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Glucose oxidation to formic acid and methyl formate in perfect.^{View Article Online} selectivity

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Abstract

We report the highly remarkable discovery that glucose oxidation catalysed by polyoxometalates (POMs) in methanolic solution enables formation of formic acid and methyl formate in close to 100% combined selectivity, thus with only negligible sugar oxidation to CO_2 . In detail, we report oxidation of a methanolic glucose solution using H_8 [PV₅Mo₇O₄₀] (HPA-5) as catalyst at 90°C and 20 bar O_2 pressure. Experiments with ¹³C-labelled glucose confirm unambiguously that glucose is the only source of the observed formic acid and methyl formate formation under the applied oxidation conditions. Our results demonstrate a very astonishing solvent effect for the POM-catalysed glucose oxidation. In comparison to earlier work, a step-change in product yield and selectivity is achieved by applying an alcoholic reaction medium. The extremely high combined yields of formic acid and methyl formate from the reaction as low-boiling methyl formate (bp= 32°C) can simply be isolated from the reaction mixture by distillation.

Keywords:

Biomass oxidation, polyoxometalates, methanol, formic acid, methyl formate

Introduction

View Article Online DOI: 10.1039/D0GC01169J

So far, the industrial production of formic acid uses fossil resources. The most common pathway for industrial formic acid production is carbonylation of methanol followed by hydrolysis of the resulting methyl formate. This process currently covers 90% of the global formic acid production with a total capacity of 770 kton/a (2014) [1]. Alternative pathways for formic acid production include the electrochemical reduction of CO_2 [2-4] and the catalytic hydrogenation of CO_2 [5]. Both processes suffer from scale-up problems and operation challenges as well as thermodynamic restrictions in the case of the thermocatalytic conversion [6, 7].

Formic acid is a broadly used industrial chemical. Prominent application examples include its use as feed additive, for leather tanning, as drilling fluid, as acidifier, as cleaning agent or as anti-icing substance for roads and airport runways [8, 9]. Formic acid is also discussed as hydrogen and as CO storage molecule. Its catalytic decomposition has been shown to deliver hydrogen and carbon dioxide in excellent selectivity [10, 11], and even the use as fuel for direct formic acid fuel cells (DFAFCs) has been proposed [12-14]. Thermal decomposition of formic acid in the presence of an acid delivers CO in high selectivity. Thus, depending on the decomposition conditions, formic acid can serve as precursor for syngas production in various H_2/CO ratios, depending on the applied process scheme [15].

In general, biomass is a promising feedstock for the production of high-value chemicals with high oxygen content [16]. Glucose, in particular, has been examined in detail as starting material for oxidation reactions leading to formic acid, acetic acid, glycolic acid or gluconic acid [17]. Several recent studies demonstrate the oxidative conversion of carbohydrate biomass into formic acid [18-21]. Typically, a two step procedure is applied: First, acid hydrolysis of the biomass leads to the formation of monosaccharides, such as e.g. glucose, fructose, or xylose. Second, C-C bond cleavage by catalytic oxidation produces formic acid [22]. Vanadium-containing catalysts, for instance NaVO₃ or VOSO₄ or polyoxometalates (POM), have been shown to exhibit activity for the second reaction step, but formic acid yields are low to date [23-28]. To improve the performance, strong mineral acids such as H₂SO₄ or HCl were applied to reduce the pH-value of the reaction media to support dissociation and re-oxidation of the catalyst [29-31].

More specific, the conversion of glucose to formic acid via oxidation in aqueous media has been successfully promoted by various vanadium-based Keggin-type POM catalysts (Scheme 1) [32-36]. The applied catalysts activate oxygen for the conversion and are reoxidized by molecular oxygen after each reaction cycle. The POMs provide strong Brønsted acidity, high proton mobility, fast multi-electron transfer, high solubility in various solvents, and excellent resistance against hydrolytic or oxidative degradations [37, 38]. A remarkable

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feature of this oxidation process is that formic acid and CO_2 are the only products when the Article Online oxidation process is completed. At full glucose conversion, formic acid yields of up to 60% can be achieved, a value that is further improved to 85% by working in a water/1-heptanol biphasic system with *in situ* product extraction [39] Vanadium-based POM catalysts are also active with other starting materials, such as pomace or humins. However, formic acid yields are lower with these more complex substrates, e.g. 55% in case of pomace oxidation [40, 41]



Scheme 1: POM catalysed oxidation of glucose to formic acid in aqueous media [29, 36].

