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Hetropolyacid-Catalyzed Oxidation of Glycerol into Lactic Acid under Mild Base-Free Conditions

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Lactic acid (LA) is a versatile platform molecule owing to the opportunity to transform this compound into useful chemicals and materials. Therefore, efficient production of LA based on inexpensive renewable feedstocks is of utmost importance for insuring its market availability. Herein, we report the efficient conversion of glycerol into LA catalyzed by heteropolyacids (HPAs) under mild base-free conditions. The catalytic performance of molecular HPAs appears to correlate with their redox potential and Brønsted acidity. Namely, $H_3PMo_{12}O_{40}$ (HPMo) exhibits the best selectivity towards LA (90%) with 88% conversion of glycerol. Loading of HPMo onto a carbon support (HPMo/C) further improves LA productivity resulting in 94% selectivity at 98% conversion under optimized reaction conditions. The reaction takes place through the formation of dihydroxyacetone/glyceraldehyde and pyruvaldehyde as intermediates. No leaching of HPMo was observed under the applied reaction conditions and HPMo/C could be recycled 5 times without significant loss of activity.

Introduction

The interest in platform molecules deriving from biomass resources to produce fuels, chemicals, and materials is growing because of the progressive depletion of fossil feedstocks and the increase in greenhouse gas emission causing global warming.[1] Glycerol is an abundant and inexpensive compound as it is a by-product of biodiesel production by trans-esterification of vegetable oils.[1] The growing production of biodiesel is accompanied by increasing interest in the development of potential valorization strategies of glycerol.[2] Glycerol contains three hydroxyl groups that can undergo selective hydrogenolysis, oxidation, esterification, and dehydration reactions.[2b, 3] Among these reactions, the oxidation of glycerol gives rise to valuable oxygenated derivatives including lactic acid (LA), glyceric acid (GlyA), dihydroxyacetone, or hydroxypyruvic acid. Significant effort was recently devoted to the development and optimization of catalysts for the selective oxidation of glycerol.

Among the listed products of selective oxidation, LA attracts attention as a very promising platform chemical.[1, 4] Nowadays LA is utilized in production of poly(lactic acid) (PLA), as well as in food industry, for leather and textile technologies, and in pharmaceutics.[4a] Recent studies predicted considerable expansion of the application field of LA and its esters. The latter bear great potential as organic solvents and could be used for production of highly pure lactic acid.[4] Currently LA is manufactured biotechnologically with a capacity estimated to 300–400 kt per annum.[5] The fermentative production of LA has the advantage of very high enantiomeric purity of the product. This is of utmost importance for the polymer industry, which relies mainly on L-LA as substrate for the production of high-quality crystalline PLA.[6] Nevertheless, the microbial production of LA also possesses drawbacks, such as utilization of expensive feedstocks and co-production of enormous amounts of wastes. Although utilization of various carbon-containing sources for fermentation, including glycerol, is possible, most of producers rely on pure and thus more expensive carbohydrate feedstocks including sucrose, dextrose corn syrups, or starch hydrolysates.[7] Additionally, fermentation proceeds most efficiently in neutral medium, therefore calcium hydroxide or calcium carbonate is added to the broth during fermentation for neutralization of the formed LA.[7] As a result, calcium lactate is produced instead of LA. Traditionally, the calcium lactate solution is acidified with sulfuric acid to precipitate calcium sulfate leaving LA in aqueous phase. The need for disposal of calcium sulfate co-produced in equimolar amounts with LA presents a major drawback of biotechnological processes.

Alternatively, glycerol can be transformed into LA chemocatalytically. Although different catalysts were proposed for this transformation, it is remarkable that the same intermediates were detected for various catalytic systems (Scheme 1).[8] First,

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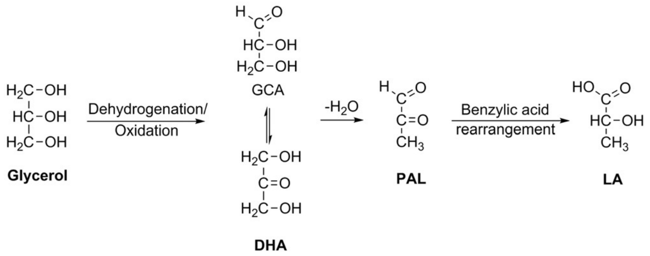


Scheme 1. Transformation of glycerol into lactic acid (LA) through formation of glyceraldehyde (GCA), dihydroxyacetone (DHA), and pyruvaldehyde (PAL).

glycerol undergoes oxidation to form dihydroxyacetone (DHA) in equilibrium with glyceraldehyde (GCA). Dehydration of DHA and GCA gives rise to pyruvaldehyde (PAL). The last step is the benzylic acid rearrangement-like transformation of PAL to LA.

Glycerol was converted to LA when treated in aqueous solution of base under harsh conditions at 280–300 °C.[8a,b,9] Strong bases such as potassium and sodium hydroxide demonstrated the highest catalytic activity among other alkali and alkali earth hydroxides resulting in up to 90% yield of LA.[8a] For this process, the first step, dehydrogenation of glycerol, appeared to be rate limiting, whereas further conversion of DHA and GCA to LA can be performed over basic catalysts under milder conditions.[10] Thus, a combination of a dehydrogenation catalyst with a base enables a decrease in the processing temperature to 90–200 °C.[8c–i,11] Dehydrogenation catalysts such as supported noble metals,[8c,d,g,h,11b,c,12] molecular iridium complexes,[8i] and copper(I) oxide[8e] were reported to be catalytically active in tandem with a base. The latter is believed to have a double function. First, the base eliminates a proton from glycerol facilitating dehydrogenation;[13] second, the base catalyzes the transformation of DHA and GCA into LA.[10] Interestingly, the LA synthesis was investigated under reducing (hydrogen),[8d,11] inert (nitrogen or helium),[8d,e] and oxidizing (oxygen)[8c,f–j,12] atmosphere. In the presence of hydrogen, the formation of LA competes with hydrogenation of the intermediates into 1,2-propanediol.[8d,11] This results in a low selectivity towards LA of ~40%.[8d,11b] The performance under inert atmosphere is more selective and enables formation of LA in high yields of 80 and 75% in the presence of base-promoted copper(I) oxide[8e] and iridium on carbon (Ir/C),[8d] respectively. Finally, syntheses of LA in the presence of metal catalysts with base under oxygen atmosphere were reported.[8c,f–j,12] A mechanistic study by Zope et al. demonstrated that the metal performs dehydrogenation of the alcohol, whereas oxygen serves as scavenger for the metal surface.[13] The great challenge of the latter approach is that the aldehyde functionality of GCA can be readily oxidized once this intermediate is formed (Scheme 1). Therefore, over-oxidation of GCA into GlyA usually accompanies the formation of LA.[8c,g,h,j] Nevertheless, tailoring the catalyst and adjusting the reaction conditions enables high yields of LA. The formation of LA with selectivities of 80–87% was reported in the presence of bases in combination with Au-Pt/TiO$_2$,[8c] Au/CeO$_2$,[8f] and Au-Pt/CeO$_2$.[8h] 91% LA yield was obtained with an iridium complex in the presence of a base.[8i]

