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Expanding the scope of biogenic substrates for the selective production of formic acid from water-insoluble and wet waste biomass†

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The selective oxidation of complex, water-insoluble and wet biomass from second and third generation to formic acid including effective catalyst recycling is reported. Additionally, the relevance and limits of potential contaminants are illustrated by different experimental approaches. By using a very robust homogeneous polyoxometalate catalyst in aqueous solution, molecular oxygen as an oxidant and an acid as a solubilizer, it is possible to convert different lignocellulosic and algae feedstock into formic acid and pure carbon dioxide. The applied green oxidation system benefits from its low reaction temperature (below 100 °C) and its very selective nature. Furthermore, catalyst recycling over three batches has been successfully carried out.

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Introduction

The upcoming requirements for sustainable production of chemicals will lead to an increasing substitution of fossil fuels by biorenewable feedstock. This is mainly due to the fact that almost all uses of hydrocarbon fossil fuels in production processes are directly or indirectly linked to carbon dioxide (CO₂) emissions that contribute to global warming.¹ However, biomass conversion is usually characterized by complex feedstock compositions leading to sophisticated processes with many parallel and consecutive reactions involved. This often results in low yields of the designated products.^{2,3} Consequently, only few processes for directly converting biomass into value-added chemicals have been established in academic research. These include the production of levulinic acid,⁴ 5-HMF,⁵ ethylene glycol,⁶ lactic acid,⁷ gluconic acid⁸ and several pentanoic esters.⁹ The high oxygen content of biomass requires typically a number of reductive conversion steps in biomass valorization sequences leading almost unavoidably to drawbacks like formation of tar or gluey byproducts. Moreover, the ultimate goal of producing valuable chemicals in high yields by direct conversion of complex biomass, such as *e.g.* lignocellulosic substrates or algae is still far ahead. Major difficulties arise from the fact that such substrates are not well

soluble in conventional solvents and are very resistant to chemical and biological transformations.^{10,11}

Other important considerations for the chemical use of biogenic feedstock arise from conflicts with the use of biomass as food and animal nutrition.¹² To characterize the potential for such conflicts, the broad range of biogenic feedstock conversion processes has been classified into three generations:¹³ the first generation of biomass conversion processes deals with feedstock that is in direct conflict with the supply of food. Examples are sugars, starch and vegetable oils. Conversion processes that utilize lignocellulosic biomass like wood or herbage do not use feedstock that is in direct conflict with food supply and belong to the second generation. However, these biomass grow on farmland and are therefore in indirect conflict with food supply.¹⁴ The use of microorganisms, such as algae, to produce fuels or chemicals is denoted as the third generation biomass conversion processes. These processes are preferred as future biomass conversion processes as no direct or indirect conflict with food and nutrition applications arises from large scale, industrial realization.¹⁵

Formic acid (FA) is a basic chemical that is widely used in chemical, textile, leather, pharmaceutical, rubber and other industries.^{16,17} Recently, FA is discussed in addition as a fuel for direct FA fuel cells,^{18,19} and as a hydrogen storage material.^{20,21} FA can be easily and selectively decomposed to hydrogen and CO₂ through metal catalysed processes under very mild conditions.^{22–24} In addition, thermal decomposition of FA (above 373 K) forms CO and water. Thus, FA can be regarded as a liquid syngas equivalent and conversion of biomass to FA can be regarded as up-grading an abundant natural resource into a green energy and synthesis equivalent.

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Oxidative conversion of wet biomass to formic acid using homogeneous POM catalysts has been developed by our group in the recent five years (OxFA-process).^{25–27} The concept essentially overcomes all major problems of classical biomass gasification or reforming processes.^{28,29} The interesting difference of the OxFA route compared to reductive biomass valorization approaches is that all the thermally induced formation of solid or gluey by-products is completely avoided. Moreover, all heteroatoms in the biomass are converted into their highest oxidized, water-soluble forms (e.g. sulfates, nitrates) in contrast to the formation of H₂S and ammonia encountered under reductive conditions.

The OxFA-process is mildly exothermic and operates under mild temperature conditions of typically below 373 K. As water is applied as a solvent, biomass of different origins, compositions and humidities can be applied without drying. Formic acid is produced as the only product in the liquid phase avoiding tedious liquid phase separation processes. The only side-product is pure carbon dioxide that forms in the gas phase and can be re-used for the production of new biomass substrates (e.g. for the production of algae in an algae farm). As the OxFA process converts a very broad range of biogenic raw materials into only two products that separate nicely into gas and liquid phases its simplicity and robustness are clear advantages compared to other biomass valorization technologies. The OxFA process applies homogeneous polyoxometalate (POM) complexes as redox catalysts. POMs are characterized by strong Brønsted acidity, high proton mobility, fast multi-electron transfer, high solubility in various solvents and excellent resistance against hydrolytic or oxidative degradations in solution.^{30,31} The named properties make this class of catalysts very attractive for the oxidative conversion of biomass in aqueous media. In particular, their tunable redox potential and acidity offer enormous potential for their future use in oxidation chemistry.³² To increase the efficiency of the OxFA process for the conversion of water-insoluble, complex biomass, we recently introduced the use of sulfonic acids as additives. The latter have been found to act as efficient depolymerization catalysts, solubilizers and promoters.²⁶ These findings have paved the way for the oxidative processing of e.g. lignocellulosic biomass, a class of substrates that is notoriously difficult to convert in aqueous phase reforming.²

