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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201901057

Link to VoR: http://dx.doi.org/10.1002/cssc.201901057



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# A Polyoxometalate-Based Microfluidic Device for Liquid Phase Oxidation of Glycerol

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**Abstract:** Peroxidation of glycerol has been performed in microfluidic reactor based on polyoxometalates (POMs), which has been fabricated on a capillary using a layer-by-layer strategy. Lactic acid (LA) is produced selectively in high yield with a TOF as high as 20,000 h<sup>-1</sup> compared to a TOF of 200 h<sup>-1</sup> in batch mode. This POM microfluidic reactor is readily prepared, scalable, highly stable, reusable, and also potentially applicable to selective oxidation of other bio-wastes.

Liquid phase oxidation is central to the conversion of petroleum or biomass-based materials into important chemicals, especially fine chemicals,[1] It is also important for the treatment of environmental pollutants.<sup>[2]</sup> Polyoxometalates (POMs), which are multi-metal-oxide cluster anions of W, Mo or V in their highest oxidation states,<sup>[3]</sup> are well-established to be important catalysts for the selective oxidation of organic substrates by O2,<sup>[4]</sup> H2O2 <sup>[5]</sup> and organic peroxides.<sup>[6]</sup> Some of the long-time and general problems in catalytic oxidation are (a) selectivity (avoiding overoxidation, competing low-selectivity autoxidation sidereactions, etc.), (b) safety, particularly in peroxide-based oxidations and O<sub>2</sub>-based ones with high-vapor-pressure organic substrates under pressure, and (c) catalyst stability.<sup>[7]</sup> (d) In addition. green heterogeneous catalytic reactions conventional batch or semi-batch mode frequently have mass transfer challenges involving multiple phases (substrates, oxidants and solid catalysts). Catalyst leaching and recovery can also be issues in batch reactors.<sup>[8]</sup> Microfluidic systems or continuous-flow microreactors (MRs) have some competitive advantages over microscopic batch or semi-batch reactors: MRs (a) are frequently more environmentally benign, (b) have higher mass and heat transfer efficiencies,<sup>[9]</sup> (c) exhibit higher surfaceto-volume ratios, and (d) generate higher outputs at higher levels of safety. Such benefits have led to increasing use of MRs by both academic and industrial investigations.<sup>[10]</sup> Micro-reactor technology has been reviewed for use in both oxidative or hazardous reactions.[11]

In this communication, we describe for the first time a microfluidic catalytic system based on POMs for organic cascade reactions. We henceforth refer to this device as POMmicrofluidic reactor (POM-MR). The  $H_2O_2$  oxidation of glycerol, a large-tonnage by-product of biodiesel production, that is highly efficient and highly selective for the desired product, lactic acid

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(LA), which proceeds in a continuous flow, an approach that is potentially scale and safer than under conventional reaction conditions.

The fabrication procedure for the  $H_3PMo_{12}O_{40}$  (henceforth "HPMo")-MR(2) is as follows (Scheme 1):

(1) A commercial glass capillary of 0.5-mm wall thickness (Yongnian Company) is rinsed with 0.1 M NaOH for 1 h then with deionized water for 30 min at room temperature (RT).

(2) The capillary is sequentially filled and flushed with a poly dimethyl diallyl ammonium chloride (PDDA) solution (2 wt% in 0.1 M NaCl) for 1 h at RT to generate the capillary-PDDA assembly. The interface of capillary is negative charged, which can connect with the positive charged PDDA successfully through electrostatic interaction.

(3) Subsequently, HPMo (0.5 mg/mL) is dispersed on the surface of the capillary-PDDA by rinsing at RT for 30 min. The HPMo trianion is readily bound electrostatically to the highly positive PDDA-decorated surface forming the capillary-PDDA-single-layer-HPMo assembly (denoted as HPMo-MR(1), where"1" represents one layer of HPMo). Finally, repeating the above treatment several times affords HPMo-MRs(n). Between each repeat, the capillary is washed with deionized water for 5 min. The HPMo-MRs(n) are stored in deionized water at 4 °C after each use until next use.



