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Molybdenum arsenate crystal: A highly efficient and recyclable catalyst for hydrolysis of ethylene carbonate

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ABSTRACT

A simple one-step hydrothermal reaction was employed to synthesize the molybdenum arsenate crystallite catalyst, $[\{Cu(imi)_2\}_3As_3Mo_3O_{15}]\cdot H_2O$ (**1**) (imi = imidazole). The catalyst was characterized using X-ray crystallographic analyses, FT-IR, TGA, XRD, ICP-AES, NH_3-TPD and BET techniques. Moreover, we performed evaluation on its catalytic activity towards the hydrolysis of ethylene carbonate to produce ethylene glycol. Interestingly, the conversion of this reaction reaches 96.5% and the selectivity is close to 100% at optimum conditions. No polyoxometalate leaching or framework decomposition was observed and the catalyst can be recovered and reused with slight loss of reactivity under identical reaction conditions.

1. Introduction

Polyoxometalates (POMs) chemistry continues to be an interesting subject due to their diverse structures and unique properties [1–5]. The POMs with strong Brønsted acidity have shown great potentiality in catalysis [6–8], such as in water splitting [9,10], epoxidation of alkenes and alkenols [11–14], hydration of alkenes, esterification, alkylation [15–19], bromination of alkenes, alkynes and aromatics [20,21], and biphasic oxidations with hydrogen peroxide [22]. However, catalyst separation and reuse have imposed great limitations for the applications of POMs for catalyzing most of homogeneous reactions. Moreover, many reported heterogeneous POM catalysts supported on silica [23–27], activated carbon [28,29] and mesoporous molecular sieves [30–33], always suffer from slow reaction rates, leaching of the active species, low loading, deactivation of acid sites, conglomeration or very complex preparation process, which are also not conductive to their applications as solid catalysts. Therefore, it is desirable to develop an efficient heterogeneous system with active, selective, environmentally benign, and recyclable POMs catalyst without additives. The POMs crystal has a suitable solid matrix and framework with integrity and stability, which can overcome the above-mentioned drawbacks and possess appropriate openings allowing for the diffusion of reactants and products. Thus, the POMs crystal is a promising material towards the challenging goal of catalysis.

The production of ethylene glycol from ethylene carbonate by hydrolysis is a well-known process. However, low ethylene glycol selectivity and use of large excess amount of water would cause high energy expenditure, making this process economically unattractive [34–37]. Hence, extensive efforts have been paid to explore the suitable catalyst for catalytic hydrolysis of ethylene carbonate. Here, we present a POM crystalline catalyst, $[\{Cu(imi)_2\}_3As_3Mo_3O_{15}]\cdot H_2O$ (**1**), whose crystal structure has been reported previously by our group [38]. The catalyst **1** was also characterized by X-ray crystallographic analyses, FT-IR, TGA, XRD, ICP-AES, NH_3-TPD and BET. In addition, the dependence of the conversion of hydrolysis on the reactions variables such as the large excess water, the amount of catalysts used, reaction temperatures, reaction time, reusability were also appraised. To the best of our knowledge, catalyst **1** represents the first example of efficient heterogeneous catalyst for preparation of ethylene glycol via hydrolysis of ethylene carbonate.

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Table 1
Catalytic performance of various catalysts for hydrolysis of ethylene carbonate.[a]

Entry	Catalyst	Solubility	Conversion[b] [%]	Selectivity[c] [%]
1	$[Ni_6(imi)_6(B\text{-}\alpha\text{-}H_3AsW_9O_{33})_2]\cdot 2H_2O$	Insoluble	0	–
2	$[Zn_6(imi)_6(B\text{-}\alpha\text{-}H_3AsW_9O_{33})_2]\cdot 2H_2O$	Insoluble	0	–
3	$[Mn_6(imi)_6(B\text{-}\alpha\text{-}H_3AsW_9O_{33})_2]\cdot 4H_2O$	Insoluble	0	–
4	$[Cu_4(phen)_4(HPO_4)_2(H_2O)_2(OH)_2]\cdot[HPMo_{12}O_{40}]\cdot H_2O$	Part of soluble	0	–
5	$[(CuO_6)(As_3O_3)_2Mo_6O_{18}][imi]_2$	Insoluble	90.7	>99
6	$(en)_6\{Cu(H_2O)Na[(Mo_6O_{12})(OH)_3(PO_4)(H_2PO_4)(HPO_4)_2][(Mo_6O_{12})\cdot(OH)_3(H_2PO_4)_2\cdot(HPO_4)_2]\}\cdot 5H_3O$	Part of soluble	27.2	92
7	$[\{Cu(imi)_2\}_3As_3Mo_3O_{15}]\cdot H_2O$	Insoluble	94.5	>99

