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Facile Synthesis of a Polycatenane Compound Based on Ag-triazole Complexes and Phosphomolybdic Acid for the Catalytic Epoxidation of Olefins with Molecular Oxygen

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Abstract: A simple and efficient approach was developed for synthesizing a metal-organic polycatenated compound composed of Ag-triazole complexes and phosphomolybdic acid (PMA) clusters. The hybrid compound, namely $\{[Ag_2(trz)_2][Ag_{24}(trz)_{18}][PMo_{12}O_{40}]_2\}$ (1) ($trz = 1,2,4$ -triazole), showed high catalytic activity, selectivity and recyclability for the epoxidation of olefins with molecular oxygen as the oxidant and isobutyraldehyde as the co-reagent, and could even work well under ambient conditions. The special polycatenane framework, formed by interlocking $[Ag_{24}(trz)_{18}]^{6+}$ nanocages, provides suitable space for filling the PMA clusters. The existence of multi-interactions, including π - π stacking, Ag-Ag interactions, and electrostatic interactions, should play a determinative role in fabricating the catalytically active and stable PMA-based polycatenane catalyst for aerobic epoxidation of olefins.

Keywords: metal-organic polycatenane; heterogeneous catalysis; aerobic epoxidation; olefin

1. Introduction

Recently, a new family of supramolecular assemblies based on metal-organic compounds and polyoxometalates (POMs) has attracted great interest due to their potential applications in material science, magnetism, electrochemistry, nanomaterials, and catalysis [1–6]. As commonly used ligands, N-donor bridging bis(triazole) compounds have shown great advantages in constructing the POM-based metal-organic compounds with special structure and physicochemical properties [7–12]. Compared with conventional bipyridine ligands, bis(triazole) ligands are more flexible and have more coordination sites, which allow them to better conform to the coordination environments of POMs and metal cations.

By utilizing triazole and its derivatives as bridging ligands, some novel POM-based metal-organic compounds have been obtained [13–17]. Among them, a very interesting example reported by Lu's group showed that an infinite three-dimensional polycatenated framework of $\{[Ag_2(trz)_2][Ag_{24}(trz)_{18}][PW_{12}O_{40}]_2\}$ ($trz=1,2,4$ -triazole) could be synthesized by a hydrothermal reaction of trilacunary Keggin $Na_9[A-PW_9O_{34}]\cdot 7H_2O$, $Ag(O_2CCH_3)$ and 1,2,4-triazole [17]. The framework of the compound is composed of catenated polyhedral cages, which are constructed by mechanical interlocking of all of the vertices of the cages. The penetration of polycatenanes creates

nanosized voids for accommodating the POM anions, thus resulting in the formation of interpenetrated supramolecular architectures. Notably, the examples of the POMs-based polycatenated framework are rather rare, and it would be highly desirable to study its physicochemical properties, including its catalytic properties. However, the relatively complicated synthesis procedure, the usage of the scarcely used reagent of $\text{Na}_9[\text{A-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$, as well as the low synthesis yield (below 50% based on W) are a serious limitation towards further exploring the structure and function of this hybrid material.

Recently, Sha and coworkers reported a new route to synthesize three new POM-based Ag-trz compounds with polycatenane structure, which contain different Keggin ions ($[\text{SiW}_{12}\text{O}_{40}]^{4-}$, $[\text{AsW}_{12}\text{O}_{40}]^{3-}$, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$) [18]. In their work, corresponded polyoxometalic acid could be directly used for the synthesis of the hybrid compounds in case of a certain amount of NH_4VO_3 was added into the synthesis system. These POM-based polycatenanes exhibited promising discharge capacity and stable electrochemical performance as an anode material in Li-ion batteries.

In this work, we reported a very simple and efficient method for the synthesis of PMA-based Ag-trz polycatenane compound. The resulting compound was characterized by a variety of characterization means, and its catalytic performance was investigated for the so-called “Mukaiyama” epoxidation of olefins, in which molecular oxygen was used as the oxidant and isobutyraldehyde was used as the co-reagent. Previous literature studies suggested that a few Ag-complexes are moderately active homogeneous catalysts for these attractive O_2 -mediated hydrocarbon/olefin oxidation processes [19–24]. Our present work shows that the hybrid polycatenane compound shows much higher catalytic activity than the corresponded POM or Ag-trz complexes. More interesting, the hybrid compound is quite stable and easily recycled under the tested conditions, which could act as truly heterogeneous catalyst for achieving the molecular oxygen activation at quite a mild reaction condition.