In this contribution, we significantly expand on the scope of biogenic substrates that can be processed with the OxFA-process. Moreover, we demonstrate for the first time in detail all the additional necessary steps to close the catalyst cycle for a future continuous OxFA process. In this context effective ways to recycle the homogeneous polyoxometalate catalyst from the OxFA process are reported.

Results and discussion

Oxidation experiments for expanding the substrate scope

To expand the scope of biogenic substrates for the POM catalyzed, selective oxidative conversion to FA, we first studied a

range of second generation feedstock like cane trash, pomace, fruit pulp, bark from hard and softwood, leaves, straw, grass clippings and aerated materials. As representatives for third generation biomass, we tested green algae like *Chlorella* and *Ulva lactuca*, brown algae like *Ascophyllum nodosum*, blue-green algae like *Spirulina* or *Cyanobacter* and *Chondrus crispus* as red algae.

To enlarge the list of feedstock even for the treatment of problematic and contaminated biological waste materials, we also used effluent sludge and deinking sludge from a paper manufacturing plant under typical OxFA process conditions. Additionally, we used railway sleepers and beech condensates as substrates for the process. The effluent sludge contained about 80 wt% organic materials with a high nitrogen content of about 10 wt%. This substrate also contained large amounts (ca. 10 wt% in total) of inorganic materials and salts like calcium oxide and different phosphates. The used deinking sludge was of even more inhomogeneous composition. Besides 35 wt% of organic material, it contained many different heavy metal salts like copper, lead, cadmium and nickel compounds. Furthermore, this substrate contained highly volatile halogenated hydrocarbons, like chloroethane and vinyl chloride as well as polycyclic and polychloric hydrocarbons. The railway sleepers used were characterized by a high content of aromatic compounds. The beech condensate used was also rich in aromatic compounds. The analysis of all substrates used in this study (highlighting their chemical nature and composition in much more detail) is given in the ESI.†

Based on our previous findings,²⁶ for the screening experiments of the named new substrates we used molecular oxygen as the oxidant, the polyoxometalate H₅[PV₂Mo₁₀O₄₀] (HPA-2) in aqueous solution as a catalyst and *para*-toluenesulfonic acid (p-TSA) as an additive and solubilizer. The conversion of all substrates was performed in a 600 mL Hastelloy autoclave with a gas entrainment impeller and additional cooling to deal with the exothermicity of the reaction. The effects of different liquid volumes in the reactor (100 mL of the reaction mixture in a reactor volume of 600 mL) can be excluded as the reaction takes place only in the liquid phase where the oxygen is entrained by the impeller. In particular, there is no further reaction in the gas phase. All biogenic feedstock were processed for 24 hours at 90 °C under 30 bar oxygen pressure. The initial composition of the reaction mixture in each oxidation experiment was 100 g of water as a solvent, 1.74 g (0.9 mmol) of HPA-2 polyoxometalate as a catalyst, 1.90 g (11 mmol) of TSA as an additive/solubilizer and 3.30 g of the substrate under investigation. To enable the calculation of yields based on comparable carbon atoms available in the substrate, we performed an elemental analysis of each substrate prior to our catalytic experiments (for results see Table 1).

For the determination of FA-yield and FA-selectivity it is important to note that only two detectable C₁-products, FA and CO₂, were found in the system after complete substrate conversion. Successful closing of the mass balance of the transformation could be proven by NMR- and GC-results. The yield of FA

Table 1 Oxidative conversion of complex, water-insoluble biomass of 2nd and 3rd generation in the presence of the additive TSA using a HPA-2 POM-catalyst