Although glycerol can be converted in high yields to LA in the presence of (metal)base-catalysts, application of soluble bases entails separation and corrosion problems. Consequently, transforming glycerol into LA under base-free conditions was investigated. Lewis acids were recently found to be efficient for the conversion of DHA into LA, analogous to basic catalysts.[14] Tsuj et al. investigated a tandem of Au-Pd/TiO$_2$ with AlCl$_3$ and reported 85.6% selectivity at 30% conversion.[15] Later on, Cho et al. reported synthesis of a bifunctional Pt-Sn-MFI catalyst possessing both metal (Pt) and Lewis acidic (Sn) active sites. In the presence of Pt-Sn-MFI, 80.5% LA selectivity at 89.8% conversion of glycerol was reported, but the reaction lasted as long as 24 h to reach high conversion.[8j] Consequently, catalysts for a more efficient conversion of glycerol into LA under base-free conditions are desirable.

Herein we report heteropolyacids (HPAs) as very active catalysts for a selective conversion of glycerol to LA. HPAs proved to be excellent catalysts for a number of processes owing to very well-tuned Brønsted acidic and redox properties.[16] This study addressed two main objectives: (i) the optimal composition of HPAs was identified to optimize the LA yield, and (ii) a promising HPA was supported onto carbon to facilitate catalyst recovery and recyclability.[17] Preparation of the supported HPA was performed through an assembly based on ionic interactions between a surfactant cation and the HPA anion.[18]

Results and Discussion

Screening molecular HPA catalysts

Oxidation of glycerol into LA is a cascade of reactions that includes dehydrogenation/oxidation, dehydration, and isomerization of a benzylic-acid-type rearrangement (Scheme 1). One-pot implementation of these reactions was performed mostly over a tandem of catalysts, that is, metal catalyst with base[8c–i,11] or metal catalyst with Lewis acid.[15] At the same time, being a multifunctional catalyst, HPAs can potentially catalyze these transformations alone. This concept encouraged us to screen molecular HPAs with different Brønsted acidity and oxidation potential, namely the HPAs in proton form $H_5PMo_{10}V_2O_{40}$, $H_3PMo_{12}O_{40}$, and $H_3PW_{12}O_{40}$ as well as cation-exchanged HPAs $Ag_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$.

The results of the screening are summarized in Table 1, entries 1–5 as well as in Table S1 in the Supporting Information, showing that glycerol was converted to LA with rather high selectivity. The stepwise transformation of glycerol to LA (Scheme 1) suggests the following required functionalities of the catalyst: (i) the first step demands the presence of a redox catalyst to convert glycerol to DHA and GCA; (ii) the second step is dehydration of DHA and GCA into PAL that proceeds efficiently over Brønsted acids; and (iii) the third step is rearrangement of PAL into LA that can efficiently be catalyzed by Lewis acids. The results from Table 1 (entries 1–5) enable understanding the roles of different functionalities of HPAs in catalysis. Selectivities for DHA and GCA were quantified by HPLC and the formation of PAL was observed using GCMS. Addition-

Table 1. Oxidation of glycerol in the presence of HPAs as catalysts. Reaction conditions: 5 mL of 10 wt% aqueous solution of glycerol, 50 mg catalyst, 60 °C, 5 h, 5 bar O_2, 800 rpm.

Entry	Catalyst	Conv. [%]	LA yield [%]	TOF[a] [h^{-1}]	Selectivity [%] DHA	GCA	LA	GlyA	AcA
1	$H_5PMo_{10}V_2O_{40}$	93	42	16	6	5	45	21	23
2	$H_3PMo_{12}O_{40}$	90	79	32	3	4	88	2	3
3	$Ag_3PMo_{12}O_{40}$	89	72	34	9	6	81	2	3
4	$K_3PMo_{12}O_{40}$	68	44	19	20	11	65	2	2
5	$H_3PW_{12}O_{40}$	48	29	19	26	14	60	1	0
6	HPMo/C[b]	98	92	124	3	3	93	0.4	0.6
7	HPMo/SiO_2[b]	70	43	29	20	14	61	2	3
8	Carbon	9	0.3	0.01	54	42	3	0	0
9	SiO_2	6	0	0	61	39	0	0	0

[a] Turnover frequency calculated as TOF = (concentration of formed LA, mol L^{-1})/[(amount used HPA, mol L^{-1}) × (reaction time, h)]. [b] 30 wt%.

ally, the oxidation products such as GlyA and acetic acid (AcA) were identified.

Redox properties of HPAs are determined by the nature of heteropoly anion and acidity of the reaction medium.[16,19] Thus, the order of redox potentials increases as follows: $H_3PW_{12}O_{40} < H_3PMo_{12}O_{40} < H_5PMo_{10}V_2O_{40}$ with ~0.7 V for vanadium-containing HPAs at pH 1.[16,19] This means that $H_5PMo_{10}V_2O_{40}$ is the strongest oxidant and $H_3PW_{12}O_{40}$ exhibits the mildest oxidation properties. As can be seen from Table 1, conversion of glycerol correlates with the redox potential of the HPAs and increases in a row: $H_3PW_{12}O_{40} < H_3PMo_{12}O_{40} < H_5PMo_{10}V_2O_{40}$. Meanwhile, the highest selectivity for LA was observed for $H_3PMo_{12}O_{40}$, pointing at optimal redox properties of this catalyst. Thus, oxidation of the GCA into GlyA and over-oxidation to AcA takes place in the presence of $H_5PMo_{10}V_2O_{40}$ (entry 1, Table 1). At the same time, the redox potential of $H_3PW_{12}O_{40}$ is not sufficient for efficient catalysis: conversion of glycerol over $H_3PW_{12}O_{40}$ was much lower compared to $H_3PMo_{12}O_{40}$ and $H_5PMo_{10}V_2O_{40}$ (entry 5 vs. entries 1 and 2, Table 1).

