Switchable Catalytic Polyoxometalate-Based Systems for Biomass Conversion to Carboxylic Acids

Dorothea Voß, Regina Dietrich, Maria Stuckart, and Jakob Albert*

ABSTRACT: We present the Keggin-type polyoxometalate H$_6$[PV$_3$Mo$_9$O$_{40}$] as a switchable catalyst being able to catalyze the transformation of both glucose and glyceraldehyde to formic acid (42%) and lactic acid (40%), respectively, within 1 h reaction time by simply changing the reaction atmosphere at 160 °C from oxygen to nitrogen in one reactor setup. In detail, we report the influence of different gas atmospheres and reaction temperatures on various vanadium-containing catalysts in the selective transformation of several biogenic substrates to carboxylic acids with a special emphasis on reaction pathways and switchability of the catalyst systems. All investigations were carried out in parallel using either an oxygen or a nitrogen atmosphere of 20 bar performing time-resolved experiments between 0.25 and 5 h and a temperature variation from 160 to 200 °C. Furthermore, a catalyst and a substrate variation led to the reaction system consisting of glyceraldehyde and the Keggin-type polyoxometalates (POM) H$_6$[PV$_3$Mo$_9$O$_{40}$] as the best switchable reaction system under the applied conditions. This study shows interesting potential for using both Keggin-type and Lindqvist-type POMs as switchable catalysts for selective biomass conversion to platform chemicals.

INTRODUCTION

The application of polyoxometalates (POMs) in science is already well established. A large number of research studies on their synthesis and application are published in numerous reviews.$^{1-9}$ POMs are complex compounds consisting of metal oxide units of the general formula M$_{x}$O$_{y}$, with $x = 4-7$, where M represents early transition metals such as molybdenum (Mo) and tungsten (W), which are present in their highest oxidation state.$^{7,9-11}$ POMs can also contain a multitude of heteroatoms to improve their chemical and thermal stabilities.$^7$ Due to the large number of already known POMs with different physical and chemical properties, as well as a wide variety of sizes, shapes, and structures, POMs are classified by different categories.$^7$ The first group describes the iso(poly)oxometalates (IPAs), which consist of metal oxide units of similar species.$^7$ The most common representative of this group are anions of the Lindqvist type. The composition and stoichiometry of Lindqvist-type POMs can be tuned on the molecular level to form structures with the formula [M$_n$M'$_{n-1}$O$_{2n}$]$^{3-}$ (M = V, M' = W, Mo), making it an ideal prototype cluster family with respect to synthetic accessibility and structural simplicity.$^7,11$ The second group describes the heteropolyoxometalates (HPAs), which contain one or more transition metal and a main group oxoanion, often phosphate or silicate.$^7$ Derivatives of the Keggin-type POMs with the molecular structure [XM$_{12}$O$_{40}$]$^{3-}$ are by far best investigated. They contain a template of various coordinating anions, e.g., o xo anions, oxometalates, or halides, together with a framework metal being typically an early, high-valent transition metal. The whole framework structure has a typical size of 1–4 nm and contains typically 2–368 metal centers.$^{12-14}$ The catalytic activity is mostly introduced by substituting some of the framework metals with heterometals from the s-, p-, d-, or f-block. For example, the substitution of molybdenum atoms in the structure [PMo$_9$O$_{40}$]$^{3-}$ with easily reducible heterometals like vanadium, niobium, or tantalum results in shifting their reactivity from acidic to redox-dominance and compounds with the general empirical formula [PV$_n$Mo$_{12-n}$O$_{40}$]$^{(3+n)-}$.

Depending on the degree of substitution $n$, heteropolyanions of this structure are abbreviated as HPA-$n$. Wells–Dawson (WD) POMs have the general formula [X$_2$M$_3$O$_{19}$]$^{9-}$ and consist of two trilacunary Keggin structures (XM$_6^{9-}$) linked in a corner-sharing manner. Removal of a metal oxide (e.g., tungstate oxide) unit leaves a free position for incorporation of a catalytically active metal, e.g., vanadium.$^{15,20}$ Their remarkable redox properties have found application in oxidation or hydrogenation of various organic compounds.$^{21-23}$
POMs have a wide range of applications due to their diverse structures and high reactivity. The applications include more than just analytical chemistry and catalysis. POMs are used in biochemistry and medicine, as well as in geochemistry and material sciences.$^{5,24,25}$ Despite the fact that the POM research field is quite small compared to other research areas, the field continues to grow vibrantly in terms of new compounds,
interesting structures, exploitation of physical properties, and catalysis.\textsuperscript{26,27} Especially, the enormous multifunctionality of POMs results in various homogeneous and heterogeneous applications in catalysis.\textsuperscript{28–30}

A very interesting field with respect to a more sustainable chemical industry is their use as highly selective catalysts in the conversion of biogenic raw materials.\textsuperscript{31} Making use of the oxygen-rich character of the feedstock, it seems promising to convert biomass into valuable oxygen-containing bulk and fine chemicals.\textsuperscript{32} Especially, the selective catalytic oxidation of biomass into carboxylic acids is of particular importance as the latter are widely used platform chemicals.\textsuperscript{33} Due to the efforts made in the chemical industry to move away from fossil resources such as coal, gas, and oil toward sustainable organic resources, biomass is gaining increasing importance as the only regenerative carbon source.\textsuperscript{34,35}

One promising approach for the use of Keggin-type POMs as selective oxidation catalysts for the conversion of biomass to carboxylic acids is the OxFA process.\textsuperscript{36–38} The latter is mildly exothermic and operates under mild temperature conditions of typically below 100 °C using molecular oxygen or synthetic air as environmental benign oxidants. As water is used as a solvent, biomass of different origin, composition, and humidity can be applied without drying. By applying the OxFA process, a very broad range of biogenic raw materials can be converted into only two products that separate nicely into gas phase (carbon dioxide) and liquid phase (formic acid); its simplicity and robustness are clear advantages compared to other biomass valorization technologies.

