Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Study on one-pot oxidative esterification of glycerol with MOF supported polyoxometalates as catalyst

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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In this work, glycerol was treated seeking for its additional values under green and mild conditions (water solvent, H_2O_2 oxidant, 40°C). With metal organic framework (MOF) supported polyoxometallate (POM) as catalyst, esters was generated as one of the major products which could serve for various industrial applications. The selectivity of esters reached 34.5% in this one-pot oxidative esterification process. Benefiting from the pore limitation effect of MOF, diffusion was restricted and the original products could be further transformed into esters with the existence of POM. No other reagents were needed during this process, and all of the intermediates were produced by glycerol itself. The oxidative esterification reaction was studied in detail including the role of MOF, the influence of pH value and POM type, the mechanism and so on. It was concluded that POM served as active site for this oxidative esterification process and H_2O_2 provided weak acidity in addition to the source of oxygen. Too stronger acidity and oxidizability were unfavourable to the generation of esters. Also, the catalysts could be recovered after reaction, exhibiting good stability and reusability.

Introduction

Considering environmental and energy issues, biodiesel fuel as one of biomass-derived energy is now becoming a promising alternative resource instead of fossil fuel gradually.[1] It is usually produced through transesterification reactions of triglycerides, which could be obtained from vegetable oils or animal fats.[2] Glycerol (GLY) as a by-product during the production process, is excessively supplied and rapidly accumulated due to its low utilization while the growing demands of biodiesel. So how to deal with the huge amount of GLY, or even create additional values from GLY, is of great concern that affects the development of biodiesel industry.[3]

According to reported works, there are four major types of glycerol transformation products.[4] First is acrolein, which is generally obtained from gas phase dehydration at 150°C~300°C, with selectivity of about 30%~84%. Noble metal supported on activated carbon or metal oxide is usually used as catalyst for this process, with polyoxometallate (POM) occasionally reported as well.[5] The advantage of this method lies in its high conversion and sometimes the selectivity is also good under certain conditions. But large amounts of aromatic compounds and coke would deposit on catalyst, leading to its quick deactivation. Secondly, alcohols, with reactions also carried out under gas phase. Alkali metals and their oxides are used as catalysts in this process forming a hydrogenation system, but catalyst deactivation phenomenon still exists.[6] The third class of products consists of various acids which were obtained through oxidations with selectivity of 50%~90% probably. Reported catalysts for this process often serve for a liquid phase oxidation process, including Al_2O_3/HPW,[7] PtAu/HT,[8] $Cu/SiO_2/MoO_3$ [9] and so on [10]. Fourthly, esterification products are usually generated under acid conditions.[11] Unlike the esterification method that we will discuss below, the addition of equimolar amount of acid is essential to accomplish this process, with glycerol just acting as an alcohol. Furthermore, for some of the esterification reactions, glycerol may be generated again through transesterification process. So, glycerol is not digested indeed.

In view of the current situation of GLY, we are trying to deal with it in a better way and create its additional values. Metal-organic frameworks (MOFs), a relatively new class of materials consisting of metal ions/clusters and organic linkers attracted our attention. Except for their use in gas storage, separation, detection and drug release, encapsulation of active species could also be achieved. [12] In particular, the environment in MOFs can be fine-tuned by selecting the appropriate building blocks and/or by post-synthetic treatment, resulting in various possibilities that might allow us to adjust the selectivity in GLY treatment. [13]

Herein in this work, a novel method was developed for oxidative esterification of GLY utilizing metal organic framework (MOF) supported POM as catalysts (MOF-POM). GLY was transformed into esters with various applications such as chemical synthesis, organic solvents, paint and so on due to their specific properties including non-pungent smell, high solvency and moderate volatility. Also, esters could be separated from substrates and other products easily. This oxidative esterification process was based on the diversity of products in POM catalyzed aqueous transformation of glycerol, and also, the porosity of MOF. Due to the specific structure of MOF, diffusion was restricted and the original products could be further transformed into esters in the presence of POM. No other reagents were needed during the process except for H_2O_2 and catalyst. All of the intermediates were produced by glycerol itself, leading to a green and clean process which may open up new vistas for GLY treatment and pave path for the development of biodiesel industry in future.

Results and discussion

Preparation and Characterization of the catalysts

A series of nano-sized metal-organic frameworks were synthesized with different POMs encapsulated including $H_3PW_4O_{12}$, $H_5PMo_{12}O_{40}$, $H_5PVMo_{10}O_{40}$, $H_5PV_2Mo_{10}O_{40}$, $H_5PV_3Mo_{10}O_{40}$ (noted as MOF-HPW, MOF-HPMo, MOF-HPMoV, MOF-HPMoV2, MOF-HPMoV3 respectively). Synthesis of MOF-POM catalysts was carried out at room temperature through stirring and aging process rather than hydrothermal process at higher temperature. With low-price and easy-obtaining raw materials, the MOF-POM catalysts could be prepared conveniently and economically from a mixture containing molar composition of 18 Cu/10 BTC/POM/CTAB/170 EtOH/2000 H_2O (BTC: benzenetricarboxylic Acid, CTAB: cetyltrimethyl ammonium bromide). The easy-preparation and low-cost property of catalysts also contributed to this green and economic treatment for GLY in whole.

Before utilization of the catalysts for oxidative esterification of GLY, their morphology, structure and composition were studied in detail. TEM images of MOF-HPW and MOF-HPMo in Figure 1 showed that the catalysts were of framed structure with uniform size and morphology. The highly ordered one-dimensional mesostructures could be clearly observed, which looked like railings viewing from the long-range. It testified the structure that Keggin ions were contained in microporous wall structures, next to the less dense mesopores. When compared with literature,[12a] similar parallel lines with a distance of 3.6 nm could be observed, which means that the structure of catalyst we prepared also followed space group P2/m. As for MOF-HPMo, the size of framework changed greatly, but the meso-structures were still clearly visible, which also confirmed that the Keggin ion acted as template species during the synthesis of MOF. In vanadium containing POMs, molybdenum was substituted by 1-3 vanadium atoms. With the increasing vanadium content, the framework of MOF-HPMoV1, MOF-HPMoV2 and MOF-HPMoV3 also tended to be different. As shown in Figure 1, TEM image of MOF-HPMoV1 was similar to that of MOF-HPW, with railings observed obviously; while for MOF-HPMoV2, some of the railings disappeared; as for MOF-HPMoV3 with 3 vanadium atoms, almost no railing was observed. It was conjectured that MOF structure changed under the influence of vanadium: 1) the structure turned to be 2D/3D distribution instead of 1D linearity; 2) A long-range disorder state was presented gradually.

