



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



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## ARTICLE INFO

### Article history:

Received 13 August 2013

Received in revised form

14 November 2013

Accepted 23 November 2013

Available online 1 December 2013

### Keywords:

POMs crystal

Heterogeneous catalysis

Hydrolysis

Ethylene glycol

## ABSTRACT

A simple one-step hydrothermal reaction was employed to synthesize the molybdenum arsenate crystallite catalyst,  $[\{\text{Cu}(\text{imi})_2\}_3\text{As}_3\text{Mo}_3\text{O}_{15}]\cdot\text{H}_2\text{O}$  (**1**) (imi = imidazole). The catalyst was characterized using X-ray crystallographic analyses, FT-IR, TGA, XRD, ICP-AES,  $\text{NH}_3$ -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.

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## 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 conducive 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,  $[\{\text{Cu}(\text{imi})_2\}_3\text{As}_3\text{Mo}_3\text{O}_{15}]\cdot\text{H}_2\text{O}$  (**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,  $\text{NH}_3$ -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.<sup>a</sup>

Entry	Catalyst	Solubility	Conversion <sup>b</sup> [%]	Selectivity <sup>c</sup> [%]
1	[Ni <sub>6</sub> (imi) <sub>6</sub> (B-α-H <sub>3</sub> AsW <sub>9</sub> O <sub>33</sub> ) <sub>2</sub> ].2H <sub>2</sub> O	Insoluble	0	–
2	[Zn <sub>6</sub> (imi) <sub>6</sub> (B-α-H <sub>3</sub> AsW <sub>9</sub> O <sub>33</sub> ) <sub>2</sub> ].2H <sub>2</sub> O	Insoluble	0	–
3	[Mn <sub>6</sub> (imi) <sub>6</sub> (B-α-H <sub>3</sub> AsW <sub>9</sub> O <sub>33</sub> ) <sub>2</sub> ].4H <sub>2</sub> O	Insoluble	0	–
4	[Cu <sub>4</sub> (phen) <sub>4</sub> (HPO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (OH) <sub>2</sub> ].[HPMo <sub>12</sub> O <sub>40</sub> ].H <sub>2</sub> O	Part of soluble	0	–
5	[(CuO <sub>6</sub> )(As <sub>3</sub> O <sub>3</sub> ) <sub>2</sub> Mo <sub>6</sub> O <sub>18</sub> ][imi] <sub>2</sub>	Insoluble	90.7	>99
6	(en) <sub>6</sub> {Cu(H <sub>2</sub> O)Na[(Mo <sub>6</sub> O <sub>12</sub> )(OH) <sub>3</sub> (PO <sub>4</sub> )(H <sub>2</sub> PO <sub>4</sub> )(HPO <sub>4</sub> ) <sub>2</sub> ]}[(Mo <sub>6</sub> O <sub>12</sub> )(OH) <sub>3</sub> (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> .(HPO <sub>4</sub> ) <sub>2</sub> ].5H <sub>2</sub> O	Part of soluble	27.2	92
7	[{Cu(imi) <sub>2</sub> }] <sub>3</sub> As <sub>3</sub> Mo <sub>3</sub> O <sub>15</sub> .H <sub>2</sub> O	Insoluble	94.5	>99

<sup>a</sup> Reaction conditions: catalyst (0.05 mmol), ethylene carbonate (22.67 mmol), H<sub>2</sub>O (30 mL), 95 °C, 4 h.

<sup>b</sup> Conversion of ethylene carbonate.

<sup>c</sup> 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<sup>-1</sup> region. The crystal data were collected on a Bruker SMART APEX II CCD diffractometer using Mo-Kα radiation (0.71073 Å) at 273 K. Thermal gravimetric analyses (TGA) were performed on a PerkinElmer TGA7 instrument in flowing N<sub>2</sub> with a heating rate of 10 °C/min. The acidity of the catalyst was studied by temperature programmed desorption using NH<sub>3</sub> as probe molecule. NH<sub>3</sub>-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<sub>2</sub> (20 mL/min). 10% NH<sub>3</sub> in helium gas was ramped at 1 °C/min for 60 min. The purging with N<sub>2</sub> was done at room temperature for 45 min to remove NH<sub>3</sub> in the gas phase. The analysis of NH<sub>3</sub> 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<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O (0.72 g, 0.58 mmol), NaAsO<sub>2</sub> (0.40 g, 2.96 mmol), CuCl<sub>2</sub>.2H<sub>2</sub>O (0.35 g, 2.05 mmol), imidazole (0.27 g, 4.01 mmol) and H<sub>2</sub>O (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<sub>2</sub>O (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<sub>3</sub>Mo<sub>3</sub>O<sub>15</sub>]<sup>3-</sup>, decorated with three [Cu(imi)<sub>2</sub>] complexes. The molybdenum arsenate fragment is constructed from three MoO<sub>6</sub> octahedras and three AsO<sub>3</sub> trigonal pyramids. The three MoO<sub>6</sub> octahedra are joined to each other by edge-sharing. The As<sub>3</sub>O<sub>7</sub> group consists of three AsO<sub>3</sub> pyramids linked in a triangular arrangement by sharing corners and bonded to three MoO<sub>6</sub> 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.

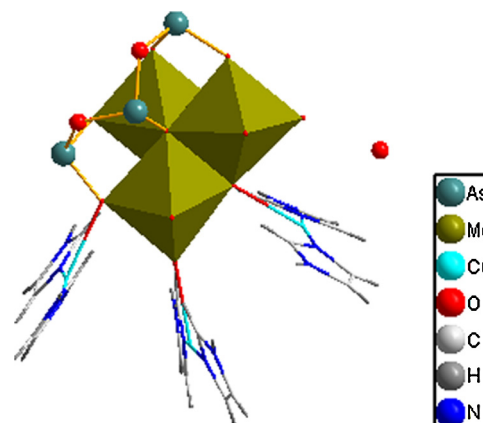


Fig. 1. Molecular structure of catalyst **1**.

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