One promising approach for the use of Keggin-type POMs as selective oxidation catalysts for the conversion of biomass to carboxylic acids is the OxFA process.\textsuperscript{36–38} The latter is mildly exothermic and operates under mild temperature conditions of typically below 100 °C using molecular oxygen or synthetic air as environmental benign oxidants. As water is used as a solvent, biomass of different origin, composition, and humidity can be applied without drying. By applying the OxFA process, a very broad range of biogenic raw materials can be converted into only two products that separate nicely into gas phase (carbon dioxide) and liquid phase (formic acid); its simplicity and robustness are clear advantages compared to other biomass valorization technologies.

Furthermore, Lindqvist-type isopolyoxometalates with the molecular structure $K_{11}[V_nW_{6-n}O_{19}]$ (also known as IPA-n) have also been studied as alternative catalysts for the selective oxidation of biomass to formic acid.\textsuperscript{39,40}

Recently, HPA-\textsuperscript{n} catalysts have also been found to catalyze the formation of lactic acid (LA) from glucose under nitrogen atmosphere and temperatures of 160 °C.\textsuperscript{41–43} It could be shown that higher substituted heteropolyacids containing vanadium in its highest oxidation state are predominant for the glucose conversion to formic acid under aerobic conditions, whereas paramagnetic acid-bound vanadyl species seem to be predominantly responsible for LA formation from glucose under anaerobic conditions.\textsuperscript{44} A similar effect was also observed by Tang et al.\textsuperscript{45} using VOSO\textsubscript{4} as a catalyst in aqueous solution. These investigations show that especially homogeneous V-containing catalysts are sensitive to the reaction atmosphere, pH level, and reaction temperature with respect to their catalytic activity.

In this contribution, we further expand our studies on the above-described effects of manipulating the composition of different vanadium-containing POM-based systems in aqueous solution and their catalytic activity by varying gas atmospheres, reaction temperatures, and pH levels. Hereby, we want to demonstrate the switchability of the catalytic activity of vanadium-containing POM catalysts in the conversion of several biogenic model substrates. Moreover, we focus not only on the oxidative conversion but also on heat-induced and acid-catalyzed reaction pathways under aerobic as well as anaerobic conditions. The main goal of these studies was to find the POM-based system with the most prominent switchable catalytic ability to produce several carboxylic acids in one single reactor setup by simply changing extensive state variables like reaction temperature or gas atmosphere from oxygen to nitrogen.

## RESULTS AND DISCUSSION

**Time-Resolved Experiments under Different Gas Atmospheres and Temperatures.** To investigate the conversion pathways of glucose under both oxygen and nitrogen atmospheres using the Lindqvist-type POM $K_{11}[V_nW_{6-n}O_{19}]$ from our previous studies\textsuperscript{42,43} as a catalyst, we performed time-resolved experiments for each gas atmosphere separately. The experiments were carried out in a 10-fold screening plant with a batch-mode reactor setup consisting of ten 20 mL autoclaves. For each gas atmosphere, seven reactors were filled with 2 mmol of glucose, 0.167 mmol of catalyst (0.5 mmol of vanadium content), and 10 g of demineralized water as the solvent. The reactions were performed under 20 bar of oxygen or nitrogen pressure at 160 °C using a stirrer speed of 1000 rpm. After a certain reaction time, one reactor at a time was removed from the heating plate and rapidly cooled down in a water bath to stop the catalytic conversion. This procedure was done after reaction times of 0.25, 0.5, 0.75, 1, 3, and 5 h. Additionally, one sample was taken directly after the heating period and used as zero sample. Detailed results of all detected

![Figure 1. Time-dependent product distribution in the $K_{11}[V_nW_{6-n}O_{19}]$-catalyzed glucose conversion under (A) oxygen and (B) nitrogen atmospheres. Reaction conditions: 2 mmol of glucose, 0.167 mmol of $K_{11}[V_nW_{6-n}O_{19}]$, 10 g of water as solvent, 160 °C reaction temperature, 20 bar pressure, 1000 rpm stirrer speed, 0–5 h reaction time.](https://dx.doi.org/10.1021/acsomega.0c02430)
species are summarized in Supporting Information Tables S1 and S2.

The time-dependent liquid product distributions and the glucose conversions under both atmospheres (oxygen and nitrogen) are shown in Figure 1. In addition, the yield of CO₂ is only shown in the diagram for the conversion under oxygen atmosphere (Figure 1A) as no CO₂ was formed under nitrogen (Figure 1B).

Full glucose conversion (X > 99%) could be achieved within 5 h reaction time under oxygen and 95% under nitrogen pressure.

Performing the experiments under oxygen atmosphere (Figure 1A) primarily led to the formation of formic acid (FA), following a literature-known reaction pathway.44,45 After initial heating, the yield of formic acid already reached 20%. Interestingly, the amount stayed almost constant during the first hour and decreased only slightly in the following with progressing reaction time due to thermal decomposition to CO (maximum yield of 1%) and water. Additionally, acetic acid (AA) was detected as the second main liquid product based on a reaction pathway described by Niu et al.46 The yield of acetic acid increased with prolonging the reaction time up to 12% after 5 h. Moreover, a significant amount of CO₂ (maximum yield of 35% after 5 h) was detected, resulting as a byproduct from competing noncatalyzed total glucose oxidation.

