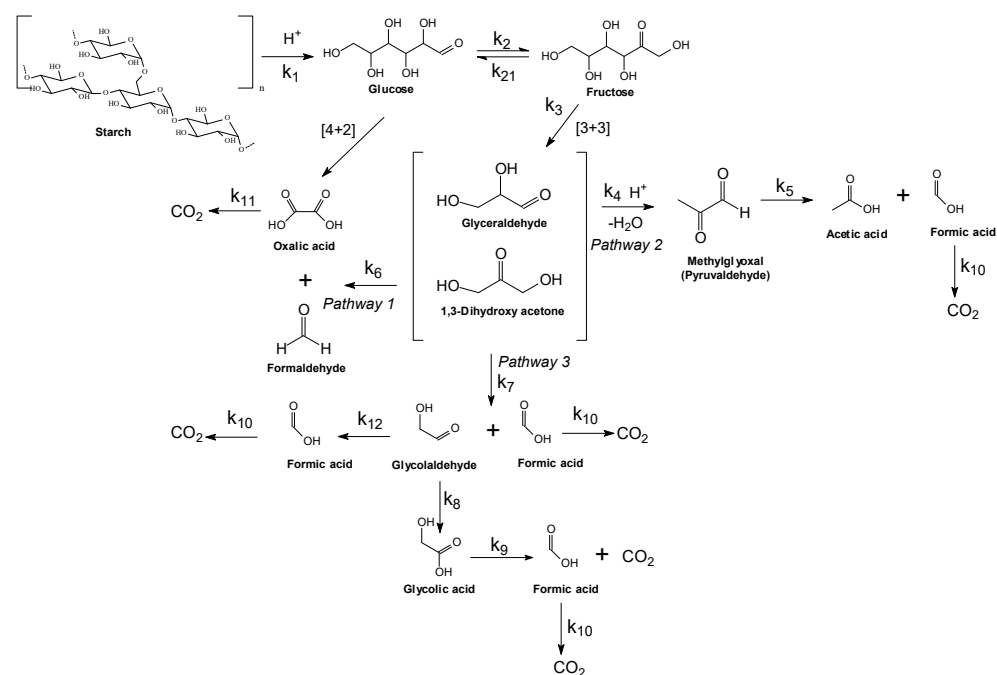
Table 2. Yield of products of hydrolysis-oxidation of potato starch in the presence of R_{3.5}H_{0.5}PMo₁₁VO₄₀ salts ^a.

№	Catalyst	T (°C)	Starch/Catalyst (wt./wt.)	TOF mol _{FA} /(mol _[V] ·h)	X (mol%)	Yield of Products in 7 h (mol%)					Maximum Product Yield ^b (mol%)			
						Gaseous		Water-Soluble ^c			Glucose		FA	
						CO ₂	CO	FA	AA	Other	τ (h)	Y _{max} (%)	τ (h)	Y _{max} (%)
1	blank	140	–	–	–	–	–	2	0	8	7	8	7	2
2	Bu ₄ N-SiWV	140	1:1	1.0	84	37	2	30	9	<6	3	25	7	30
3	Bu ₄ N-PMoV	140	1:1	2.7	100	52	3	30	12	<3	0.5	2	2	33
4	Et ₄ N-PMoV	140	1:1	3.4	100	46	2	50	1	<2	0.75	5	2	50
5	Et ₄ N-PMoV	120	1:1	0.7	72	26	2	35	1	<7	7	4	7	35
6	Et ₄ N-PMoV	170	1:1	13.5	100	47	3	40	1	0	0	16	0.5	50
7	Et ₄ N-PMoV	140	8:1	27.0	100	46	2	50	1	<2	0.5	5	2	50
8	Et ₄ N-PMoV	140	16:1	13.0	92	39	2	42	5	<4	1	4	7	42
9	Hex ₄ N-PMoV	140	1:1	0.6	85	–	–	24	3	12	5	13	7	24

[^a] Experimental conditions: 11.9 g/L of starch (10 g/L of dry starch), 0.3–10 g/L of catalyst, 60 mL of reaction volume, 2 MPa of air mixture, reaction time 7 h; X—Starch conversion. [^b] Maximum yields of glucose and formic acid achieved during the experiment and the time of its achievement. [^c] FA—Formic acid; AA—Acetic acid; Other—glucose, fructose, succinic acids, glycolic acid, hydrated formaldehyde (methyleneglycol).