In recognition of the significant advantages offered by the POM-catalysed, selective biomass oxidation, some of us have developed the so-called OxFA-process [22, 32-35]. This continuous process applies $H_8[PV_5Mo_7O_{40}]$ (HPA-5) at low pressure (\leq 20bar) of molecular oxygen or synthetic air as the oxidant in aqueous solution. The process can be applied to a broad range of biogenic raw material including a lot of complex water-insoluble biomass compounds of the 2nd and 3rd generation if *para*-toluenesulfonic acid (*p*-TSA) is used as an additive to assist feedstock hydrolysis [32, 41] Despite its versatility, the classical OxFA process – as all other POM catalysed conversion of biomass to date - suffers from a maximum formic acid yield of 60% in a monophasic reaction system. This means that ca. 40% of the carbon present in the biomass substrate is converted to CO₂ [17, 22].

In this contribution we describe the incidental and very remarkable discovery that a simple change in the reaction medium of the POM-catalysed glucose oxidation leads to a step-change in performance. In detail, we report a remarkable influence of methanol as solvent onto the formic acid selectivity in glucose oxidation at 20 bar initial O_2 and 90 °C reaction temperature.

Results and Discussion

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Solvent selection

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Our initial intention was to study the influence of the reaction medium on the POM-catalysed glucose oxidation reaction. We selected solvents of interest according to the following requirements: i) The applied solvent should dissolve the HPA-5 catalyst and the substrate glucose at room temperature; ii) the mixture should be liquid at room temperature; iii) the solvent must be stable under the oxidative reaction conditions (for all stability tests of the applied solvents see Supporting Information, Table S1); iv) the solvent should enable straightforward isolation of the desired formic acid product. In the light of these requirements the glucose oxidation was performed in methanol, ethanol, n-propanol and n-butanol, and the results were compared to the original reaction in water. The results are shown in Figure 1.



Figure 1: Solvent screening. Reaction conditions: 1 mmol glucose, 0.1 mmol HPA-5 catalyst dissolved in 10 mL solvent, 20 bar initial O_2 , 90 °C, 24 h, 1000 rpm.

All systems achieved full glucose conversion within 24 h reaction time. It is important to note that for all experiments using alcoholic solvents, the organic acids formed during oxidation were present in the reaction mixture as either free acids or esterification products with the respective alcohol solvent. With all alcoholic solvents, formic acid and its respective ester were formed as the dominant product. Very surprisingly, however, the yield in methyl formate exceeded 99% in the case of methanol being the solvent. In this case neither CO nor CO_2 were detectable in our gas phase analysis by gas chromatography. In contrast, the combined yield of formic acid and the respective esters using C_2 - C_4 alcohols was only between 30-50%, significantly lower than the aqueous benchmark system. Moreover, in ethanol, n-propanol and n-butanol as reaction solvent, significant amounts of CO_2 , CO and acetic acid (and its respective esters) were found as side products. The carbon mass balance (expressed as total carbon yield TOC, for details see Equation (3) in the Supporting Information) could be closed

to over 95% for each experiment. Blank experiments without the HPA-5 catalyst didn't showice Online DOI: 10.1039/DOGC01169J any product formation in any of the solvents under investigation.

Labelling experiments

In order to further elucidate the outstanding catalytic performance in methanol, the reaction in this solvent was investigated in more detail. Our aim was to unambiguously prove that the formic acid equivalent in the formed methyl formate origins solely from glucose oxidation and not from oxidation of the solvent methanol followed by esterification. In order to address these questions we performed oxidation experiments with ¹³C labelled glucose. Scheme 2 shows the expected reaction for the combination of ¹³C labelled glucose and ¹²C methanol.



Scheme 2: POM-catalysed oxidation of ¹³C labelled glucose in ¹²C methanol as solvent – expected reactivity for the case of glucose serving as sole source of the formic acid equivalent formed.