Brønsted acidity is important for efficient dehydration of DHA and GCA to obtain PAL. Indeed, $K_3PMo_{12}O_{40}$ demonstrated somewhat lower conversions than its protonated counterpart $H_3PMo_{12}O_{40}$ (entries 2 and 4, Table 1). Nevertheless, even the heteropolysalts exhibited considerable conversion for the glycerol oxidation. This is probably a result of dissociation of coordinated water molecules that induces Brønsted acidity for neutral HPAs.[19] Brønsted acidity of Keggin HPAs is known to depend weakly on their composition.[16,19] Therefore, variation in catalytic activities of the protonated HPAs for dehydration of DHA and GCA is surprising. $H_3PW_{12}O_{40}$ demonstrated lower activity in dehydration of the DHA and GCA intermediates compared to $H_5PMo_{10}V_2O_{40}$ and $H_3PMo_{12}O_{40}$. After the reaction, the summed selectivity for the intermediates DHA+GCA over $H_3PW_{12}O_{40}$ was 40%, whereas the selectivity to intermediates did not exceed 11% in the presence of $H_5PMo_{10}V_2O_{40}$ and $H_3PMo_{12}O_{40}$ (entries 1, 2 and 5, Table 1). Apparently, the formation of PAL depends not only on Brønsted acidity but also on the structure of heteropolyanion. Further investigations are required for understanding this observation on a molecular level.

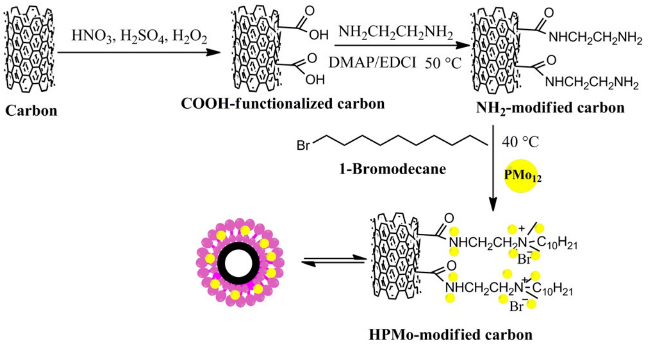
The last step of the transformation of glycerol into LA is most probably catalyzed by molybdenum- or tungsten-containing heteropolyanions. Indeed, complexation of LA with molybdenum and tungsten is well known.[20] Moreover, recent investigations uncovered an efficient rearrangement of PAL into LA in the presence of metal salts.[14a,21] The Brønsted acidic sites are known to be moderately active for the benzylic-acid-type rearrangement.[14a]

The results of the screening of molecular HPAs were very promising as these compounds exhibited excellent catalytic performance for oxidation of glycerol into LA. The highest yield of LA was obtained over $H_3PMo_{12}O_{40}$ owing to optimal redox and Brønsted acidic properties of this catalyst. Despite very promising results, application of molecular catalysts is problematic mainly owing to separation issues. Therefore, we aimed at preparation of supported $H_3PMo_{12}O_{40}$ (referred to as HPMo in the following sections) to facilitate catalyst recycling. Two solid supported catalysts, namely HPMo/C and HPMo/SiO_2, were prepared and tested under the screening conditions (entries 6 and 7, Table 1). Remarkably, HPMo/C was very efficient, even outperforming the molecular counterpart in terms of activity and selectivity. The following studies were focused on detailed investigations of HPMo/C.

Conversion of glycerol in the presence of supported HPA

Preparation and characterization of HPMo/C

HPMo was loaded onto a carbon support by way of surfactant-assisted synthesis.[18] This approach includes immobilization of heteropolyanions by means of their electrostatic interactions with a hydrophobic cation covalently bonded to the carbon surface. Specifically, the protocol of the HPMo/C synthesis included three main steps as shown in Scheme 2: (1) surface oxidation of a carbon material by successive treatments with $H_2SO_4 + HNO_3$ and $H_2SO_4 + H_2O_2$ mixtures; (2) covalent binding of ethanediamine to the surface carboxylic groups; and (3) functionalization with 1-bromodecane and loading of HPMo through self-assembly to form a lipid-like layer on the surface of the carbon materials. Literature data suggest that surrounding the support with a lipid-like layer improves the resistance of HPA against leaching as well as stability in case of pH and temperature changes.[22] Loaded HPAs serve not only as catalytically active sites, but also as hydrophilic moieties for tuning



Scheme 2. Synthetic progresses of HPMo-modified carbon catalysts.

the amphiphilic properties of the catalyst. Consequently, such lipid-like bilayers can enhance the adsorption of oxygen and glycerol molecules, which could cause an accelerated reaction.

The modified carbon materials were characterized by IR spectroscopy (Figure S1). The IR spectrum of the oxidized carbon exhibits vibration bands at 1089 and 1640 cm^{-1} corresponding to the primary hydroxyl groups[23] and carboxylate groups,[24] respectively (Figure S1 a). The IR spectrum of the NH_2-modified carbon (Figure S1 b) contains signals at 1564, 3016 and 1733 cm^{-1} for N–H[25] and C–H stretching vibrations in the alkyl chain of ethanediamine and C=O vibrations of an amide bond, respectively. Four characteristic peaks at 1137, 1036, 942, and 870 cm^{-1} were present in the IR spectrum of HPMo/C (Figure S1 c). These signals were attributed to the characteristic stretching vibrations of the Keggin anion $PMo_{12}O_{40}{}^{3-}$ at 1084, 977, 880, and 799 cm^{-1}, respectively. This result demonstrates that HPMo was successfully loaded on the surface of carbon materials. Furthermore, vibrations at 1220–1600 and 2800–3000 cm^{-1} confirm the presence of an alkyl group belonging to the long carbon chain of 1-bromodecane (Figure S1 c).