[a] Reaction conditions: catalyst (0.05 mmol), ethylene carbonate (22.67 mmol), H_2O (30 mL), 95 °C, 4 h.
[b] Conversion of ethylene carbonate.
[c] Selectivity for the ethylene glycol product; by-products: diethylene glycol.

2. Experimental

2.1. Reagents and catalyst characterization

All reagents and solvents were purchased from commercial sources and were used as received. The IR spectra were obtained on Alpha Centauri Fourier transform IR (FT-IR) spectrometer with KBr pellet in the 400–4000 cm^{-1} region. The crystal data were collected on a Bruker SMART APEX II CCD diffractometer using Mo-Ka radiation (0.71073 Å) at 273 K. Thermal gravimetric analyses (TGA) were performed on a PerkinElmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C/min. The acidity of the catalyst was studied by temperature programmed desorption using NH_3 as probe molecule. NH_3–TPD experiment was performed using a Thermo Finnigan TPDRO 1100 apparatus equipped with a thermal conductivity detector. The catalyst **1** (0.1 g) was placed in the reactor, treated under 200 °C for 15 min in N_2 (20 mL/min). 10% NH_3 in helium gas was ramped at 1 °C/min for 60 min. The purging with N_2 was done at room temperature for 45 min to remove NH_3 in the gas phase. The analysis of NH_3 desorption was then carried out between 100 and 700 °C under helium flow (15 °C/min, 20 mL/min) and detected by thermal conductivity detector. Elemental analysis was performed on ICP-AES spectrometer (Thermo Scientific iCAP 6000 series). Surface area measurement (by BET method) was carried out on Micromeritics Gemini at −196 °C using nitrogen adsorption isotherms. The products of the catalytic hydrolysis reaction were analyzed using a gas chromatograph (Shimadzu, GC-14) equipped, with a FID detector and Agilent DB-1 column.

2.2. Preparation of catalyst 1

The POM crystal was prepared and characterized according to the literature. The detailed procedure is as follows: a mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.72 g, 0.58 mmol), $NaAsO_2$ (0.40 g, 2.96 mmol), $CuCl_2\cdot 2H_2O$ (0.35 g, 2.05 mmol), imidazole (0.27 g, 4.01 mmol) and H_2O (22 mL) was stirred for 60 min in air. The resulting gel was then transferred to a 30 mL Teflon-lined autoclave and kept at 160 °C for 6 days. After the mixture was slowly cooled to room temperature, light-yellow block crystals were isolated (yield ca. 42% based on Mo).

2.3. Typical procedure for hydrolysis of ethylene carbonate

In a typical experiment, ethylene carbonate (22.67 mmol), catalyst **1** (0.02 mmol) and H_2O (2 mL) were added to a 3-neck Pyrex flask (ca. 20 mL) equipped with a refluxing condenser, sampling tube and thermometer. Then the reaction mixture was stirred for 8 h under refluxing conditions and vigorous stirring, at a temperature of about 95 °C. After reaction, the catalyst was separated by filtration and subjected to a recycling experiment. The liquid was analyzed with the gas chromatograph.