The first way was the formation of FA from fructose derived from glucose via its isomerization as proposed by Tang et al. [19]. The second way was a [4+2] retro-aldol decomposition of glucose to form oxalic acid as an intermediate product. The maximum yield of FA was reached in 2 h. Moreover, acetic and glycolic acids and hydrated formaldehyde (methyleneglycol) were registered in the reaction mixture. The formation of gaseous products, such as CO and CO₂, was also observed. According to the reaction mass balance revealed by HPLC, GC and NMR and weighting of catalyst after the reaction there was no formation of solid side products such as humins under air atmosphere. Note, that the formation of humins could be possible when hydrolyzing polysaccharides under acid aqueous media and inert atmosphere [25].

Effect of the reaction temperature. The effect of the reaction temperature was investigated in the presence of Et₄N-PMoV at 1/1 of weight ratio of starch/catalyst (molar coefficient 13.5/1 of starch/catalyst) and 2 MPa of air. The main results are shown in Table 2 (lines 4–6). Decreasing the reaction temperature to 120 °C declined the reaction rate, the formic acid yield and starch conversion (Table 2, lines 4 and 5, Figure S4, SI). Only 35 mol% of FA was obtained at 72% of substrate conversion in 7 h. On the other hand, increasing temperature up to 170 °C made it possible for the highest FA yield equal to 50 mol% to be obtained in 0.5 h (Table 2, line 6). However, such an increase in reaction temperature seems to be disadvantageous because of formic acid instability and significant energy consumption under harsh conditions.



Scheme 1. Possible mechanism of formic acid formation from starch based on the literature data [12,18,19,26,27] and the present study.

Effect of the catalyst amount. The influence of catalyst loading was studied at 140 °C and air pressure 2 MPa (Table 1, lines 4, 7–8). The results obtained showed that decreasing the starch/catalyst weight ratio from 1/1 to 8/1 (molar ratio from 13.5/1 to 108/1 respectively) did not adjust the process parameters, i.e., reaction rate, starch conversion, FA yield (Table 1, lines 6 and 7, Figure S5, SI). Only the following decreasing catalyst loading declined the efficiency of the catalyst (Table 1, line 8, Figure S5, SI). Thus, the TOF number of the Et₄N-PMoV catalyst was 27.0 under the optimum conditions (140 °C, 2 MPa of air, 108/1 of molar ration of starch/catalyst).

2.2.2. Activity of Solid HPA Catalysts

It was interesting to evaluate the efficiency of Et₄N-PMoV as a bifunctional catalyst. It is with this aim in mind that we compared the catalytic properties of Et₄N-PMoV with Bu₄N-PMoV and Bu₄-SiWV (Table 2, lines 2–4). The reaction was investigated at 140 °C, 2 MPa of air mixture and 1/1 of weight ratio of starch/catalyst (13.5/1 of molar ratio of starch/catalyst). According to experimental data, the yield of FA depends on the alkyl group length in cation of R_{3.5}H_{0.5}PMo₁₁VO₄₀. The increasing the alkyl group length leads to the decreasing yield of FA (Figure 1C). The yield of FA for 7 h is higher in the presence of Et₄N-PMoV (50%) in comparison to Bu₄N-PmoV (33%) and Hex₄N-PMoV (24%). This trend agrees with the changing of surface acidity of salts (Table 1).

The activity (TOF) of Hex₄N-PMoV is lower (0.6 mol_{FA}/(mol_[V]·h)) due to the lower surface acidity (pH_{PZC} 5.2) in comparison to Bu₄N-PMoV (pH_{PZC} 5.0) and Et₄N-PMoV (pH_{PZC} 3.5). It is interesting that in the presence of Bu₄N-PMoV acetic acid (12%), CO (3%) and CO₂ (52%) are formed in a larger amount compared with Et₄N-PMoV (1, 2 and 46%, respectively) (Table 2, lines 3–4). These differences can be explained by the reaction mechanism (Scheme 1). First, starch was hydrolyzed to glucose onto the acid sites. Then glucose can be transformed to fructose under acidic medium. Formaldehyde can be formed from [C₃] intermediates simultaneously with oxalic acid which seems to be the main way of evolution of CO₂ (pathway 1). The oxidation of glycerinaldehyde or 1,3-dihydroxyacetone can lead to the formation of pyruvaldehyde (pathway 2) and glycolaldehyde and glycolic acid (pathway 3). Based on the catalytic data (Table 2, lines 3–4) and difference in pH_{PZC} of Bu₄N-PMoV and Et₄N-PMoV (Table 1), we can suggest that the high surface acidity of Et₄N-