The ^{31}P magic angle spinning (MAS) NMR spectrum of HPMo/C possesses two signals at −2.35 and −5.48 ppm originating from the central PO_4 unit of the $PMo_{12}O_{40}{}^{3-}$ anion at −3.8 ppm (Figure S2 a). The split of this resonance can be explained by interaction between $PMo_{12}O_{40}{}^{3-}$ anion and grafted cation.[26]

HPMo/C was further characterized by TEM and energy-dispersive X-ray (EDX) techniques. Figure 1 a shows that the original carbon material was tubular with uniform carbon walls. Particles of irregular shape and overall sizes ranging from 50 to 150 nm were observed on the surface of HPMo/C (Figure 1 b). Moreover, the wall of the functionalized carbon was surrounded by a layer shown in the inset of Figure 1 b, which might be a lipid-like bilayer containing the surfactant 1-bromodecane and HPMo. EDX analysis (Figure 1 c) revealed the presence of phosphorous, molybdenum and oxygen on HPMo/C. 30 wt% loading of HPMo onto carbon was confirmed by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis.

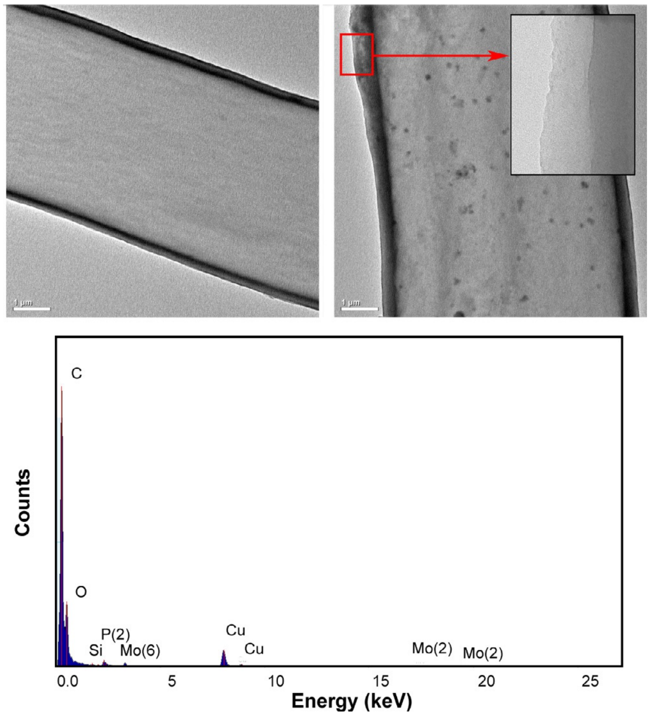


Figure 1. TEM micrographs of (a) carbon used as support and (b) HPMo/C; (c) EDX of HPMo/C.

Catalytic activity of HPMo/C for transformation of glycerol into LA

HPMo/C-catalyzed glycerol oxidation was very efficient yielding 92% of LA. To the best of our knowledge, this is the highest yield of LA achieved using a solid catalyst under very mild base-free conditions with short reaction time. The high activity of HPMo/C was attributed to the unique structure of the catalyst: The lipid-like environment of HPAs on the surface of carbon adsorbs glycerol and oxygen molecules to concentrate the reaction reagent around the catalytic sites. Adsorption of glycerol was performed on HPMo/C and the catalyst was characterized by IR spectroscopy (Figure S3). Comparison of the IR spectra of as-prepared HPMo/C and HPMo/C after adsorption of glycerol reveals more intensive vibrational bands at 3287 and 994–1115 cm^{-1} for the latter. Most probably, these signals correspond to –OH groups of glycerol. In addition, the adsorption of oxygen on catalysts was performed to verify if the presence of lipid-like layer increases the oxygen uptake. Indeed, the oxygen uptake was found to be significantly higher (2×10^{-5} mol g^{-1}) for HPMo/C. This value exceeds those of HPMo (2×10^{-7} mol g^{-1}), carbon support (6×10^{-7} mol g^{-1}), and HPMo/SiO_2 (5×10^{-7} mol g^{-1}). Probably, the structure of HPMo/C can be described as a supported HPA ionic liquid. We prepared and tested an unsupported HPA ionic liquid [DTAB]$H_2PMo_{12}O_{40}$ (DTAB = dodecyltrimethylammonium bromide-phosphomolybdic acid). For conversion of glycerol into LA, [DTAB]$H_2PMo_{12}O_{40}$ demonstrated a TOF of 21 h^{-1}(Table S1), which is comparable with molecular HPAs (Table 1).

We investigated the reaction network for glycerol oxidation. DHA and GCA were found as intermediates converted into LA during the course of reaction (Figure 2). PAL was identified in the reaction mixture by GCMS. AcA was found as side product formed in minor amounts. Importantly, both DHA and GCA can be converted into LA in the presence of HPMo/C.

The dependency of the catalyst productivity on the reaction conditions was investigated. Increasing the reaction temperature from 60 to 90 °C results in gradual decrease of selectivity for LA owing to over-oxidation of intermediates (Figure 3 a).The optimal weight ratio of glycerol to HPMo/C appeared to be 10:1 to complete the reaction within 5 h. When using more concentrated solutions of substrate (Figure 3 b) or lower amounts of catalyst (Figure 3 c), lower selectivity for LA was observed after 5 h of reaction owing to incomplete conversion of the intermediates. Use of high amounts of catalyst (0.06 or 0.07 g, Figure 3 c) or performing the oxidation for 6 h (Figure 3 d) did not result in a decrease of LA selectivity. This indicates that LA is stable in the presence of HPMo/C under the