3. Results and discussion

3.1. Screening of catalyst

Catalytic performance of POMs crystal for hydrolysis of ethylene carbonate is listed in Table 1. POMs crystals (entries 1–4) do not show catalytic activity for hydrolysis of ethylene carbonate. The POMs crystal (entry 7) was insoluble in the reaction and thus led to a liquid–solid heterogeneous system, exhibiting close to 100% selectivity with a high conversion of 94.5%. Moreover, POMs crystal (entry 5) also caused similar heterogeneous reactions and close to 100% selectivity with high conversions of 90.7%, indicating highly catalytic activity and selectivity of molybdenum arsenate crystal. In contrast molybdenum phosphate crystal (entry 6) was inactive and showed a low conversion of 27.2%.

3.2. Structure of catalyst 1

The structure of **1**, shown in Fig. 1, consists of a new molybdenum arsenate fragment $[As_3Mo_3O_{15}]^{3-}$, decorated with three $[Cu(imi)_2]$ complexes. The molybdenum arsenate fragment is constructed from three MoO_6 octahedras and three AsO_3 trigonal pyramids. The three MoO_6 octahedra are joined to each other by edge-sharing. The As_3O_7 group consists of three AsO_3 pyramids linked in a triangular arrangement by sharing corners and bonded to three MoO_6 octahedra via bridging oxygen atoms. In compound **1**, the N atoms of organic ligands and the O atoms of polyanions are linked to each other by means of hydrogen bonds, which make the crystal structure of compound **1** more stable (Fig.S1). Important atomic distances and bond angles are listed in Table S1.

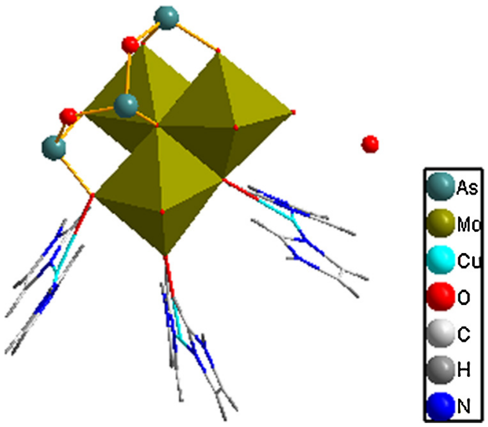


Fig. 1. Molecular structure of catalyst **1**.

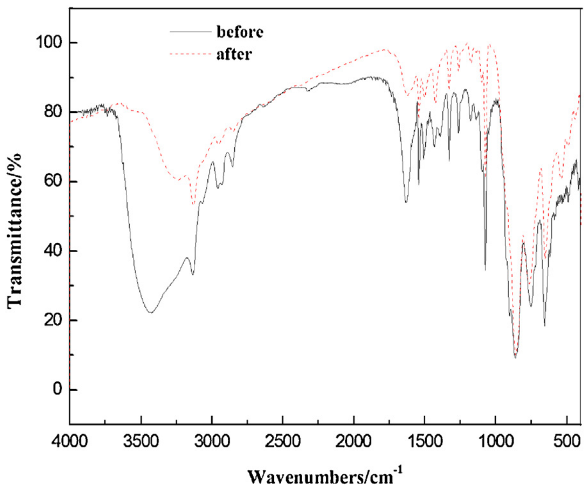


Fig. 2. The IR spectra of catalyst **1** before and after heated at 200 °C.

3.3. *Charaterization of catalyst **1***

An essential property of solid catalyst is the stability of the active component with respect to leaching and other transformations, and toleration for thermal or acid–base conditions. Catalyst **1** was stable for months under air atmosphere, and no efflorescence was observed. After rinsing in 0.02 M sodium hydroxide solution, or 0.02 M hydrochloric solution, or one of common organic solvents (methanol, ethanol, acetonitrile, acetone, chloroform, and DMF) under stirring at 80 °C for 10 h, no compound dissolution or framework decomposition occurs on catalyst **1**, or POM leaching from it, as evidenced by the single-crystal X-ray diffraction analysis. Moreover, after heated at 200 °C for 10 h, leading to the loss of isolated water molecule, catalyst **1** showed no evidence of POM framework decomposition in IR spectra (Fig. 2), confirming the maintenance of crystalline framework and indicating its high thermal stability.