The analysis of the GC-MS data of the respective reaction is shown in Figure 2. Four experiments were performed: Figure 2A shows the GC-MS for the reaction product of the benchmark experiment with ¹²C glucose in ¹²C methanol indicating the mass of 60 g/mol for the exclusively formed ¹²C methyl formate. Figure 2 B shows the mass spectrum of the reaction of glucose in a 9:1 ¹²C/¹³C methanol mixture indicating only ¹²C methyl formate formation. Figure 2C shows the GC-MS for the same product but this time obtained from a 1:1 mixture of ¹²C glucose and ¹³C glucose in ¹²C methanol. As a result, a roughly 1:1 mixture of the masses 60 and 61 g/mol was found for the reaction product. Figure 2D, finally, shows the GC-MS for the main product in the experiments in which solely ¹³C glucose was used as the feedstock. As expected, the product with the mass of 61 g/mol was found almost exclusively, the remaining traces of 60 g/mol may be explained with the fact that the applied ¹³C glucose was only of 99% isotopic purity. No doubly labelled product of mass 62 g/mol was detected in any of the samples indicating that the formic acid unit origins from glucose while the methyl ester group origins uniquely from the solvent as indicated in Scheme 2. Consequently, our labelling experiments provide convincing evidence that methanol is not the source of formic acid in the applied reaction system. Instead, the methanolic reaction medium changes in a very remarkable manner the selectivity of the HPA-5 catalyst in glucose oxidation, avoiding almost

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III MS Spectrum Results 2 ++ \$ Q 1 1 1 1 2 A O C 1 • 👖 🛏 🗳 况 % 🌾 🖄 🗢 🤳 x102 + Scan (1.492-1.511 min, 4 Scans) 4_konz_Mth_g_s200_lnj.D 21 A) 0.8 29.1 0.6 60.0 0.4 0.2 18.1 44.0 53.1 56.0 70.1 73.1 78.1 + Scan (1.492-1.562 min, 12 Scans) 3_konz_Mth_g_s200_Inj.D x101 B) 4 29.1 3 60.03 2 34 18.1 41.1 44.0 51.1 56.1 70.1 73.1 78.1 1 1 0. + Scan (1.492-1.550 min. 10 Scans) 2 konz Mth g s200 Ini.D x101 5 C) 4 3 29.1 2 60.0 18.1 56.1 41.1 45.0 51.1 70.1 73.0 78,1 0 x10² + Scan (1.499-1.511 min, 3 Scans) 1_konz_Mth_g_s200_Inj.D D) 0.8 0.6 0.4 0.2 15.1 18.1 15 20 30 35 40 45 50 70 80 75 unts (%) vs. Mass-to

all side product formation and leading to an extremely high methyl formate selectivity Notecte Online DOI: 10/10/39/D0GC01169J that TOC almost reached 100% in all experiments.

Figure 2: Mass spectra of the main product in glucose oxidation experiments as analysed by GC-MS: A) Mass spectrum of the main product obtained from ¹²C-glucose oxidation in ¹²C methanol, B) Mass spectrum of the main product obtained from ¹²C-glucose oxidation in a 9:1 ¹²C/¹³C methanol mixture, C) Mass spectrum of the main product obtained from oxidising a ¹²C/¹³C-glucose mixture (1:1) in ¹²C methanol, D) Mass spectrum of the main product obtained from ¹³C-glucose oxidation in ¹²C methanol. Reaction conditions: 1 mmol ¹³C-glucose/¹²C-glucose, 0.1 mmol HPA-5 catalyst dissolved in 10 mL methanol, 20 bar initial O₂, 90 °C, 24 h, 1000 rpm.

Mechanistic investigations – the pathway from glucose to methyl formate

To learn more about the oxidation pathway leading to methyl formate formation in almost perfect selectivity in the methanolic HPA-5 reaction solution, we performed a time-resolved glucose conversion experiment (Figure 3). Already after one hour reaction time, full conversion of glucose was achieved. Erythrose, glyoxal and glycolaldehyde were detected as reaction intermediates while around 50% of the initial glucose was already converted to formic

acid/methyl formate. With increasing reaction time, erythrose and glyoxal decreased fasterice online DOI: 10.1039/D0GC01169J than glycolaldehyde which is a hint that the latter is a secondary intermediate on the way to formic acid. After 24 hours, all intermediates were fully oxidised to formic acid that forms methyl formate under the reaction conditions in almost quantitative manner. The mass balance was always closed to 100% in the liquid phase and no gaseous side products were detected throughout the entire course of the experiment.



Figure 3: Glucose oxidation catalysed by HPA-5 in methanol as solvent – product formation over reaction time. Reaction conditions: 1 mmol glucose, 0.1 mmol HPA-5 catalyst dissolved in 10 mL methanol, 20 bar initial O_2 , 90 °C, 1-24 h, 1000 rpm.