2. Results and Discussions

2.1. Synthesis and Structure of the Catalysts

The one-pot reaction for the synthesis of catalyst **1** was used, which similar to the literature [17]. Some modifications were made in order to improve the successful rates and the product yield. For instance, the unsaturated phosphotungstic acid $\text{Na}_9[\text{A-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ was used for the synthesis of catalyst **1** in the literature [17], which needs to be synthesized beforehand. Our present work confirmed that the usage of $\text{Na}_9[\text{A-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ was not the best option due to the cumbersome synthesis strategy and the very low yield. A simpler synthesis strategy and relatively high yield of catalyst **1** can be achieved by optimizing synthesis conditions as described in the experimental section.

X-ray single crystal diffraction analysis revealed that catalyst **1** has a metal-organic polycatenation structure consisted of a three-dimensional infinite metal-organic polycatenated framework and $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ polyanions (Figure 1). This structure is consistent with the previous reported structure in literature [17]. As shown in Figure 2a, Ag^+ cations and triazole ligands generated the $\{\text{Ag}_{24}(\text{trz})_{18}\}^{6+}$ nanocage through Ag-N bonds. One nanocage, which has six-connected vertex angles, interlocked with other six ones through its vertices to form a 3D polycatenated framework (Figure 2b). The twofold 3D polycatenated frameworks interpenetrate one another to form the final structure (Figure 2c). PMA anions and Ag-trz framework combined through charge interactions between terminal oxygen atoms in polyanions and Ag^+ atoms in the 3-D framework. The Keggin $[\text{PW}_{12}\text{O}_{40}]^{3-}$ polyanions function not only as counteranions but also as templates to direct the formation of the polycatenated framework.

Figure 1. The metal-organic polycatenation structure of catalyst 1.

Figure 2. (a) The structure of one $\{Ag_{24}(trz)_{18}\}^{6+}$ nanocage. (b) View of a $\{Ag_{24}(trz)_{18}\}^{6+}$ nanocage (yellow) catenated by six others through its vertices. (c) The overall structure of the three-dimensional infinite polycatenated framework.

Figure 3 shows the SEM micrograph of catalyst 1. It can be seen that the crystal of catalyst 1 has uniform positive octahedral structure. The macroscopic crystal structure is consistent with the microscopic positive octahedral cage structure.

Figure 3. The SEM micrograph of catalyst 1.

The FT-IR spectrum of reference sample Ag- trz_3 is given in Figure 4. The peak at 1650 cm^{-1} belongs to the $-C=N-$ stretching vibration, and the two peaks appeared at 1147 cm^{-1} and 1062 cm^{-1} are attributed to the N-N stretching vibration in triazole ligand [25–28]. These results suggest that the structure of the triazole ring is well preserved in the reference sample Ag- trz_3 . Compared with the infrared spectrum of 1,2,4-triazole ligand (also shown in Figure 1), three new peaks appear at 2542 cm^{-1} and 2673 cm^{-1} and 2755 cm^{-1} in the infrared spectrum of Ag- trz_3 , while the two peaks belonging to

the >N-H stretching vibration at 3130 cm^{-1} and 1547 cm^{-1} disappear [29,30]. These changes should be an indication that triazole molecules are bonded with silver cations.

Figure 4. FT-IR spectra of fresh reference sample Ag-trz₃, fresh 1,2,4-triazole and fresh catalyst **1**.

2.2. Catalytic Properties

The catalytic performance of catalyst **1** and the reference samples of Ag-trz₃, CH₃COOAg and PMA were investigated for the epoxidation of *cis*-cyclooctene and 1-octene with air as the oxidant and IBA as co-reagent. As shown in Table 1, all catalysts are active for the epoxidation of olefins with nearly 100% selectivity to the corresponding epoxides. Among these, catalyst **1** shows the highest activity. The result of *cis*-cyclooctene epoxidation by catalyst **1** exhibits that about 40% conversion is achieved after 1 h and the reaction is over after 3 h at the temperature of 40 °C. In comparison, the conversions of *cis*-cyclooctene by the reference samples of Ag-trz₃, CH₃COOAg and PMA are much lower (23%, 51% and 5% conversions of cyclooctene after 3 h, respectively). Notably, the pure PMA has very low catalytic activity under the tested conditions, while the Ag salts (CH₃COOAg) and the related Ag-trz₃ complex show moderate activity for the epoxidation of cyclooctene. These results suggest that silver species rather than PMA clusters are the main catalytically active sites for this reaction. Under the same reaction conditions, the reaction hardly proceed without a catalyst.