The different published reaction pathways for the conversion of glucose under oxidative atmosphere are compared in Scheme 1.44−48

Generally, glucose or its isomer fructose can react in two ways under oxidative reaction conditions in aqueous solution.
On the one hand, glucose can undergo an oxidative carbon–carbon bond cleavage catalyzed by redox-active V$^{5+}$ in the POM structure to the shown intermediates glyceraldehyde, and its isomer dihydroxyacetone, glycolaldehyde, and glyoxal on the way to formic acid (right reaction pathway in Scheme 1), whereby up to 9% glyceraldehyde after initial heating and small amounts of dihydroxyacetone could be detected (see Figure 1A and Table S1). Moreover, also up to 11% glycolaldehyde could be observed after 0.25 h reaction time. As expected, the yields of these intermediates decreased with increasing reaction time. However, glyoxal could not be detected with the analysis used. This is probably due to the fast conversion of the latter at the applied high temperatures. On the other hand, glucose can undergo acid-catalyzed dehydration to 5-hydroxymethylfurfural (HMF) and further on to levulinic acid (acid-catalyzed), furfural (heat-induced), or succinic acid (oxidative-catalyzed by V$^{5+}$) on the way to acetic acid (left reaction pathway in Scheme 1). However, only small amounts of levulinic acid and succinic acid (maximum yields of around 3%) could be detected in the reaction solution. Furfural could not be detected with the analysis used. Instead, in addition to the gaseous and liquid products, the formation of dark-colored and solid humins could be observed resulting from heat-induced HMF conversion.

Performing the experiments under a nitrogen atmosphere (Figure 1B) led primarily to the formation of lactic acid with yields up to 17% after 1 h. Furthermore, the carboxylic acids formic acid (7%), acetic acid (7%), and levulinic acid (5%) were also formed in the reaction mixture. In addition, different reaction pathways for the conversion of glucose under a nitrogen atmosphere were already published for different catalytic systems. The different reaction pathways for the conversion of glucose under reductive atmosphere are compared in Scheme 2.

Herewith, glucose or its isomer fructose can also react in two ways under reductive reaction conditions in aqueous solution. One possibility (left pathway in Scheme 2) is again acid-catalyzed dehydration to HMF, followed by either heat-induced conversion to furfural or acid-catalyzed reaction to levulinic and formic acid. The intermediate HMF could also be detected with yields up to 4% after 1 h in our reaction solution. Moreover, up to 5% levulinic acid and 7% formic acid could be observed. However, again no furfural could be detected by the applied analytics. Interestingly, also propionic acid was detected in small amounts (maximum yield of 3%). On the redox-catalyzed reaction pathway toward lactic acid (right pathway in Scheme 2), the intermediate glyceraldehyde was formed with yields up to 12% after initial heating of the reaction mixture. In the following, the yield decreased to around 7%, indicating its status as intermediate. Although the reaction was performed under a nitrogen atmosphere, small amounts of carbon dioxide ($Y_{CO_2} < 3\%$) were also formed. This indicates that the system was not completely free of oxygen. In addition, the catalyst was present in the oxidized form at the beginning of the reaction. This also enabled the oxidative conversion of glucose. However, due to the lack of oxygen in the reaction atmosphere, the reoxidation of the catalyst could not take place afterward. Again, the formation of dark-colored and solid humins could be observed.

Analogous to the conversion under an oxygen atmosphere, the conversion of the substrate glucose reached 92% after already 1 h reaction time. For this reason, the following investigations were performed with a reaction time of 1 h.

Figure 2. $^{51}$V NMR spectra of the catalyst K$_5$[V$_3$W$_3$O$_{19}$] before reaction (top) at pH = 5.9, after reaction under oxygen atmosphere (middle) at pH = 2.7, and after reaction under nitrogen atmosphere (bottom) at pH = 3.3.

19085
The spectrum became more complex. The peak at 517.4 ppm can be assigned to the trans-[V3W3O19]5− polyanion. Figure 2 clearly shows that the [V3W3O19]5− polyanion undergoes structural changes already after dissolution of the parent solid K5[V3W3O19] compound in water as well as during catalytic reaction. In the spectrum of the concentrated solution of K5[V3W3O19] in H2O/D2O (top), the significant peaks for [V2W4O19]3− (~ −510.3 ppm (the largest peak) and ~ −517.4 ppm) and [V3W3O19]5− (~ −497.9 and ~ −504.2 ppm) as well as the presence of different VO3− species (around ~ −575 ppm) are visible. After 5 h reaction under nitrogen atmosphere (middle), due to the decrease in pH of the reaction mixture (pH = 2.7 compared to 5.9 before reaction) and, as a result, the formation of many different V-containing species, the spectrum became more complex. The peak at ~ −521.5 ppm can be assigned to trans-[V3W3O19]5− and that at ~ −527.5 ppm can be assigned to cis-[HV2W4O19]3− and trans-[HV2W4O19]5−. The peaks in the range of ~ −533 to ~ −564 ppm can be attributed to various [VO3−(H2O)n]n+ species. 49, 50

After the reaction under nitrogen atmosphere (bottom), the 51V NMR spectrum changed completely. The increasing background noise results from paramagnetic V4+ species formed under reductive conditions. 44 Therefore, only a minor signal is visible in the spectrum, showing the presence of only traces from diamagnetic V5+ species.

To investigate the influence of temperature on the K5[V3W3O19]-catalyzed glucose conversion under oxygen and nitrogen, we performed additional experiments at 180 and 200 °C, respectively. The results of the temperature variation experiments are summarized in Supporting Information Tables S3 and S4. The temperature variation under oxygen atmosphere showed almost full conversion (X > 96%) at all tested temperatures. With increasing temperature, the formic acid yield decreased from 20% at 160 °C to 10% at 200 °C, whereas the yield of CO2 increased from 16 to 23%, indicating a higher conversion of glucose by the noncatalyzed total oxidation. At the same time, the yield of acetic acid only slightly increased from 9% (160 °C) to 12% (200 °C). The temperature variation experiments under nitrogen atmosphere showed no influence of the reaction temperature on product yields. The yield of lactic acid reached a constant value of 17− 18%. As an increased temperature led not to higher yields of formic acid (under oxygen) and lactic acid (under nitrogen), we performed the following experiments at 160 °C.

To identify the different vanadium species being present using the Lindqvist-type POM catalyst K5[V3W3O19] under both oxygen and nitrogen atmospheres, we performed 51V NMR measurements of the aqueous phase before and after reaction at 160 °C under oxygen and nitrogen, respectively. Figure 2 shows that the [V3W3O19]5− polyanion undergoes structural changes already after dissolution of the parent solid K5[V3W3O19].