Based on these time-resolved experiments, we propose the following reaction mechanism for the HPA-5-catalysed glucose oxidation in methanolic solution to formic acid and further esterification to methyl formate (Scheme 3). In the first step, glucose undergoes an oxidative C-C bond cleavage under water elimination to form one molecule of erythrose and one molecule of glyoxal. Hereafter, erythrose is cleaved by a similar oxidative reaction step to form one molecule glyoxal and one molecule glycolaldehyde. All C₂-intermediates are subsequently oxidised to formic acid. The latter is rapidly transformed into methyl formate via esterification with methanol. The esterification is fast and almost complete due to the enormous excess of the solvent methanol. Obviously, no undesired total oxidation of any carbon intermediate to CO or CO_2 takes place in methanol. The amount of water that is overall produced (six equivalents per glucose substrate) correspond well to the amount of water that we have measured after full conversion in our Karl-Fischer titration experiments.



Scheme 3: Proposed reaction mechanism for the HPA-5-catalysed glucose oxidation to methyl formate in methanol.

Methanol stability under oxidative conditions

Published on 11 June 2020. Downloaded on 6/14/2020 2:55:13 AM.

To critically evaluate the stability of the solvent methanol under the reaction conditions further, we performed methanol oxidation experiments with the same HPA-5 catalyst under the same conditions but without adding glucose. For comparison, we also performed an experiment under nitrogen atmosphere to clarify whether oxygen is transferred from the POM catalyst to the methanol. The resulting ¹³C-NMR spectra (Figure 4) and headspace GC-MS measurements (see Supporting Information, Figures S1 and S2) show that under oxidative conditions small amounts of dimethoxymethane are formed from methanol at 90 °C and 110 °C, respectively. At 110 °C under oxygen atmosphere small amounts of dimethylether are formed in addition. Both products are not detectable under nitrogen atmosphere.



Figure 4: Methanol stability under oxidative conditions in presence of HPA-5. Reaction conditions: 0.1 mmol catalyst, 10 g MeOH, 20 bar initial O_2 or N_2 pressure, 24

To clarify the role of the HPA-5 catalyst in methanol oxidation, we performed control experiments without catalyst both under oxygen and nitrogen atmosphere at 90°C. Interestingly, we could not find neither dimethoxymethane nor dimethylether without the POM

catalyst under O_2 atmosphere but methoxymethanol (Figure 5). As expected, no products cle Online could be detected under nitrogen atmosphere without catalyst.



Figure 5: ¹³C-NMR spectra of the product mixture obtained from methanol oxidation at 90 °C without catalyst. Further reaction conditions: 10 g MeOH, 20 bar, 24

Based on a published mechanism for gas-phase methanol oxidation [42], we propose that formaldehyde must be formed as an intermediate on the way to methoxymethanol (Scheme 4), although we couldn't detect this compound in our experiments due to its fast consecutive reaction with methanol. To verify this hypothesis, we performed control experiments using all suggested intermediates and products as substrates under the same oxidative reaction conditions of 90°C and 20 bar oxygen pressure. The corresponding ¹³C-NMR spectra can be found in the Supporting Information (Figures S6-S8).

As expected, the use of dimethoxymethane and dimethylether as substrates did not show any conversion under the applied reaction conditions in absence of the catalyst confirming that these compounds are stable under the reaction conditions in methanolic solution. Using formaldehyde resulted in the formation of methoxymethanol as the only product, as expected. Compared to the experiment in pure methanol this compound was formed in much larger quantities with added formaldehyde confirming that formaldehyde is indeed an intermediate on the way to methoxymethanol (without HPA-5 catalyst) and dimethoxymethane (with HPA-5 catalyst). Based on these results, we propose the following reaction scheme for methanol oxidation in the absence of glucose in our HPA-5 reaction system (Scheme 4). Note that these experiments were only performed on a qualitative manner. Therefore we cannot comment on the mass balance here.



dimethylether

dimethoxymethane

Scheme 4: Reaction pathway of oxidative methanol conversion in the HPA-5 catalysed reaction system in the absence of glucose.

Product composition depending on water content

As six moles of water are formed per conversion of one mol of sugar to six moles of methyl formate (see Scheme 3), we were interested to understand in more detail the role of small amounts of water in our methanolic reaction system. In the following set of experiments, we therefore varied the amount of water from zero (pure methanol) to 100% (pure water). The results are depicted in Figure 6.