<Insert Figure 1 here>

To further confirm the structure of MOF-POMs, X-ray Diffraction (XRD) studies were carried out. Figure 2 showed XRD patterns of MOF-HPW, MOF-HPMo, MOF-HPMoV, MOF-HPMoV2 and MOF-HPMoV3 respectively, and the results for MOF and POM raw materials were listed in supplementary information. As demonstrated in Figure 2, XRD patterns of MOF-POMs exhibited combination of MOF and POM raw materials when compared with those of pure POMs. Viewing the sharp reflections at low angles, mesoscopic structure of high degree of ordering was confirmed. Also, it could be found that though XRD patterns of MOF-HPW and MOF-HPMo were similar, the results changed a lot for MOF-HPMoV series. It was in accordance with TEM results that one-dimensional structure of MOF may be changed under the influence of vanadium. Furthermore, the intensity of small-angle diffraction weakened gradually with increasing vanadium contents, indicating that the structure of MOF-POMs became less ordered, and a short-range order state was seen away the long-range one.

<Insert Figure 2 here>

Thermogravimeric (TG) analysis was also applied to the catalysts as shown in Figure 3. Within 100°C, the weight loss was probably attributed completely to the absorbed water molecules, with MOF-HPMo being the most obvious one. Weight loss at 320~370°C could be exhibited for all the MOF-POMs, which was due to the decomposition of organic skeleton, while the weight loss between 400~450°C was attributed to the decomposition of POMs, with MOF-HPW at 400°C and MOF-HPMo at 450°C. As for MOF-HPMoV series, the two sections were a little merged probably due to the similar decomposition temperature. Besides, loading amount of POMs could be further calculated from the TG results, which would be useful in the following discussion. Interestingly, for MOF-HPW catalysts of different loading amount, the ratio of weight loss for organic frameworks also tended to be different. As shown in Figure 3, when the loading amount of HPW increased, the weight loss at 320~370°C reduced gradually. It was conjectured that POM in cavity stabilized the microporous structure by means of synergism between the metal and Keggin ions.[12a] With the increment of POM contents, the ratio of cavity reduced accordingly, resulting in the reduction of weight loss for bare MOF decomposition.

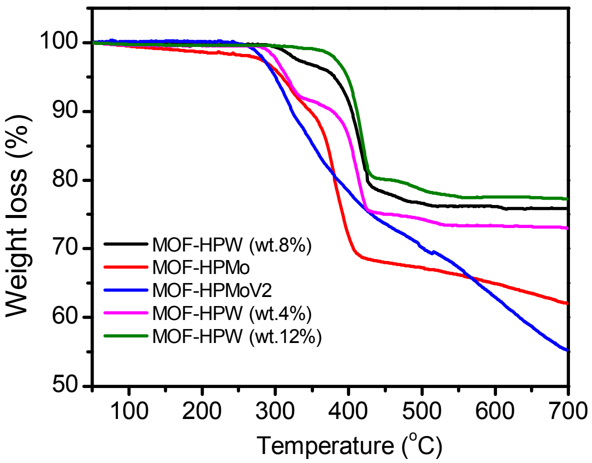

Fig. 3 Thermogravimeric analysis of prepared MOF-POMs.

Analysis of products distribution

To study the catalytic performance of MOF-POMs and establish reaction pathways, reaction samples (0.1mL each time) were taken at 0.5 h, 6 h, 12 h, 24 h and 48 h respectively, and assessed by GC-MS after removing the catalyst. Taking MOF-HPW as a typical catalyst, products distribution at different reaction time was shown in Figure 4, and the results for other catalysts were listed in supplementary information. As can be seen, detected main products consisted of ethanol, acrolein, 3-hydroxy-2-oxopropanal (HOP), ethyl propanoate, propyl acetate, 2,4-dimethyl-1,3-dioxolane(DMDO), 2-methyl-1,3-dioxolane-4-methanol (MDM) (DMDO and MDM together were termed as DOA) and aromatics. Except for gaseous products, ethanol was the smallest molecule detected in GC-MS and its concentration was always at a low level. Acrolein was only found during the beginning 0.5 h and disappeared after 6 hours. Acids took up about 40% in products distribution. Though it still accounted for the majority, the value was obviously much lower compared with other POM catalyzed systems. This was because acids were further reacted and transformed into esters such as ethyl propanoate and propyl acetate, which occupied about 30% in the products distribution. DMDO and MDM constituted another series of products with a total percentage around 10-15% during the whole reaction process. By-product aromatic compounds could be observed after long time reaction. Among all the products, acrolein and aromatic were either of low concentration or non-existent, which were difficult and also did not need to be analyzed for comparison. So they were ignored in the following discussion. Unlike gas phase reaction at high temperature (more than 200°C), coke was completely avoided in this system at least within 48 hours, which was benefit for the life length of catalysts. During the reaction, bubble was observed all the time and gas products were collected and assessed to contain CO and CO_2. Limit to the experimental condition, it was difficult for us to make sure the accurate ratio of the gas. But their percentages were usually no more than 10% in total according to reported results by Corma and Martinuzzi,[14] so they were not taken into account in the total conversion.