Three Lindqvist-type POMs (K5[V3W3O19], (NH4)5[V3W3O19], and H5[V3W3O19]) as well as the Keggin-type POM H8[VP3Mo9O40] and the Wells–Dawson-type POM K8H[P2W15V3O62] were used as catalysts for this study. Additionally, the commercial vanadium salts NH4VO3, NaVO3, and VOSO4 were tested for a comparison. The catalyst concentration was always kept constant regarding the amount of vanadium (0.5 mmol of vanadium content). The reactors were filled in addition with 2 mmol of glucose and 10 g of demineralized water as solvent. The reactions were performed under 20 bar of oxygen or nitrogen pressure at 160 °C using a stirrer speed of 1000 rpm. After the reaction time of 1 h, the reactors were removed from the heating plate and rapidly cooled down in a water bath.

The results of the catalyst variation experiments are presented in Figure 3 and Tables S5 and S6 in the Supporting Information. For a better comparison, only the yields of the main products are shown in Figure 3 (formic acid and acetic acid for the experiments under oxygen atmosphere as well as lactic acid and formic acid for the experiments under nitrogen atmosphere). The catalyst variation experiments under oxygen atmosphere (Figure 3A) demonstrated full glucose conversion after 1 h except for using the Wells–Dawson-type POM (X = 89%). Hereby, the Keggin-type POM catalyst H8[VP3Mo9O40] showed the highest activity with a formic acid yield of 36% and a glucose conversion of almost 100% after 1 h reaction time. Glucose oxidation with the three tested Lindqvist anions...
Table 1. Product Yields of the Substrate Variation Experiments under Oxygen Atmosphere Reaction Conditions: 2 mmol of Substrate, 0.5 mmol of (Vanadium Content) H$_6$[PV$_3$Mo$_9$O$_{40}$] Catalyst, 10 g of Water, 160 °C Reaction Temperature, 20 bar Oxygen Pressure, 1000 rpm Stirrer Speed, 1 h Reaction Time$^a$

| entry | substrate | FA (%) | AA (%) | LA (%) | HMF (%) | LA (%) | CO (%) | CO (%) | X (%) |
|-------|-----------|--------|--------|--------|---------|--------|--------|--------|-------|
| 1     | glucose   | 36.0   | 7.9    | 3.9    | 27.6    | 1.2    | 100    |
| 2     | xylose    | 39.5   | 7.7    | 0      | 25.6    | 1.3    | 100    |
| 3     | glyceraldehyde | 41.7 | 16.1   | 0      | 22.5    | 2.4    | 100    |
| 4     | dihydroxyacetone | 33.6 | 18.8   | 0      | 20.9    | 1.0    | 100    |
| 5     | glycolaldehyde | 35.1 | 0      | 0      | 8.7     | 1.9    | 100    |
| 6     | glyoxal   | 29.0   | 0      | 0      | 5.2     | 0      | 100    |

$^a$Abbreviations: formic acid (FA); acetic acid (AA); glyceraldehyde (glyceral).

Table 2. Product Yields of the Substrate Variation Experiments under Nitrogen Atmosphere Reaction Conditions: 2 mmol of Substrate, 0.5 mmol of (Vanadium Content) K$_5$[V$_3$W$_3$O$_{19}$] Catalyst, 10 g of Water, 160 °C Reaction Temperature, 20 bar Nitrogen Pressure, 1000 rpm Stirrer Speed, 1 h Reaction Time$^a$

| entry | substrate | FA (%) | AA (%) | LA (%) | HMF (%) | LA (%) | CO (%) | CO (%) | X (%) |
|-------|-----------|--------|--------|--------|---------|--------|--------|--------|-------|
| 1     | glucose   | 7.5    | 7.2    | 17.3   | 3.7     | 3.2    | 8.1    | 2.5    | 0     | 2.0    | 90.5 |
| 2     | xylose    | 6.8    | 5.1    | 15.4   | 0.6     | 1.9    | 4.2    | 1.0    | 0     | 2.1    | 93.6 |
| 3     | glyceraldehyde | 6.2  | 8.3    | 17.9   | 0.5     | 2.5    | 7.7    | 2.4    | 0     | 2.8    | 92.3 |
| 4     | dihydroxyacetone | 4.9  | 9.3    | 17.6   | 0       | 3.2    | 6.2    | 1.7    | 0     | 3.4    | 100  |
| 5     | glycolaldehyde | 14.2 | 7.3    | 0      | 0       | 1.9    | 5.9    | 2.4    | 14.1  | 0     | 78.8 |
| 6     | glyoxal   | 14.7   | 0      | 0      | 0       | 0      | 20.6   | 0      | 0     | 99.0   |

$^a$Abbreviations: formic acid (FA); acetic acid (AA); lactic acid (LA), hydroxymethylfurural (HMF); levulinic acid (LevA); glyceraldehyde (glyceral); propionic acid (PA); glycolaldehyde (glycolal).

With the different counter cations K$^+$, NH$_4^+$, and H$^+$ led to formic acid yields between 18 and 20%. This indicates that the counter cation does not influence the reaction mechanism under the applied reaction conditions. The Wells–Dawson-type POM K$_6$H$_2$[P$_2$W$_{15}$V$_3$O$_{62}$] showed the second highest formic acid yield with 28%. In comparison, all selected POM catalysts showed a higher activity under oxygen atmosphere compared to the commercial vanadium salts, except for VOSO$_4$ giving formic acid yields of 14% (NH$_4$VO$_3$), 16% (NaVO$_3$), and 23% (VOSO$_4$). It has to be noted that no other intermediates or side products could be detected with any of the catalysts used than described in Scheme 1. Regarding different side products, using the protonated [V$_3$W$_3$O$_{19}$]$^{5-}$ POM catalyst resulted in the highest detected acetic acid yield of 12%. With respect to the CO$_2$ yield, the Keggin-type POM led to the highest amounts of 28%. However, this catalyst was the most selective as only formic acid, CO$_2$, acetic acid (8%), glyceraldehyde (4%), and CO (1%) could be detected after reaction. Very importantly, no solid residues could be observed using this catalyst compared to most of the other compounds used.