As expected, glucose conversion is not a strong function of the water content, the reaction converts all glucose in pure methanol, pure water and most of the solvent mixtures (see Figure 6A). The amount of CO_2 formed shows, however, a very interesting dependency on the actual water content in the methanolic reaction mixture. Up to 90% water content, the degree of undesired CO_2 formation stays as low as 3.3% and only increases to the typical values of 43% with pure water as a solvent. This shows impressively that already a small amount of methanol in the reaction system has a quite significant influence on the suppression of the unwanted CO_2 production during glucose oxidation.



Figure 6: Influence of water in the HPA-5-catalysed oxidation of glucose in methanolic solution: A) Glucose conversion and CO_2 yield as function of the water content. B) Methyl formate and formic acid yields as function of the water content. Reaction conditions: 1 mmol glucose, 0.1 mmol HPA-5 catalyst dissolved in 10 mL solvent, 20 bar initial O_2 , 90 °C, 24 h, 1000 rpm.

The yield of methyl formate depends also on the water content of the reaction mixture and decreases linearly from almost 100% yield in pure methanol to almost 0% yield in pure water, as expected (Figure 6B). The yield of formic acid depends also strongly on the water content. Without water the formic acid yield is almost zero as it immediately reacts with methanol to methyl formate. The higher the water content, the higher is the formic acid yield. The maximum formic acid selectivity is found at 90% water with 78 % (formic acid yield of 72%). At even higher water content, the selectivity decreases slightly due to the increasing CO_2 formation. Moreover, again no intermediates were left after 24 h reaction time whereby CO_2 and CO

could be detected as byproducts in the gas phase (for details see Supporting information ticle Online DOI: 10.1039/D0GC01169J Table S2). The carbon mass balance was always closed to >99% in this study.

Reaction rate comparison of HPA-5-catalysed glucose oxidation in water vs. methanol

Finally, we were interested to compare the kinetics of our new HPA-5-catalysed glucose oxidation in methanol with the same reaction in the state-of-the-art aqueous system. Therefore, we performed for both reaction systems time-resolved experiments with sampling of both the gas and the liquid phase over the course of the reaction. In order to further approach reaction conditions of technical interest, we performed these comparison experiments at reduced oxygen pressure using 5 bar synthetic air (21 vol% oxygen), i.e. a twenty-fold reduced oxygen partial pressure compared to our standard reaction conditions, at 90°C reaction temperature. Figure 7 shows that the glucose concentration drops much faster in methanol compared to the reaction in water. The fact that under these relatively oxygen-lean conditions a full glucose oxidation is possible in methanol while only 40 % of the glucose is oxidised in water demonstrates that re-oxidation of the HPA-5 catalyst is possible at lower oxygen partial pressure in methanol compared to water. The fact that re-oxidation of the HPA-5 catalyst at the here applied low O₂ partial pressure of only 1.02 bar is indeed possible in methanol as solvent is visually confirmed by the different colour of the reaction solution. While the reaction mixture in water is dark blue at the end of the reaction in water (indicating vanadium in its +IV oxidation state), it stayed in its original orange colour (indicating vanadium in its +V oxidation state) throughout the experiment in methanolic solution. This interpretation was further confirmed by our ⁵¹V-NMR spectroscopy measurements (see Figures S9-S10 in the Supporting Information). Thus, the HPA-5-catalysed glucose oxidation is not only significantly faster in methanol than in water (for detailed experimental data see Supporting Information Tables S3, S4 and Figure S11, respectively). It is also feasible at significantly lower oxygen partial pressure which is another big advantage. The reason can be found in the higher oxygen solubility in methanol compared to water (2.15 mM in methanol compared to 0.26 mM in water at 20°C and 1 atm) [44, 45].

The use of our new methanolic reaction system enables operation with air (instead of pure oxygen) and/or at significantly lower total pressure. Both aspects reduce equipment and operation cost of a potential glucose oxidation process and add significantly to the economic attractiveness of our new methanolic oxidation process.

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Figure 7: Glucose concentration over time in water (blue) and methanol (orange). Reaction conditions: 1 mmol glucose, 0.1 mmol HPA-5 catalyst dissolved in 10 mL solvent, 5 bar synthetic air (21 vol% O_2), 90 °C, 1-24 h, 1000 rpm.