Entry	Substrate	Molecular composition ^a	Combined yield ^b FA + CO ₂ [%]	FA-yield ^b [%]	FA : CO ₂ -selectivity ^b [%]
1	Pomace	C _{0.24} H _{1.59} O ₁	97.3	54.6	56 : 44
2	Cane trash	C _{0.92} H _{2.04} O ₁	97.5	48.9	50 : 50
3	Fruit pulp	C _{1.00} H _{1.92} O ₁	99.0	45.3	46 : 54
4	Spruce chips	C _{1.30} H _{1.98} O ₁	89.5	34.6	39 : 61
5	Poplar splint	C _{1.32} H _{1.98} O ₁	66.0	30.8	47 : 53
6	Grass clippings	C _{1.17} H _{2.05} O ₁	74.6	29.9	40 : 60
7	<i>Chondrus crispus</i>	C _{0.71} H _{1.30} O ₁	48.3	21.7	45 : 55
8	<i>Chlorella</i>	C _{1.69} H _{2.92} O ₁	53.7	21.6	40 : 60
9	Oak bark	C _{1.21} H _{1.87} O ₁	56.0	21.1	38 : 62
10	Willow bark	C _{1.34} H _{2.15} O ₁	59.5	16.1	27 : 73
11	<i>Cyanobacter</i>	C _{0.72} H _{1.32} O ₁	27.4	15.8	58 : 42
12	<i>Spirulina</i>	C _{1.70} H _{2.99} O ₁	40.6	15.7	39 : 61
13	Birch bark	C _{1.39} H _{2.29} O ₁	41.0	15.5	38 : 62
14	<i>Ascophyllum nodosum</i>	C _{0.82} H _{1.42} O ₁	29.2	14.8	51 : 49
15	Straw	C _{1.04} H _{1.62} O ₁	53.1	11.9	22 : 78
16	Nettle leaves	C _{1.10} H _{1.98} O ₁	54.2	11.0	20 : 80
17	<i>Ulva lactuca</i>	C _{0.75} H _{1.53} O ₁	16.4	7.6	46 : 54
18	TSA	C ₇ H ₈ O ₃ S	—	—	—
19	FA	CH ₂ O ₂	—	—	—
20	Neat pomace ^c	C _{0.24} H _{1.59} O ₁	52.0	12.5	24 : 76
21	Neat <i>Cyanobacter</i> ^c	C _{0.72} H _{1.32} O ₁	14.8	4.3	29 : 71

Reaction conditions: 3.3 g substrate, 1.9 g (11 mmol) additive and 1.74 g (0.9 mmol) catalyst dissolved in 100.0 mL H₂O, 30 bar O₂, 90 °C, 24 h, 1000 rpm. ^a Determined via C, H, N, S elemental analyses. ^b Yield and selectivity determined by means of ¹H-NMR using benzene as an external standard according to $n(\text{FA})/n(\text{C-atom feedstock})$. ^c Reference experiments without the TSA additive.

was determined by means of ¹H-NMR using benzene as an external standard. FA yields were calculated as $Y_{\text{FA}} = n(\text{FA})/n(\text{C-atom feedstock})$. The yield of CO₂ was determined by means of GC-analysis as $Y_{\text{CO}_2} = n(\text{CO}_2)/n(\text{C-atom feedstock})$. The combined yield of formic acid and CO₂ was calculated by $n(\text{FA}) + n(\text{CO}_2)/n(\text{C-atom feedstock})$, respectively. This value was applied to describe the degree of substrate oxidation of FA and CO₂ after a given reaction time. The results of the biomass oxidation experiments using the above described substrates are shown in Table 1.

The results in Table 1 clearly show that the applied homogeneous oxidation system is able to convert all 2nd and 3rd generation biomass used predominantly to formic acid and carbon dioxide. Under the applied conditions no CO formation from FA decomposition and no catalytic FA decomposition to CO₂ and hydrogen were detected (see Table 1, entry 19). The yield in FA was found to depend strongly on the structure of the substrate and the number of oxygen-functionalities in the carbon framework. Among the tested new substrates, the best raw material for producing formic acid was found to be pomace with 55% FA yield (entry 1) followed by cane trash with 49% FA yield (entry 2) and fruit pulp with 45% FA yield (entry 3). Note that all these three originate from commercial and industrial biomass conversion processes making the here presented technology an interesting add-on to widely practiced processes of the food industry.

Interestingly, also substrates from the third generation biomass like red algae (*Chondrus crispus*) or green algae (*Chlorella*) gave surprisingly high FA yields. Note, that for these substrates the selected reaction time of 24 hours was definitely too

short, so not all the substrate was converted to FA and CO₂. From our experience, it can be expected that prolonged reaction times would lead to a final FA yield for these substances close to the FA selectivity obtained after 24 h reaction time.