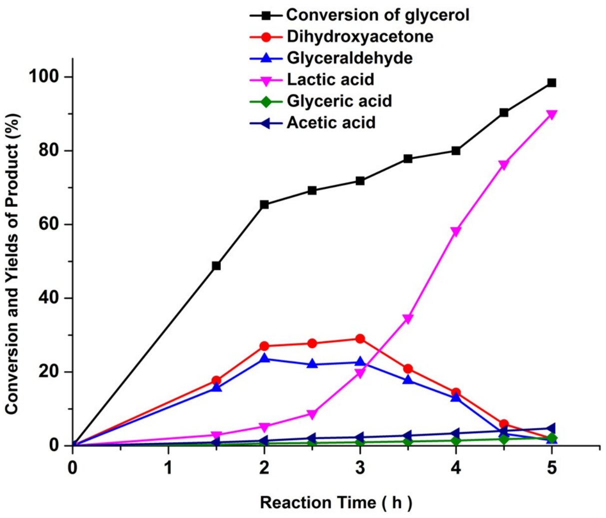


Figure 2. Time course of glycerol and the products. Reaction conditions: 5 mL 10 wt% aqueous solution of glycerol, 50 mg 30 wt% HPMo/C, 5 bar O_2, 800 rpm.

applied reaction conditions. An increase of HPA loading from 10 to 30 wt% improved glycerol conversion. Under the applied reaction conditions, 30 wt% HPMo/C was efficient enough for full conversion of the substrate with excellent selectivity for LA (Figure 3 e).

Interestingly, even neat glycerol could be successfully converted to LA under the optimized reaction conditions [5 mL neat glycerol, 50 mg 30 wt%HPMo/C, 5 bar (1 bar = 0.1 MPa) O_2, 800 rpm, 60 °C]. The conversion of neat glycerol and the selectivity for LA were 66% and 56% for 18 h, and 84% and 68% for 24 h, respectively. This result is very important for practical applications. Another crucial aspect for industrial use is purity of the substrate. Utilization of crude glycerol produced as by-products at bio-diesel plants is highly interesting from a commercial point of view. Conversion of crude glycerol is challenging owing to the impurities, which usually negatively influence the catalytic upgrading of glycerol.[8i,27] In this study, crude glycerol was obtained from biodiesel production comprising 71 wt% of glycerol, 28 wt% of methanol, and other minor organic admixtures. Surprisingly, HPMo/C displayed good activity in converting crude glycerol to LA with almost the same conversion (98%) and selectivity (90%) under mild conditions (10 wt% aqueous solution of crude glycerol, 50 mg 30 wt% HPMo/C, 60 °C, 5 bar O_2, 5 h). This result suggests HPA/C to be a methanol-tolerant catalyst capable of converting crude glycerol.

The HPMo/C catalyst was successfully reused five times without significant loss of catalytic activity and selectivity for LA formation (Figure 4). After each catalytic run, the catalyst was recovered by centrifugation, washed with ethanol and dried before reuse. To investigate a potential leaching of HPMo under the reaction conditions, the reaction mixture after the catalytic experiment was studied by UV/Vis spectroscopy. As the UV/Vis spectrum of the reaction mixture does not exhibit characteristic peaks of HPMo in the range of 200–400 nm, we suppose that no leaching of HPA takes place under our reaction conditions (Figure S4). Therefore, minor loss of catalytic activity of HPMo/C can be explained by loss of the catalyst

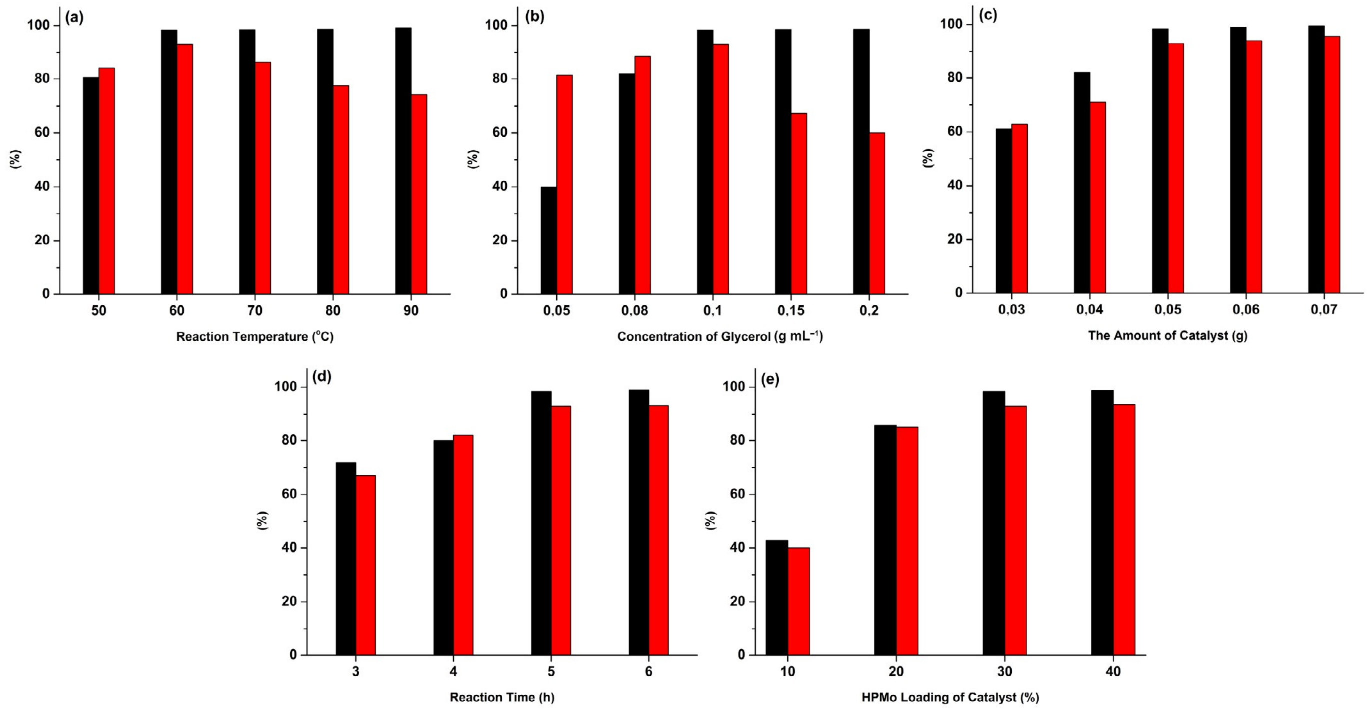


Figure 3. Conversion of glycerol (black) and selectivity for LA (red) observed under the following reaction conditions: (a) 5 mL 10 wt% aqueous solution of glycerol, 50 mg 30 wt% HPMo/C, 5 bar O_2, 800 rpm, 5 h; (b) 5 mL aqueous solution of glycerol, 50 mg 30wt.% HPMo/C, 5 bar O_2, 800 rpm, 60 °C, 5 h; (c) 5 mL 10 wt% aqueous solution of glycerol, 5 bar O_2, 800 rpm, 60 °C, 5 h; (d) 5 mL 10 wt% aqueous solution of glycerol, 50 mg 30 wt% HPMo/C, 5 bar O_2, 800 rpm, 60 °C; (e) 5 mL 10 wt% aqueous solution of glycerol, 50 mg HPMo/C, 5 bar O_2, 800 rpm, 60 °C.