Table 1. Catalytic epoxidation of cyclooctene and 1-octene with O₂/IBA over various catalysts ^a.

Catalyst	Substrate	Product	Time (h)	Conversion (%)	Related work
1			3	96	this work
Ag-trz ₃			3	23	this work
CH ₃ COOAg			3	51	this work
PMA			3	5	this work
1 ^b			2.5	94	this work
POM@MOF ^c			4	95 ^d	Ref-31
1			4	90	this work
Ag-trz ₃			4	15	this work
CH ₃ COOAg			4	37	this work
PMA			4	11	this work
POM@MOF ^c			7	73 ^d	Ref-31

^a Reaction conditions: catalyst 10 mg (0.001 mmol), substrate 1.0 mmol, CH₃CN 10 mL, flow of air 10 mL/min, IBA 2.0 mmol, reaction temperature 40 °C. All selectivities for the epoxide are ≥99%. ^b CH₃CN 5 mL.

^c [Ni(4,4'-bpy)₂]₂[V^{IV}₇V^V₉O₃₈Cl]₂·(4,4'-bpy)·6H₂O. ^d Reaction conditions: substrate 2.9 mmol, catalyst 0.02 mmol, IBA 5 mmol, CH₃CN 5 mL, air as oxidant at 35 °C.

Moreover, the reference samples Ag-trz₃, CH₃COOAg and PMA were obviously dissolved in the reaction mixture, revealing the homogeneous nature of these catalysts. By comparing with the related heterogeneous catalysts reported in literature work [31], we used less catalyst and isobutyraldehyde in the reaction, and also used a higher solvent dose. We therefore found that catalyst **1** has a much

higher activity than the nickel-complex modified polyoxometalate catalyst in literature [31] for the epoxidation of cyclooctene with O₂/IBA (Table 1).

In addition, the relatively inert terminal olefin of 1-octene can be also converted rapidly to the corresponding epoxide (90% conversion, nearly 100% epoxide selectivity after 4 h reaction) when 1 was used as catalyst. The activity of catalyst 1 is much higher than the other three reference samples.

These results proved that catalyst 1 not only exhibits much higher activity than reference sample Ag-trz₃, CH₃COOAg and PMA, but also has efficient selectivity in the epoxidation reaction systems of several olefins.

The effect of solvents on the catalytic activity of 1 was also investigated by the epoxidation reaction of cyclooctene with air/IBA (Table 2). It can be seen that CHCl₃- and EtOH- and CH₃CN- mediated reactions give the increasing conversions in turn at 60 °C. These results suggest that the catalytic performance of catalyst 1 was solvent dependent [32]. According to the characteristics of the solvent, it can be inferred that the conversions is related to the polarity of the solvent. The bigger the polarity is, the more favorable the reaction is.

Table 2. Effect of solvents on the epoxidation of cyclooctene over catalyst 1.

Entry	Solvent	Temperature (°C)	Conversion (%)
1	EtOH	60	64
2	CHCl ₃	60	62
3	CH ₃ CN	25	81
4	CH ₃ CN	35	89
5	CH ₃ CN	40	96
6	CH ₃ CN	60	98

Reaction conditions: catalyst 10 mg (0.001 mmol), cyclooctene 1.0 mmol, solvent 10 ml, flow of air 10 ml/min, IBA 2.0 mmol, time = 3 h. All selectivities for the epoxide are ≥ 99%.

Using CH₃CN as solvent, the temperature effect on the catalytic performance was also studied (Table 2, entries 3–6). “Green” in consideration of reaction conditions, the optimum temperature of the reaction is 40 °C.

In addition, the catalytic properties of catalyst 1 were also investigated for the epoxidation of other olefins. As shown in Table 3, relatively high activity and epoxide selectivity could be achieved for the epoxidation cyclohexene and styrene at mild reaction conditions. In particularly, this catalyst could also efficiently convert the bulky molecular of cyclododecene to the corresponding epoxide, with 82% conversion and 99% selectivity of epoxide at 61 °C after 6 h reaction. These results illustrate that catalyst 1 is highly efficient for the O₂/IBA-mediated epoxidation of a large scope of olefins.

