

Mn-, Ru- Coordinated Covalent Triazine Framework as Catalysts for Epoxidation of Cyclohexene

Xue Liu

Hubei Key Laboratory of Natural Products Research and Development, College of Biological and Pharmaceutical Sciences, China Three Gorges University, Yichang 443002, China
e-mail: 934349496@qq.com

Wei-Qiao Deng

State Key Laboratory of Molecular Reaction Dynamics, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics Chinese Academy of Science, Dalian 116023, China
e-mail: wqdeng@dicp.ac.cn

Ling Zhang

Hubei Key Laboratory of Natural Products Research and Development, College of Biological and Pharmaceutical Sciences, China Three Gorges University, Yichang 443002, China
e-mail: 593305836@qq.com

Nian-Yu Huang

Hubei Key Laboratory of Natural Products Research and Development, College of Biological and Pharmaceutical Sciences, China Three Gorges University, Yichang 443002, China
e-mail: hny115@126.com (Corresponding author)

Abstract—The alkene epoxidation is an important reaction for organic synthesis and the catalytic epoxidation of cyclohexene can be widely used for the synthesis of fine chemicals. In this work, a new kind of heterogeneous catalysts, Mn/Ru coordinated covalent triazine framework (Mn-CTF and Ru-CTF), for oxidation of cyclohexene to epoxy hexane were designed. The catalyst Mn-CTF/Ru-CTF was prepared via coordination of manganese chloride hydrate/ruthenium trichloride (III) hydrate with CTF, which was obtained by self-polymerization of 2, 6-pyridinedicarbonitrile. Reducing and oxidizing agents are isobutyraldehyde and molecular oxygen. The yield of epoxidation reaction of cyclohexene catalyzed by the Mn-CTF and Ru-CTF can be up to 97% and 99% under room temperature and atmospheric pressure, respectively.

Keywords-Covalent triazine framework; polymerization; cyclohexene epoxidation; catalysis; coordination

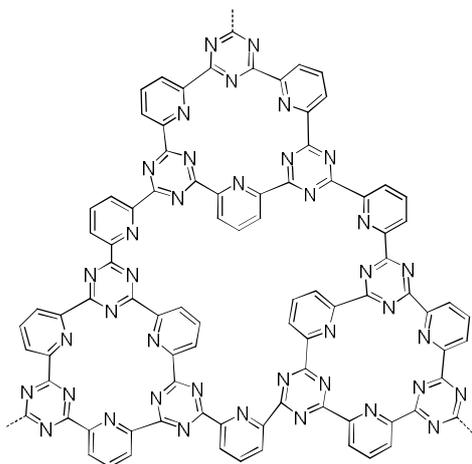
I. INTRODUCTION

Cyclohexane oxide is one of the important materials in organic synthesis. It can be used for the manufacture of ethylene glycol, detergents, emulsifiers, nonionic surfactants, antifreeze agents, plasticizers, lubricants and pesticides [1-2]. The epoxidation of cyclohexene has been studied extensively and many groups have made breakthrough over the past few decades [3-4]. However, in most cases, the catalyzed epoxidation of cyclohexene requires special conditions such as higher temperature or pressure, and large amounts of catalyst, etc. These conditions inevitably produced a lot of by-products, which not only resulted in a waste of raw materials, but also greatly enhanced the industrial production costs [5-8].

Covalent triazine frameworks (CTFs) have attracted widespread attention because of its high specific surface

and low cost [9-10]. Subsequently, CTFs have been demonstrated potential applications in many fields, such as gas storage, organic dyes separation and heterogeneous catalysis. Therefore, it is no doubt that since a few years, more and more research groups became interested in the development of CTFs, and a lot of different types of covalent triazine frameworks have been synthesized [11-12]. Especially, the excellent stability to acids, alkalis and high temperature of CTFs makes them one of the most studied catalyst supports. Recently, CTF-Pt was used as a catalyst by Ferdi Schuth's groups in methane oxidation to methanol and high catalytic efficiency was achieved [13]. Carine E. Chan-Thawa, etc. used one kind of CTFs as support for Pd nanoparticles, and the resulting Pd-CTF can be used as an efficient catalyst for glycerol oxidation [14].

In this work, we synthesized CTF by ionothermal trimerization of carbonitrile groups in molten $ZnCl_2$ which acts as both solvent and catalyst at temperatures $400^\circ C/600^\circ C$ and developed Mn(II) and Ru(II) coordinated CTF, and then used them as heterogeneous catalysts for the epoxidation of cyclohexene by molecular oxygen in the presence of isobutyraldehyde. The catalytic reaction can be achieved in ambient conditions. Moreover, facile operation of the reaction and high catalytic efficiency promise a potential application of the new CTFs as catalysts in cyclohexene epoxidation.



