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# Catalytic Air Oxidation of Biomass-Derived Carbohydrates to Formic Acid

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An efficient catalytic system for biomass oxidation to form formic acid was developed. The conversion of glucose to formic acid can reach up to 52% yield within 3 h when catalyzed by 5 mol% of  $H_5PV_2Mo_{10}O_{40}$  at only 373 K using air as the oxidant. Furthermore, the heteropolyacid can be used as a bifunctional catalyst in the conversion of cellulose to formic acid (yield = 35%) with air as the oxidant.

### Introduction

With the diminishing reserves of fossil fuels, worldwide researchers have focused their studies on renewable biomass conversion. Cellulose, which has the highest content of biomass raw material, can be transformed into a series of top value-added chemicals and fuels, such as levulinic acid, sorbitol,<sup>[1]</sup> ethylene glycol,<sup>[2]</sup> hydroxymethylfurfural,<sup>[3]</sup> lactic acid,<sup>[4]</sup> dimethylformamide,<sup>[5]</sup> and pentanoic acid esters.<sup>[6]</sup> Because of the high oxygen content of biomass, the conversion of biomass to fuel must go through the process of hydrogenation and the addition of hydrogen from outside sources is unavoidable.<sup>[3,7]</sup> Such outside hydrogen is usually produced from nonrenewable materials, such as natural gas and petroleum.<sup>[8]</sup> To make hydrogen generation and biomass conversion more environmentally benign, it is ideal if hydrogen can be obtained from water or biomass.<sup>[9]</sup> To date, efficient production of hydrogen from water has remained difficult; the most efficient method of hydrogen production from biomass-derived glucose is aqueous-phase reforming catalyzed by Pt/Al<sub>2</sub>O<sub>3.</sub><sup>[10]</sup> However, the operation temperature is as high as about 500 K and precious metal catalysts are required. Thus, it is highly attractive to achieve the conversion of biomass-derived carbohydrates into compounds from which hydrogen is generated more easily, such as sugar alcohols.<sup>[1,9]</sup> Recently, the replacement of hydrogen with formic acid (FA) in some important biomass hydrogenation processes has been developed<sup>[11-13]</sup> (Scheme 1). The reversible formation of hydrogen from FA occurred through metal catalysis,<sup>[14]</sup> especially when catalyzed by iron complexes.<sup>[15]</sup> The reaction temperatures were below 373 K, showing the potential of using FA as a hydrogen carrier for biomass conversion.<sup>[16]</sup> Although FA can be generated from the acid hydrolysis of biomass as a byproduct,<sup>[17]</sup> the amount of such FA production cannot meet the hydrogen needs in the hydrogenation process in biomass conversion. Therefore, if FA can be obtained in high yield from biomass-derived carbohydrates, such as glucose or cellulose, under mild conditions, it can be used as a hydrogen source for biomass conversion.

The conversion of cellulose into FA must undergo two processes: 1) acid hydrolysis of cellulose to give glucose and 2) oxidation of glucose to give FA. The oxidation conditions for glu-



**Scheme 1.** Several examples of the hydrogenation of sugar-derived building blocks to give biofuels with a focus on FA as the hydrogen source.

cose have been investigated for many years, but oxygen or air have rarely been used as oxidants at low temperatures. McGinnis et al.<sup>[18]</sup> reported that favorable conditions for carbohydrate oxidation in water using O<sub>2</sub> as the oxidant were an oxygen atmosphere (1.5 MPa) and temperatures of 443–493 K. The highest yield of FA from glucose was 25 mol% with the presence of Fe<sup>3+</sup> as a co-oxidant at 463 K for 30 min in 1.5 MPa O<sub>2</sub>. Jin et al.<sup>[19]</sup> reported that a 75% yield of FA during glucose oxidation could be attained by using H<sub>2</sub>O<sub>2</sub> as the oxidant at 523 K in 60 s, but alkali bases (5 equiv) had to be added to prevent the oxidative decomposition of FA. In these studies, the tempera-