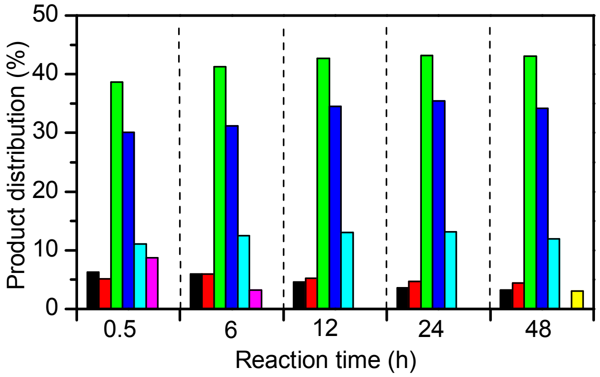

Fig. 4 Products distribution of glycerol transformation over MOF-HPW (8%). Reaction conditions: glycerol 5 mmol, deionized H_2O 2 mL, H_2O_2 (1 mL a.q., 30% w.t.), MOF-HPW 20 mg, 40°C, 24 h. ■: ethanol; ■: HOP; ■: acids; ■: esters; ■: DOA; ■: acrolein; ■: aromatics

Based on the aforementioned results, Scheme 1 summarized a proposed reaction network of glycerol and its sub-products in this system. Products detected by GC-MS were labeled by dashed lines. As shown in the scheme, the main reaction was the dehydration of glycerol with H_2O elimination, including inter-molecular dehydration and intra-molecular dehydration. The former one gave DOA as the main and also the final products. As for the latter one, 3-hydroxypropanal and hydroxyacetone were generated as products, but further reaction would proceed for both of them. 3-hydroxypropanal would be dehydrated into acrolein, which was oxidized into propionic acid finally. The transformation of hydroxyacetone was a little complex. Different products were obtained with the leaving of OH group or H only, which would turn into various acids and alcohols through a series of transformations, acting as the resources for esterification. Even if some other compounds such as acetaldehyde, formaldehyde, 1-propanol, 1,3-propanediol and so on were not detected in the final products, it is interesting to see what type of products they formed over the catalyst. For example, we confirmed the presence of 2-methyl-1,3-dioxolane-4-methanol (MDM) during glycerol transformations, which was supposed to be created by cyclizing of glycerol and acetaldehyde. Ethanol was also generated though hydrogenation of acetaldehyde. Moreover, acetaldehyde and formaldehyde may also be decomposed into CO/CO_2 and H_2. So acetaldehyde was the key intermediate to produce subsequent products which has been confirmed by Corma as well.[14a] Actually, some authors have captured some of the intermediates in their experiments.[15]

<Insert Scheme 1 here>

Study on the mass-transfer effect and loading amount

In usual case, as reported by other researchers,[14a,15b,16] transformation of GLY would stop at certain steps, with acrolein, several acids, dioxolane derivatives and sometimes aromatics generated as the final products. However, in our

MOF-POM catalytic system, an interesting phenomenon was observed that the percentage of acids decreased, while their esterified products were found to be part of main products. We conjectured that there was a factor that forwarded the further reaction: the pore limitation of MOF structure. As shown in Figure 5, for reactions catalyzed by pure POMs or metal oxides supported POMs in either liquid or gas phase, the catalytic site was entirely exposed. In this case, the formed acrolein and acids, after leaving the catalyst surface, would be easily taken away by solvent or gas. Thus their concentration around the surface was too low for further reaction and they become the final products. While for MOF-POM catalyst, the pore limitation of MOF introduced a mass-transfer effect thus a unique condition for reaction was provided. Although the formed acrolein and acids desorbed from catalyst surface, it was difficult for them to diffuse into solvent immediately. Thus, the diffusion limitation created an environment easy for accumulation of acrolein and acids around catalyst surface in pore. Afterwards, they may be adsorbed again and decomposed or oxidized into other compounds. But another possibility, especially for the acids, is that they reacted with alcohols to form esters derivatives. Here in our study, with the existence of alcohols, it was reasonable that esters become one of the main products as detected by GC-MS. As is known,[17] Fischer-Speier esterification is easy to happen in acidic and oxidative (metal oxides on surface) conditions between these acids and alcohol derivatives.

The mass-transfer effect can be further confirmed when comparing the results in Scheme 1 and Figure 3 carefully. It was found that ethanol, the smallest molecule except for gas products, was the only intermediate in cavity that released and detected. The size of MOF pore and POM was about 5 and 3 nm respectively. Other intermediates of larger molecule were restricted in the narrow pathway where they could react with other species benefitting from the assistance of POM catalyst and its own high activity. Ester products could gradually diffuse to the solvent attributed to their relative inertia under this condition.

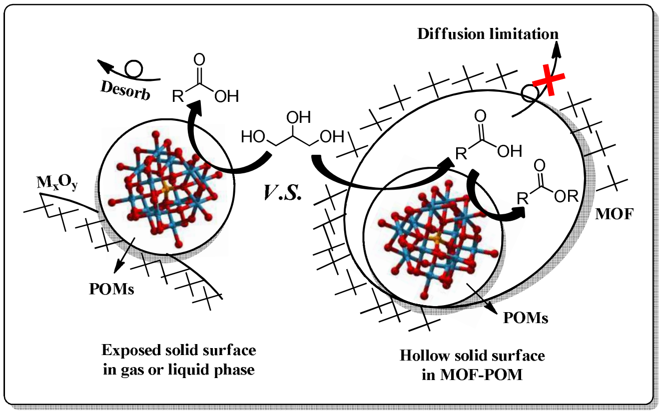

Fig. 5 Diffusion limited glycerol transformation on MOF-POMs.

The effect of loading amount was studied as shown in Figure 6. Conversion showed a raising trend when loading amount increased, as it also led to the increment of catalytic active sites. But the growth from 4% loading amount to 8% was more obvious than that from 8% to 12%, indicating that catalytic performance was also affected by mass-transfer effect in addition to loading amount. When catalyst of 4% loading amount was used, proportion of esters in products was lower than that of 8% and 12%. It was conjectured that the poor conversion led to lower concentration of acid, which was unfavorable for further esterification. Furthermore, it was found that the generation of esters was retarded with catalyst of 12% loading amount when compared with the results of 8%, since the formation of alcohols was also slowed down. The ratio of DOA in 4% catalytic system was much higher than the other two. It increased along with reaction time, but for 8% catalyst almost no changes were observed. As for 12% catalyst, the value decreased instead. The reason was supposed to be the substantial transformation of glycerol, resulting in the reduction of glycerol that adsorbed on the surface of catalyst, and the chance for DOA generation as well. Considering both conversion and selectivity of esters, MOF-HPW of 8% loading amount was used unless otherwise noted.