Scheme 1. The structure of CTF

II. EXPERIMENTAL

A. Reagents and Physical Measurements

Unless otherwise noted, all reagents and materials were used without further purification. 2, 6-Pyridinedicarbonitrile was purchased from Sigma-Aldrich Group Company. Anhydrous zinc chloride, ruthenium trichloride (III) hydrate (38.0-42.0% Ru basis), manganese chloride hydrate and isobutyraldehyde (AR) were all purchased from Aladdin Reagent Company.

The synthesis of CTF was carried out in a muffle burner (TSX1200). The specific surface area of CTF was measured on adsorption instrument (Quantachrome QUADRASORB SI). The yield of cyclohexane oxide was tested on GC-MS spectrometry (QP2010SE).

B. Synthesis Procedure of CTF

Triazine-based material was synthesized as described elsewhere [15]. Specifically, 2,6-Pyridinedicarbonitrile (1g, 7.75 mmol) and anhydrous $ZnCl_2$ (5.3g, 39.0 mmol) were transferred into a pyrex ampoule (3×15 cm) under an inert atmosphere. The ampoule was evacuated by a vacuum pump, sealed, and heated to $400^\circ C$ for 20h, after which the temperature was turned to $600^\circ C$ for another 20h. The ampoule was then cooled down to room temperature and opened carefully. *Caution:* the ampoule is under pressure, which is released during opening. The reaction mixture was subsequently grounded and then washed thoroughly with large amounts of water to remove most of the $ZnCl_2$. Further stirring in diluted HCl for 15h was carried out to remove the residual salt. After this purification step, the resulting black powder was filtered, washed successively with water and THF, and dried in vacuum at $120^\circ C$. Yield: 91%.

C. Synthesis Procedure of $MnCl_2$ -CTF ($RuCl_3$ -CTF)

For Mn coordination, CTF (500 mg) and $MnCl_2 \cdot 4H_2O$ (800 mg) were reacted in water under argon atmosphere for 6 h at $60^\circ C$, then the reactant was cooled down to room temperature and filtered, washed with water and tetrahydrofuran, and dried overnight at $100^\circ C$.

D. Epoxidation of Cyclohexene Catalyzed by Mn-CTF (Ru -CTF)

A solution of cyclohexene (2 mmol) in dichloromethane (5 mL) was added to catalyst (50 mg), isobutyraldehyde (10 mmol). The reaction mixture was vigorously stirred at room temperature with oxygen in a balloon for 6h, 12h, 18h and 24h. The reaction solution was filtered and the filtrate was diluted by dichloromethane and then tested on GC-MS. The residue was washed by dichloromethane and dried in a vacuum oven at $60^\circ C$ for 12 h and recycling.

III. RESULTS AND DISCUSSION

A. Nitrogen Adsorption and Desorption Isotherms

Nitrogen adsorption and desorption isotherms of CTF, Mn-CTF, Ru-CTF were measured on an adsorption instrument before degassed at $200^\circ C$ for 10 h. The analysis of porosity of CTF, Mn-CTF, Ru-CTF were listed in TABLE I. As shown in Fig. 1, the nitrogen isotherms at 77 K indicate that the polymers are microporous. The surface area of the CTF, calculated by the Brunauer-Emmett-Teller (BET) equation, is $1680 \text{ m}^2 \text{ g}^{-1}$. However, it reduced to 1466 and $1370 \text{ m}^2 \text{ g}^{-1}$ after coordinated with Mn^{2+} and Ru^{3+} . Moreover, the overall micropore volume are 0.69, 0.44, $0.48 \text{ cm}^3 \text{ g}^{-1}$ and the total pore volume are 0.86, 0.74, 0.77, corresponding to CTF, Mn-CTF and Ru-CTF, respectively. The reduction of the porosity is ascribed to the clog of the micropores by metal ions.