These experiments could also confirm the very positive effect of the toluenesulfonic acid (TSA) as additive and solubilizer on the POM-catalyzed biomass oxidation. Experimental evidence is provided by the reactions with and without the TSA additive (compare Table 1, entries 1 and 11 against entries 20 and 21). For pomace, the experiment without TSA (entry 20) showed only very little FA formation ($Y_{\text{FA}} = 12.5\%$) compared to a FA-yield of 54.6% (entry 1) with TSA for otherwise identical conditions. For *Cyanobacter*, the experiment without TSA (entry 21) yielded only 4.3% FA after 24 h reaction time, in contrast to the experiment with the TSA additive in entry 11 (15.8% FA-yield). Based on these results, it is obvious that the TSA additive does not only act as a solubilizer but also as a reaction accelerator and selectivity enhancer. The latter can be explained by the solubilizing effect of the TSA additive giving the homogeneous POM catalyst more access to the functional groups within the substrate carbon framework. As these groups are normally carbonyl- or hydroxy-groups this leads to an increase in the FA-yield based on our previous findings with different functionalized C₂-model compounds.²⁵ These results are in good agreement with previous findings concerning the suitability of the TSA additive for the transformation of weekly water soluble biomass substrates using homogeneous POM catalysts in water.²⁶ A baseline experiment using pure TSA as the substrate showed again no oxidation neither to FA nor to CO₂ (see Table 1, entry 18).

Table 2 Oxidative conversion of chemically contaminated biomass substrates with the HPA-2 catalyst

Entry	Substrate	Molecular composition ^a	Combined yield ^b FA + CO ₂ [%]	FA-yield ^b [%]	FA : CO ₂ -selectivity ^b [%]
1	Effluent sludge	C _{6.31} H _{11.35} O _{6.63} N ₁	46.1	15.7	34 : 66
2	Railway sleeper	C _{1.25} H _{1.90} O ₁	39.5	11.2	29 : 71
3	Beech condensate	C _{1.21} H _{1.86} O ₁	2.5	1.0	41 : 59
4	Deinking sludge	C _{0.38} H _{0.47} O ₁	—	—	—

Reaction conditions: 100 mmol substrate (1.85 g for entry 1; 5 g for entry 2; 10 g for entry 3 and 5.35 g for entry 4) depending on the molecular weight; 1.74 g (0.9 mmol) catalyst dissolved in 100.0 mL H₂O; 30 bar O₂, 90 °C, 24 h, 1000 rpm. ^a Determined *via* C, H, N, S elemental analyses. ^b Yield and selectivity determined by means of ¹H-NMR using benzene as an external standard according to $n(\text{FA})/n(\text{C-atom feedstock})$.

In an additional set of experiments, we tested the conversion of the chemically contaminated substrates in the POM catalyzed oxidation. For this purpose, we processed effluent sludge, railway sleepers, beech condensate and deinking sludge under typical OxFA conditions. In these experiments, the initial composition of the reaction mixtures contained 100 g of water as a solvent, 1.74 g (0.9 mmol) of HPA-2 as a catalyst and between 1.85 g and 10 g (100 mmol) of the substrate dependent on its water content. The additive TSA was not used in these experiments as the unknown composition of the applied “real life” substrates was expected to open additional but unknown reaction pathways for TSA (*e.g.* salt formation with metal ions). This would lead to consecutive reactions and uncontrollable loss of the additive which would have made interpretation of the obtained results rather difficult. For all experiments of this series the reaction temperature was maintained at 90 °C in order to prevent thermal FA decomposition. The oxidation reactions were carried out at 30 bar oxygen atmosphere with stirring of 1000 rpm for 24 h reaction time. The obtained results are summarized in Table 2.

It is obvious that the HPA-2 catalyst also works with contaminated feedstock and is highly robust against many impurities. Thus effluent sludge with the highest amount of organic and oxidisable matter yields nearly 16% FA at a combined FA + CO₂ yield of 46% after 24 h reaction time. The high nitrogen content within the sludge from a wastewater treatment plant has a negative effect on the conversion rate but does not prevent the oxidation reaction. Also for railway sleepers containing high amounts of aromatic compounds, the oxidation to FA and CO₂ is observed. A FA + CO₂ combined yield of 40% is observed after 24 h resulting in FA selectivity of 29%. In contrast to the latter two substrates, highly diluted beech condensate and deinking sludge show almost no oxidative conversion after 24 h reaction time.

Defined poisoning experiments for the POM catalyst

In order to elucidate the complete lack of reactivity with the deinking sludge substrate we performed a couple of poisoning experiments to learn more about the sensitivities of the applied POM oxidation system. Our first hypothesis was that the heavy metal content in the applied deinking sludge (Palm GmbH & Co. KG, a paper manufacturing company) could be responsible for the observed catalyst deactivation. Such heavy-

Table 3 HPA-2 catalysed glucose oxidation – defined poisoning experiments with typical impurities from paper manufacturing to elucidate the lack of catalytic activity for deinking sludge as a substrate