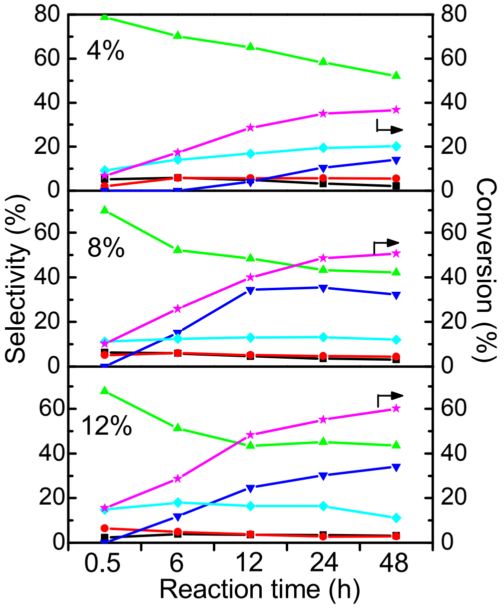

Fig. 6 Glycerol transformations on MOF-HPW with different loading amount. Reaction conditions: glycerol 5 mmol, deionized H_2O 2 mL, H_2O_2 (1 mL a.q., 30% w.t.), MOF-HPW 20 mg, 40°C. ■: ethanol; ●: HOP; ▲: Acids; ▼: Esters; ◆: DOA; ★: Conv.

When turnover frequency (TOF) was used to evaluate the reaction, mass-transfer effect could be demonstrated more clearly according to the results of loading amount, The number of active sites per nm^2 for POM could be calculated according to equation 1 and TOF was obtained based on equation 2, representing the conversion rate per active site per second. The results of BET, POM density and TOF with MOF-HPW of different loading amounts were listed in Table 1. As can be seen, when loading amount increased from 4% to 8%, TOF could not maintain at the same level and decreased by about 30%. With loading amount further increased to 12%, a more obvious reduction in TOF was observed. That is to say, the reaction per active site turned to be slower with the increment of loading amount. Also, the decrease of TOF was more obvious when compared with other reported catalysts with higher density (due to the smaller surface area). So we concluded that it was not loading amount but mass-transfer effect that restricted TOF, as it led to the difficulty for GLY to go into MOF cavity. Without enough GLY existed around HPW catalyst, reaction was slowed down. Considering this, TOF was not suitable to describe the reaction rate hence conversion would be still used in the following discussion.

Equation1:

$$\text{POM density (nm}^{-2}\text{)}=\frac{[\text{POM loading (wt\%)}]\times 6.02\times 10^{5}\,(\text{mol}^{-1})}{\text{BET area of Cat. (m}^{2}\bullet\text{g}^{-1})\times\text{M.W. of POM (g}\bullet\text{mol}^{-1})}$$

Equation 2:

$$\text{TOF [mol (mol POM*h)}^{-1}]=\frac{\text{Num. of reacted GLY (mol)}}{\text{Num. of POM loading(mol)}\times\text{ Time (hour)}}$$

Table 1 BET and POM density

Catalyst	HPW loading (w.t.%)	BET surface area (m^2/g)	POM density (nm^{-2})	TOF (mol(mol POM*h)$^{-1}$)
MOF-HPW(4%)	4.3	710	1.28×10^{-2}	243.49
MOF-HPW(8%)	8.1	660	2.57×10^{-2}	180.02
MOF-HPW(12%)	11.3	430	5.49×10^{-2}	159.84

Reaction conditions: glycerol 5 mmol, deionized H_2O 2 mL, H_2O_2 (1 mL a.q., 30% w.t.), catalyst 20 mg, 40°C, 24 h.

The role of each element in catalytic system

To highlight the advantage of our catalytic system and determine the role of each element, comparison experiments were carried out and the results were listed in Table 2. As can be seen, in blank experiment without catalyst, only 6.1% of glycerol was reacted even increasing the temperature to 90°C. Only acid derivatives were detected as main product such as glycolic acid, formic acid and acrylic acid. When bare MOF without POM was added to reaction mixture, the conversion improved slightly, and ester products appeared, although of a low percentage. Sarkar [9] described that Cu nano-cluster was benefit for the generation of acids in the form of Cu^+-Cu^{2+} on its surface under oxidative condition. But it was not clear whether the Cu^{2+} in our MOF would play the same role that led to the growth of conversion. To our knowledge, few reports about similar situation are available until now and our further research is still ongoing [19]. The difference of results between POM and MOF-POM confirmed that POM was the real catalytic site for the whole reaction while MOF provided a particular environment which would significantly vary the products distribution. Besides, if O_2 was used as oxidant instead of H_2O_2, the conversion dropped greatly to 12.7%. It was indicated that the weak acidity of H_2O_2, except for its oxidative property, may be also essential for this catalytic cycle. Also, the high potential of polyoxometalates (POMs) for activation of H_2O_2 has been established generating metal-oxo species, thanks to the nanoarrays of d^0 transitionmetal ions such as W^{VI}, Mo^{VI}, and V^{V} exposed on their surfaces. [20]

Two other types of supported POM catalysts, for liquid and gas phase GLY transformations respectively, were listed here for comparison. Since there was no pore limitation for these two catalysts as that for MOF, almost no mass-transfer effect was observed. Acids or acrolein as the intermediate in our catalytic system easily diffused into the environment and became final product. On the other hand, however, the mass-transfer effect of nano-pore also led to lower conversions compared with the exposed condition.

<Insert Table 2 here>

Study on the effect of acidic and oxidative conditions

According to the above mentioned speculations, both acidic and oxidative conditions seemed to be essential factors for the reaction cycle. Further experiments were carried out varying pH values and POM types with different oxidative ability to investigate their importance.

The catalytic performance with different pH values (adjusted by diluted HCl or NaOH solution) was tested and compared as shown in Figure 7. Reactions of pH=4 and pH=6 gave almost the same results, with both similar yields and similar products distribution. When reactions were carried out under neutral or alkali conditions, however, conversion decreased by a half compared with acid conditions. Lower proportion of acids, DOA and esters while higher proportion of alcohols at pH=8 demonstrated that esterification was impeded with decreased H^+ concentration. The pH values after reactions were measured again. With original pH values set at 4, 6 and 8, they turned to be 4, 4 and 6.5 respectively when reaction completed, which all tended towards the formation of acids. The concentration of H_2O_2 after reaction was also determined through titration, as listed in Table S1 in supplementary information. Similar products distribution and H_2O_2 concentration for pH = 4 and 6 may be just resulted from their similar variation trend in pH value. Organic acid was not very strong in acidity and pH=4 may be its low limitation. As for the solution of pH=8, the concentration of H_2O_2 was much lower, probably due to the faster decomposition in such conditions. If another 1 mL of H_2O_2 was added again to continue the reaction, the pH value would be finally similar to the other two conditions and the concentration of H_2O_2 also increased a little, exhibiting a similar trend of pH value. The products distribution, variation trend of pH value and concentration of H_2O_2 were consistent with each other. The results indicated that reaction in water solvent (with the weak acidity of the catalyst) gave the best results and no adjustment of pH value was needed. Thus a relative mild system was achieved.