PMoV (pH_{PZC} 3.5) does not favor the *pathway* 2 in contrast to $\text{Bu}_4\text{N-PMoV}$ (pH_{PZC} 5.0). These results can point out that the type of cation plays an important role in one-pot hydrolysis-oxidation of starch. Note that similar trend is observed for $\text{Bu}_4\text{N-SiWV}$. The difference in the catalytic properties of $\text{Bu}_4\text{N-SiWV}$ and $\text{Et}_4\text{N-PMoV}$ can also be explained by an influence of W and Mo on electron density of V, which is responsible for the oxidation of glucose to formic acid. This is confirmed by electron affinity (W (78.6 kJ/mol) and Mo (71.9 kJ/mol)). Similar catalytic behavior of W and Mo containing catalysts were observed for cesium salts of HPA [18].

2.2.3. Investigation of Reaction Mechanism

To investigate possible pathways of formic acid formation from starch experiments with main reaction intermediates were carried out. The reactions were made in the presence of $\text{Et}_4\text{N-PMoV}$ catalyst 140 °C, 2 MPa of air mixture and 108/1 of molar ratio of substrate/catalyst. The conditions used were equal to ones applied for starch transformations. The transformation of glucose, methylglyoxal, glycolaldehyde, glyceraldehyde, glycolic, oxalic, acetic and formic acids were studied. Maltose was processed as the simplest disaccharide, which contains a α -1,4-glycosidic bond, to investigate the hydrolysis step of the process. Kinetic curves of the intermediate transformations are shown in Figure 2.

Hydrolysis-oxidation of maltose disaccharide made it possible to evaluate the initial rate of hydrolysis first step via cleavage of the α -1,4-glycosidic bond. Quite fast consumption of maltose was established (Figure 2). The conversion of the disaccharide achieved 96% in 0.5 h of the reaction. Maltose hydrolysis-oxidation was revealed as an irreversible process. Interestingly, consumption of glucose as a substrate was faster than transformation of maltose meaning that the hydrolysis of starch is a limiting stage of the process. When transforming maltose and glucose the formation of fructose was observed under acidic reaction conditions. The formation of fructose as one of the intermediates of biomass OxFA processing is usually out of consideration.

To our knowledge, only Tang et al. proposed the way of FA formation from fructose [19]. Retro-aldol cleavage of the monosaccharides occurs via two possible pathways. First, glucose can be directly cleaved via a [4+2] mechanism [26]. To form [3+3] products glucose is firstly transformed to fructose which undergoes retro-aldol reaction [26]. Glycolaldehyde can be converted to FA with the yield of 70 mol%. It should be noted that oxidation of glycolic acid is a slow process and only 50 mol% yield of FA was observed (Figure 2). The results obtained demonstrate that FA can be formed from glycolaldehyde via two possible reaction pathways. The first one proposes oxidation of glycolaldehyde to glycolic acid and its subsequent retro-aldol cleavage to form FA and CO_2 . Another way is a direct oxidation of glycolaldehyde to form FA. Oxalic acid is oxidizing to CO_2 without formation FA. Similar results were reported previously [12].

It seems to be the main rout of CO_2 generation under hydrolysis-oxidation conditions. Experiments with acetic and formic acids as substrates demonstrated there quite high stability under hydrothermal conditions, negligible consumption of the chemicals was detected (Figure 2).

All the intermediates and products identified and proposed were taken into account when describing the scheme of the starch hydrolysis-oxidation process (Scheme 1). The reaction scheme proposed was based on the data described in the literature [12,18,19,26,27] and our experimental observations. The constants of the reactions and chemical interactions were revealed by the experimental kinetic curves (Table 3). The kinetic modelling was based on the following assumptions. The first orders of all the stages were assumed.