The TGA curve shows a three-step weight-loss process (Fig.S2). The first step in the temperature range 160–193 °C corresponds to the loss of isolated water molecule. The second step occurs between 200 and 350 °C and corresponds to the loss of two imi ligands. The third step in the temperature range 370–436 °C is probably due to the loss of organic components and As_2O_3. The result of TG analysis basically agrees with that of the structure determination, reflecting that POMs have highly stable framework.

NH_3-TPD measurements were carried out to determine the acid strength and amounts of acid sites on the catalyst surface using ammonia as an adsorbate. The NH_3-TPD profile showed that the catalyst **1** had four desorption peaks (Fig. 3). Two peaks from 240 to 340 °C and the other two from 350 to 700 °C that were assigned to two types of acid site. These peaks corresponded to medium and strong acid sites with total acid density of about 2.1 mmol/g. The acid sites may be Brønsted acidity because imidazole ligands can give proton [39,40]. Surface area (BET method) for catalyst **1** was found to be 10.4 m^2/g.

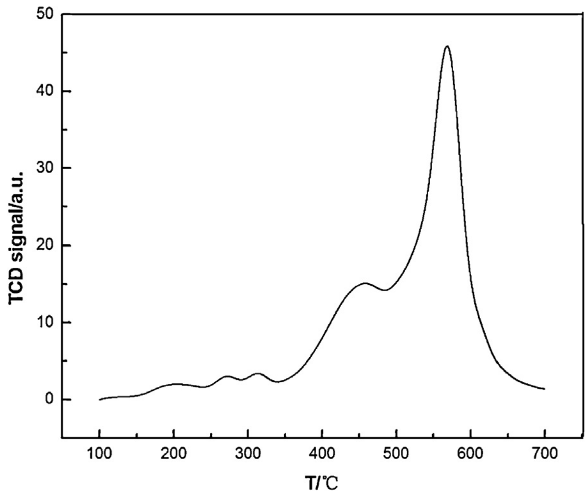


Fig. 3. NH_3-TPD of catalyst **1**.

3.4. *Catalytic performance*

To explore the optimum conditions for hydrolysis reaction on catalyst **1**, we studied effects of difference reaction conditions including temperature, time, the amount of catalyst and large excess water for hydrolysis of ethylene carbonate. Firstly, the effect of temperature on hydrolysis reaction was investigated at 45–95 °C (Fig. 4a). At 95 °C, 100% selectivity to ethylene glycol was achieved at a conversion closes to 80%. As expected, the conversion increased steadily as the temperature was raised from 45 to 95 °C. Based on the obtained results, the optimum catalytic performance (highest yield of ethylene glycol) was achieved at 95 °C. Secondly, the effect of reaction time on the catalytic performance is shown in Fig. 4b. When the time was less than 1 h, catalytic activity was almost unchanged. However, the activity increased remarkably when the time was over 6 h, and ethylene carbonate conversion exceeded 70%, when the reaction time reached 10 h. Thirdly, the catalytic performance is also influenced by the catalyst amount. In the present study, the catalyst amount was varied within the 0.005–0.02 mmol range and the reactant conversion increased remarkably with the catalyst amount, as shown in Fig. 4c. This can be explained by an increase in the number of acid sites. Beyond 0.02 mmol, the catalytic conversion curve was found to be almost flat. Finally, ethylene carbonate conversion reaches the highest value of 96.46% with 2 mL water (Fig. 4d), which shows that large excess water is adversely for the reaction. The experimental results show that 96.5% conversion and close to 100% selectivity could be achieved under the optimum conditions (catalyst (0.02 mmol), ethylene carbonate (22.67 mmol), H_2O (2 mL), temperature (95 °C) and time (8 h)).