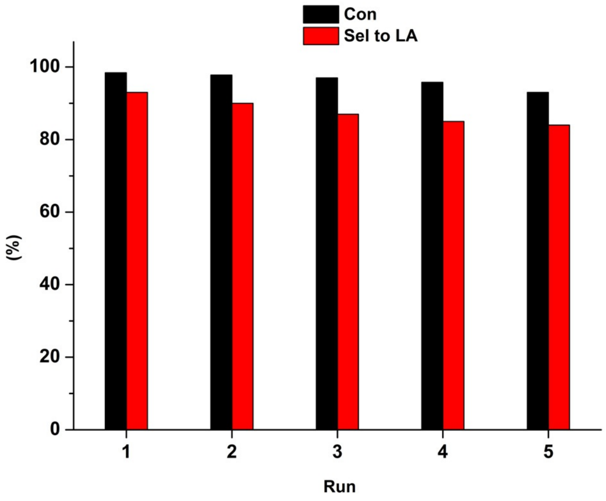


Figure 4. Reusability test catalyzed by HPMo/C in oxidation of glycerol. Reaction conditions: 5 mL of 10 wt% aqueous solution of glycerol, 50 mg catalyst, 60 °C, 5 h, 5 bar O_2, 800 rpm.

during recycling. The IR spectrum of the used HPMo/C does not significantly differ from that of fresh HPMo/C, indicating that the structure of the heteropolyanion remains intact (Figure S1 d). The characteristic vibration bands of heteropolyanions with the Keggin structure at 1055, 951, 867, and 791 cm^{-1} were observed in IR spectrum of the used HPMo/C. The ^{31}P MAS NMR also confirms stability of the HPMo/C catalyst exhibiting two signals at −2.24 and −5.43 ppm (Figure S2 b). Stability of HPMo/C was also suggested by X-ray photoelectron spectroscopy (XPS) spectra, which do not differ for the fresh and used catalysts (Figure S5).

Conclusions

This study demonstrates heteropolyacids (HPAs) as outstanding catalysts for oxidation of glycerol into LA. Dihydroxyacetone (DHA), glyceraldehyde (GCA), and pyruvaldehyde (PAL) were identified as reaction intermediates. The first step of the transformation is a heteropolyanion-catalyzed oxidation of glycerol into DHA and GCA. Dehydration of these intermediates is the second step of the process promoted by Brønsted acidic centers and leading to the formation of PAL. Finally, the rearrangement of PAL gives rise to lactic acid (LA). Most probably, the rearrangement is also catalyzed by a heteropolyanion. Productivity of molecular HPAs is mainly a function of redox potential and Brønsted acidity of the catalyst. The optimal oxidation properties were demonstrated by $H_3PMo_{12}O_{40}$ (HPMo) that produced LA by aerobic oxidation of glycerol in aqueous solution in 79% yield at 60 °C. Loading of HPMo on carbon was performed through a three-step procedure, resulting in inclusion of the HPA in a lipid-like layer on the surface of the support. The catalyst HPMo/C demonstrated excellent activity for glycerol oxidation. 94% selectivity of LA was reached at 98% conversion of glycerol under optimized reaction conditions: 10 wt% aqueous glycerol solution, 30 wt% HPMo/C, 10:1 *w/w* glycerol/catalyst, 60 °C, 5 bar O_2, 5 h. Most importantly, HPMo/C was stable for 5 catalytic runs and exhibited no leaching of the HPA. Very high potential of HPMo/C as catalyst for LA synthesis can be highlighted by capability of this material to convert crude glycerol (LA yield 88% under optimized conditions) as well as neat glycerol (LA yield 58% under optimized conditions for 24 h).

Experimental Section

Catalyst preparation

The following molecular HPAs were synthesized according to the previously reported methods: $H_5PMo_{10}V_2O_{40}$,[28] $H_3PMo_{12}O_{40}$,[29] $Ag_3PMo_{12}O_{40}$,[30] $K_3PMo_{12}O_{40}$,[30] and $H_3PW_{12}O_{40}$.[31]

Synthesis of HPMo/SiO_2 and HPMo/C

The HPMo was supported on carbon or silica to produce HPMo/C or HPMo/SiO_2. HPMo/SiO_2 was synthesized following the method reported by Guo et al.[32] The Brunauer–Emmett–Teller (BET) surface area and pore size of HPMo/SiO_2 were measured as 645 $m^2 g^{-1}$ and 5.7 nm, respectively.

The HPMo/C catalyst was prepared according to Scheme 2. Carbonized willow catkins were used as support. First, the surface of carbon support was oxidized. Carbon (1 g) was dispersed under stirring in concentrated sulfuric acid and concentrated nitric acid with a volume ratio of 3:1 and sonicated for 1 h. Thereafter, the solution was stirred for 24 h at room temperature. The reaction mixture was diluted, filtered, and washed with deionized water. The mixture was added then to 50 mL of a 4:1 (volume ratio) mixture of concentrated sulfuric acid and hydrogen peroxide and stirred for 30 min at 70 °C. The obtained oxidized carbon material was washed with deionized water until the media of the effluent became neutral. Finally, the product was dried at 80 °C.