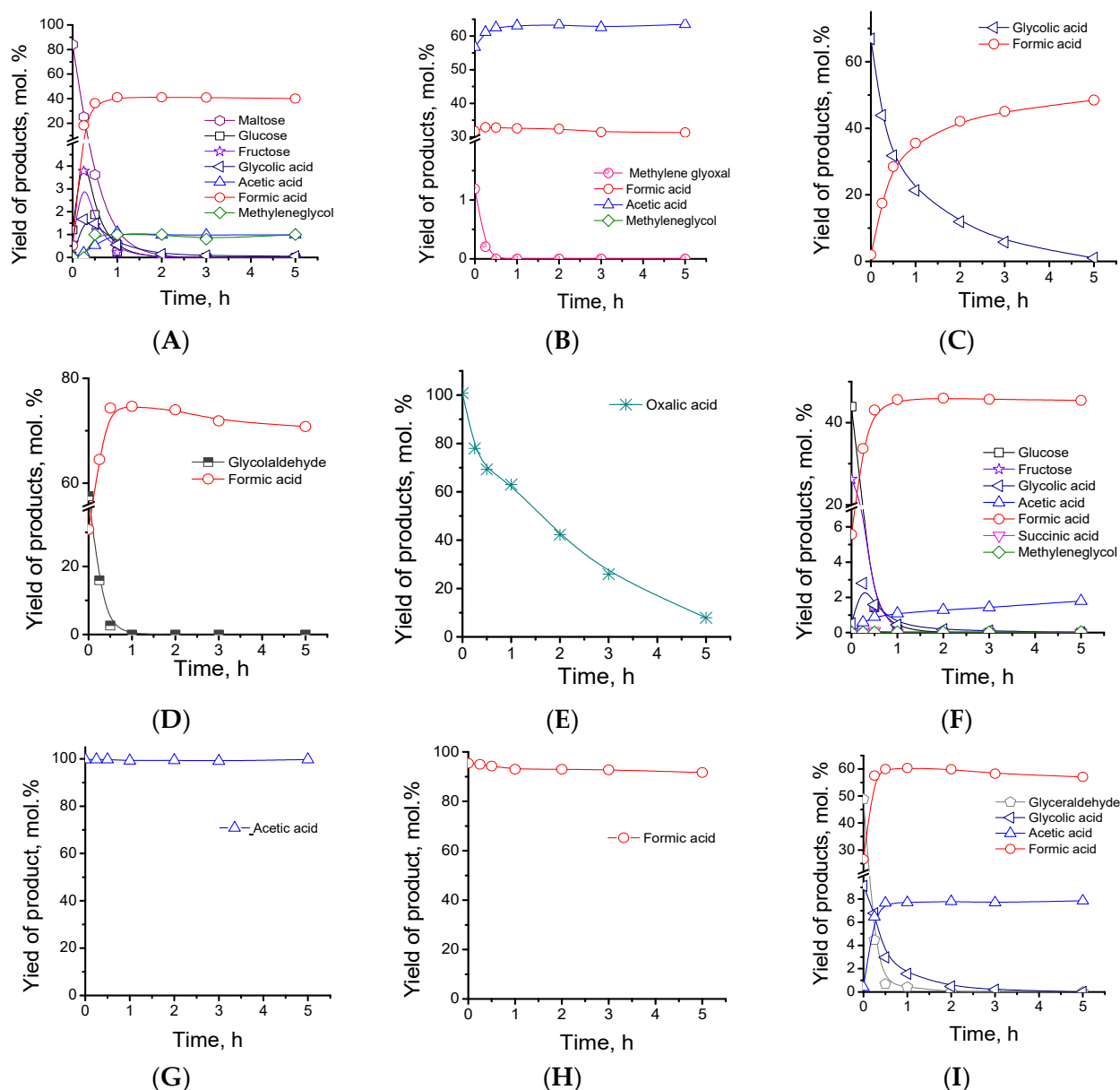


Figure 2. Kinetic curves of accumulation of water-soluble products during hydrolysis-oxidation of maltose (A) and oxidation of other reaction intermediates; transformation of methylglyoxal (B), glycolic acid (C), glycolaldehyde (D), oxalic acid (E), glucose (F), acetic acid (G), formic acid (H), glyceraldehyde (I) are shown. (Experimental conditions: 1.25 g/L of Et₄N-PMoV, 108/1 of starch/catalyst molar ratio, 60 mL of the reaction volume, 2 MPa of air, 140 °C).

Table 3. Constants of the starch hydrolysis-oxidation process.

Constant	Interaction	$k \cdot 10^3 \text{ (min}^{-1}\text{)}$
k_1	Starch hydrolysis to glucose	84
k_2	Glucose isomerization to fructose	46
k_{21}	Fructose isomerization to glucose	0.1
k_3	Fructose retro-aldol cleavage to C ₃ intermediates	114
k_4	Dehydration of C ₃ intermediates to methylglyoxal (pyruvaldehyde)	12.8
k_5	Transformation of methylglyoxal to acetic and formic acids	1.0

Table 3. Cont.