The catalyst screening under nitrogen atmosphere (Figure 3B) showed different results. With respect to lactic acid formation, the Lindqvist-type POM K$_5$[V$_3$W$_3$O$_{19}$] showed the highest activity with a lactic acid yield of 17% after 1 h reaction time. However, all other catalysts used achieved lactic acid yields between 10 and 15% at glucose conversions >95%, except the Wells–Dawson-type POM with only 6% lactic acid yield at 31% conversion. Contrary to the results under oxygen atmosphere, the tested Keggin-type POM H$_6$[PV$_3$Mo$_9$O$_{40}$] only showed a lactic acid yield of 10% under the applied reaction conditions. Interestingly, all commercial vanadium salts gave high amounts of glyceraldehyde (14–18%) and thus low selectivities to lactic acid. VOSO$_4$ also showed a high amount (15%) of HMF demonstrating its low selectivity to the desired vanadium-catalyzed reaction pathway. Moreover, again no other intermediates or side products could be detected with any of the catalysts used than described in Scheme 2.

Due to the different catalyst performances under oxygen and nitrogen atmospheres, we decided to continue the substrate variation in the following with the best catalyst system for each particular gas atmosphere. Specifically, we continued with the Keggin-type POM H$_6$[PV$_3$Mo$_9$O$_{40}$] for the investigations under oxygen atmosphere and the Lindqvist-type POM K$_5$[V$_3$W$_3$O$_{19}$] for the experiments under nitrogen atmosphere.

Substrate Variation. In the next set of experiments, we wanted to identify a suitable model substrate to investigate whether the two selected POMs can be regarded as “switchable catalysts” by simply changing the reaction atmosphere in situ. Therefore, we performed the substrate variation experiments as well under both gas atmospheres in parallel. In addition to the already used substrate glucose (C$_6$ sugar), the C$_5$ sugar xylose was tested as well as the intermediates glyceraldehyde, dihydroxyacetone, glycolaldehyde, and glyoxal were detected.

The reactors were filled with 2 mmol of substrate, either the catalyst K$_5$[V$_3$W$_3$O$_{19}$] or H$_6$[PV$_3$Mo$_9$O$_{40}$] (0.5 mmol of vanadium content), and 10 g of demineralized water as solvent. For each substrate, a blank experiment (without catalyst) was performed as well. The reactions were carried out under 20 bar of nitrogen or oxygen pressure at 160 °C using a stirrer speed of 1000 rpm. After the reaction time of 1 h, the reactors were removed from the heating plate and rapidly cooled down in a water bath.

The yields of the main products formic acid (for the experiments under oxygen atmosphere) and lactic acid (for the experiments under nitrogen atmosphere) of the substrate variation experiments are presented in Tables 1 and 2.

The substrate variation experiments under oxygen atmosphere (Table 1) using the Keggin-type POM H$_6$[PV$_3$Mo$_9$O$_{40}$] showed full conversion of all substrates used within 1 h reaction time. With respect to the formic acid yield, using glyceraldehyde as a substrate showed the highest yield of 42%.
Also xylose ($Y_{FA} = 40\%$) showed a higher value than glucose ($Y_{FA} = 36\%$). While the use of dihydroxyacetone and glycolaldehyde led to similar yields of formic acid ($Y_{FA} = 34\text{--}35\%$) compared to the experiment with glucose as a substrate, the conversion of glyoxal resulted in a slightly lower formic acid yield of 29\%. Interestingly, the intermediates glycer aldehyde and dihydroxyacetone also gave higher yields of acetic acid ($Y_{AA} = 16\text{--}19\%$) compared to glucose and xylose, whereby using glycolaldehyde and glyoxal only resulted in formic acid formation besides CO$_2$. In all blank experiments, formic acid could be detected in small amounts as well due to the heat-induced reaction pathway described in Scheme 1.

If the substrate variation was performed under nitrogen atmosphere using the Lindqvist-type POM K$_5$[V$_3$W$_3$O$_19$] (see Table 2), the results show a different behavior of the substrates. Again, lactic acid could be detected as the main product with yields up to 18\% using glycer aldehyde or its isomer dihydroxyacetone. Interestingly, using glucose nearly gave the same amount of lactic acid ($Y_{LA} = 17\%$). As expected, using the intermediates glycer aldehyde and glyoxal of the oxidative route toward formic acid (see Scheme 1) did not produce lactic acid. Here, formic acid as the main product with yields between 14 and 15\% was achieved. Additionally, formation of formic acid as well as small amounts of CO$_2$ in entries 1\textendash}4 could be detected. In the blank experiments without any catalyst, the different substrates could not be converted into lactic acid under nitrogen atmosphere at 160 °C. Only small amounts of formic acid, acetic acid, and levulinic acid with yields less than 5\% could be detected after the reaction.

Based on these results, we decided to investigate the switchability of the catalytic activity of K$_5$[V$_3$W$_3$O$_19$] and H$_6$[PV$_3$Mo$_9$O$_40$]-based systems using the two different substrates glucose and glycer aldehyde.

**Switchability Experiments.** Finally, we combined the results of the aforementioned studies to find a suitable switchable catalytic system at 160 °C. Using oxygen atmosphere, the conversion of glycer aldehyde with the Keggin-type POM H$_6$[PV$_3$Mo$_9$O$_40$] led to the highest yield of formic acid ($Y_{FA} = 42\%$), whereby glucose gave 36\% FA yield. Under nitrogen atmosphere, the conversion of both glucose and glycer aldehyde with the Lindqvist-type POM K$_5$[V$_3$W$_3$O$_19$] showed good results regarding the obtained lactic acid yield ($Y_{LA} = 17\text{--}18\%$). With these two different substrates and catalysts each, we generated an experiment matrix where every combination of substrate and catalyst was tested. This matrix is shown in Figure 4.