Second, ethanediamine was grafted to the oxidized carbon material. COOH-functionalized carbon (0.2 g) was suspended in 20 mL of 2:1:1 (volume ratio) mixture of DMF, chloroform, and methanol and sonicated for 1 h. Ethanediamine (2.24 mL) along with a 10× molar excess 4-dimethylaminopyridine (DMAP) and 10× molar excess 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) was added to the reaction mixture as the catalyst for amide formation, sonicated for 1 h, and stirred for 48 h at 50 °C. The reaction mixture was centrifuged for 20 min at 4000 rpm to separate the carbons and remove unbound ethanediamine. The modified carbon was washed with 1:1 (volume ratio) mixture of chloroform and methanol until all the ethanediamine was removed. Lipid-modified carbon was dried overnight under vacuum at 30 °C.

Finally, HPMo was loaded on the produced carbon material. The NH_2-functionalized carbon (0.2 g) was mixed with 1-bromodecane (5 mmol) in 10 mL toluene. HPMo (0.06 g) was added to the mixture, sonicated for 1 h, and stirred for 24 h at 110 °C. The catalyst was recovered by filtration, washed with toluene (10 mL) five times and dried under vacuum at 60 °C for 4 h.

Characterization of supported HPMo/C

HPMo/C was characterized by XPS, FTIR, ^{31}P MAS NMR, and TEM. XPS spectra were recorded on an Escalab-MK II photoelectronic spectrometer with $Al_{K\alpha}$ (1200 eV). IR spectra (4000–400 cm^{-1}) were acquired as potassium bromide discs on a Nicolet Magna 560 IR spectrometer. The ^{31}P MAS NMR spectra were obtained using a Bruker AM500 spectrometer at 202.5 MHz using 85% H_3PO_4 as external standard. TEM micrographs and EDX spectra were collected using a JEOL-2020F electron microscope with accelerating voltage of 200 kV. Powder samples of the catalysts were ultrasonicated in ethanol and dispersed on copper grids. The loading of HPMo onto HPMo/C and HPMo/SiO_2 was determined by ICP-OES.

Catalytic tests

Glycerol oxidation was performed in a high-pressure batch autoclave of stainless steel with a polytetrafluoroethylene inlet (10 mL). The autoclave was equipped with gas supply system and a magnetic stirrer. A catalyst was suspended in 5 mL aqueous glycerol, and the mixture was heated up to 60 °C. During the reaction, oxygen pressure was maintained at 5 bar. When DHA or GCA were used as substrates, the same reaction conditions as for glycerol transformation were used. Concentrations of glycerol, LA, DHA, GCA, GlyA, and AcA were determined by HPLC. After the experiment, the reaction mixture was diluted 10 times with distilled water and analyzed by HPLC using a Shimadzu LC10A-VP chromatograph equipped with a SPB-10 A Variable UV (210 nm) and a RID-10A R.I. detectors. Prevail TM C18 column (4.6×250 mm) was used with a solution of H_2SO_4 (0.1% *w/w*) in H_2O/acetonitrile (1/2 *v/v*, 1.0 mL min^{-1}) as the eluent at 50 °C.