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ture of oxidation was very high and alkali bases were added to prevent decomposition. Phosphovanadomolybdates with a Keggin structure,  $[PV_xMo_{12-x}O_{40}]^{(3+x)-}$  (particularly for x=2), perform well in liquid-phase aerobic catalytic oxidation reactions and  $\left[\text{PV}_2\text{Mo}_{10}\text{O}_{40}\right]^{5-}$  can be re-oxidized by oxygen after oxidation of the substrate.<sup>[20]</sup> In addition, a Keggin-structure heteropolyacid has been used as a homogeneous catalyst in biomass conversion, particularly in cellulose conversion. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> combined with Ru/C can efficiently catalyze the conversion of cellulose into sugar alcohol.<sup>[21]</sup> The results for the acid hydrolysis of cellulose catalyzed by a Keggin-structure heteropolyacid were better than those obtained for common mineral acids.<sup>[22]</sup> In the study of glucose oxidation catalyzed by  $H_5PV_2Mo_{10}O_{40}$ , we found good yields of FA when using air as the oxidant. Efficient conversion of cellulose into FA also occurred.

### **Results and Discussion**

### **Catalyst screening**

Initially, weakly oxidative heteropolyacids and the mineral acid  $H_2SO_4$  were selected for glucose oxidation (Table 1, entries 1– 6). No FA was detected when  $H_3PW_{12}O_{40}$  and  $H_3PMo_{12}O_{40}$  were used (Table 1, entries 1–4). When  $H_2SO_4$  was employed, no oxidation occurred at 373 K (Table 1, entry 6); however, when the temperature increased to 423 K, acid hydrolysis of glucose to levulinic acid and FA occurred, but gave only 9% yield of FA (Table 1, entry 5). These results demonstrate that the yield of FA has no relationship with the acidity of the catalyst.

Table 1. Results for glucose oxidation into FA with different catalysts. <sup>[a]</sup>							
Entry	Catalyst	<i>t</i> [h]	Т [K]	Conversion [%]	Yield <sup>[b]</sup> [mol %]		
1	$H_3PMo_{12}O_{40}$	3	423	100	0		
2	$H_3PMo_{12}O_{40}$	2	373	0	0		
3	$H_3PW_{12}O_{40}$	3	423	50	5		
4	$H_{3}PW_{12}O_{40}$	2	373	0	0		
5	$H_2SO_4$	3	423	80	9		
6	$H_2SO_4$	2	373	0	0		
7	$H_5PV_2Mo_{10}O_{40}$	3	423	100	29		
8	$H_5PV_2Mo_{10}O_{40}$	2	373	90	36		
9	V <sub>2</sub> O <sub>5</sub>	3	423	100	30		
10	V <sub>2</sub> O <sub>5</sub>	2	373	33	12		
11	NaVO <sub>3</sub>	3	423	90	27		
12	NaVO <sub>3</sub>	2	373	25	10		
13	VOHPO <sub>4</sub>	3	423	99	5		
14	VOHPO <sub>4</sub>	2	373	52	24		
15	VOPO <sub>4</sub>	3	423	99	6		
16	VOPO <sub>4</sub>	2	373	65	27		
17	VOSO <sub>4</sub>	3	423	99	7		
18	VOSO <sub>4</sub>	2	373	55	25		

[a] Reaction procedure: glucose (2.5 g) was added to H<sub>2</sub>O (50 mL), then mixed with catalyst, which contained 10 mol% vanadium. The concentration of H<sup>+</sup> was equivalent to H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> when H<sub>2</sub>SO<sub>4</sub> was used. The pressures of oxygen were 1 and 2 MPa when the reaction temperatures were 423 and 373 K, respectively. [b] The yield of FA was calculated based on 1 mol glucose producing 6 mol FA.