Scheme 1. Schematic for preparation of HPMo-MR(2) based on electrostatic assembly.

Features of these HPMo-containing microfluidic reactors include: (1) easy fabrication of POM active sites via layer-bylayer incorporation of polyoxometalate anions to PDDA polycation polymers; (2) excellent retention of the POM by the PDDA-surface, a feature illustrated recently by quantitative removal of POM water oxidation catalysts from aqueous solutions by semi-conductor photo-electrode surfaces bearing surface-bound ammonium cations;<sup>[12]</sup> (3) low restriction of substrate fluid flowing through the reactor; (4) a very large specific interfacial area per unit of volume in the MR, which leads to efficient liquid-solid reaction.

The fabrication procedure can be followed to some extent by the SEM images (Figure 1). The initial smooth surface of the bare capillary becomes covered with small mounds of uniform depth, width, and shape in the capillary-PDDA. The surface of

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the capillary-PDDA-HPMo bears some uniform and well defined particles with a size of ~10 nm. When this MR has two and three HPMo coating layers, HPMo-MRs(2 or 3), more particles with 30-nm diameters are observed.



Figure 1. SEM images illustrating fabrication of HPMo-MRs through layer-by-layer assembly. (a) bare capillary, (b) capillary-PDDA, (c) HPMo-MR(1), (d) HPMo-MR(2), and (e) HPMo-MR(3). The coated capillary was cut at an inclined angle to expose the inner wall of the capillary under the SEM lens.

Electroosmotic flow (EOF) was also used to determine the successful fabrication of HPMo-MRs. The bare capillary being coated by negatively charged silanol groups showed a positive EOF (from anode to cathode). After application of the PDDA coating, the EOF was reversed due to the residues of the positively charged PDDA units. After treatment of the capillary-PDDA with HPMo solution, the direction of EOF changed back to positive. As a result, the alternative direction of the EOFs supports the successful formation of the HPMo-modified capillary. Clearly, the existence of the positively-charged PDDA and the negatively-charged HPMo leading to multiple strong anion-cation interactions kept the POM molecules tightly bound on the microfluidic reactor surfaces.

The FTIR spectra of HPMo-MRs with varying layers are illustrated in Figure S1. The four characteristic POM peaks from 1056 to 720 cm<sup>-1</sup>, are similar to and in registry with the corresponding bands in pure H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (1060 (vas P-O), 965 (vas Mo=O), 882 (vas Mo-O-Mo) and 748 cm<sup>-1</sup> (vas Mo-O-Mo)) with some red shifts. The broader bands may because of the grinding before recording on the KBr pellets. This indicates that after coating the capillary PDDA with the POM catalyst, HPMo, this Keggin POM structure remains intact. Further, these vibrational bands are consistent with some interaction between PDDA and a terminal oxygen of Mo=O which results in red shifting of the asymmetric stretch, vas, of Mo=O.[13] The shifts increase from 4, 10 and to 18 cm<sup>-1</sup>, for HPMo-MR(1), HPMo-MR(2) and HPMo-MR(3), respectively, which is attributed to the increasing interaction between the PDDA and the HPMo units. The amount of HPMo in the MRs was determined by Uv-Vis spectroscopy from the intensity of peaks at 220 and 260 cm<sup>-1</sup> corresponding to the Keggin structure of HPMo <sup>[14]</sup> (Figure S2). A certain length (20 cm) of HPMo-MR(n) were immersed in HF (1 M) for a while under vacuum until the capillary was dissolved, and then the final solutions were tested by Uv-vis. The concentration of HPMo-MR(1), HPMo-MR(2) and HPMo-MR(3) divided by capillary internal area were  $2.8 \times 10^{-7}$ ,  $6.7 \times 10^{-7}$ , and  $8.3 \times 10^{-7}$  mol/cm<sup>2</sup>, respectively. Thermogravimetric analysis (TGA) was used to confirm the successfully fabrication of HPMo-MR via the layer-by-layer method. The evident weight reduction around 550 °C is due to HPMo decomposition.<sup>[15]</sup> The TGA data indicate that a loss of  $2.7 \times 10^{-7}$ ,  $6.4 \times 10^{-7}$ , and  $8.9 \times 10^{-7}$  mol/cm<sup>2</sup> in HPMo-MR(1), HPMo-MR(2), and HPMo-MR(3), respectively (Figure S3).