We examined the hydrolysis of ethylene carbonate catalyzed by two molybdenum arsenate crystals (Table 2). Among them, catalyst **1** shows the highest activity, and a 96.5% conversion and close to 100% selectivity could be achieved after 8 h of reaction,

Table 2
The hydrolysis of ethylene carbonate catalyzed by molybdenum arsenate crystals.[a]

Entry	Catalyst	Time [h]	Conversion[b] [%]	Selectivity[c] [%]
1	$[\{Cu(imi)_2\}_3As_3Mo_3O_{15}]\cdot H_2O$	2	56.91	>99
2	$[\{Cu(imi)_2\}_3As_3Mo_3O_{15}]\cdot H_2O$	4	90.36	>99
3	$[\{Cu(imi)_2\}_3As_3Mo_3O_{15}]\cdot H_2O$	6	91.81	>99
4	$[\{Cu(imi)_2\}_3As_3Mo_3O_{15}]\cdot H_2O$	8	96.46	>99
5	$[(CuO_6)(As_3O_3)_2Mo_6O_{18}][imi]_2$	8	90.06	>99

[a] Reaction conditions: catalyst (0.02 mmol), ethylene carbonate (22.67 mmol), H_2O (2 mL), 95 °C.
[b] Conversion of ethylene carbonate.
[c] Selectivity for the ethylene glycol product; by-products: diethylene glycol.