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c02430) Experimental matrix for the investigation of the switchability of the POM catalysts K$_5$[V$_3$W$_3$O$_19$] and H$_6$[PV$_3$Mo$_9$O$_40$] using the substrates glucose and glycer aldehyde.

The results of these experiments are presented in the same matrix system in Figure 5. For both gas atmospheres, the yields of the main formed carboxylic acids (formic acid for the experiments under oxygen atmosphere and lactic acid for the experiments under nitrogen atmosphere) showed a maximum using glycer aldehyde as a substrate and the Keggin-type POM H$_6$[PV$_3$Mo$_9$O$_40$] as a catalyst.

Comparing the yields of the formed carboxylic acids, the best switchable system could be determined. Under both atmospheres, the conversion of glycer aldehyde using the Keggin-type POM as a catalyst H$_6$[PV$_3$Mo$_9$O$_40$] led to the highest yields of formic acid (42\%) and lactic acid (40\%) (highlighted in green in Figure 5). The latter was very surprising as this behavior was not expected based on neither the substrate screening nor the catalyst screening studies.

**CONCLUSIONS**

In this contribution, we have successfully presented the switchability of POM-based catalytic systems concerning the formation of different carboxylic acids by simply changing the gas atmosphere from oxygen to nitrogen at 160 °C.

First, we started the investigation using the Lindqvist-type POM K$_5$[V$_3$W$_3$O$_19$] and glucose as a model substrate. All investigations were carried out in parallel using either an oxygen or a nitrogen atmosphere of 20 bar. After performing time-resolved experiments between 0.25 and 5 h and a temperature variation from 160 to 200 °C, we found that 160 °C and 1 h reaction time are sufficient to study the switchability of the catalytic POM-based system. Moreover, using $^{51}$V NMR spectroscopy revealed that the applied reaction atmosphere influences the structural rearrangement of K$_5$[V$_3$W$_3$O$_19$]. Thus, the composition of vanadium-containing species under aerobic reaction conditions differs from that under anaerobic conditions. In turn, the difference in the compositions may be one of the reasons for the observed atmosphere-dependent variations of catalytic activity as various vanadium-containing species exhibit dissimilar catalytic properties.

Furthermore, a catalyst and a substrate variation led to the reaction system consisting of glycer aldehyde and the Keggin-type POM H$_6$[PV$_3$Mo$_9$O$_40$] as the best switchable reaction system under the applied conditions.
Performing the experiments with glyceraldehyde as a substrate and \( \text{H}_6[\text{PV}_3\text{Mo}_9\text{O}_{40}] \) as a catalyst using oxygen as reaction gas, we achieved a formic acid yield of 42% within 1 h reaction time. Executing the same experiment simply changing the gas atmosphere from oxygen to nitrogen at the same reaction time, the main product changed to lactic acid with a yield of 40%. This shows interesting potential for using both Keggin-type and Lindqvist-type POMs as switchable catalysts for selective biomass conversion to platform chemicals.

**EXPERIMENTAL SECTION**

**Chemicals.** All reagents and substrates were obtained commercially and used as received without further purification. The polyoxometalate catalysts \( \text{K}_6[\text{PW}_{12}\text{O}_{48}]\cdot10\ \text{H}_2\text{O} \), \( \text{H}_6[\text{PV}_3\text{Mo}_9\text{O}_{40}]\cdot10\ \text{H}_2\text{O} \), \( \text{K}_5[\text{V}_3\text{W}_3\text{O}_{19}]\cdot8\ \text{H}_2\text{O} \), \( (\text{NH}_4)_5[\text{V}_3\text{W}_3\text{O}_{19}]\cdot3\ \text{H}_2\text{O} \), and \( \text{H}_6[\text{V}_6\text{W}_6\text{O}_{19}] \) were synthesized according to literature procedures (for details, see the Catalyst Synthesis and Characterization section in the Supporting Information). The gases oxygen 4.5 and nitrogen 5.0 were obtained by Linde AG. Demineralized water was used as a solvent.

**Experimental Setup.** All experiments were performed in a 10-fold screening plant with a batch-mode reactor setup. It consists of ten 20 mL autoclaves made of Hastelloy C276. All pipes, valves, and fittings were made of stainless steel 1.4571. The gaskets were made of Teflon. The autoclaves were connected in parallel to a single gas supply line via individual couplings and placed inside a heating plate to adjust the required temperature. The heating plate was equipped with a magnetic stirrer, whereby magnetic stirrer bars could be used. Additionally, each reactor was connected to a rupture disk with a burst pressure maximum of 90 bar.

**Typical Work-Up Procedure.** For each experiment, an autoclave was filled with substrate, catalyst, and water as the solvent. The used system was purged twice with more than 10 bar of oxygen or nitrogen to remove the residual air out of the reactor. In the following, the reactor was prepressurized, the stirrer was set to 300 rpm, and the heating was switched on. When the desired temperature was reached, the pressure was increased to the desired reaction pressure and the stirrer speed was set to 1000 rpm to start the gas entrainment. This moment was set as starting time of the experiment. After the total reaction time, the reactors were removed from the heating plate and cooled down in a water bath. Samples were taken from the liquid and gas phases to analyze the composition.