No.	Impurity	Potential source of origin	Combined yield ^a FA + CO ₂ [%]	FA-yield ^a [%]	FA : CO ₂ -selectivity ^a [%]
1	CuSO ₄	Printer's ink	39.8	—	0 : 100
2	CdCl ₂	Printer's ink	87.6	44.4	51 : 49
3	NiCl ₂	Printer's ink	n.d.	n.d.	n.d.
4	PbCl ₂	Printer's ink	6.2	4.4	71 : 29
5	Gypsum	Filler	89.9	47.5	53 : 47
6	Kaoline	Filler	93.7	49.2	53 : 47
7	TiO ₂	Filler	72.3	44.4	61 : 39
8	ZrO ₂	Paper varnish	83.0	38.8	47 : 53
9	—	—	100	46.2	46 : 54

Reaction conditions: 5 g (25 mmol) glucose as a substrate; 1.74 g (0.9 mmol) HPA-2 as a catalyst dissolved in 100.0 mL H₂O; 8 mmol (0.63–2.18 g) of the impurity depending on the molecular weight; 30 bar O₂, 90 °C, 6.5 h, 1000 rpm. ^a Yield and selectivity determined by means of ¹H-NMR using benzene as an external standard according to $n(\text{FA})/n(\text{C-atom feedstock})$.

metal cations are expected to form water-insoluble and inactive complexes with the anion of the polyoxometalate catalyst. To confirm this hypothesis, we added on-purpose water-soluble salts of higher transition metals like copper, lead, cadmium and nickel as contaminants to a glucose oxidation experiment. Moreover, similar contamination experiments were performed with other typical components of deinking sludge, such as *e.g.* gypsum, kaoline, TiO₂ or ZrO₂. For these experiments, 5 g (25 mmol) of glucose as a water-soluble substrate and 1.74 g (0.9 mmol) of the catalyst dissolved in 100 mL water, together with 8 mmol (0.63–2.18 g) of the impurity were processed at 90 °C, 30 bar oxygen with 1000 rpm for 6.5 h in a 600 mL high-pressure autoclave. All results are displayed in Table 3; the baseline result for a non-contaminated glucose oxidation experiment is shown as entry 9.

The results in Table 3 clearly indicate a strong influence of Pb- and Cu-salts on the catalytic activity for glucose oxidation. Other heavy metal ions, like Cd²⁺, appear to be of little effect. Interestingly, the presence of copper ions does completely inhibit the formation of FA from glucose oxidation, and only CO₂ is detected as a product. This goes along with the observation that copper ions form water-insoluble complexes with the catalyst heteropolyanion in the form of small blue particles

at the bottom of the reaction vessel. Unfortunately, the oxidation result with the added NiCl_2 could not be quantified by the usual NMR method due to the strong deformation of the spectra due to the paramagnetic nature of Ni(II) in the sample. Nevertheless, also for this case, the formation of FA could be qualitatively confirmed by the help of ^{13}C -NMR (see the ESI†). In contrast to the experiments with Cu, no formation of water-insoluble crystals was observed in the case of NiCl_2 addition. Finally, the addition of Pb(II) species to the aqueous glucose solution resulted in an immediate color change from orange to a blue-green solution. The ^{51}V -NMR spectra of the obtained solution strongly indicate complexation of the heteropolyanion with the Pb^{2+} cations. In addition, the formation of yellow crystals at the bottom of the reaction vessel was observed thus removing the active catalyst from solution. In general, ^{51}V -NMR spectra of the reaction solutions containing late transition-metal cations show significant changes after addition of Cu-, Ni- and Pb-salts (see the ESI†).

In contrast, the ^{51}V -NMR spectra with added fillers do not show significant changes of the polyoxometalate catalyst (see the reference spectrum in the ESI†). Addition of these water-insoluble fillers, like gypsum, kaoline, titanium dioxide and zirconia, resulted in an increase of the viscosity of the reaction mixture; however, this had very little effect on the observed glucose oxidation reaction.

Recycling experiments for catalyst and additive

Finally, we performed in this study a more detailed investigation into catalyst and additive recycling in order to evaluate the economic feasibility of the POM-catalyzed biomass oxidation to formic acid (OxFA-process). For our recyclability test of the applied HPA-2 catalyst, we first used glucose and cellobiose oxidation as these water-soluble substrates react very smoothly without addition of the TSA additive. For the catalyst recycling test with glucose as a substrate, we used 3.61 g (20 mmol) of glucose and 1.74 g (0.9 mmol) of the HPA-2 catalyst and dissolved both in 100 mL of water. This aqueous solution was processed at 90 °C under 30 bar of pure oxygen and 1000 rpm for 6 h reaction time. Afterwards, the reaction mixture was analysed by GC and ^1H -NMR. Subsequently, 3.61 g (20 mmol) of fresh glucose as a substrate were added and again processed under identical reaction conditions for 6 h. This addition of fresh glucose was repeated three times while the formed formic acid was allowed to accumulate in the reaction mixture. As shown in Table 4, entries 1–3, the repetitive use of the HPA-2 catalyst in several subsequent glucose oxidation runs showed no significant decrease in both conversion and selectivity over three runs. The combined FA + CO_2 yields are in the range of 95% for all three batch experiments while the FA-selectivity slightly decreased from 52% to 50% over three batches.