Constant	Interaction	$k \cdot 10^3 \text{ (min}^{-1}\text{)}$
k_6	Transformation of C ₃ intermediates to oxalic acid and formaldehyde	42.8
k_7	Degradation of C ₃ intermediates to glycolaldehyde and formic acid	110
k_8	Oxidation of glycolaldehyde to glycolic acid	34
k_9	Oxidation of glycolic acid to formic acid and CO ₂	13.1
k_{10}	Degradation of formic acid to CO ₂	~0
k_{11}	Oxidation of oxalic acid to CO ₂	7.8
k_{12}	Transformation of glycolaldehyde to formic acid	4.82
k_{13}	Glucose retro-aldol [4+2] cleavage	1

Based on the experimental data (Scheme 1), the following system of differential Equations (2)–(13) was proposed for modelling the kinetic curves.

$$\frac{d[\text{Star}]}{dt} = -k_1 \cdot [\text{Star}] \quad (2)$$

$$\frac{d[\text{Glu}]}{dt} = k_1 \cdot [\text{Star}] - k_2 \cdot [\text{Glu}] - k_{13} \cdot [\text{Glu}] \quad (3)$$

$$\frac{d[\text{Fru}]}{dt} = k_2 \cdot [\text{Glu}] - k_{21} \cdot [\text{Fru}] - k_3 \cdot [\text{Fru}] \quad (4)$$

$$\frac{d[\text{GCA}]}{dt} = 2k_3 \cdot [\text{Fru}] - k_4 \cdot [\text{GCA}] - k_6 \cdot [\text{GCA}] - k_7 \cdot [\text{GCA}] \quad (5)$$

$$\frac{d[\text{Met}]}{dt} = k_4 \cdot [\text{GCA}] - k_5 \cdot [\text{Met}] \quad (6)$$

$$\frac{d[\text{Gly_Ald}]}{dt} = k_7 \cdot [\text{GCA}] - k_8 \cdot [\text{Gly_Ald}] - k_{12} \cdot [\text{Gly_Ald}] \quad (7)$$

$$\frac{d[\text{Gly_Ac}]}{dt} = k_8 \cdot [\text{Gly_Ald}] - k_9 \cdot [\text{Gly_Ac}] \quad (8)$$

$$\frac{d[\text{Oxal}]}{dt} = k_6 \cdot [\text{GCA}] + k_{13} \cdot [\text{Glu}] - k_{11} \cdot [\text{Oxal}] \quad (9)$$

$$\frac{d[\text{FA}]}{dt} = k_7 \cdot [\text{GCA}] + k_5 \cdot [\text{Met}] + k_9 \cdot [\text{Gly_Ac}] + 2k_{12} \cdot [\text{Gly_Ald}] - k_{10} \cdot [\text{FA}] \quad (10)$$

$$\frac{d[\text{Formald}]}{dt} = k_6 \cdot [\text{GCA}] \quad (11)$$

$$\frac{d[\text{CO}_2]}{dt} = k_{10} \cdot [\text{FA}] + k_9 \cdot [\text{Gly_Ac}] + 2k_{11} \cdot [\text{Oxal}] \quad (12)$$

$$\frac{d[\text{Acetic}]}{dt} = k_5 \cdot [\text{Met}] \quad (13)$$

where Star is starch, Glu is glucose, Fru is fructose, GCA is glyceraldehyde, Met is methylglyoxal (pyruvaldehyde), Gly_Ald is glycolaldehyde, Gly_Ac is glycolic acid, FA is formic acid, Oxal is oxalic acid, Formald is formaldehyde, Acetic is acetic acid, CO₂ is carbon dioxide.

The system of differential equations was solved by the Mathcad 15.0 software with function the Odesolve based on the Runge–Kutta method with an automatic step-size for solving. The developed kinetic model described FA formation accurately enough (Figure 3).

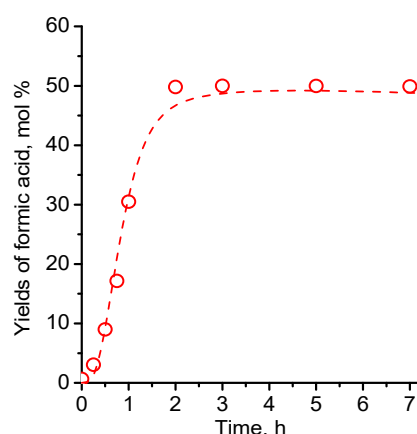


Figure 3. The experimental data (points) compared with simulated kinetic curves (dotted line) for the formation of formic acid during starch hydrolysis-oxidation. (Experimental conditions: 11.9 g/L of starch (10 g/L of dry polysaccharide), 1.25 g/L of $\text{Et}_4\text{N-PMoV}$, 8/1 of starch/catalyst weight ratio (108/1 of starch/catalyst molar ratio), 60 mL of the reaction volume, 2 MPa of air, 140 °C).