Table 3. Epoxidation of Various Substrates with O₂ in Air Catalyzed by catalyst 1.

Entry	Substrate	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)	
					Epoxidation	Others
1		35	3	96	84	16
2		61	8	74	75	25
3		61	6	82	>99	–

Reaction conditions: catalyst 10 mg (0.001 mmol), substrate 1.0 mmol, CH₃CN 10 ml, flow of air 10 ml/min, IBA 2.0 mmol.

To verify the heterogeneity of the catalytic process, a leaching test was performed for the epoxidation of *cis*-cyclooctene and 1-octene over the catalyst 1. As shown in Figure 5, catalyst 1 shows

very high stability against leaching of the active species. Besides, catalyst **1** can be easily recovered from the reaction system by filtration. The recovered solid could be reused directly as catalyst for the next run after washing with water. Catalyst **1** can be reused for at least ten cycles without significant change of conversions, proving that this system has persistent activity during the recycling experiments (Figure 6). These results suggested that the metal-organic polycatenation is truly heterogeneous catalyst under the reaction conditions employed. The high structural stability of catalyst **1** might be mainly attributed to the formation of the hybrid framework based on the Ag-triazole framework and the PMA clusters, and the relatively strong interaction between them.

Figure 5. Kinetic profiles of the epoxidation of cyclooctene and 1-octene over the catalyst **1**. (x) Leaching experiments of the catalyst indicating conversion of cyclooctene and 1-octene with the catalyst removed after 4h at reaction temperature. Reaction conditions: catalyst 10 mg, substrate 1.0 mmol, CH_3CN 10 mL, flow of air 10 mL/min, IBA 2.0 mmol, reaction temperature 40 °C. All selectivities for the epoxide are $\geq 99\%$.

Figure 6. Recycling experiments of catalyst **1** for epoxidation of cis-cyclooctene with air/IBA. Reaction conditions: catalyst 10 mg, cis-cyclooctene 1.0 mmol, CH_3CN 10 mL, flow of air 10 mL/min, IBA 2.0 mmol, reaction temperature 40 °C, reaction time 3 h. All selectivities for the epoxide are $\geq 99\%$.

For oxidation/epoxidation reaction, utilization efficiency of sacrificial reductant and material balance is shown in Table S1. In addition, the typical GC charts are shown in supplementary materials.

FT-IR and XRD measurements were carried out to investigate the structural stability of catalyst **1**. The FT-IR spectra show that there is no obvious difference between the used catalysts (after the reaction of cyclooctene and 1-octene epoxidations) and the fresh one (Figure 7). The XRD patterns indicate that the characteristic diffraction peaks for the used catalysts are consistent with the fresh catalyst **1** (Figure 8). These results suggested that the structure of catalyst **1** is kept well during the reaction process.

Figure 7. FT-IR spectra of fresh catalyst **1** (a) and used one in cyclooctene epoxidation (b) and used one in 1-octene epoxidation (c).

Figure 8. XRD patterns of fresh catalyst **1** (a), used one in cyclooctene epoxidation (b), used one in 1-octene epoxidation (c) and the simulated pattern.

The XPS measurements were carried out for various samples. Figure 9 shows the Ag 3d spectra of catalyst **1**, Ag-trz₃ and CH₃COOAg. There are two major peaks of Ag 3d, assigned to Ag 3d_{5/2} at 368.55 eV and Ag 3d_{3/2} at 374.6 eV photoelectrons, respectively, indicating that Ag species existed in the form of Ag⁺ [29,33–38]. The Ag BE values for catalyst **1** shift positively compared with other samples, which can be assigned to the charge interaction between PMA ions and silver cations.

Figure 9. X-ray photoelectron Ag 3d spectra of catalyst **1**, Ag-trz₃ and CH₃COOAg.

The XPS spectra of N 1s is shown in Figure 10. For trz and Ag-trz₃, the appearance of binding energies at 399.7 eV is attributed to the N 1s of =N- or -NH- on triazole ring [39–41]. Compared with triazole, the binding energies of N 1s in the catalyst **1** shift positively (from 399.7 eV to 399.85 eV),

suggesting that relatively strong coordinative interaction is present between Ag^+ and triazole ligands in this catalyst.