Using cellobiose as another water-soluble substrate (6.85 g (20 mmol) cellobiose, 1.74 g (0.9 mmol) HPA-2 catalyst in 100 mL water, 24 h, 90 °C, 30 bar O_2 , 1000 rpm) in the same type of repetitive batch experiment resulted in a very similar behaviour of the HPA-2 catalyst. The combined yields are

Table 4 Recycling of the HPA-2 catalyst over three batches with water-soluble substrates

Entry	Substrate	Reaction time [h]	Combined yield ^a FA + CO_2 [%]	FA-yield ^a [%]	FA : CO_2 -selectivity ^a [%]
1	Glucose	6	95.9	49.8	52 : 48
2		6	94.4	47.3	50 : 50
3		6	94.9	47.4	50 : 50
4	Cellobiose	24	72.9	42.8	59 : 41
5		24	69.4	40.5	58 : 42
6		24	67.9	38.5	57 : 43

Reaction conditions: 3.61 g resp. 6.85 g (20 mmol) glucose resp. cellobiose as a substrate; 1.74 g (0.9 mmol) HPA-2 as a catalyst dissolved in 100.0 mL H_2O ; 30 bar O_2 , 90 °C, 6 resp. 24 h, 1000 rpm. ^aYield and selectivity determined by means of ^1H -NMR using benzene as an external standard according to $n(\text{FA})/n(\text{C-atom feedstock})$.

somewhat lower with 73% after the first and 68% after the third approach. The FA-selectivities decrease but only very little from 59% to 57% after the third run. As for glucose oxidation, no drastic decrease in conversion and FA-selectivity is observed over three batches (Table 4, entries 4–6).

In a further set of experiments we wanted to investigate the recyclability of the HPA-2 catalyst in combination with the TSA additive for the oxidation of water-insoluble substrates. A first series of experiments in the same repetitive batch mode was carried out with beech wood as a substrate. The experiments used 3.25 g of beech wood, 1.74 g (0.9 mmol) HPA-2 as a catalyst and 1.9 g (11 mmol) of TSA as an additive and in 100 g of water. This suspension was heated up to 90 °C and stirred with 1000 rpm under 30 bar oxygen pressure for 24 h reaction time. Afterwards, the reaction mixture was analysed by GC and ^1H -NMR. Subsequently, 3.25 g of fresh beech wood were added again and processed under identical reaction conditions for 24 h. This procedure was repeated three times while the formed formic acid accumulated in the reaction mixture.

While the results in Table 5 (entries 1–3) indicate a slight decrease in beech wood conversion over three batches from 85% after the first run down to 75% combined FA + CO_2 yield after the third run, FA-selectivity remained nearly constant at a level of 40%. It may add to the slight deactivation observed that the remaining non-converted beech residues tend to increase the viscosity of the reaction mixture for the next run. Increasing viscosity is of negative influence on the oxygen entrainment into the reaction solution.

A second recycling test with water-insoluble biomass was carried out using pine wood. We used 3.30 g of this substrate, 1.74 g (0.9 mmol) HPA-2 as a catalyst and 1.9 g (11 mmol) of TSA as an additive together with 100 g of water. This suspension was heated to 90 °C and stirred with 1000 rpm under 30 bar oxygen pressure for 24 h reaction time. Again, the reaction mixture was analysed by GC and ^1H -NMR after each run. Subsequently, 3.30 g of fresh pine wood as a substrate were added and processed under identical reaction conditions for another 24 h using the same catalyst solution. This procedure was

Table 5 Recycling of the HPA-2 catalyst and the TSA additive over three batches with complex, water-insoluble substrates

Entry	Substrate	Molecular composition ^a	Combined yield ^b FA + CO ₂ [%]	FA-yield ^b [%]	FA : CO ₂ -selectivity ^b [%]
1	Beech wood	C _{1.21} H _{1.86} O	84.7	33.7	40 : 60
2			80.8	33.6	42 : 58
3			75.4	32.0	42 : 58
4	Pine wood	C _{1.41} H _{2.12} O	59.9	28.6	48 : 52
5			58.6	24.4	42 : 56
6			59.0	24.3	41 : 59

Reaction conditions: 3.25 g beech wood resp. 3.30 g pine wood as a substrate; 1.74 g (0.9 mmol) HPA-2 as a catalyst dissolved in 100.0 mL H₂O; 30 bar O₂, 90 °C, 24 h, 1000 rpm. ^a Determined *via* C, H, N, S elemental analyses. ^b Yield and selectivity determined by means of ¹H-NMR using benzene as an external standard according to $n(\text{FA})/n(\text{C-atom feedstock})$.

repeated three times while the formed formic acid accumulated in the reaction mixture.