Strikingly, the glucose oxidation process could be catalyzed by  $H_{s}PV_{2}Mo_{10}O_{40}$  at a lower temperature (373 K) with a higher selectivity of FA and a maximal yield of 36% (Table 1, entry 8). When compared with the oxidation results for catalysis by  $H_{3}PMo_{12}O_{40}$ , we found that more FA was generated when two molybdenum atoms in the Keggin-structure heteropolyacid were substituted by vanadium atoms. This result indicated that the vanadium atom played an important role in glucose oxidation. Other vanadium catalysts, such as  $V_{2}O_{5}$ , NaVO<sub>3</sub>, and some homogeneous vanadium oxides, gave rise to a much lower conversion rate of glucose and yield of FA (Table 1, entries 9– 18). Complex products with a low selectivity of FA were detected when homogeneous vanadium oxides were used at 423 K. Thus, we used  $H_{5}PV_{2}Mo_{10}O_{40}$  as the catalyst for the glucose oxidation and explored the best reaction conditions.

### Effect of reaction temperature

First, we investigated the effect of reaction temperature (Figure 1) on the formation of FA by glucose oxidation. Experiments were carried out at 353, 373, 398, and 423 K. Higher conversion rates were observed at 398 and 423 K. At these temperatures, complete conversion of glucose was detected in less than 1 h and the maximum yield of FA was about 30%. Under these conditions, the selectivity of FA was low.

When the temperature was 373 K, complete conversion of glucose and a yield of 47 % of FA were obtained in 3 h. However, the yield of FA decreased when the reaction time was extended, indicating that decomposition of FA occurred.

When the temperature was reduced to 353 K, a slower conversion rate of glucose was observed and the highest yield of HCOOH was 30% in 12 h. Thus, we selected 373 K as the optimized reaction temperature.

### Effect of substrate concentration

We prepared glucose solutions with different concentrations (1, 2.5, and 5%) for the oxidation reaction and the results are shown in Figure 2. When the substrate concentration increased, the yield of FA and the conversion rate of glucose clearly decreased. Reaction with a 1 wt% aqueous solution of glucose gave a 55% yield of FA with complete decomposition of glucose in 3 h. However, only a 36% yield of FA was detected when the concentration of the solution was 5 wt%. In addition, FA yields decreased in all cases as the reaction time was extended. These results showed that a low concentration was beneficial to the oxidation reaction.

### Effect of catalyst loading

We carried out the reaction with different catalyst loadings, and the results are shown in Figure 3. It was found that the catalyst concentration had a great impact on the conversion rate of glucose, but little effect on the yield of FA. When 2.5 mol% catalyst was added, complete conversion of glucose required a longer reaction time of about 12 h, whereas when the catalyst concentration was increased to 10%, glucose was



**Figure 1.** Results for the oxidation of a 2.5 wt% aqueous solution of glucose oxidation catalyzed by 5 mol%  $H_5PV_2Mo_{10}O_{40}$  under an oxygen atmosphere at different temperatures (**a**: 353 K, **b**: 373 K, **b**: 398 K, **v**: 423 K). The oxygen pressure was 2 MPa.

converted completely within 3 h. However, the highest yields of FA under the different conditions were about 50%.

#### Effect of reaction atmosphere

Oxygen pressures of 0.5, 1, 2, and 4 MPa were examined, and the results are shown in Figure 4. The conversion rate was substantially improved when higher oxygen pressure was employed, and the optimal pressure was 2 MPa. When the conversion of glucose was 100%, the only product in the solution was FA. To identify the product distribution during oxidation, we detected the gaseous product in the reaction when the selectivity of FA was 55%. The carbon selectivity of CO<sub>2</sub> was nearly 40%; no CO was detected. When different amounts of CO<sub>2</sub> (1, 2, 3, 4 MPa) were mixed with O<sub>2</sub> (2 MPa) as a complex reaction atmosphere, no improvement in the FA yield was observed, indicating that the addition of CO<sub>2</sub> before the reaction did not improve the selectivity of FA. When using air as the oxidant at 5 MPa, a 52% yield of FA was achieved in 3 h, which was higher than that of the oxidation in oxygen. The purity of FA in the product solution was more than 99%. This phenom-



**Figure 2.** Results for the oxidation of different concentrations (**a**: 1 wt %, **e**: 2.5 wt %, **a**: 5 wt %) of glucose catalyzed by 5 mol %  $H_5PV_2Mo_{10}O_{40}$  at 373 K. The oxygen pressure was 2 MPa.

enon indicated that using air as the oxidant could efficiently improve the selectivity for FA.