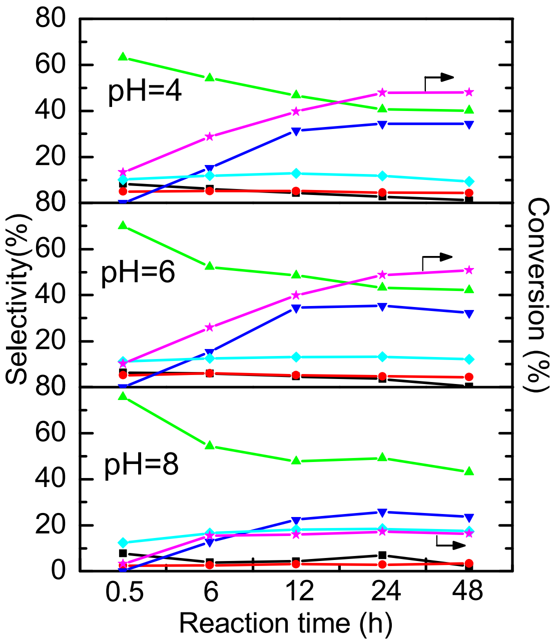

Fig. 7 Effect of different pH values on selectivity and conversion of glycerol transformation. The pH value with MOF-HPW and H_2O_2 in water solvent without adjustment was about 6. Reaction conditions: glycerol 5 mmol, aqueous solvent with appropriated pH value 2 mL, H_2O_2 (1 mL a.q., 30% w.t.), MOF-HPW 20 mg, 40°C, 24 h. ■: ethanol; ●: HOP; ▲: acids; ▼: esters; ◆: DOA; ★: Conv.

The influence of POM type which could affect the oxidation results of glycerol was also studied. Several MOF supported POMs with different oxidizability were prepared and used for catalytic oxidation of glycerol for comparison. As shown in Figure 8, MOF-HPW and MOF-HPMo gave almost the same results, probably due to their similar oxidizability. When vanadium was introduced into POMs, oxidizability of the catalysts increased along with the V contents, so was the conversion. Also, stronger oxidizability led to higher proportion of acids but lower proportion of esters. It was resulted from the decreased ratio of alcohols as their intermediate aldehydes turned into acids more easily under stronger oxidizability. Generation of DOA was almost not influenced by POM type, because the concentration of glycerol and pH value that would affect its generation remained almost the same with various POM types. On the other hand, HOP increased obviously along with V contents, showing a tendency similar to acids. It was indicated that analogous formation mode and environmental condition were shared between HOP and acids.

As analyzed above, the structure of catalysts tended to be 2D/3D distribution instead of 1D linearity with the introduction of vanadium atom, but its influence on catalytic performance was not obvious. This was because the introduction of vanadium atom into POM was of atom substitution, and the main part of POM remained almost unchanged. So was the pore size and POM size. The factor that affected by POM variation was oxidizability which worked in catalytic performance.

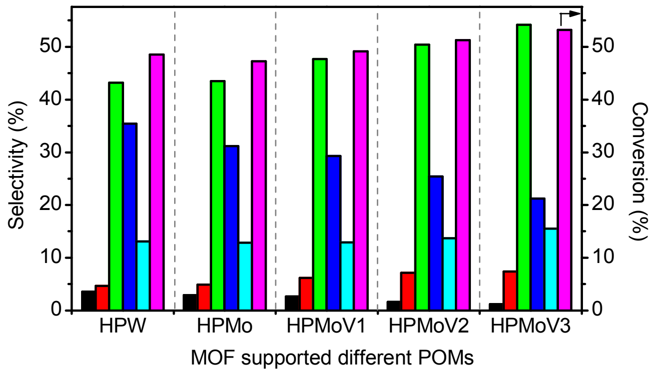

Fig. 8 Effect of different POM types on selectivity and conversion of glycerol transformation. Reaction conditions: glycerol 5 mmol, deionized H_2O 2 mL, H_2O_2 (1 mL a.q., 30% w.t.), catalyst 20 mg, 40°C, 24 h. ■: ethanol; ■: HOP; ■: acids; ■: esters; ■: DOA; ■: Conv.

Study on recycling and mechanisms

With MOF-HPW as model catalyst, the reusability was further studied. As shown in Figure 9, recovered MOF-HPW can be reused for at least 4 times without great loss of activity, with conversion decreased a little after each run. XRD pattern of the reused catalyst in supplementary information (Figure S4) disclosed that the structure of MOF remained relatively stable during 4 times' cycles. The existence of POM improved the stability of MOF, as mentioned above. On the other hand, esters and acids were always the main products, but the selectivity of esters dropped gradually as opposed to acids. It was probably due to the gradual collapsing of MOF structure during the repeated tests, as the reflections at low angles for the reused catalyst weakened gradually in XRD pattern. The pore limitation effect or more exactly the mass-transfer effect was lost gradually, leading to the tendency for generation of acids under the catalysis of exposed POM.

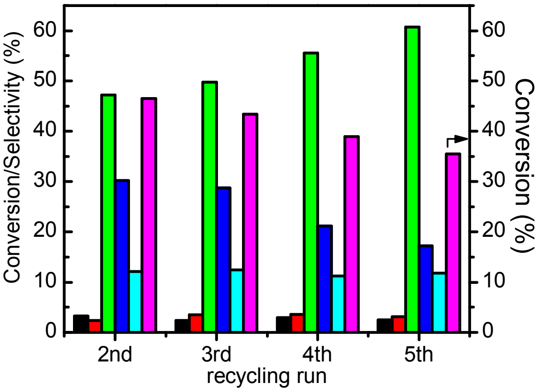

Fig. 9 The recycling study of MOF-HPW. Reaction conditions: glycerol 5 mmol, deionized H_2O 2 mL, H_2O_2 (1 mL a.q., 30% w.t.), 40°C, 24 h. ■: ethanol; ■: HOP; ■: acids; ■: esters; ■: DOA; ■: Conv.