The initial reaction rates are very fast. Consequently, we have further investigated the influence of possible mass transfer limitations. In detail, we have performed variations of oxygen partial pressure and stirring speed (for details see Supporting Information, Figures S13 and S14). Both studies confirmed that sufficient oxygen is available for catalyst re-oxidation in methanol under the applied reaction conditions whereby it is limited in water.

It remains to be noted that we could already demonstrate the stability of our HPA-5 catalyst system in pure methanolic solution as evidenced by three consecutive catalytic runs without any catalyst treatment or product removal in-between and without any loss in performance (see Supporting information, Figure S12).

Experimental section

Materials

D(+)-glucose (99.4%) was purchased from Merck KGaA and used without further purification. The ¹³C-glucose (99%) was obtained from Eurisotop and used as received. A list of all solvents previously tested in the POM catalysed glucose oxidation and the corresponding sources can be found in the Supporting Information, Table S1. The solvents used in this work, i.e. demineralized water, methanol (99.0%), ethanol (99.5%), n-propanol (98%) and *n*-butanol (99.9%) were all purchased from Merck KGaA. For our mechanistic investigations formic acid (99.5%) from VWR, methyl formate (97%) from Alfa Aesar, dimethoxymethane (98%) from Alfa Aesar, and formaldehyde (50 wt% aqueous solution) from Merck KGaA were used.

All gases applied for the described experiments (oxygen 5.0, helium 5.0, nitrogen 5.0, and warticle Online Synthetic air) were purchased from Linde AG. Argon 5.0 and hydrogen 5.0 from Linde AG were additionally used as carrier gases for the GC analysis.

For the synthesis of the HPA-5 ($H_8PV_5Mo_7O_{40}$) catalyst, V_2O_5 (99.5%) from Alfa Aesar, MoO_3 (99%) from Alfa Aesar, H_3PO_4 (25 wt% aqueous solution) from AppliChem and H_2O_2 (30 wt% aqueous solution) from Alfa Aesar were used.

Catalyst preparation and characterisation

Our synthesis of Keggin heteropolyoxometalates was based on a method published by Odyakov and Zhizhina [43] and was optimised for the synthesis of HPA-5 by Albert et al .[33]. This procedure consists of a two-step synthesis, with the first step producing the stable vanadium precursor $H_9[PV_{14}O_{42}]$. HPA-5 is obtained in the second step by synthesising the molybdenum precursor (HPA-0) followed by subsequent addition of the vanadium precursor.

For the synthesis of the vanadium precursor, V_2O_5 is first suspended in about 8°C cold water (<10°C) with constant stirring. Slow dropwise addition of 30 wt% hydrogen peroxide solution at lower than 10°C results in the dark red coloration of the vanadium (V) peroxo species formed. Reaction induced warming to 30-35 °C (due to removing of the cooling bath) causes the release of O_2 accompanied by a colour change to brown orange by forming the unstable $H_6[V_{10}O_{28}]$. When the evolution of the gas stops, the stable dark brown $H_9[PV_{14}O_{42}]$ vanadium precursor is obtained by slow addition of 25 wt% phosphoric acid.

To prepare the molybdenum precursor (HPA-0), MoO₃ is first suspended in water at room temperature with constant stirring. The subsequent addition of 25 wt% H₃PO₄ and heating to the boiling point of about 140 °C leads to the formation of the yellow H₃[PMo₁₂O₄₀] precursor (HPA-0). Thereafter, the reaction mixture is further boiled while adding portions of the H₉[PV₁₄O₄₂] precursor from the first reaction step. Depending on the stoichiometric ratio of the starting materials, the finished polyoxometalate with the corresponding degree of substitution n is formed. The reaction mixture is then concentrated by evaporation and cooled to room temperature. This process is followed by a dead-end filtration of the concentrated mixture to remove unreacted starting materials (V₂O₅ or MoO₃) or other impurities. The remaining filtrate is then dried by rotary evaporation at 55 °C in the water bath under a vacuum (the end pressure is ca. 50 mbar) to obtain a crystalline solid. The obtained crystals are finally dried overnight at 30 °C and 50 mbar vacuum. As a result, HPA-5 is obtained as a powdery, crystalline, reddish-brown solid in high yields of over 90%.