2.3. Efficiency of Acidic Quaternary Ammonium Salts of HPA

2.3.1. Stability of $\text{Et}_4\text{N-PMoV}$ Catalyst

Under the optimized reaction conditions, we investigated the reusability and catalytic potential of $\text{Et}_4\text{N-PMoV}$. After each operation cycle, the catalyst was separated, washed with water, dried at room temperature, then dried at 100 °C for 12 h and used in the next run. It was found that this sample could be used repeatedly without significant loss of catalytic activity during at least seven catalytic cycles (Figure 4). The yield of FA was 50–51% after each cycle.

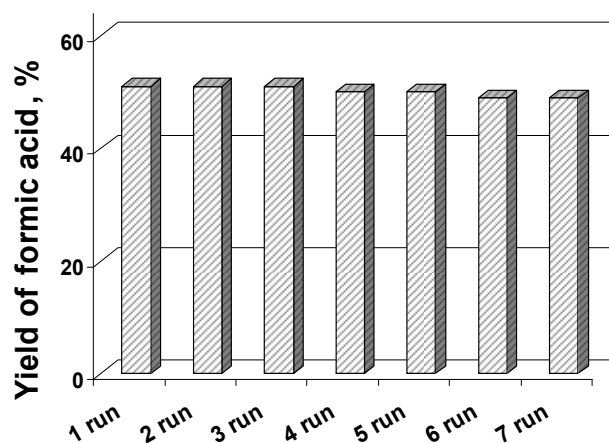


Figure 4. The yield of formic acid achieved during seven runs in the presence of $\text{Et}_4\text{N-PMoV}$ catalyst. (Experimental conditions: 11.9 g/L of starch (10 g/L of dry polysaccharide), 1.25 g/L of $\text{Et}_4\text{N-PMoV}$, 8/1 of starch/catalyst weight ratio (108/1 of starch/catalyst molar ratio), 60 mL of the reaction volume, 2 MPa of air, 140 °C).

According to the analysis of the reaction mixture by the ICP-AES method, in reaction mixture V was registered. V content was 1.1 mg/L, i.e., about 0.4 wt.% of the active component was leached to the reaction solution.

According to the IR spectroscopy, the Keggin structure of heteropoly anion of $\text{Et}_4\text{N-PMoV}$ after seven cycles is not much different from that of the fresh sample (Figure 5). New bands in the region of 1150–1250 cm^{-1} are due to a small amount of reaction products. The oxidation state of vanadium ion change in the course of the reaction can be seen from the change in spectrum of $\text{Et}_4\text{N-PMo}_{11}\text{V}$ pristine and after seven cycles (Figure 5). In spectrum of pristine salt, we can reveal two bands at 320 and 405 nm assigned to the ligand-to-metal

charge transfer bands $\text{Mo} \rightarrow -\text{O}$ and $\text{V}^{\text{V}} \rightarrow \text{O}$, respectively. The appearance of new bands at 375 nm can be assigned to the ligand-to-metal charge transfer band ($\text{V} \rightarrow \text{O}$) due to the small changing the charge state of V.

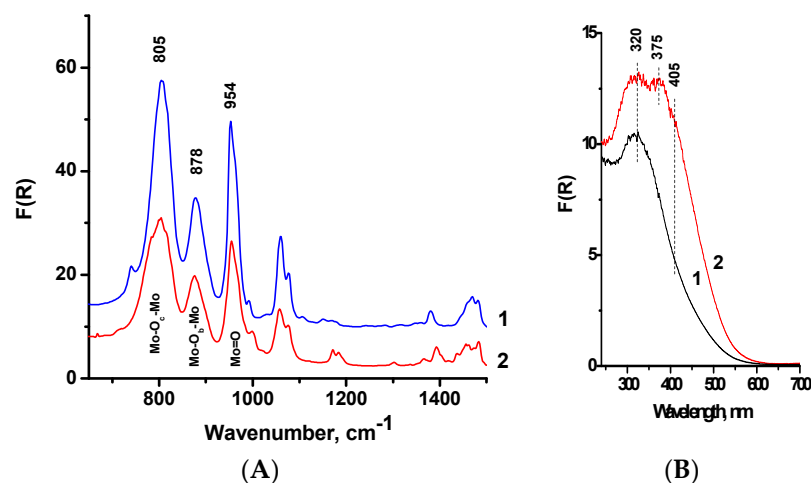


Figure 5. IR (A) and DR-UV-vis (B) spectra of Et₄N-PMoV pristine (1) and after seven runs (2).