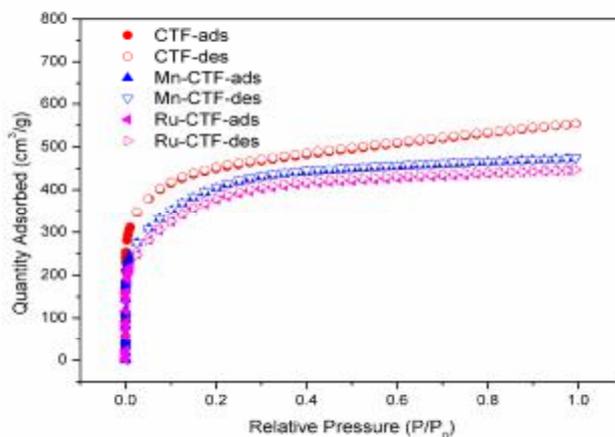


Figure 1. Argon adsorption (ads) and desorption (des) isotherms of CTF, Mn-CTF and Ru-CTF at 77K

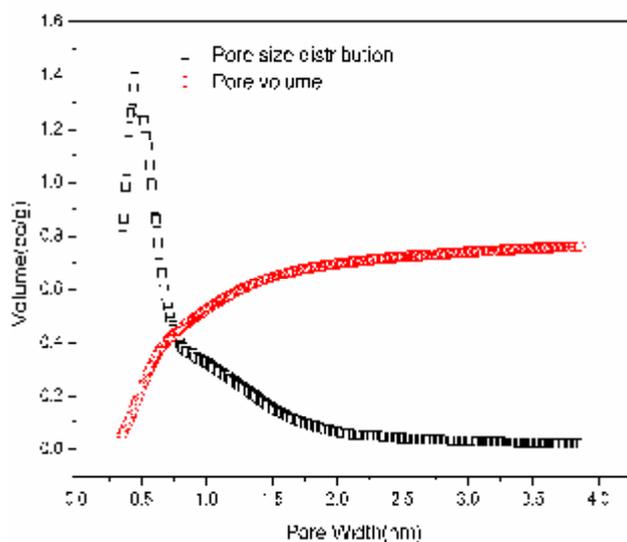


Figure 2. The pore size distribution and pore volume isotherms of CTF

TABLE I. CHARACTERIZATIONS OF CTFs BY NITROGEN SORPTION MEASUREMENTS

Material	S_{BET} (m^2/g) ^[a]	V_{tot} (cm^3/g) ^[b]	V_{micro} (cm^3/g) ^[c]
CTF	1680	0.86	0.69
Mn-CTF	1466	0.74	0.44
Ru-CTF	1370	0.77	0.44

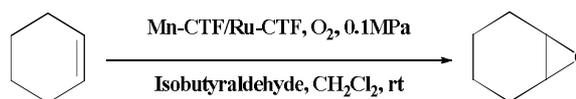
[a] Brunauer-Emmett-Teller (BET) surface area calculated over the pressure range (P/P_0) 0.05-0.3.

[b] Total pore volume at $P/P_0=0.99$.

[c] Micropore volume calculated using the t-plot method.

B. The Catalytic Performance of the Mn-CTF and Ru-CTF

The catalytic performance of the Mn-CTF and Ru-CTF on cyclohexene epoxidation was listed in TABLE 2. Firstly, a benchmark experiment was carried out for comparison. The yield for epoxidation of cyclohexene was just 17% and 46% in the time of 6h and 24h without the use of catalyst (Entry 1 and 6). Only 35% yield for cyclohexane oxide was achieved by Mn-CTF after 6h at the room temperature and atmospheric pressure (Entry 2). However, the yields increased from 35% to 97% (Entry 2-5) when the reaction time prolonged from 6h to 24h. Compared to Mn-CTF, Ru-CTF shows more excellent catalytic activity under the same conditions (6h) (Entry 2 and 7). Nevertheless, both high yields for cyclohexane oxide were obtained catalyzed by Mn-CTF (97%) and Ru-CTF (99%) after 24h (Entry 5 and 10). The high catalytic activity can be attributed to the enrichment of O_2 concentrations near the catalytic center located in the pore structures of Mn/Ru-CTF [16].



Scheme 2. Synthesis of the cyclohexane oxide

TABLE II. EPOXIDATION OF CYCLOHEXENE BY MOLECULAR OXYGEN IN THE PRESENCE OF Mn-CTF AND Ru-CTF WITH ISOBUTYRALDEHYDE

Entry	Time (h)	Catalyst (mg)	Yield (%)
1	6	None	17
2	6	Mn-CTF	35
3	12	Mn-CTF	64
4	18	Mn-CTF	80
5	24	Mn-CTF	97
6	24	None	46
7	6	Ru-CTF	55
8	12	Ru-CTF	79
9	18	Ru-CTF	89
10	24	Ru-CTF	99

IV. SUMMARY

The special micropore structures of CTFs show good adsorption of gas molecules, which can enrich the concentrations of gaseous molecular near the catalytic center when they are used as catalysts. As a new kind of heterogeneous catalysts, Mn-CTF and Ru-CTF showed high catalytic efficiency for the cyclohexene oxidation. In addition, the excellent performance of the CTFs offers a useful way to find new catalysts with high efficiency and superior activity.

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