The characterisation of the so-prepared HPA-5 catalyst was carried out by ICP-OES, FT-IR, TGA, ³¹P- and ⁵¹V-NMR spectroscopy. Elemental analysis by ICP-OES (Perkin Elmer Plasma 400) resulted in a ratio of P/V/Mo of 1/5/7. Infrared spectroscopy of the solid catalyst

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was recorded using a Shimadzu Prestige-21 FT-IR spectrophotometer in combination with warticle Online diamond crystal ATR unit from L.O.T., Golden Gate in the range of 4000 to 400 cm⁻¹. The spectra showed the expected stretching vibrations for the Keggin-oxoanion (see Supporting Information, Figure S3). Thermogravimetric analyses (TGA) were conducted using a SETSYS-1750 CS Evolution from SETARAM Instruments resulting in the two-step loss of water that is typical for Keggin-heteropolyacids (see Supporting Information, Figure S4). 11 wt% loss of crystallisation water and 5 wt% loss of constitutional water resulted in 14 moles of hydrated water per mole of HPA-5. Using this value, a molar mass of M_{HPA-5}=1857 g/mol can be calculated. The NMR spectra were recorded using a Jeol ECX-400 MHz spectrometer (9.4 Tesla) at 293 K. The ³¹P NMR spectra were recorded at 161.98 MHz with 512 scans in the range of -7 to +5 ppm, resulting in a resolution of 0.24 Hz. The field frequency stabilisation was locked to deuterium by placing a coaxial inner tube with 1 wt% H_3PO_4 in D_2O into a 5 mm tube containing the sample. The ⁵¹V NMR spectra were measured with 2024 scans in a range of -580 to -460 ppm with an excitation frequency of 105.25 MHz and a resolution of 0.77 Hz. The field frequency stabilisation was locked to deuterium by placing a coaxial inner tube with D_2O into a 10 mm tube containing the sample. The corresponding spectra are shown in Figure S5 in the Supporting Information. The experimental data confirmed that HPA-5 was synthesized successfully.

Experimental setup and procedure for the glucose oxidation experiments

The catalytic oxidation experiments were performed in a dedicated screening device, a parallel autoclave reactor system consisting of ten parallel 20 mL Hastelloy C-276 autoclaves. All ten autoclaves were connected individually to an oxygen/nitrogen supply line. For safety reasons, a rupture disk was installed with a maximum burst pressure of 100 bar. All pipes, fittings, and valves were made of stainless steel 1.4571. A PTFE sealing was located between headcover and vessel of the reactor for protection against pressure leaks. The reactors were placed into a heating hole on the top of a magnetic stirrer system. The system works with magnetic bars placed in each of the ten 20 mL autoclaves and can be heated up to 200°C. The kinetic experiments were carried out in a 600 mL Hastelloy C276 autoclave equipped with a gas entrainment impeller.

It should be generally noted that all oxidation experiments involving oxidisable solvents, such as methanol, ethanol, n-propanol or n-butanol come with some intrinsic risk of thermal runaway if the oxidation reaction is not carefully controlled. In the here described case all autoclaves used were constructed to withstand a complete oxidation of all organic material in the reactor or a complete consumption of the oxygen provided to the reaction.

For a typical glucose oxidation experiment, 0.1 mmol of HPA-5 catalyst and 1 mmol of glucose were filled into the 20 ml autoclave, subsequently solvent (10 mL) was added. A

For the kinetic experiments in the 600 ml Hastelloy C autoclave, water, glucose and catalyst were charged into the vessel. The system was purged three times with oxygen to remove the remaining air, the stirrer speed was set to 300 rpm and heating was switched on. As soon as the desired temperature of 90°C was reached, the oxygen pressure was adjusted to the desired value. At the beginning of the experiment, a liquid and a gas sample were taken in order to determine the initial substrate and product concentrations. Then the stirrer speed was set to 1000 rpm to start the reaction. Liquid and gas samples were taken at regular intervals to follow the reaction. To interrupt the oxidation reaction during sampling, the gas entrainment was stopped by reducing the stirrer speed to 300 rpm. Each kinetic experiment was carried out for 24 h reaction time.

For the catalyst stability, three consecutive runs with only adding fresh substrate (1 mmol of glucose) after each run were performed in a similar manner as described before.