**Analytics.** Characterization of the synthesized catalysts has been carried out using different analytical techniques. Elemental analysis has been done using a PerkinElmer Plasma 400 ICP-OES device. The determination of hydration water content was done by performing thermogravimetric analysis (TGA) on a Setysys 1750 CS Evolution. Solid-state Fourier transform infrared (FTIR) spectra were recorded in KBr disks on a Jasco FT/IR-4100 spectrometer. CHNS elemental analyses were performed on a UNICUBE analyzer. The synthesized catalysts were further characterized in aqueous solutions (\( \text{H}_2\text{O}/\text{D}_2\text{O} \)) by \( ^{31}\text{V} \) NMR spectroscopy using a JEOL ECX-400 MHz spectrometer (9.4 T) at 293 K in 5 mm tubes. The \( ^{31}\text{V} \) NMR spectra were measured in a range of \(-670\) to \(-360\) ppm with an excitation frequency of 105.12 MHz. The characterization of the POM catalysts and the analytical results are summarized in the Catalyst Synthesis and Characterization section in the Supporting Information.

Analysis of reaction mixtures has been carried out using solid, liquid, and gaseous samples. Solid residues were characterized by FTIR and CHNS analysis using the same equipment as mentioned above. Liquid products were analyzed by means of high-performance liquid chromatography (HPLC) measurements using a high-performance liquid chromatograph from Jasco equipped with a 300 mm \( \times \) 8 mm SH1011 Shodex column. As eluent, 5 mmol of an aqueous sulfuric acid solution was applied. The liquid phases were also analyzed by \( ^{31}\text{V} \) NMR spectroscopy using the equipment as mentioned above. Gaseous product analysis was performed using a Varian GC 450 equipped with a 2 m \( \times \) 0.75 mm ID ShinCarbon ST column.

The yields of the liquid and gaseous products were calculated by eq 1

\[
Y_i = \frac{n_{\text{product},i}}{n_{\text{C-atoms, glucose}}}
\]

The substrate conversion was calculated using the molar amount of C atoms in the reaction mixture before and after the reaction by eq 2

\[
X = \frac{n_{\text{C-atoms,substrate,0}} - n_{\text{C-atoms,substrate,0}}}{n_{\text{C-atoms,substrate,0}}}
\]

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02430.

Catalyst synthesis and characterization; tables with the product yields of the different variation experiments (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Jakob Albert – Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany; orcid.org/0000-0002-3923-2269; Email: jakob.albert@fau.de

**Authors**

Dorothea Voß – Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

Regina Dietrich – Institut für Technische und Makromolekulare Chemie, Rheinisch-Westfälische Technische Hochschule Aachen, 52074 Aachen, Germany

Maria Stuckart – Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02430

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge financial support from the Cluster of Excellence “Engineering of Advanced Materials (EAM)” and the Vector-Stiftung (2016-033).
REFERENCES

(1) López, X.; Carbó, J. J.; Bo, C.; Poblet, J. M. Structure, properties and reactivity of polyoxometalates: a theoretical perspective. Chem. Soc. Rev. 2012, 41, 7537−7571.

(2) Wang, S.-S.; Yang, G.-Y. Recent advances in polyoxometalate-catalyzed reactions. Chem. Rev. 2015, 115, 4893−4962.

(3) Mizuno, N.; Kamata, K. Catalytic oxidation of hydrocarbons with hydrogen peroxide by vanadium-based polyoxometalates. Coord. Chem. Rev. 2011, 255, 2358−2370.

(4) Gumerova, N. I.; Rompel, A. Synthesis, structures and applications of electron-rich polyoxometalates. Nat. Rev. Chem. 2018, 2, No. 0112.

(5) Pope, M. T.; Müller, A. Chemie der Polyoxometallate: Aktuelle Variationen über ein altes Thema mit interdisziplinären Bezügen. Angew. Chem. 1991, 103, 56−70.

(6) Long, D.-L.; Tsunashima, R.; Cronin, L. Polyoxometalate as Bausteine für funktionelle Nanosysteme. Angew. Chem. 2010, 122, 1780−1803.

(7) Ammac, M. Polyoxometalates: formation, structures, principal properties, main deposition methods and application in sensing. J. Mater. Chem. A 2013, 1, 6291−6312.

(8) Müller, A.; Peters, F.; Pope, M. T.; Gattesch, D. Polyoxometalates: very large clusters nanoscale magnets. Chem. Rev. 1998, 98, 239−272.

(9) Kozhevnikov, I. V. Catalysis by heteropoly acids and multi-component polyoxometalates in liquid-phase reactions. Chem. Rev. 1998, 98, 171−198.

(10) Hill, C. L.; Prosser-McCartha, C. M. Homogeneous catalysts for direct production of clean-gasoline fuel through selective oxidation of biomass to formic acid (OxFA Process) using Dawson polyoxometalate as efficient catalysts for transformations of cellulose into platform chemicals. Dalton Trans. 2012, 41, 9817−9831.

(11) Xu, C.; Arancon, R. A. D.; Labidi, J.; Luque, R. Lignin depolymerisation strategies: towards valuable chemicals and fuels. Chem. Soc. Rev. 2014, 43, 7485−7500.

(12) Zhang, Z.; Huber, G. W. Catalytic oxidation of carbohydrates into organic acids and furan chemicals. Chem. Soc. Rev. 2018, 47, 1351−1390.

(13) Chiheda, J. N.; Huber, G. W.; Dumesic, J. A. Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. Angew. Chem., Int. Ed. 2007, 46, 7164−7183.

(14) Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. Integrated catalytic conversion of γ-valerolactone to liquid alkenes for transportation fuels. Science 2010, 327, 1110−1114.

(15) Albert, J.; Maud, D.; Göttel, R.; Streb, C. Challenges in polyoxometalate-mediated aerobic oxidation catalysis: catalyst development meets reactor design. Dalton Trans. 2016, 45, 16716−16726.

(16) Keita, B.; Nadjo, L. Polyoxometalate-based homogeneous catalysis of electrode reactions: Recent achievements. J. Mol. Catal. A: Chem. 2007, 262, 190−215.

(17) Pettersson, L.; Andersson, I.; Grate, J. H.; Selling, A. Multicomponent polyoxometalates: a family of zeolite polyoxometalate frameworks from a minimal building block library. J. Am. Chem. Soc. 2017, 139, 5930−5938.