Initially the influence of the molar ratio of  $H_2O_2$  to glycerol was evaluated (Table 1) at 2:1, 4:1, 6:1, and 8:1 values. As expected, increasing  $H_2O_2$  enhances the conversion with a maximum value of 77 % in the case of HPMo-MR(2) at the molar ratio of 4:1. The maximum yield to LA (54 %) is obtained at this molar ratio, and decreases at higher peroxide concentrations due to overoxidation. The products of overoxidation include acetic acid, formic acid,  $CO_2$ , et al.<sup>[16]</sup> In order to evaluate the efficiency of HPMo-MR(2) in peroxidative conversion of glycerol, the reaction was conducted in batch mode under the  $H_2O_2$ -to-glycerol molar ratio (4:1) and same temperature (60 °C) using 50 cm of ground HPMo-MR(2) (Table S1, entries 1-5). In batch mode, the highest yield to LA obtained as 50 % at 75 % conversion of glycerol after 480 min.

The product distribution was determined to be LA, glyceraldehyde (GCA) and dihydroxyacetone (DHA), and other uncertain oxidative products. According to a previous report,<sup>[13]</sup> glycerol can be oxidized by H<sub>2</sub>O<sub>2</sub> through several pathways (Scheme S1) in batch mode. H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub>@SiO<sub>2</sub> was reported to show 68 % selectivity to formic acid and 27 % selectivity to glycolic acid at 61 % conversion using a H<sub>2</sub>O<sub>2</sub> to glycerol molar ratio = 5:1 at 70 °C for 12 h with 0.06 mg of catalyst.<sup>[13c]</sup> The reaction proceeded via pathway I for peroxidation of glycerol with a TOF =195 h<sup>-1</sup> (TOF = [Gly]×conversion/usage of POM ×reaction time). Under our batch reaction conditions, glycerol was oxidized to LA via pathway II with a TOF =200 h<sup>-1</sup> in the presence of ground HPMo-MR(2). This noteworthy rate is attributed to the molecular environment in HPMo-MR, in which HPMo is embedded in the hydrophobic PDDA molecules which favors LA generation.<sup>[17]</sup> In our previous report, homogeneous HPMo (no PDDA present) had a TOF of 32 h<sup>-1</sup> in batch mode <sup>[18]</sup> PDDA clearly alters the microenvironment of HPMo-MR and thus influences the efficiency of glycerol peroxidation. In addition, the residence time also plays an important role in glycerol conversion and LA yield (Table 1, entries 8). These increase to 98 and 93 %, respectively, as the residence time is increased to 16 min.

The performance (yield and rate) of HPMo producing LA increases dramatically ongoing from batch mode to microreactor mode: (TOF<sub>LA</sub> = molar yield of LA/molar of catalyst × reaction time) increases from 200 h<sup>-1</sup> to 20000 h<sup>-1</sup>.

A further attempt to increase the concentration of glycerol from 0.2 to 1.0 M (Table S1, entries 7, 11-14) was conducted.