2.3.2. Efficiency of Acidic Quaternary Ammonium Salts of HPA

Catalytic performance of Et₄N-PMoV was compared with that of VOSO₄ applied in starch hydrolysis-oxidation to FA by Tang et al. [19] (Table 4, lines 1 and 6). The TOF was significantly higher in the presence of Et₄N-PMoV (27.0 mol_{FA}/(mol_[V]·h)) compared to the one observed in the presence of VOSO₄ (3.1 mol_{FA}/(mol_[V]·h)). Moreover, a higher yield of formic acid (50 vs. 46%) is reported in this work at a higher starch/catalyst ratio and identical temperature and air pressure.

Table 4. Comparative catalytic properties of Et₄N-PMoV catalyst in hydrolysis-oxidation of starch.

Nº	Catalyst	T (°C)	P (MPa)	Time (h)	Starch/V Atom (mmol _{glucose unit} /mmol _V)	Starch/V Active Site (mol/mol)	FA Yield (%)	TOF mol _{FA} /(mol _[V] ·h)	Ref.
1	Et ₄ N-PMoV	140	5	2	62/0.57	108/1	50	27.0	This work
2	Bu ₄ N-PMoV	140	5	2	62/0.57	108/1	33	16.3	This work
3	Bu ₄ N-SiWV	140	5	7	62/0.57	108/1	30	4.7	This work
4	Co-PMoV ₂	150	5	1	62/20	3.1/1	50	1.5	Gromov et al. [18]
5	Cs-PMoV	150	5	2	62/0.5	124/1	51	32.0	Gromov et al. [18]
6	VOSO ₄	140	5	1.5	1/0.1	10/1	46	3.1	Tang et al. [19]

It is more interesting to compare heterogeneous and homogeneous approaches for the hydrolysis-oxidation of starch in the presence of HPA catalysts. Our investigations led us to conclude that a heterogeneous solid bifunctional HPA catalyst is significantly more active and perspective than a homogeneous soluble heteropoly acid for OxFA processing of biomass to biogenic formic acid (Table 4, lines 1 and 4).

3. Materials and Methods

3.1. Synthesis of Acidic Quaternary Ammonium Salts of HPA

The synthesis of the solid X₄N-PMoV (X = Et, Bu and He) catalysts was carried out by partial neutralization of a 0.20 M aqueous solution of H₄PMo₁₁VO₄₀ obtained at a separate stage using tetraethyl-, tetrabutyl- and tetrahexylammonium bromides, respectively (Supplementary Material, SI). The synthesis of the solid Bu₄N-SiWV catalyst was carried out by partial neutralization of a 0.12 M aqueous solution of H₅SiW₁₁VO₄₀ obtained at a separate stage using Et₄NBr [28] (SI). The following chemicals were applied to prepare the catalysts: oxide of vanadium (V) V₂O₅ (99%, Vectron), oxide of molybdenum (VI) MoO₃ (99%), H₂O₂ (high purity, Gamma), H₃PO₄ (99.4%, Acros), tetraethylammonium

bromide Et_4NBr (98%, Vecton), tetrabutylammonium bromide Bu_4NBr (99%, Vecton) and tetrahexylammonium bromide Hex_4NBr (99%, Vecton).

3.2. Characterization of Catalysts

Textural properties of salts are shown in Table 1 and Figure S6 (SI). Textural property measurements are described in detail in SI. Adsorption–desorption isotherms of N_2 onto solid heteropoly acid-based catalysts are described in Figure S1 (SI).

Leaching of the Mo and V from the catalysts in the course of reaction was carried out by means of inductively coupled plasma-atomic emission spectrometry (ICP-AES) using Perkin-Elmer instrument OPTIMA 4300.

The structures of quaternary amines of heteropoly acids were verified by IR spectroscopy (Shimadzu FTIR-8300 equipment). The spectra were recorded in the range of $400\text{--}1800\text{ cm}^{-1}$. A resolution of the spectrometer was 4 cm^{-1} .

The point of zero charge of the samples (pH_{PZC}) was also studied (Table 1, Figure S2, SI).

3.3. Starch Characterization

Commercial potato starch (Amilloros Co., Novosibirsk Oblast, Russia) was used to investigate the hydrolysis-oxidation of the polysaccharide to FA. The purity (99.2%) and moisture content (15.0%) was proven according to the techniques we previously applied [18] and SI. The moisture content was determined according to the Russian National State Standard 16932-82 procedure [29].