Through refereeing literatures and our experimental results, a hypothetical possible reaction mechanism containing catalytic cycle was proposed as shown in Figure 10. The main reaction started from the adsorption and dehydration of glycerol on catalytic site. Dehydration of glycerol could occur at both terminal and secondary OH group. When it dehydrated at the terminal OH group, 2,3-dihydroxypropene was generated, which could further rearrange into 1-hydroxyl-2-propanone (Step 1.1). With the help of oxidative species, H^+ or the whole OH group were extruded at another terminal OH group to form two species: 2-oxopropanal and acetone (Step 1.2.1 and Step 1.2.2). Both of them were detected in GC-MS, demonstrating that there was an equilibrium between desorption and adsorption. The two species that still adsorbed on catalyst would be further oxidized, generating C1 and C2 compounds accompanying with the break of C-C bond (Step 1.3.1 and Step 1.3.2). C1 compounds were mainly released as CO_x gases while C2 compounds would turn into acids and alcohols.[21] Part of the acids, activated by Lewis acid site on POM surface, would undergo Fischer-Speier esterification process to produce ester products through removing one H_2O molecular (Step 1.4).

As for the dehydration at secondary OH group, either 1,3-dihydroxypropene or 3-hydroxypropanal would be generated (Step 2.1). They were further dehydrated into acrolein also because of their high reactivity (Step 2.2), which was the identified product before 6 h. Furthermore, C-C bond in 3-hydroxypropanal tended to cleave, leading to the formation of formaldehyde and acetaldehyde (Step 2.3), exactly as the reports of Chai et al. [22] and Tsukuba et al. [23]. According to previous computational study,[16] they proposed that the decomposition of 3-hydroxylpropenal would yield these two aldehydes through retro-aldol condensation. The aldehydes protonated by H^+ could 1) become their corresponding acids through oxidation; 2) decompose into CO/CO_2 and H_2; 3) form $-OH^+$ group with H^+ or -OH alcohol with H_2. With GLY adsorbed on catalyst, aldolization reaction may take place with the generated aldehydes (Step1.2.1) before it could go through dehydration process. Carbon of aldehyde group became more active under acid conditions as H^+ attacked the aldehyde group, followed by the combination with O from the two OH groups in GLY (Step 3.1 and Step 3.2). DOA was finally obtained after dehydration (Step 3.3).

<Insert Figure 10 here>

Conclusions

In general, a series of novel catalysts with MOF supported POMs were prepared and applied to the transformation of glycerol under mild conditions (water solvent, H_2O_2 oxidant, 40°C). Esters, which could serve for various industrial applications, were found to be one of the major products in addition to acids in this system. The investigation showed that they were generated through oxidative esterification of GLY. Different from other reported methods of GLY esterification where GLY served as alcohols and the addition of equimolar amount of acid was essential, no other reagents were needed during this process except for H_2O_2 and catalyst, which could be recovered after reaction for recycling. MOF in the catalyst provided a mass-transfer effect while POMs acted as active site in catalytic cycle. Acidic and oxidative conditions were also proved to be essential in the reaction. It was believed that this green, clean and mild process supplied a new way for GLY treatment which may be helpful to development of biodiesel industry in future.

Experimental section

Materials and Methods

All of the solvents and reagents in this work were purchased from commercial sources and used without purification. XRD data were collected with Cu_{Ka} radiation on Bruker C8 ADVANCE. GC-MS (Thermo ITQ 1100) equipped with capillary columns, TRACE TR-35MS (30 m × 0.25 mm ID × 0.25 µm film) and connected to a flame ionization detector (FID) was used to identify the composition. Gas chromatograph (Agilent 7890A) equipped with capillary columns, Agilent HP-5 (30 m x 0.25 mm ID x 0.25 µm film) and connected to a thermal conductivity detector (TCD) was used to identify the gas products. TEM images were taken on JEM-2100. Thermo gravimetric analysis (TGA) was performed on TGA/SDTA851e under N_2 atmosphere from 50°C to 700°C, with a heating rate of 10°C/min and N_2 flowing rate of 30 mL/min.

Synthesis of MOF-POM

MOF-POM was prepared according to ref. [12a] with some expansion. In a typical synthesis, copper (II) nitrate trihydrate (1.45 g, 6 mmol) and polyoxometalates of Keggin type (0.33 mmol) were dissolved in 12 mL distilled water. Another solution containing BTC (98%, 0.70 g, 2.8 mmol) and CTAB (0.12 g, 0.33 mmol) dissolved in 16 mL absolute ethanol was prepared and mixed with the solution above under vigorous stirring. The mixture was kept stirring for approximately 30 min at room temperature and then aged without stirring for further 5 days. After filtration, the solid product and washed with water before dried in air at 60°C for 24 h. To remove CTAB, Soxhlet extraction with ethanol was performed for 48 h at 105°C. Finally, the product was dried in air at 60°C.

General procedure for oxidative esterification of GLY

To a vial containing MOF-POM powder (20 mg, 8% w.t. loading amount) was added 2 mL deionized H_2O. The mixture was sonicated for 20 min followed by the addition of GLY (5 mmol) and H_2O_2 (1 mL a.q., 30% w.t.) respectively. The solution was stirred at 40°C for certain time. Samples (0.1 mL) were withdrawn periodically at 0.5, 6, 12, 24, 48 hours and centrifuged to separate the catalyst before analysis. However, due to the potential damage of water solvent to GC-MS instrument, samples in water solvent were tried to be avoided. So before injection into GC-MS to identify the composition and ratios of esterification products and DOA, samples were extracted with ethyl acetate. And MS was used assisting the identification under other conditions. If water was inevitable, for example, when quantifying acid products, ethanol was used to dilute samples. Since bubble was observed during reaction process, gaseous envelope (Teflon FEP, 250 mL) was used here to collect the gaseous products. Identification of the collected chemical gas was then performed with gas chromatograph.

Acknowledgements

We thank the Natural Science Foundation of China (NSFC No. 51374131) for support of this research.

Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of XRD results for MOF and POM raw materials, products distribution over MOF-HPMo and MOF-HPMoV1 series, as well as typical GC-MS results]. See DOI: 10.1039/b000000x/

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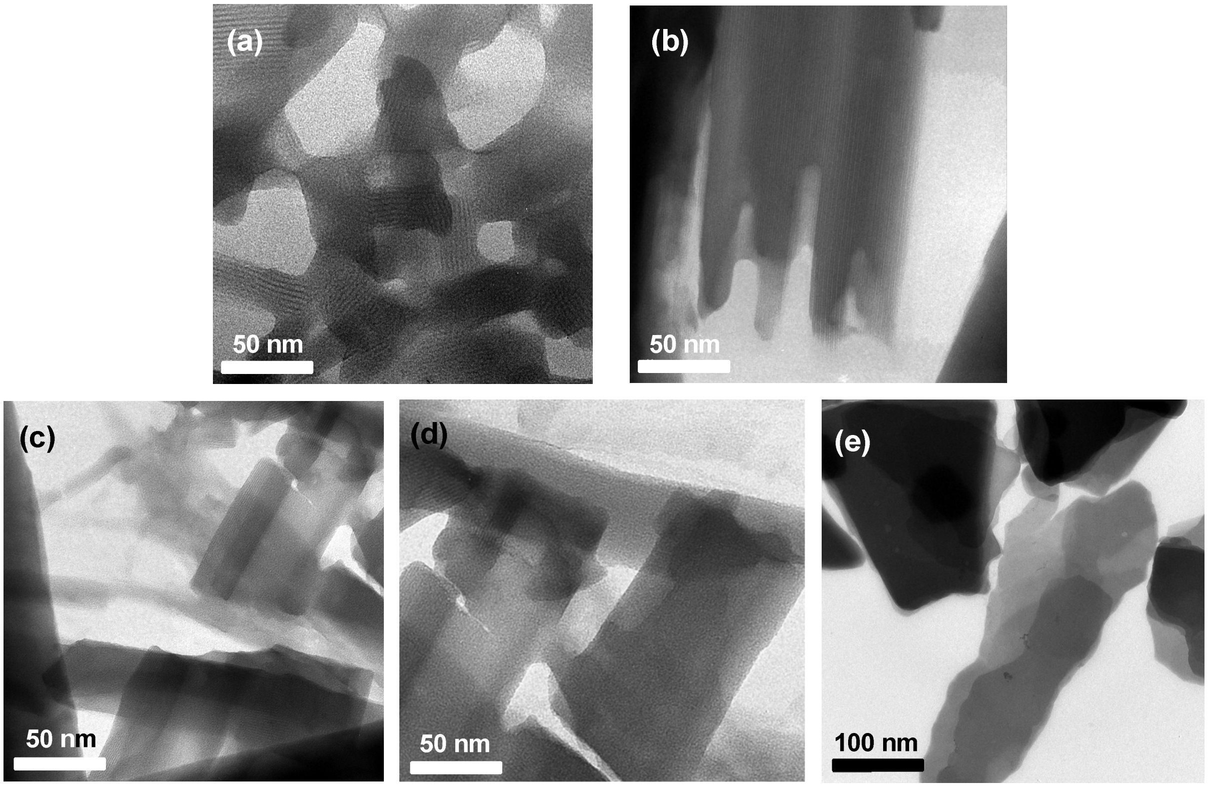


Fig. 1 TEM images of prepared samples: (a) MOF-HPW; (b) MOF-HPMo; (c) MOF-HPMoV1; (d) MOF-HPMoV2; (e) MOF-HPMoV3.

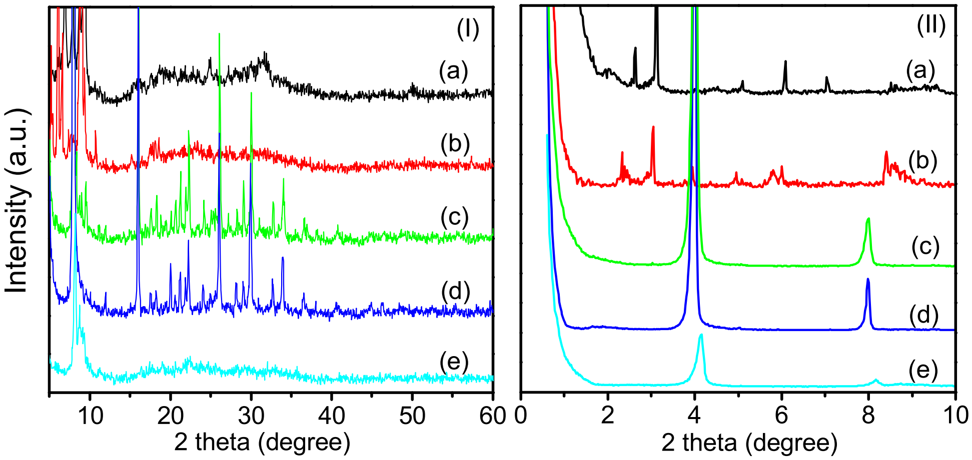
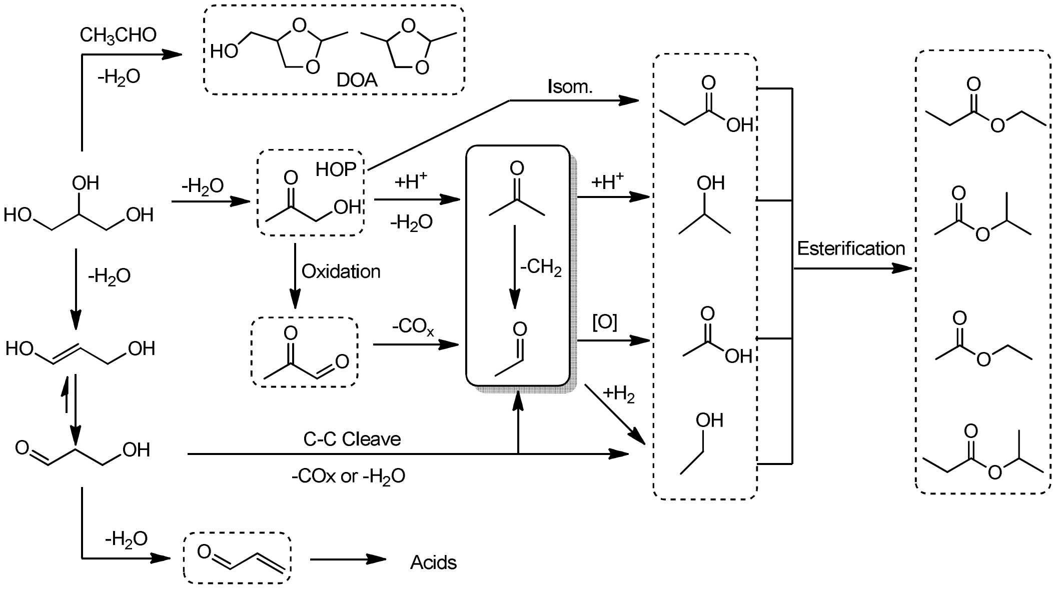