#### Possible mechanism for glucose oxidation by H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub>

Some possible intermediates were studied to give indirect evidence for the mechanism of glucose oxidation (Table 2). First, for the considerable generation of CO<sub>2</sub> during the reaction, we used 5 wt% FA solution for the reaction substrate (Table 2, entry 1) and less than 10 mol% of FA decomposed at 373 K in 6 h. Therefore, most of the CO<sub>2</sub> produced cannot be attributed to the degradation of FA. Furthermore, when methanol and formaldehyde were employed as the substrates (Table 2, entries 2 and 3, respectively), no FA was detected after a long reaction time, indicating that the reaction mechanism could not be the  $\alpha$ -cleavage of glucose to form methanol or formaldehyde, which would subsequently be oxidized to FA. The results for 1,3- and 1,2-propylene glycol (Table 2, entries 8 and 9, respectively) demonstrated that oxidation could not occur without the pinacol structure. The conversion of ethylene glycol, glycolaldehyde dimer, and glyoxal over the same reaction time

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**Figure 3.** Results for the oxidation of a 2.5 wt% aqueous solution of glucose with different catalyst loadings ( $\equiv$  2.5 mol%,  $\in$  5 mol%,  $\triangleq$ : 10 mol%) of H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> at 373 K. The oxygen pressure was 2 MPa.

showed that the active center of the substrates should be the aldehyde group. A long oxidation time for oxalic acid, glycolic acid, and glyoxylic acid was used, but very low conversion rates of the substrates were observed. Because only FA was detected in the product solution, the reaction intermediates could not be these carboxylic acids.

The X-ray photoelectron spectra of V and Mo atoms in the catalyst revealed their valence during the reaction. In the presence of oxygen, the valence of the V and Mo atoms in the catalysts were the same as that of the fresh catalyst, but when oxygen was absent, the peak position of the Mo catalysts remained basically unchanged, whereas the change in the peak position of V indicated that the valence changed from five to four (Figure S1 in the Supporting Information). Thus, the reaction center of catalyst should be the V atom, as proposed in the literature.<sup>[20]</sup> Combining the reaction results for possible intermediates and the pinacol oxidation mechanism proposed by Neumann and Khenkin, we proposed that a possible mechanism for glucose oxidation in-



**Figure 4.** Results for the oxidation of a 2.5 wt% aqueous solution of glucose catalyzed by 5 mol%  $H_5PV_2Mo_{10}O_{40}$  at 373 K with different oxygen pressures (**=**: 0.5 MPa, **•**: 1 MPa, **\***: 2 MPa, **\***: 4 MPa).

volved electron and oxygen transfer processes catalyzed by the heteropolyacid (Scheme 2) and that the reaction intermediates might be aldehydes.

lyzed by Entry	y $H_5PV_2Mo_{10}O_{40}$ heteropolyacids. <sup>(a)</sup> Substrate ([g mL <sup>-1</sup> ])	t [h]	T [K]	Conversion [%]	Yield <sup>[b]</sup> [mol %]
1	FA (0.05)	6	373	9	_
2	methanol (0.025)	6	373	0	0
3	formaldehyde (0.025)	6	373	13	0
4	ethylene glycol (0.01)	3	373	10	0
5 <sup>[c]</sup>	2,5-dihydroxy-1,4-dioxane (0.01)	3	373	90	56
6	glyoxal (0.01)	3	373	100	65
7	glyceraldehyde (0.01)	3	373	100	55
8	1,3-propylene glycol (0.05)	2	398	0	0
9	1,2-propylene glycol (0.05)	3	398	50	17
[a] Reaction conditions: 5 mol% of $H_5PV_2Mo_{10}O_{40}$ catalystwas added to the mixture. The pressure of oxygen was 2 MPa. [b] The yield of FA was calculated based on 1 mol of glucose producing 6 mol of FA. [c] The substrate was the glycolaldehyde dimer.					

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Scheme 2. Possible pathway for glucose oxidation catalyzed by  $H_5PV_2Mo_{10}O_{40}$  through an electron (ET) and oxygen transfer (OT) reaction mechanism.