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The conversion initially increased together with the selectivity for LA, and the maximum value was obtained at 0.6 M glycerol. The decrease in conversion and selectivity was observed as more DHA formed with increasing glycerol concentration; the DHA requires more time to transform to LA than GCA does. Increasing the temperature leads to an expected decrease in selectivity (Table S1, entries 6-10): LA is easily over-oxidized at the higher temperature in the presence of  $H_2O_2$ . The most important parameters for microfluidic reactor performance are the length and diameter of the HPMo layer. Increasing the layers in the MR from one to three doesn't increases conversion and Table 1. Optimization of the peroxidation of glycerol under the catalysis of HPMo-MR<sup>a</sup>

ent ry	catalyst	H2O2: Gly (mol/ mol)	Con% <sup>b</sup>	Yields %		
				DHA+GCA	LA	others
1	none	4:1	2	0	0	2
2	HPMo-MR(1)	4:1	31	5	24	2
3	HPMo-MR(2)	2:1	23	1	18	3
4	HPMo-MR(2)	4:1	77	20	54	3
5	HPMo-MR(2)	6:1	88	31	42	13
6	HPMo-MR(2)	8:1	94	38	32	20
7	HPMo-MR(3)	4:1	51	19	28	4
8°	HPMo-MR(2)	4:1	98	4	93	1

[a] The length and the diameter of HPMo-MR are 50 cm and 100  $\mu$ m, respectively. Conditions: 0.6 M glycerol, 60 °C, residence time 8 min. [b] Conversion (percent). [c] Residence time 16 min.

selectivity necessarily (Table 1, entries 2, 4, 7), and the highest yield of LA is obtained by HPMo-MR(2). It is likely that there are too few active sites in HPMo-MR(1), while too many layers might lead to the stacking inside the capillary which decreases the fluidity. The performance of HPMo-MR(2) with different diameters is consistent with this hypothesis (Figure S4a). The length of microfluidic reactor also influences the efficiency: longer MR give rise to higher yields of LA (Figure S4b).





The HPMo-MR(2) was reused several times with very little loss inactivity (Figure 2). Conversion and selectivity decreased from 98 % and 95 % to 93 % and 86 %, respectively. After each catalytic run, the catalytic MR was not treated before reuse. We attempted to clarify the loss of the activity by examination of the solution from the HPMo-MR(2) reactions. No HPMo was detected in most cases (assessed by UV-Vis spectra). The strong electrostatic attraction of the multicharged PDDA surfaces and the multicharged (3-) HPMo polyanion appears to eliminate POM leaching. The loss in activity is likely attributable to the adsorption of products during the peroxidation reaction. Conversions of glycerol as high as 93 % are maintained after ten cycles. The FTIR and SEM of HPMo-MR(2) after reaction also confirmed its stability (Figure S5-6). In normal peroxidatic reaction in the presence of  $H_3PMo_{12}O_{40}$  and  $H_2O_2$ , metal peroxide is usually formed. While in the FTIR spectrum after reaction, no peaks of molybdenum peroxide (around 578 and 532 cm<sup>-1</sup>) appeared.<sup>[19]</sup> It means the HPMo-MR(n) catalysts were stable under the reaction condition, which was attributed to the capillary-PDDA microfluidic structure.

#### Conclusions

In summary, a POM-containing microfluidic reactor leads to a scalable, selective and high yield production of lactic acid (LA). A facile protocol for fabrication of these POM-MR catalysts is given. Their use eliminates the catalyst-product separation problem, minimizes mass transfer difficulties, and facilitates a very short residence time. The use of HPMo-MR(2) produces LA in 95 % selectivity at 98 % conversion of glycerol under optimized reaction conditions, with a TOF 100 times higher than batch mode.

#### **Experimental Section**

The materials and methods are described in the supporting information (SI). The main components of the HPMo-MR microreactors are illustrated in Scheme 2. Details of fabrication and the catalytic oxidation procedures are given in the SI.



Scheme 2. Key components in glycerol peroxidation to LA catalyzed by HPMo-MR.

#### Acknowledgements

We thank the National Natural Science Foundation of China (51578119) and Jilin Provincial Science and Technology Department (20180414069GH) for support of this research.

**Keywords:** Microfluidic reactors • Electrostatic interaction • Glycerol oxidation • Lactic acid

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Glycerol Lactic acid H <sub>2</sub> O <sub>2</sub> TOF 20000 h <sup>-1</sup>