Product analysis

Published on 11 June 2020. Downloaded on 6/14/2020 2:55:13 AM

After cooling down, all gaseous products (CO, CO₂) were analysed with a gas chromatograph Varian GC 450-TCD-FID equipped with a Shin Carbon ST column (2 m x 0.75 mm ID). The yields of CO₂ and CO were determined by calculating $n(CO_2)/n(C$ atoms feedstock) and n(CO)/n(C atoms feedstock), respectively. The liquid phase was analysed by ¹³C-NMR spectroscopy (Jeol ECX-400 MHz Spectrometer, 9,4 Tesla) at 20°C as well as high-performance liquid chromatography (HPLC, Jasco instrument with a Shodex SUGAR SH1011 300 mm x 8 mm column). The calculation of glucose conversion and product selectivity was carried out on a carbon basis and is shown in detail in the Supporting Information, Equations S1 and S2. The ¹³C-labelling experiments were performed using a GC-MS Agilent 7890B GC/ 5977A MSD-system with HP-5ms Ultra Inert column (30 m x 250 µm x 0.25 µm) and a single quadrupole MS. For double checking of the ¹³C-labelling measurements, the samples were analysed in addition by headspace GC-MS (Shimadzu QC 2010/ QP2010 SE GCMS-system equipped with CTC combi PAL headspace and separated with CP-Sil PONA CB column, 50 m x 210 µm x 0.5 µm) with liquid injection method. Moreover, water content of the alcoholic

solutions was quantified by Karl-Fischer Titration (KFT) using a Coulometer 756 from Metrohymice Online By electrochemical means, iodine is generated directly in the iodide-containing electrolyte. The generator electrode without diaphragm was used for producing iodine at the anode. Karl Fischer reagent was supplied by Merck KGaA, with a type of "CombiCoulomat fritless" for coulometric water. With the limitation of the method and the Karl Fischer reagent used, it is suitable for a range of water content between 0.1 and 20 wt.%

Conclusions

View Article Online DOI: 10.1039/D0GC01169J

We have discovered a very remarkable solvent effect in the polyoxymetalate-catalysed oxidation of glucose. Replacing the well-investigated aqueous reaction system by a methanolic solution, we demonstrate HPA-5-catalysed glucose oxidation under mild conditions (90 °C) in almost perfect yield to methyl formate (> 99% yield). Undesired side products that have been typically found in the traditional aqueous oxidation system, such as CO or CO₂, can be completely avoided in this way. As the mass balance in the here-presented glucose oxidation in methanol is perfectly closed, we claim a new option for glucose valorisation in hitherto unmatched efficiency. Experiments with labelled ¹³C glucose have unambiguously proved that glucose is converted completely to formic acid which subsequently forms methyl formate by esterification in the excess of methanolic reaction medium. Stability tests of the solvent methanol (under the identical oxidation conditions but without added glucose) showed that methanol is converted to small amounts of dimethylether and dimethoxymethane but not to methyl formate.

Based on the detailed analysis of all reaction intermediates formed during glucose oxidation, we are able to propose a conclusive reaction pathway from glucose to methyl formate via formic acid. As water forms in the reaction system during esterification from the latter to methyl formate, we have also studied methanol/water mixtures as reaction medium for HPA-5-catalysed glucose oxidation. Remarkably, a 90:10 water/methanol reaction system still shows a very pronounced enhancement of combined formic acid+methyl formate selectivity and a very effective suppression of gaseous side products. Higher water contents shift the esterification equilibrium towards the free acid, as expected. A highly important finding is that glucose oxidation in methanol benefits from a faster re-oxidation of the HPA-5 catalyst. This enables effective re-oxidation at lower oxygen partial pressures and allows to work with air as oxidant at pressures as low as 5 bar. In conclusion, our findings constitute a new, technically highly attractive approach to convert glucose in perfect selectivity to methyl formate. As the latter is a valuable intermediate this opens new attractive routes for biomass valorisation, in particular if the here presented oxidation catalysis can be extended in the future to more technical carbohydrate feedstocks, such as industrial sugar solutions, hemicellulose fractions of the pulping process or cellulose hydrolysates.

Acknowledgements

The authors acknowledge financial support from the Cluster of Excellence "Engineering of Advanced Materials (EAM)". CK acknowledges in addition support of the Office of the Civil Service Commission (OCSC) scholarship of the Republic of Thailand. Moreover, we thank Birgit Brunner from Bayreuth University for performing GC-MS measurements and Peter Schulz from CRT, University Erlangen-Nuremberg for Headspace-GC measurements.

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