### Degradation of cellulose by using $H_5PV_2Mo_{10}O_{40}$ as a bifunctional catalyst

Due to the acidic system of glucose oxidation, we tried to combine acid hydrolysis and oxidation in a one-pot reaction for cellulose conversion to FA.  $\alpha$ -Cellulose without pretreatment was used as the reactant, and the results are shown in Table 3. When the heteropolyacid was used as a bifunctional catalyst for acid hydrolysis and oxidation, only 3% yield of FA was detected with complete conversion of cellulose (Table 3, entry 1), and the yield of glucose was less than 1% with more than 50% of the carbon in the reactant converted into CO<sub>2</sub>. This result showed that H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> had a comparative ability for the decomposition of cellulose, but a poor selectivity to produce FA under these reaction conditions. When we added inorganic acids to the reaction system, a substantial enhancement in the yield of FA was observed, and the yield of FA was about 30%. Moreover, the type of inorganic acid did not lead to a clear variation in FA yield, and the maximum yield of FA was 34% in 9 h when HCl was added (Table 3, entry 6); a 14%

Table 3. The results for the conversion of cellulose to FA under different conditions. $^{\left[ a\right] }$							
Entry	Catalyst additive	t [h]	T [K]	Conversion [%]	Yiel FA	d <sup>[b]</sup> [mol %] glucose	
1	-	9	443	100	3	-	
2	$H_2SO_4$	9	423	56	23	9	
3	$H_2SO_4$	9	443	100	28	9	
4	$H_2SO_4$	3	443	98	6	27	
5 <sup>[c]</sup>	H₂SO₄	9	443	90	18	4	
6	HCI	9	443	100	34	14	
7	$H_3SiW_{12}O_{40}$	9	443	100	27	7	
8	H₃PO₄	9	443	100	29	-	
9 <sup>[d]</sup>	$H_2SO_4$	9	443	100	27	10	
10 <sup>[d]</sup>	-	9	443	100	35	5	

[a] Reaction procedure: cellulose (0.5 g) was added to an aqueous solution of acid (50 mL), then mixed with  $H_5PV_2Mo_{10}O_{40}$  (5 mol%). The concentration of  $H^+$  was  $10^{-2}$  mol  $L^{-1}$  when  $H_2SO_4$  and HCl was used; 2.5 and 1 wt%  $H_3PO_4$  and  $H_3SiW_{12}O_{40}$  were added to the mixture. The autoclave was heated to the desired temperature in less than 30 min with stirring at 500 rpm. The pressure of oxygen was 1 MPa. [b] The yield of FA is calculated based on 1 mol glucose producing 6 mol FA. [c] The reaction was carried out without  $H_5PV_2Mo_{10}O_{40}$ . [d] The reaction atmosphere was 5 MPa air.

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yield of glucose was also detected. Then, we analyzed the reaction solution reacted for 3 h and found a cellulose conversion of 98%, a glucose yield of 27%, and an FA yield of only 6% (Table 3, entry 4). This phenomenon indicated that, during the first 3 h of the reaction, the main reaction was the acid hydrolysis of cellulose. Afterwards, the product glucose was converted into FA. When the reaction was carried out with only mineral acid (Table 3, entry 5), the yield of FA was 18%. The yield of FA was lower than the reaction result when  $H_5PV_2Mo_{10}O_{40}$  was present (Table 3, entry 3), which indicated that the presence of  $H_5PV_2Mo_{10}O_{40}$  promoted the selectivity of FA. When we used air as the oxidant, the yield of FA was 27% (Table 3, entry 9), indicating that air was also suitable for the oxidation of cellulose. Surprisingly, when the reaction was carried out without mineral acid under an air atmosphere, the amount of glucose in the reaction mixture decreased from 10 to 5% and the yield of FA increased to 35% (Table 3, entry 10). This result indicated that the heteropolyacid could be used as a bifunctional catalyst in the conversion of cellulose to FA when using air as the oxidant.