Figure 10. X-ray photoelectron N1 spectra of catalyst 1, Ag-trz_3 and trz.

Figure 11 shows the Mo 3d spectra of PMA and catalyst 1. For PMA, the Mo 3d spectrum is deconvoluted into one doublet Mo3d5/2 at 233.3 eV and Mo3d3/2 at 236.5 eV, which is attributed to the Mo^{6+} oxidation state [42–44]. After introducing the PMA into the infinite three-dimensional polycatenated framework, the Mo3d peaks shift slightly toward lower binding energies (Mo3d5/2 at 232.75 eV and Mo3d3/2 at 235.85 eV), further reflecting the presence of interaction between PMA units and the polycatenated framework.

Figure 11. X-ray photoelectron Mo3d spectra of PMA and catalyst 1.

In general, the polycatenane compounds have a relatively large open framework, which is suitable for the diffusion of the reactants to increase the substrate contact with the catalyst active sites, thus helping to improve the catalytic activity [31,42,44]. Meanwhile, the formation of multidimensional supramolecular structure through multiple weak interactions, such as charge interaction and hydrogen bonds, should be very critical in fabricating highly efficient and stable POM-based catalysts [12,42,45]. In our case, the relatively high stability of the catalysts 1 should be mainly due to the following reasons. First, the infinite three-dimensional polycatenated framework consisting of Ag^+ and 1,2,4-triazole ligand could effectively inhibit the aggregation of PMA clusters by space limitation. Second, the abundant electron-rich terminal oxygen atoms of PMA anions and the Ag^+ cations located in the whole 3-D framework can result in the formation of multi-interactions. In another word, the Ag^+ atoms existed in the 3-D framework can produce electrostatic interaction with the PMA anion from different directions, thus being beneficial to the formation of a highly stable PMA-based catalyst.

For the aerobic oxidation of olefin in the presence of IBA, it is believed that the epoxidation reaction may follow acylperoxy radicals (formed in autoxidation) or alkylperoxy radicals (formed in cooxidation process). In general, cooxidation affords yields of epoxides that are much higher than those obtained from the autoxidation of the olefin alone, since acylperoxy radicals are more selective than alkylperoxy radicals in favoring addition relative to abstraction [46–51]. Therefore, it seems reasonable to propose that the epoxidation of olefins over catalyst **1** should be mainly follow a cooxidation mechanism of aldehydes and olefins. This is shown in Scheme 1. The first step of the reaction should involve the adsorption/activation process of IBA on catalyst **1**, to generate carbon-center free radicals of $\text{RCO}\bullet$. Subsequently, it reacts with the surface adsorbed O_2 to produce acylperoxy radicals ($\text{RCO}_3\bullet$). After that, $\text{RCO}_3\bullet$ could either react directly with olefin to get epoxides and RCOOH , or interact with IBA to form $\text{RCO}\bullet$ and RCO_3H , which is another active intermediate for the epoxidation of olefin.

Scheme 1. Proposed mechanism for epoxidation of olefins on catalyst **1**.

3. Materials and Methods

3.1. Synthesis of the Catalysts

3.1.1. Synthesis of $[\{\text{Ag}_2(\text{trz})_2\} [\text{Ag}_{24}(\text{trz})_{18}]] [\text{PMo}_{12}\text{O}_{40}]_2$ (**1**)

CH_3COOAg (0.1001 g, 1 mmol), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (0.3651 g, 0.2 mmol), 1,2,4-triazole (0.1392 g, 2.0 mmol) and water (15 mL) were added in succession. After stirring the mixture ($\text{pH} = 4$) for 1 h at room temperature, it was sealed in a 25 mL Teflon-lined autoclave and heated at 160°C for 96 h, followed by cooling to room temperature with a rate of $10^\circ\text{C}\cdot\text{h}^{-1}$. Light green block type crystals, being suitable for X-ray analysis, were collected. The entire yield is 81% based on Mo. The CCDC number of catalyst **1** is 873140.

3.1.2. Reference Sample $\text{Ag}\text{-trz}_3$

For comparison, the silver complex derived from CH_3COOAg and 1,2,4-triazole ligand was synthesized under the similar hydrothermal condition, just without the addition of PMA. Some white powder microcrystals were obtained with a 55% yield based on Ag. The resultant complex is denoted as $\text{Ag}\text{-trz}_3$, in which the mole ratio of Ag/trz is determined by elemental analysis.