Fig. 2 X-ray Diffraction (I) and small-angle diffraction (II) patterns of (a) MOF-HPW; (b) MOF-HPMo; (c) MOF-HPMoV1; (d) MOF-HPMoV2; (e) MOF-HPMoV3.



Scheme 1 Pathway of glycerol transformation on MOF-POMs. Dashed lines represent products detected by GC-MS.

Table 2 glycerol transformation with different catalysts [a]

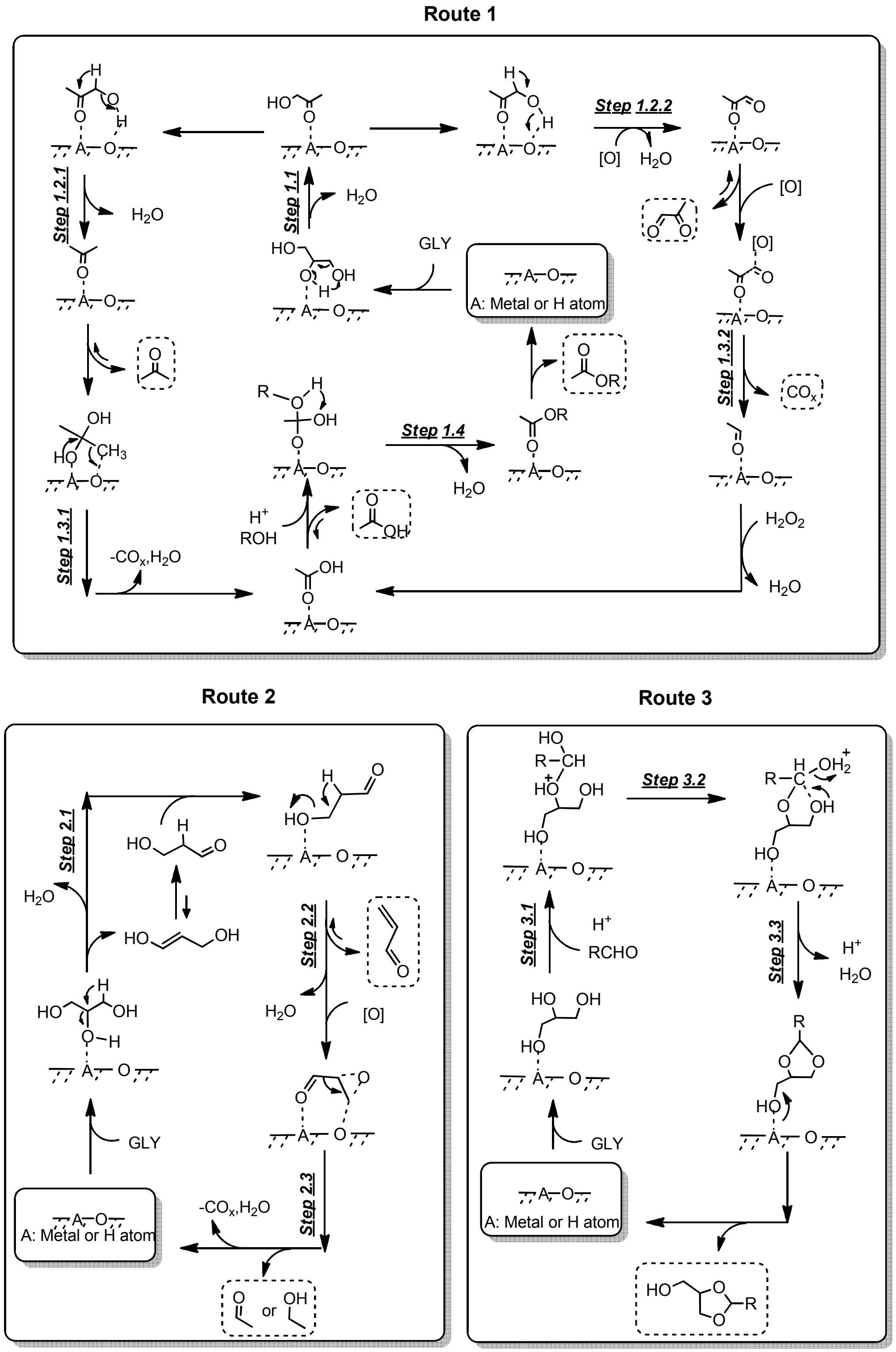
Catalyst	Glycerol conversion (%)	Product distribution (%)				
		Acids	Acrolein	Esters	DOA	Others [b]
Blank	6.1	90.0	--	--	--	10.0
MOF	10.3	30.2	3.2	9.2	16.5	40.9
HPW	50.5	45.7	10.4	--	21.9	22.2
MOF-HPW	48.6	42.7	--	34.5	13.0	9.8
MOF-HPW(O_2)	12.7	58.8	4.4	6.4	11.5	18.9
Al_2O_3-HPW(liquid) [c]	74.3	66.8	5.6	--	7.8	19.8
ZrO_2-HPW(gas) [d]	87.7	10.0	47.0	--	--	43.0

[a] Reaction conditions: glycerol 5 mmol, deionized H_2O 2 mL, H_2O_2 (1 mL a.q., 30% w.t.), catalyst 20 mg, room temperature, 24 h.

[b] Others included some detected compounds such as alcohols, HOP and aromatics.

[c] Ref. [7b].

[d] Ref. [18].



Route 1

Route 2

Route 3

Fig. 10 Possible reaction mechanism and key steps for glycerol transformation on MOF-POMs. Dashed lines represent products detected by GC-MS.