### Conclusions

Efficient conversion of biomass-derived carbohydrates into FA was achieved when catalyzed by  $H_5PV_2Mo_{10}O_{40}$ . The highest yield of FA for glucose oxidation was 55% when oxidized by oxygen<sup>[23]</sup> and 52% when oxidized by air. The X-ray photoelectron spectra and reactions of possible intermediates indirectly revealed the reaction mechanism to be electron and oxygen transfer processes.  $H_5PV_2Mo_{10}O_{40}$  can also be used as a bifunctional catalyst for the conversion of cellulose into FA at 443 K in 9 h with 35% yield when using air as the oxidant.

### **Experimental Section**

All of the catalytic experiments were carried out in a 100 mL autoclave made of zirconium alloy. The mixture of substrates and catalyst was heated to the desired temperature in less than 30 min with stirring at 500 rpm. The concentrations of glucose and FA were determined by using an HPLC system consisting of a Waters 1525 pump, a Waters  $5C_{18}$ -PAQ column (4.6×250 mm) or a D-sugar column, and a Waters 2414 refractive index detector.  $H_2SO_4$ (5 mmol) was used as the mobile phase at a flow rate of 1 mLmin<sup>-1</sup>.

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**Keywords:** biomass · carbohydrates · heterogeneous catalysis · heteropolyacids · oxidation

 [1] A. Fukuoka, P. L. Dhepe, Angew. Chem. 2006, 118, 5285-5287; Angew. Chem. Int. Ed. 2006, 45, 5161-5163.

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- [2] N. Ji, T. Zhang, M. Y. Zheng, A. Q. Wang, H. Wang, X. D. Wang, J. G. Chen, Angew. Chem. 2008, 120, 8638–8641; Angew. Chem. Int. Ed. 2008, 47, 8510–8513.
- [3] G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, Science 2005, 308, 1446–1450.
- [4] M. S. Holm, S. Saravanamurugan, E. Taarning, Science 2010, 328, 602– 605.
- [5] Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* 2007, 447, 982–985.
- [6] a) J. P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, Angew. Chem. 2010, 122, 4581–4585; Angew. Chem. Int. Ed. 2010, 49, 4479–4483; b) R. Palkovits, Angew. Chem. 2010, 122, 4434–4436; Angew. Chem. Int. Ed. 2010, 49, 4336–4338.
- [7] T. P. Vispute, H. Y. Zhang, A. Sanna, R. Xiao, G. W. Huber, Science 2010, 330, 1222–1227.
- [8] J. Rostrup-Nielsen, Phys. Chem. Chem. Phys. 2001, 3, 283-288.
- [9] G. W. Huber, J. W. Shabaker, J. A. Dumesic, Science 2003, 300, 2075– 2077.
- [10] R. D. Cortright, R. R. Davda, J. A. Dumesic, Nature 2002, 418, 964-967.
- [11] a) L. Deng, J. Li, D. M. Lai, Y. Fu, Q. X. Guo, Angew. Chem. 2009, 121, 6651–6654; Angew. Chem. Int. Ed. 2009, 48, 6529–6532; b) L. Deng, Y. Zhao, J. Li, Y. Fu, B. L, Q. X. Guo, ChemSusChem 2010, 3, 1172–1175.
- [12] a) T. Thananatthanachon, T. B. Rauchfuss, Angew. Chem. 2010, 122, 6766-6768; Angew. Chem. Int. Ed. 2010, 49, 6616-6618; b) T. Thananatthanachon, T. B. Rauchfuss, ChemSusChem 2010, 3, 1139-1141.
- [13] a) J. Q. Bond, D. M. Alonso, D. Wang, R. M. West, J. A. Dumesic, *Science* 2010, *327*, 1110–1114; b) D. M. Alonso, J. Q. Bond, J. C. Serrano-Ruiz, J. A. Dumesic, *Green Chem.* 2010, *12*, 992–999; c) J. C. Serrano-Ruiz, D. J. Braden, R. M. West, J. A. Dumesic, *Appl. Catal. B* 2010, *100*, 184–189.
- [14] a) B. Loges, A. Boddien, H. Junge, M. Beller, Angew. Chem. 2008, 120, 4026–4029; Angew. Chem. Int. Ed. 2008, 47, 3962–3965; b) H. Junge, A. Boddien, F. Capitta, B. Loges, J. R. Noyes, S. Gladiali, M. Beller, Tetrahedron Lett. 2009, 50, 1603–1606; c) B. Loges, A. Boddien, H. Junge, J. R. Noyes, W. Baumann, M. Beller, Chem. Commun. 2009, 4185–4187; d) C. Federsel, R. Jackstell, M. Beller, Angew. Chem. 2010, 122, 6392–6395; Angew. Chem. Int. Ed. 2010, 49, 6254–6257; e) C. Fellay, P. J. Dyson, G.