(18) Kozhevnikov, I. V.; Matveev, K. I. Homogeneous catalysts based on heteropoly acids. Appl. Catal. 1983, 5, 135−150.

(19) Wu, M.-T.; Cao, Y.; Zhang, Q.; Wang, Y. Polyoxometalates as efficient catalysts for selective oxidation of biomass to formic acid (OxFA Process) using model substrates and real biomass. ACS Sustainable Chem. Eng. 2017, 5, 7383−7392.

(20) Voß, D.; Ponce, S.; Wesinger, S.; Etzold, B. J. M.; Albert, J. Combining autoclave and LCWM reactor studies to shed light on the kinetics of glucose oxidation catalyzed by doped molybdenum-based heteropoly acids. RSC Adv. 2019, 9, 29346−29356.

(21) Kozhevnikov, I. V.; Matveev, K. I. Heteropolyacids as catalysts for synthesis of methyl tert-butyl ether. React. Kinet. Catal. Lett. 1989, 39, 317−322.

(22) Wang, C.; Bu, X.; Ma, J.; Liu, C.; Chou, K.; Wang, X.; Li, Q. Wels−Dawson type Cs8,H14,P2W20O84 based Co/Al2O3 as bifunctional catalysts for direct production of clean-gasoline fuel through Fischer−Tropsch synthesis. Catal. Today 2016, 274, 82−87.

(23) Maysuy, D.; Bartoli, J. F.; Battioni, P.; Lyon, D. K.; Finke, R. G. Highly oxidation resistant inorganic-porphyrin analog polyoxometalate oxidation catalysts. Synthesis of olefin epoxidation and aromatic hydroxylations starting from α-P2W9O34(MnIII−Br−I) (MnIII = MnIII,FeIII,CaIII,NiII,CuII), including quantitative comparisons to metalloporphyrin catalysts. J. Am. Chem. Soc. 1991, 113, 7222−7226.

(24) Chiheda, J. N.; Huber, G. W.; Dumesic, J. A. Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. Angew. Chem., Int. Ed. 2007, 46, 7164−7183.

(25) Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. Integrated catalytic conversion of γ-valerolactone to liquid alkenes for transportation fuels. Science 2010, 327, 1110−1114.

(26) Albert, J.; Wölfl, R.; Bösmann, A.; Wasserscheid, P. Selective oxidation of complex, water-insoluble biomass to formic acid using additives as reaction accelerators. Energy Environ. Sci. 2012, 5, 7956−7962.

(27) Albert, J.; Lüders, D.; Bösmann, A.; Guldí, D. M.; Wasserscheid, P. Spectroscopic and electrochemical characterization of heterogeneous catalytic oxidation of formic acid for their optimized application in selective biomass oxidation to formic acid. Green Chem. 2014, 16, 226−237.

(28) Reichert, J.; Albert, J. Biogenic formic acid as a green hydrogen carrier. Energy Technol. 2018, 6, 501−509.

(29) Albert, J.; Wasserscheid, P. Expanding the scope of biogenic substrates for the selective production of formic acid from water-insoluble and wet waste biomass. Green Chem. 2015, 17, 5164−5171.

(30) Reichert, J.; Brunner, B.; Jess, A.; Wasserscheid, P.; Albert, J. Biomass oxidation to formic acid in aqueous media using polyoxometalate catalysts − boosting FA selectivity by in-situ extraction. Energy Environ. Sci. 2015, 8, 2985−2990.

(31) Albert, J.; Mehler, J.; Tucher, J.; Kastner, K.; Streb, C. One-step synthesizable indirps-isopolyoxometalates as promising new catalysts for selective conversion of glucose as a model substrate for lignocellulosic biomass to formic acid. ChemistrySelect 2016, 1, 2889−2894.

(32) Albert, J. Selective oxidation of lignocellulosic biomass to formic acid and high-grade cellulose using tailor-made polyoxometalate catalysts. Faraday Discuss. 2017, 202, 99−109.
(43) Voß, D.; Pickel, H.; Albert, J. Improving the Fractionated Catalytic Oxidation of Lignocellulosic Biomass to Formic Acid and Cellulose by Using Design of Experiments. ACS Sustainable Chem. Eng. 2019, 7, 9754−9762.

(44) Albert, J.; Mendt, M.; Mozer, M.; Voß, D. Explaining the role of vanadium in homogeneous glucose transformation reactions using NMR and EPR spectroscopy. Appl. Catal., A 2019, 570, 262−270.

(45) Tang, Z.; Deng, W.; Wang, Y.; Zhu, E.; Wan, X.; Zhang, Q.; Wang, Y. Transformation of cellulose and its derived carbohydrates into formic and lactic acids catalyzed by vanadyl cations. ChemSusChem 2014, 7, 1557−1567.

(46) Niu, M.; Hou, Y.; Ren, S.; Wang, W.; Zheng, Q.; Wu, W. The relationship between oxidation and hydrolysis in the conversion of cellulose in NaVO₃−H₂SO₄ aqueous solution with O₂. Green Chem. 2015, 17, 335−342.

(47) Lu, T.; Niu, M.; Hou, Y.; Wu, W.; Ren, S.; Yang, F. Catalytic oxidation of cellulose to formic acid in H₃PV₂Mo₁₀O₄₀+H₂SO₄ aqueous solution with molecular oxygen. Green Chem. 2016, 18, 4725−4732.

(48) Flannelly, T.; Lopes, M.; Kupiainen, L.; Dooley, S.; Leahy, J. J. Non-stoichiometric formation of formic and levulinic acids from the hydrolysis of biomass derived hexose carbohydrates. RSC Adv. 2016, 6, 5797−5804.

(49) Andersson, I.; Hastings, J. J.; Howarth, O. W.; Pettersson, L. Aqueous tungstovanadate equilibria. J. Chem. Soc., Dalton Trans. 1996, 13, 2705−2711.

(50) Rehder, D. A Survey of ⁵¹V NMR Spectroscopy. Bull. Magn. Reson. 1982, 4, 33−83.