Study on photocatalytic degradation of CEES by ZIF-8, NTU-9 and MOF-525

Yi Liu *

School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China

*Corresponding author’s e-mail: xuanfengyue@126.com

Abstract. We studied the photocatalytic degradation of 2-chloroethyl ethyl sulfide (CEES) by three kinds of MOFs (ZIF-8, NTU-9 and MOF-525). Among the three kinds of MOFs, NTU-9 and MOF-525 can selectively photocatalytic oxidize CEES to 2-chloroethyl ethyl sulfoxide (CEESO). And MOF-525 showed higher catalytic activity.

1. Introduction

Sulfur mustard, also known as mustard gas, is a typical blistering agent. In recent years, there are still reports on the use of mustard gas. Sulfur mustard has always been a huge threat to human health[1]. Thus, development of new materials for mustard gas detoxification is important. Sulfur mustard can be detoxified by hydrolysis, oxidation and dehydrohalogenation (Scheme 1).

Metal organic frameworks (MOFs) are crystalline porous materials that consist of metal ions/clusters and organic ligands. MOFs have rich pore structure, high specific surface area, adjustable function and structure. MOFs have been studied for applications in catalysis, gas storage and separation, and chemical sensing. Recently, the application of MOFs in sulfur mustard degradation has been reported[2]. We studied three kinds of MOFs (ZIF-8, NTU-9 and MOF-525) for photocatalytic degradation of CEES, a sulfur mustard simulant.
2. Synthesis of MOFs

2.1. Synthesis of ZIF-8

ZIF-8 was synthesized by the previous reported [3]. 3.3 g 2-methylimidazole and 1.5 g Zn(NO₃)₂·6H₂O were dissolved in 70 mL methanol respectively. The two solutions were mixed and stirred for 24 h. After filtering the reaction liquid, the obtained white powder was repeatedly washed with methanol, then dried in a vacuum oven at 60 °C, and activated under vacuum at 120 °C.

![Figure 1. PXRD data for ZIF-8.](image)

2.2. Synthesis of NTU-9

NTU-9 was synthesized by the previous reported [4]. In a 23 mL teflon-lined stainless steel autoclave, 0.15 g H₄DOBDC was added to 3 mL acetic acid. Then, 0.2 mL Ti(i-OPr)₄ was added to the solution. The mixture was stirred to form a dark red slurry, and heated at 120 °C for 5 days. The liquid was then cooled to room temperature, and washed with ethanol to obtain dark brown crystals of the NTU-9.

![Figure 2. PXRD data for NTU-9.](image)

2.3. Synthesis of MOF-525

MOF-525 was synthesized by the previous reported [5]. 12.5 mg ZrOCl₂·8H₂O was added to 10 mL DMF and sonicated for 30 min. 2.5 mg tetrakis(4-carboxyphenyl) porphyrin was added to the solution. 2.5 mL acetic acid was added to the solution after 10 min sonication. The solution was placed in a 20 mL scintillation vial and heated at 65 °C for 3 days. After filtering the reaction liquid, the obtained powder was washed with DMF. DMF was then replaced with acetone. The powder was dried in a vacuum oven at 120 °C for 48 h.
3. Photocatalytic degradation of CEES

5 mg MOF (ZIF-8, NTU-9 or MOF-525) was added to CD$_3$OD (2 mL) in a quartz reactor and the mixture was sonicated for 5 min before purged with oxygen for 30 min. Then CEES (50 μL) was added to the reaction system with a micro syringe. The reactor was exposed to simulated solar light (1 W cm$^{-2}$) for 30 min.

$^{13}$C NMR and $^1$H NMR spectroscopy were used to identify the product. For comparison, the $^{13}$C NMR spectra and $^1$H NMR spectra of CEES and 2-chloroethyl ethyl sulfoxide (CEESO) were recorded (Figure 4).

![Figure 3. PXRD data for MOF-525.](image)

4. Results and discussion

After 30 minutes of illumination, only CEES was found in the reaction solution with ZIF-8 as catalyst (Figure 5). CEES and CEESO were found in the reaction solution with NTU-9 as catalyst (Figure 6). When MOF-525 was used as catalyst, only CEESO was found in the reaction solution (Figure 7).
Figure 5. $^{13}$C NMR spectrum (a) and $^1$H NMR spectrum (b) measured after 30 minutes of catalytic oxidation of CEES with ZIF-8.

Figure 6. $^{13}$C NMR spectrum (a) and $^1$H NMR spectrum (b) measured after 30 minutes of catalytic oxidation of CEES with NTU-9.

Figure 7. $^{13}$C NMR spectrum (a) and $^1$H NMR spectrum (b) measured after 30 minutes of catalytic oxidation of CEES with MOF-525.

The results show that ZIF-8 cannot catalyze the oxidation of CEES, NTU-9 and MOF-525 can selectively photocatalytically oxidize CEES to CEESO. And MOF-525 can fully decompose CEES, which is significantly faster than NTU-9 (70% oxidation of CEES) as the catalyst under test conditions.

5. Conclusion
In summary, we studied the activities of three kinds of MOFs (ZIF-8, NTU-9 and MOF-525) to photocatalytic degradation of CEES. Among them, MOF-525 and NTU-9 exhibit photocatalytic
activity towards CEES, which can selectively oxidize CEES to CEESO. And MOF-525 has higher catalytic activity.

References
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