Laurenczy, Angew. Chem. 2008, 120, 4030–4032; Angew. Chem. Int. Ed. 2008, 47, 3966–3968; f) Z. F. Zhang, S. Q. Hu, J. L. Song, W. J. Li, G. Y. Yang, B. X. Han, ChemSusChem 2009, 2, 234–238; g) Z. F. Zhang, Y. Xie, W. J. Li, S. Q. Hu, J. L. Song, T. Jiang, B. X. Han, Angew. Chem. 2008, 120, 1143–1145; Angew. Chem. Int. Ed. 2008, 47, 1127–1129.

- [15] a) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, R. J. Dyson, R. Scopellitti, G. Laurenczy, M. Beller, *Angew. Chem.* 2010, *122*, 9971–9974; *Angew. Chem. Int. Ed.* 2010, *49*, 9777–9780; b) A. Boddien, F. Gärtner, R. Jackstell, H. Junge, A. Spannenberg, W. Baumann, R. Ludwig, M. Beller, *Angew. Chem.* 2010, *122*, 9177–9181; *Angew. Chem. Int. Ed.* 2010, *49*, 8993–8996; c) A. Boddien, B. Loges, F. Gärtner, C. Torborg, K. Fumino, H. Junge, R. Ludwig, M. Beller, *J. Am. Chem. Soc.* 2010, *132*, 8924–8934.
- [16] a) F. Joó, ChemSusChem 2008, 1, 805–808; b) P. Makowski, A. Thomas, P. Kuhn, F. Goettmann, Energy Environ. Sci. 2009, 2, 480–490.
- [17] N. Taccardi, D. Assenbaum, M. E. M. Berger, A. Bösmann, F. Enzenberger, R. Wölfel, S. Neuendorf, V. Goeke, N. Schödel, H. J. Maass, H. Kistenmacher, P. Wasserscheid, *Green Chem.* **2010**, *12*, 1150–1156.
- [18] G. D. McGinnis, S. E. Prince, C. J. Biermann, J. T. Lowrimore, *Carbohydr. Res.* 1984, 128, 51–60.
- [19] F. M. Jin, J. Yun, G. M. Li, A. Kishita, K. Tohji, H. Enomoto, Green Chem. 2008, 10, 612–615.
- [20] A. M. Khenkin, R. Neumann, J. Am. Chem. Soc. 2008, 130, 14474-14476.
- [21] a) J. Geboers, S. Van de Vyver, K. Carpentier, K. P. de Blochouse, P. Jacobs, B. Sels, *Chem. Commun.* 2010, 46, 3577 3579; b) R. Palkovits, K. Tajvidi, A. M. Ruppert, J. Procelewska, *Chem. Commun.* 2011, 47, 576–578.
- [22] K. I. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya, A. Satsuma, Green Chem. 2009, 11, 1627-1632.
- [23] During the preparation of this paper, we found similar work published as an ASAP article in *Green Chemistry*: R. Wölfel, N. Taccardi, A. Bosmann, P. Wasserscheid, *Green Chem.* 2011, 13, 2759–2763.

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**Breathing life into new conversions**: An efficient conversion of biomass-derived carbohydrates into formic acid (FA) can be achieved when catalyzed by  $H_5PV_2Mo_{10}O_{40}$ , which can also be used for the conversion of cellulose into FA. X-ray photoelectron spectra and reactions of possible intermediates indirectly shed light on the reaction mechanism involving electron and oxygen transfer processes. J. Li, D.-J. Ding, L. Deng, Q.-X. Guo, Y. Fu\*



Catalytic Air Oxidation of Biomass-Derived Carbohydrates to Formic Acid