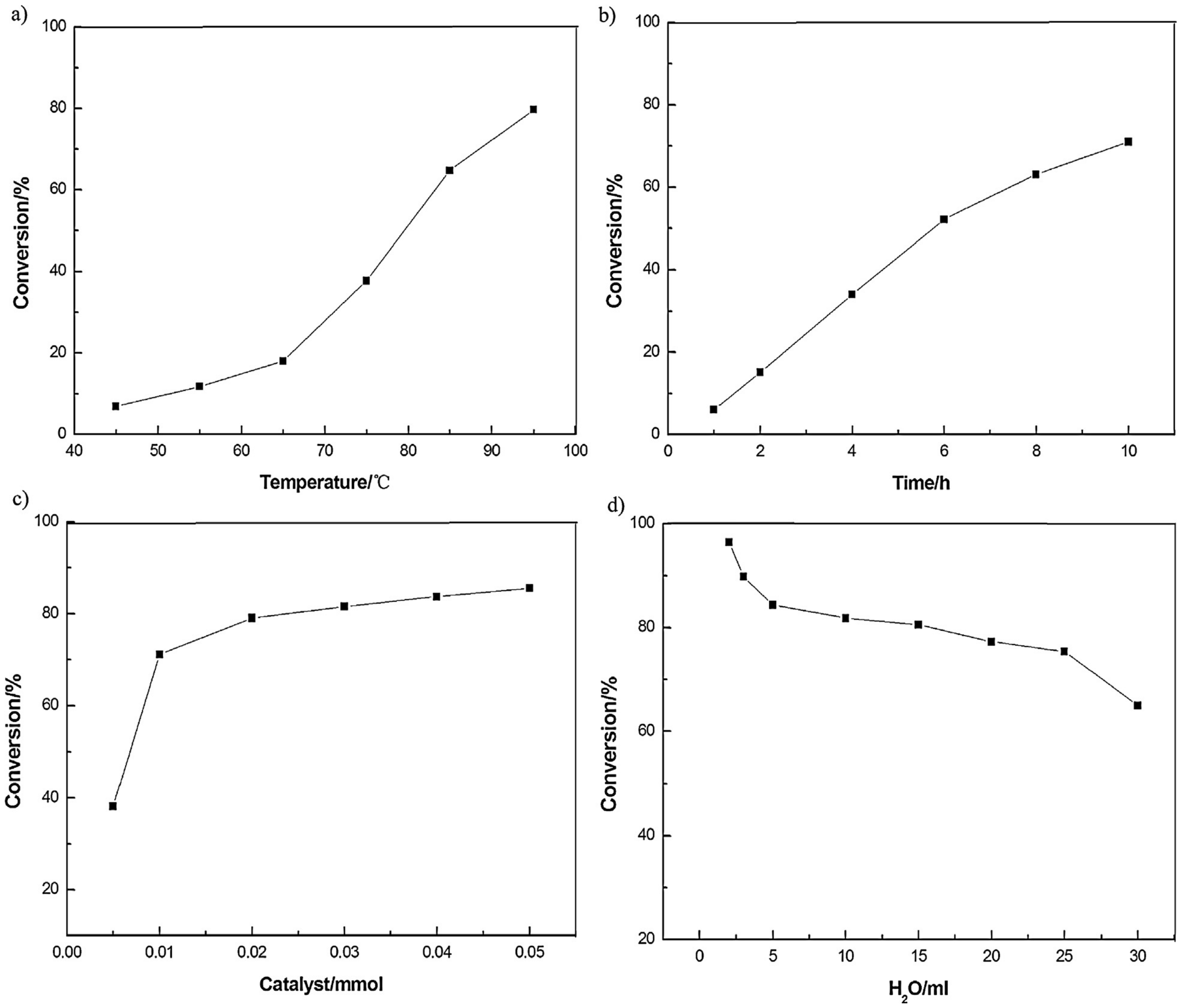


Fig. 4. Dependence of catalytic performance on (a) temperature, (b) time, (c) the amount of catalyst, (d) solvent (H_2O).

in comparison, catalyst $[(CuO_6)(As_3O_3)_2Mo_6O_{18}][imi]_2$ [41] shows a conversions of 90.1% at the same reaction condition.

3.5. Activity change after repeating of the reaction

The catalyst recycling is an important step as it minimizes the cost of the process. In order to test the reusability, the catalyst **1** was recycled and used for five times at same reaction conditions (Fig. 5). The slight drop in the activity was detected after five recycles indicating the efficiency of the catalyst. Elemental analysis performed by ICP-AES for filtrate shows Cu = 0.043%, As = 0.037% and Mo = 0.163%. The leaching amounts are negligible and the reaction completely stops after the removal of catalyst at the reaction temperature, which indicated the heterogeneous nature of the catalyst. The recovery of the present crystalline catalyst is explicitly more convenient than the previous homogeneous organic POM salt catalyst. Furthermore, not only can our new POM crystalline catalyst be comparable to the other classic POM catalysts in conversion, selectivity and reusability, but also is the preparation of the present catalyst much simpler, i.e., there is no need to strictly control the complex multiple-steps. Comparing the IR spectra (Fig. 6) of catalyst **1** before and after the reactions, it was found that there was almost no difference. Fig. 7 shows the XRD patterns of catalyst **1** before and after the reactions, exhibiting strong diffraction peaks

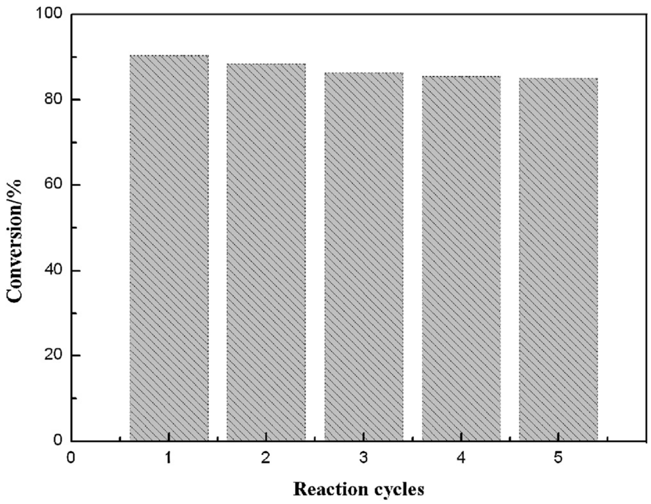


Fig. 5. Changes of catalytic activity of catalyst **1** for hydrolysis of ethylene carbonate with repeating the reactions (reaction conditions: catalyst (0.02 mmol), ethylene carbonate (22.67 mmol), H_2O (2 mL), time (4 h); temperature (95 °C)).