3.2. Materials and Methods

CH_3COOAg ($\geq 99\%$), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ($\geq 99\%$), 1, 2, 4-triazole (trz, $\geq 99\%$), *cis*-cyclooctene (95%), 1-octene (95%), chloroform ($\geq 99\%$), acetonitrile ($\geq 99\%$, AR), ethanol ($\geq 99.7\%$, AR) and isobutyraldehyde (IBA) were obtained commercially (aladdin-e Inc., Shanghai, China) and used without additional purification.

FT-IR spectra were recorded on a Nicolet AVATAR 370 DTGS spectrometer (Thermo Electron (Shanghai) Instruments Co., Shanghai, China) in the range 400–4000 cm^{-1} . FT-IR (KBr, 4000–400 cm^{-1}) of catalyst **1**: 3116(s), 1778(m), 1635(m), 1517(s), 1425(s), 1307(s), 1140(s), 1053(s), 934(m), 831(w), 626(w), 435(w).

Elemental analyses of (C, H and N) were carried out with a Vario EL III elemental analyzer. Elemental analyses of Ag and Mo were carried out with a 2100DV ICP-AES spectrometer. Elemental analysis (%) calcd for $\text{C}_{40}\text{H}_{40}\text{N}_{60}\text{O}_{80}\text{Ag}_{26}\text{P}_2\text{Mo}_{24}$ (catalyst **1** formula weight = 7809.08): Ag 35.91, Mo 29.49, C 6.15, H 0.51, N 10.76; found: Ag 35.89, Mo 29.54, C 6.22, H 0.44, N 10.73. There are no water molecules exist.

Powder X-ray diffraction (XRD) measurements were performed on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA) (Shimadzu (Shanghai) Global Laboratory Consumables Co., Ltd., Shanghai, China) using Ni-filtered $\text{Cu-K}\alpha$ radiation in the angular range $2\theta = 5^\circ\text{--}50^\circ$ at 293 K. SEM measurements were performed on JSM-6510 Series Scanning Electron Microscope.

Intensity data were measured on a Siemens SMART CCD (SLC Changchun Branch, Changchun, China) with graphite-monochromatized $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K and corrected for adsorption by the SADABS program [52]. The structure of the crystal was solved by direct method and refined by full-matrix least-squares method with the SHELXL-97 program package [53]. The hydrogen atoms attached to carbon positions were placed in geometrically calculated positions.

3.3. Catalyst Test

The catalytic oxidation reaction was carried out in a 50 mL three-necked bottle equipped with a stirring bar, reflux condenser, and gas supply. Solvent, olefin, IBA and catalyst were added into the flask respectively, and the whole device was placed in a temperature-controlled oil bath. All catalysts were ground into powder in a mortar, which is then put into the reaction system. To commence the reaction, oxygen was passed through the reactor at a flow rate of 10 mL/min^{-1} under atmosphere. The oxidation products of the reaction were analyzed and quantified by Shimadzu GC-8A gas chromatograph (Shimadzu (Shanghai) Global Laboratory Consumables Co., Ltd., Shanghai, China) with an HP-5 capillary column.

4. Conclusions

A metal-organic polycatenated compound based on PMA and Ag-triazole complexes was synthesized in a very simple and efficient way. This compound showed excellent catalytic activity and selectivity for the aerobic Mukaiyama epoxidation of olefins as a catalyst. Combined with the characteristics of the structure, we can see that the supramolecular structure is a very open framework, which is suitable for the diffusion of the reactants to increase the substrate contact with the catalyst active sites, thus helping to improve the catalytic activity. This catalyst is heterogeneous in nature and can be easily recycled without a decrease in activity. This shows that catalyst **1** has very excellent stability. This result also indicates that weak interactions such as non-covalent mechanical interactions and weak interactions should be critical for the stability of the catalyst.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/7/568/s1>, Figure S1 The GC spectrogram of 1-octene. Figure S2 The GC spectrogram of cyclooctene. Figure S3 The crystal cell structure of catalyst **1**. Figure S4 The 2D frameworks form a three-dimensional polycatenated framework through interlocking of vertex angles. Table S1. Catalytic epoxidation of cyclooctene and 1-octene with O_2 /IBA over catalyst **1**. Table S2 Crystal data and structure refinement of catalyst **1**.

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