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[1] a) J. J. Bozell, G. R. Petersen, *Green Chem.* **2010**, *12*, 539–554; b) C. Tang, J. Peng, X. Li, Z. Zhai, W. Bai, N. Jiang, H. Gao, Y. Liao, *Green Chem.* **2015**, *17*, 1159; c) J. Zhang, Y. Zhao, M. Pan, X. Feng, W. Ji, C. T. Au, *ACS Catal.* **2011**, *1*, 32–41; d) Z. Zhai, X. Li, C. Tang, J. Peng, N. Jiang, W. Bai, H. Gao, Y. Liao, *Ind. Eng. Chem. Res.* **2014**, *53*, 10318; e) J. Peng, X. Li, C. Tang, W. Bai, *Green Chem.* **2014**, *16*, 108–111; f) C. Tang, Z. Zhai, X. Li, L. Sun, W. Bai, *J. Catal.* **2015**, *329*, 206–217.
[2] a) S.-H. Chai, H.-P. Wang, Y. Liang, B.-Q. Xu, *Appl. Catal. A* **2009**, *353*, 213–222; b) J. M. Clomburg, R. Gonzalez, *Trends Biotechnol.* **2013**, *31*, 20–28.
[3] a) C.-H. Zhou, J. N. Beltramini, Y.-X. Fan, G. Q. Lu, *Chem. Soc. Rev.* **2008**, *37*, 527–549; b) B. Sels, E. D'Hondt, P. Jacobs in *Catalysis for Renewables*, Wiley-VCH, **2007**, pp. 223–255; c) J. Zhang, M. Sun, Y. Han, *RSC Adv.* **2014**, *4*, 35463–35466.
[4] a) M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina, B. F. Sels, *Energy Environ. Sci.* **2013**, *6*, 1415–1442; b) P. Mäki-Arvela, I. L. Simakova, T. Salmi, D. Y. Murzin, *Chem. Rev.* **2014**, *114*, 1909–1971.
[5] P. F. H. Harmsen, M. M. Hackmann, H. L. Bos, *Biofuels Bioprod. Biorefin.* **2014**, *8*, 306–324.
[6] G.-Q. Chen, M. K. Patel, *Chem. Rev.* **2012**, *112*, 2082–2099.
[7] P. Gruber, D. E. Henton, J. Starr in *Biorefineries-Industrial Processes and Products*, Wiley-VCH, **2008**, pp. 381–407.
[8] a) H. Kishida, F. Jin, Z. Zhou, T. Moriya, H. Enomoto, *Chem. Lett.* **2005**, *34*, 1560–1561; b) C. A. Ramírez-López, J. R. Ochoa-Gómez, M. Fernández-Santos, O. Gómez-Jiménez-Aberasturi, A. Alonso-Vicario, J. Torrecilla-Soria, *Ind. Eng. Chem. Res.* **2010**, *49*, 6270–6278; c) Y. Shen, S. Zhang, H. Li, Y. Ren, H. Liu, *Chem. Eur. J.* **2010**, *16*, 7368–7371; d) F. Auneau, S. Noël, G. Aubert, M. Besson, L. Djakovitch, C. Pinel, *Catal. Commun.* **2011**, *16*, 144–149; e) D. Roy, B. Subramaniam, R. V. Chaudhari, *ACS Catal.* **2011**, *1*, 548–551; f) P. Lakshmanan, P. P. Upare, N.-T. Le, Y. K. Hwang, D. W. Hwang, U. H. Lee, H. R. Kim, J.-S. Chang, *Appl. Catal. A* **2013**, *468*, 260–268; g) J. Xu, H. Zhang, Y. Zhao, B. Yu, S. Chen, Y. Li, L. Hao, Z. Liu, *Green Chem.* **2013**, *15*, 1520–1525; h) R. K. P. Purushothaman, J. van Haveren, D. S. van Es, I. Melián-Cabrera, J. D. Meeldijk, H. J. Heeres, *Appl. Catal. B* **2014**, *147*, 92–100; i) L. S. Sharninghausen, J. Campos, M. G. Manas, R. H. Crabtree, *Nat. Commun.* **2014**, *5*, 5084; j) H. J. Cho, C.-C. Chang, W. Fan, *Green Chem.* **2014**, *16*, 3428–3433.
[9] Z. Shen, F. Jin, Y. Zhang, B. Wu, A. Kishita, K. Tohji, H. Kishida, *Ind. Eng. Chem. Res.* **2009**, *48*, 8920–8925.
[10] a) J. F. Harris, *Carbohydr. Res.* **1972**, *23*, 207–215; b) M. Gibbs, *J. Am. Chem. Soc.* **1950**, *72*, 3964–3965; c) J. C. Sowden, E. K. Pohlen, *J. Am. Chem. Soc.* **1958**, *80*, 242–244.
[11] a) E. P. Maris, R. J. Davis, *J. Catal.* **2007**, *249*, 328–337; b) E. P. Maris, W. C. Ketchie, M. Murayama, R. J. Davis, *J. Catal.* **2007**, *251*, 281–294; c) J. ten Dam, F. Kapteijn, K. Djanashvili, U. Hanefeld, *Catal. Commun.* **2011**, *13*, 1–5.
[12] Y. Li, S. Chen, J. Xu, H. Zhang, Y. Zhao, Y. Wang, Z. Liu, *Clean* **2014**, *42*, 1140–1144.
[13] B. N. Zope, D. D. Hibbitts, M. Neurock, R. J. Davis, *Science* **2010**, *330*, 74–78.
[14] a) C. B. Rasrendra, B. A. Fachri, I. G. B. N. Makertihartha, S. Adisasmito, H. J. Heeres, *ChemSusChem* **2011**, *4*, 768–777; b) M. S. Holm, S. Saravanamurugan, E. Taarning, *Science* **2010**, *328*, 602–605; c) P. P. Pescarmona, K. P. F. Janssen, C. Delaet, C. Stroobants, K. Houthoofd, A. Philippaerts, C. De Jonghe, J. S. Paul, P. A. Jacobs, B. F. Sels, *Green Chem.* **2010**, *12*, 1083–1089.
[15] A. Tsuji, K. T. V. Rao, S. Nishimura, A. Takagaki, K. Ebitani, *ChemSusChem* **2011**, *4*, 542–548.
[16] I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171–198.
[17] L. Qian, *Ind. Catal.* **2012**, *20*, 60–62.
[18] a) J. Zhu, P.-c. Wang, M. Lu, *J. Iran Chem. Soc.* **2013**, *10*, 123–129; b) S. Zhao, C. Sun, L. Wang, X. Xu, X. Wang, *Dalton Trans.* **2010**, *39*, 5087–5090; c) C. Zhan, J. M. Cameron, J. Gao, J. W. Purcell, D.-L. Long, L. Cronin, *Angew. Chem. Int. Ed.* **2014**, *53*, 10362–10366; *Angew. Chem.* **2014**, *126*, 10530–10534.
[19] I. V. Kozhevnikov, *Catal. Rev.* **1995**, *37*, 311–352.
[20] a) M. M. Caldeira, M. L. Ramos, V. M. S. Gil, *Can. J. Chem.* **1987**, *65*, 827–832; b) M. M. Caldeira, V. M. S. Gil, *Polyhedron* **1986**, *5*, 381–385.
[21] a) Z. Tang, W. Deng, Y. Wang, E. Zhu, X. Wan, Q. Zhang, Y. Wang, *ChemSusChem* **2014**, *7*, 1557–1567; b) Y. Wang, W. Deng, B. Wang, Q. Zhang, X. Wan, Z. Tang, Y. Wang, C. Zhu, Z. Cao, G. Wang, H. Wan, *Nat. Commun.* **2013**, *4*, 2141.
[22] a) Y. Dayani, N. Malmstadt, *Langmuir* **2012**, *28*, 8174–8182; b) S. E. Baker, W. Cai, T. L. Lasseter, K. P. Weidkamp, R. J. Hamers, *Nano Lett.* **2002**, *2*, 1413–1417.
[23] O. Taran, E. Polyanskaya, O. Ogorodnikova, V. Kuznetsov, V. Parmon, M. Besson, C. Descorme, *Appl. Catal. A* **2010**, *387*, 55–66.
[24] K. V. Singh, R. R. Pandey, X. Wang, R. Lake, C. S. Ozkan, K. Wang, M. Ozkan, *Carbon* **2006**, *44*, 1730–1739.
[25] M. G. Giorgini, M. R. Pelletti, G. Paliani, R. S. Cataliotti, *J. Raman Spectrosc.* **1983**, *14*, 16–21.
[26] R. Wei, M. Guo, J. Wang, *Chin. J. Chem. Eng.* **2009**, *17*, 58–63.
[27] a) E. Skrzyńska, A. Wondołowska-Grabowska, M. Capron, F. Dumeignil, *Appl. Catal. A* **2014**, *482*, 245–257; b) F. Yang, M. Hanna, R. Sun, *Biotechnol. Biofuels* **2012**, *5*, 13.
[28] G. A. Tsigdinos, C. J. Hallada, *Inorg. Chem.* **1968**, *7*, 437–441.
[29] H. Wu, *J. Biol. Chem.* **1920**, *43*, 189–220.
[30] S. Zhu, X. Gao, F. Dong, Y. Zhu, H. Zheng, Y. Li, *J. Catal.* **2013**, *306*, 155–163.
[31] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.* **1983**, *22*, 207–216.
[32] Y. Guo, K. Li, X. Yu, J. H. Clark, *Appl. Catal. B* **2008**, *81*, 182–191.

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