3.4. Catalytic Tests

Hydrolysis-oxidation of potato starch was conducted in a high-pressure autoclave (Autoclave Engineers, USA) (1500 rpm). The reaction temperatures were in the range of $120\text{--}170\text{ }^\circ\text{C}$. All the experiments were conducted under air. To carry out any catalytic test, the mixture which consisted of O_2 (20 v/v%) and N_2 (80 v/v%) was prepared according to National State Standard 5583–78. The initial pressure of air in the autoclave was 2 MPa.

To investigate the process of starch hydrolysis-oxidation, the substrate, a catalyst and water were placed together into the autoclave. The reaction mixture was heated to the temperature desired. $\text{Et}_4\text{N-PMoV}$ catalyst was also tested in seven runs of the reaction. To carry out the investigation, the $\text{Et}_4\text{N-PMoV}$ sample was isolated from the aqueous mixture, washed with water, and dried. The step-by-step operations of the catalytic tests have been placed in the SI and described in our previous papers [11,18].

3.5. Reaction Mixture Analysis

The amounts of water-soluble products were determined by HPLC. The eluent applied for the analysis was an aqueous solution of sulfuric acid [18]. Glucose (98%, Alfa Aesar), formic acid (98%, Panreac), acetic acid (99.5%, Reakhim), levulinic acid (98%, Acros), maltose (95%, Acros), fructose (98%, Panreac), glycolic acid (Reakhim), methylglyoxal (40% solution in water, Acros), glycolaldehyde (98%, Sigma), glyceraldehyde (95%, Sigma), and oxalic acid (Reakhim) were applied as HPLC standards or reaction substrates (SI).

^1H and ^{13}C NMR were used to determine the chemicals (SI).

Gas chromatograph Kristall 2000M (Chromatec, Russia) was applied to determine the composition of gas products after the reaction (SI). The instrument was equipped with a flame-ionization detector. The column's parameters were 2 meters length and 2 mm diameter. The column was charged by sorbent Chromosorb 102. The gas carrier was Ar.

The total yield of water-soluble products was TOC analysis (SI).

The detailed information on characterization of reaction mixtures can be found in the SI and our previous works [11,18].

3.6. Computation Methods

The system of differential equations was solved by the Mathcad 15.0 software (PTC Inc., 140 Kendrick Street, Needham, MA, USA).

4. Conclusions

Thus, the potential of water-insoluble acidic quaternary ammonium salts of vanadium-containing heteropoly acids $[(C_2H_5)_4N]_{3.5}H_{0.5}PVMo_{11}O_{40}$, $[(C_4H_9)_4N]_{3.5}H_{0.5}PMo_{11}VO_{40}$, $[(C_6H_{13})_4N]_{3.5}H_{0.5}PMo_{11}VO_{40}$ and $[(C_4H_9)_4N]_{4.5}H_{0.5}SiW_{11}VO_{40}$ as heterogeneous catalysts of one-pot hydrolysis-oxidation of starch to formic acid is demonstrated. The maximum yield of the target product reaches 50% in the presence of $[(C_2H_5)_4N]_{3.5}H_{0.5}PVMo_{11}O_{40}$. The most promising catalyst has good reusability (seven cycles) and significant TOF values. The results obtained lead one to conclude that a heterogeneous catalytic approach to the production of biogenic formic acid is much more effective than a homogeneous one. The kinetic model which consisted of seventeen stages was proposed to predict the formation of formic acid via starch hydrolysis-oxidation over the most active $[(C_2H_5)_4N]_{3.5}H_{0.5}PVMo_{11}O_{40}$ catalyst. The computational model described the formic acid formation observed well.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12101252/s1>. Experimental section in detail; Figure S1: Correlation between $(\alpha h\nu)^{1/2}$ and proton energy for these samples; Figure S2: Correlation between pH and amount of solid heteropoly acid based catalysts in water; Figure S3: Kinetic curves of accumulation of water-soluble products during starch hydrolysis-oxidation; Figure S4: Effect of reaction temperature on the yield of formic acid in the presence of $[(C_2H_5)_4N]_{3.5}H_{0.5}PMo_{11}VO_{40}$; Figure S5: Correlation between formic acid yield and molar ratio of starch/catalyst; Figure S6: Adsorption-desorption isotherms of N₂ onto solid heteropoly acid-based catalysts.

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