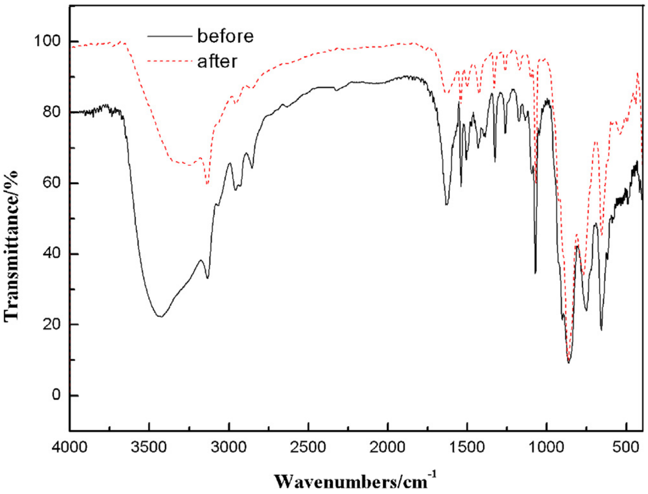


Fig. 6. The IR spectra of catalyst **1** before and after reaction.

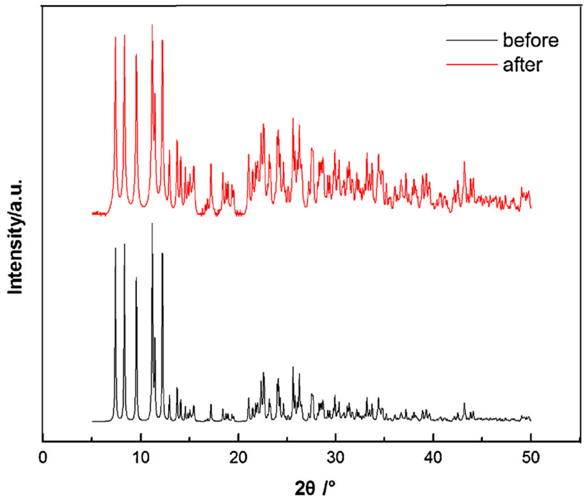
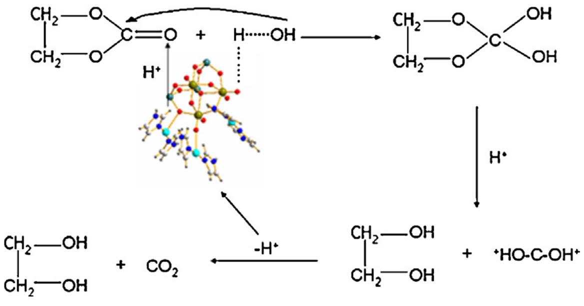


Fig. 7. XRD patterns of catalyst **1** before and after reaction.



Scheme 1. Proposed mechanism of hydrolysis catalyzed by catalyst **1**.

that correspond to fragment $[As_3Mo_3O_{15}]^{3-}$ and weak peaks that correspond to $[Cu(imi)_2]$ complexes. These results indicate a rather durable catalyst structure that accounts for the steady reusability.

3.6. Proposed mechanism

Scheme 1 shows the proposed mechanism of hydrolysis of ethylene carbonate. The ethylene carbonate and water in liquid phase penetrate and react in between in the lattice of catalyst **1**. The catalyst **1** would be expected to have a higher activity for the production of ethylene glycol from ethylene carbonate because it has more acid sites and higher acid density.

4. Conclusions

The molybdenum arsenate crystalline catalyst, $[\{Cu(imi)_2\}_3As_3Mo_3O_{15}]\cdot H_2O$, could be fabricated using the hydrothermal method. The catalyst **1** possesses 2.1 mmol/g acid density and high thermal stability, which exhibited better catalytic performance towards the hydrolysis of ethylene carbonate to produce ethylene glycol under optimum conditions. The mild and simple synthesis conditions of POM crystalline catalyst permit the one-step framework construction with integrity and stability. The new catalyst leads to the liquid solid heterogeneous hydrolysis of ethylene carbonate with green features of convenient recovery, steady reusability, high conversion and selectivity. Further studies directed to analogous reactions and their mechanistic understandings are underway. Our work may provide a useful guidance for further fabricate molybdenum-based catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.11.028.

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