With pine wood, the combined FA + CO₂ yield remained remarkably stable over the three repetitive runs (see Table 5, entries 3–6). A modest reduction in FA selectivity from 48% (first run) to 41% (third run) was observed, however. The reason for the slower conversion of pine compared to beech is in the lower amount of hemicellulose and the higher amount of lignin inside pine compared to beech.

To summarize the recycling experiments with complex, water-insoluble substrates and the additive TSA, we clearly confirm the applicability of both the HPA-2 catalyst and the TSA additive in repetitive batches of wood oxidation. This makes oxidative conversion of such complex substrates in POM catalysed reactions increasingly attractive. The expenses for the applied amount of (relatively inexpensive) catalyst are much lower compared to the large amounts of converted substrate and produced FA which makes the OxFA process economically feasible.

Conclusions

Our contribution gives strong support to the scientific and economic attractiveness of homogeneously catalyzed biomass oxidation to formic acid by polyoxometalate catalysts. We could expand the substrate scope for the reaction considerably by converting a very wide range of substrates including many complex water-insoluble biogenic feeds and also contaminated materials. While waste from the food industry, effluent sludge and even railway sleepers was found to be effectively converted under typical OxFA reaction conditions (90 °C, 30 bar O₂, 24 h reaction time), a clear and so far undetected limitation has been found for metal ion containing feedstock. Whenever contaminated biological feed with metal ions forming stable water-insoluble complexes with the catalytically active polyoxometalate ion were present in the applied feedstock, the reactivity of the oxidation system was strongly reduced or almost completely eliminated. The favorable role of the TSA additive for supporting depolymerization and solubilisation of 2nd and

3rd generation was impressively underlined by comparative oxidation experiments with pomace and *Cyanobacter*. Finally, repetitive use of the applied HPA-2 catalyst and the TSA additive could confirm the general recyclability of the applied homogeneous POM-based catalyst system for both, the conversion of water-soluble (glucose, cellobiose) and water-insoluble (beech and pine wood) substrates. Only minor losses in biomass conversion and FA selectivity were detected over three repetitive batches using the same catalyst and additive solution demonstrating the robustness and practical applicability of the catalyst system under investigation. From all the results of this study we anticipate a high potential of POM-catalyzed biomass oxidation for future decentralized biomass conversion processes of wet and contaminated substrates. As formic acid is a chemical product used in high amounts by farmers (*e.g.* in the preparation of silage) and waste streams from farming or food manufacturing represent very attractive feedstock, the technology appears particularly attractive if linked to agricultural activities or small to medium sized food industries.

Experimental details

All chemicals were obtained commercially and used without further purification. The HPA-2 catalyst H₅[PV₂Mo₁₀O₄₀]·10H₂O was synthesized according to the literature.^{27,33} Its characterization *via* ICP-OES resulted in a P/V/Mo ratio of 1/2.01/10.12. For this analysis, 20 mg of the HPA-2 catalyst were dissolved in 250 mL of double distilled water and analysed. The moles of salt hydrate water were determined *via* TGA with a three-step temperature programme up to 350 °C with helium as a gas carrier. The model substrates glucose and cellobiose were supplied by Merck KGaA while the TSA additive was obtained from Alfa Aesar. Formic acid was purchased from AppliChem. The different types of 2nd and 3rd generation complex biomass and wood samples were donated by JBACH GmbH, Scheßlitz, Germany. The chemically contaminated substrates were also kindly provided by our industrial partner JBACH GmbH. Different ingredients of paper manufacturing were purchased commercially from Sigma Aldrich (CdCl₂, NiCl₂), Alfa Aesar (ZrO₂, CuSO₄) and Merck KGaA (gypsum, kaoline, TiO₂, and PbCl₂). Elementary analysis of the complex biogenic substrates was carried out using a Euro Vector EA 3000. Product analyses of gases were performed using gas chromatography (GC) with a Varian GC 450 equipped with a 2 m × 0.75 mm ID Shin carbon ST column. Thermogravimetric analyses (TGAs) were carried out using a SETSYS-1750 CS Evolution from SETARAM Instruments. The ICP-OES measurements were performed on a Perkin Elmer Plasma 400. The NMR spectra were recorded on a JEOL ECX-400 MHz.

