



Review

Metal–organic frameworks as media for the catalytic degradation of chemical warfare agents



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ABSTRACT

Because of the highly toxic properties of chemical warfare agents (CWA), an effective technology for the deactivation/detoxification of CWAs is desperately needed. Due to the safety issues involved in treating CWAs, catalytic conversion into (an)other non-toxic or less toxic material is suggested as one of the most favorable routes for their treatment. In this respect, many materials including zeolites, activated carbon, and metal oxides have been used as catalysts for the hydrolysis/methanolysis of the highly toxic organophosphate bonds of CWAs. However, the limited structural flexibility of these catalytic materials has been a hurdle to expanding detoxification on a large scale. A new option of using various porous materials for this application, including metal–organic frameworks (MOFs), has provided the potential for structural tailoring of the deactivation of CWAs. To discuss the potential of MOFs as deactivation/detoxification platforms for CWAs, we have initially described the structural pre-requisites for improving the catalytic activity of the MOF catalysts. A detailed explanation of the MOF catalysis and suitable examples are provided along with future perspectives and recommendations for such applications. We hope that this review will help provide a new roadmap for the scientists who are working in the area of heterogeneous catalytic approaches for the efficient degradation of CWAs.

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1. Introduction

Chemical warfare agents (CWA) have been developed as materials that possess self-toxifying properties. Consequently, the degradation of these materials into non/less toxic by-products is an important concern. There are two major categories of CWAs: nerve agents and vesicants (Fig. 1) [1]. For instance, Soman (*o*-pinacolylmethylphosphonofluoridate: GD), *o*-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate (VX), and Sarin (GB) are well known as the former. In contrast, Sulfur mustard (HD) is representative of the latter. Even short-term exposure to these materials is known to cause asphyxiation, severe blisters on the skin, and irritation to the eyes and respiratory tract [2–5]. The widely used degradation method for these CWAs is based on the hydrolysis process, and the resulting products of such processes are pinacolyl methyl-phosphonic acid (PMPA), ethyl methylphosphonic acid (EMPA), diisopropylamino ethyl mercaptan (DESH), chlorohydrin (CH), and thiodiglycol (TG) [1]. An alternative strategy for the degradation of CWAs is based on the oxidation process. However, most of the time, this process can lead to poisoning of the catalyst [1].

Apart from the water used for the hydrolysis of CWA, phosphotriesterase (PTE) enzyme was also recommended for the cleavage of P–O bonds [2,6]. As of now, there has been little information regarding the mechanistic sequence of the hydrolytic procedure. Most of the hydrolysis agents (e.g., water and enzymes) were reported to form homogeneous phases so that catalytic materials (e.g., PTE) are not effective under such circumstances [7,8]. Due to the limitations encountered with homogeneous materials, researchers have tried to develop effective media for heterogeneous catalysis.

Solid sorbent materials such as activated carbon, metal oxides, and zeolites are commonly used for diverse catalytic applications. As such, they have been tested earlier for their potential in the destruction of CWAs [9–13]. Nevertheless, their use has been restricted due to some of their structural properties including: (1) low sorption capacity, (2) low number of active sites, (3) deactivation/destruction of active sites of catalysis after interaction with guest analytes, (4) slow reaction kinetics, and (5) poor structural flexibility [14,15]. These limitations suggest that there is room for novel, tailorable porous materials such as metal–organic frameworks (MOFs).

MOFs are stable crystalline materials with large porosities and surface areas that facilitate the efficient sorption of diverse targets [16,17]. MOFs have recently been studied for the degradation of various CWAs. Several deposition methods have been used for this purpose including (1) impregnation of MOFs into textile fabrics, (2) *in situ* growth of functional groups on the MOF surface, (3) electrodeposition, (4) electrospinning of MOF suspensions in polymeric fluids, and (5) use of a protective material with a reactive adhesive layer for the deposition of MOF particles through covalent attachment [18–22]. The superior performance of MOFs over other traditional materials was explained by a number of reasons including their functional moieties (e.g., –NH₂ and –OH). Moreover, further functionalisation of these materials using coordinating or conjugating agents led to considerable expansion of their removal capacity. For instance, the addition of –NH₂ groups on two MOFs (namely, NH₂-MIL-101(Al) and NH₂-MIL-53(Al)) was examined via the reaction of 4-methylaminopyridine (4-MAP) with an isocyanate adhesive layer [18]. Accordingly, the isocyanate layer was seen to act as a surface platform for the incoming –NH₂ groups (from the 4-MAP) with considerable increase in the

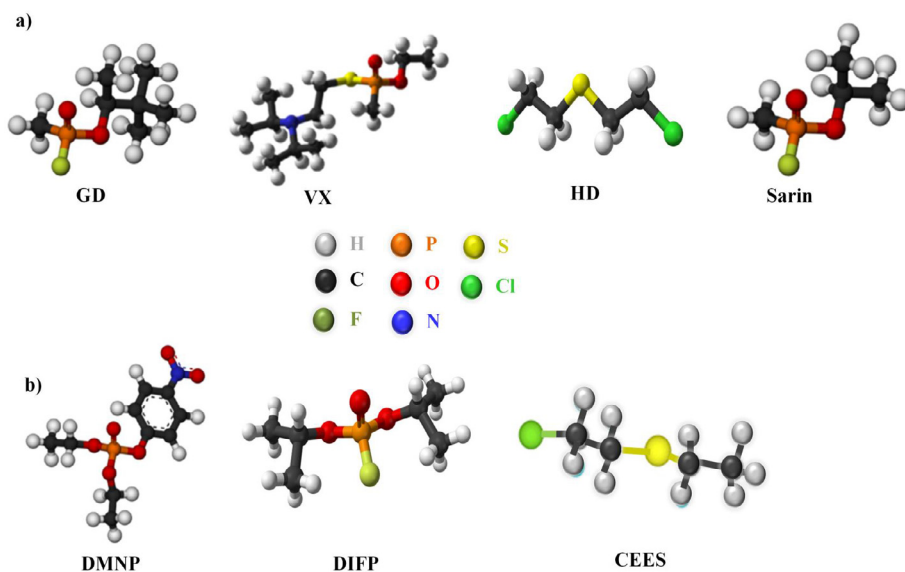


Fig. 1. Chemical structures of the real (a) and simulants (b) of CWAs explored in this review: Soman (GD), *o*-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate (VX), Sulfur mustard (HD), Sarin, dimethyl-4-nitrophenyl phosphate (DMNP), diisopropylfluorophosphates (DIFP), and 2-chloroethyl ethyl sulfide (CEES). The images were taken from Wikipedia.

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