Catalytic oxidation reactions with complex, water-insoluble substrates

All oxidation reactions shown in Table 1 were carried out in a 600 mL Hastelloy C276 autoclave equipped with a gas entrain-

ment impeller. Water (100.0 mL), $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$ catalyst (1.74 g, 0.9 mmol), TSA additive (1.9 g, 11 mmol) and the substrate (3.3 g) were charged into the autoclave. The system was purged with oxygen (2 times), then the stirrer was set to 300 rpm and the heating was switched on. When the reaction temperature of 90 °C was reached, the oxygen pressure was adjusted to 30 bar and the stirrer was set to 1000 rpm.

Catalytic oxidation reactions with chemically contaminated biomass

The oxidation reactions reported in Table 2 were carried out in a 600 mL Hastelloy C276 autoclave equipped with a gas entrainment impeller. 100 mmol of the substrate (1.85–10 g depending on molecular weight) and 1.74 g, (0.9 mmol) $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$ catalyst were dissolved in 100 mL water and charged into the apparatus. The system was purged two times with oxygen, then the stirrer was set to 300 rpm and the heating was switched on. When the reaction temperature of 90 °C was reached, the oxygen pressure was adjusted to 30 bar and the stirrer was set to 1000 rpm.

Catalytic oxidation reactions with defined impurities

The oxidation reactions shown in Table 3 were carried out in a 600 mL Hastelloy C276 autoclave equipped with a gas entrainment impeller. Water (100.0 mL), $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$ catalyst (1.74 g, 0.9 mmol) and glucose as a substrate (5 g, 25 mmol) were charged into the apparatus. Additionally, 8 mmol (0.63–2.18 g depending on molecular weight) of the respective impurities were added into the reaction vessel. The system was purged twice with oxygen, then the stirrer was set to 300 rpm and the heating was switched on. When the reaction temperature of 90 °C was reached, the oxygen pressure was adjusted to 30 bar and the stirrer was set to 1000 rpm.

Recycling experiments with the HPA-2 catalyst and water-soluble biomass

The recycling experiments with the water-soluble substrates glucose and cellobiose reported in Table 4 were carried out in a 600 mL Hastelloy C276 autoclave equipped with a gas entrainment impeller. 3.61 (20 mmol) of glucose (or 6.85 g, 20 mmol of cellobiose), water (100 mL) and 1.74 g, (0.9 mmol) $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$ catalyst were charged into the apparatus. The system was purged twice with oxygen, then the stirrer was set to 300 rpm and the heating was switched on. When the reaction temperature of 90 °C was reached, the oxygen pressure was adjusted to 30 bar and the stirrer was set to 1000 rpm. For the catalyst recycling experiments, 3.61 (20 mmol) of fresh glucose (or 6.85 g, 20 mmol of fresh cellobiose) were charged into the apparatus after each run and the setup was reprocessed for another 6 h (or 24 h in the case of cellobiose). This repetitive batch procedure with keeping the identical catalyst solution and all formed FA in the reactor was repeated three times for both substrates.

Recycling experiments with the HPA-2 catalyst and the TSA additive in the oxidation of water-insoluble biomass

The recycling experiments with the water-insoluble substrates beech wood and pine wood reported in Table 5 were carried out in a 600 mL Hastelloy C276 autoclave equipped with a gas entrainment impeller. 3.25 g (beech) resp. 3.30 g (pine) (20 mmol) of the substrate, 1.74 g (0.9 mmol) $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$ catalyst and (1.9 g, 11 mmol) of the TSA additive were dissolved in 100 mL water and charged into the apparatus. The system was purged with oxygen (2 times), then the stirrer was set to 300 rpm and the heating was switched on. When the reaction temperature of 90 °C was reached, the oxygen pressure was adjusted to 30 bar and the stirrer was set to 1000 rpm. For the catalyst recycling experiments, 3.25 g resp. 3.30 g of fresh beech or pine wood were charged in the apparatus and the setup was reprocessed for 24 h. This repetitive batch procedure with keeping the identical catalyst solution and all formed FA in the reactor was repeated three times for both substrates.

Determination of yield and selectivity

In all oxidation reactions reported in Tables 1–5 only two C_1 -products, FA and CO_2 , were quantitatively determined by NMR- and GC-analysis, respectively. The yield of FA was determined by means of ^1H -NMR using benzene and calculated as $n(\text{FA})/n(\text{C-atom feedstock})$. The yield of CO_2 was determined by means of GC-analysis and calculated as $n(\text{CO}_2)/n(\text{C-atom feedstock})$. The combined yield $\text{FA} + \text{CO}_2$ was calculated by $n(\text{FA}) + n(\text{CO}_2)/n(\text{C-atom feedstock})$ and serves as a measure for substrate conversion (other products than FA and CO_2 were not detected quantitatively). Additional information is found in the footnotes of Tables 1–5.

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