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Adsorption of sarin on MgO nanotubes: Role of doped and defect sites

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ABSTRACT

Sarin is a highly toxic organophosphorus chemical warfare agent which has been employed in various wars and terrorist attacks. Due to an urgent need of finding safe methods to decompose this toxic nerve agent, the research on decomposition of sarin gains importance. In the present work, the decomposition of sarin molecule on MgO nanotube and Ti-doped MgO nanotube has been investigated. For this purpose, the structural and electronic characteristics of nanotubes are first examined. It is seen that although doping with Ti modifies the properties of the nanotube, adsorption of sarin on both kinds of nanotubes presents similar characteristics. Adsorption is found to be more favorable at low-coordinated sites, *i.e.*, the 3c site is preferred over 4c. Five kinds of surface defect sites have been considered *i.e.*, O_{4c}, O_{4c}^{2-}, Mg_{4c}, Mg_{4c}^{2+} and $(MgO)_{4c}$. Adsorption of sarin on various defect sites produces different products. In two of the cases, the neutral oxygen defect and MgO defect, the molecule breaks completely into fragments and is destructively decomposed. Hence, our study proposes a new metal oxide system that might destructively adsorb chemical warfare agents and highlights the need for further exploration of untested metal oxide systems.

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1. Introduction

Sarin (GB), isopropyl methylphosphonofluoridate ($C_4H_{10}FO_2P$) (Scheme 1), is a chemical warfare agent (CWA), also known as a nerve agent. Named after its discoverers, **S**chrader, **A**mbros, **R**üdiger and van der L**IN**de, it is a highly toxic organophosphorus compound that inhibits the acetylcholinesterase (AChE) enzyme, which plays a significant role in the nervous system. History is witness to the use of sarin in terrorist attacks against Japan, in the Iran–Iraq war and recently in Syria, killing and injuring a large number of people. Hence, the studies on sarin are highly important for the purpose of quickly detecting and decomposing this toxic agent.

Many theoretical studies of chemical warfare agents and their simulants have been carried out by *ab initio* methods [1]. The conformations of sarin, soman and their simulant dimethyl methylphosphonate (DMMP) were thoroughly studied in vacuum using MP2 theory calculations, in conjunction with Fourier transform microwave spectroscopy [2–4]. Kaczmarek et al. [5] determined the most stable conformers of sarin and soman in high-level-correlated calculations with extended Gaussian basis sets. Majumdar et al. [6] carried out conformational analysis of sarin and soman at the DFT-B3LYP/6-31++G(d,p) level, comparing their results to MP2/6-31++G** calculations and experimental values. Bermudez [7–9] performed a series of *ab initio* calculations to describe sarin adsorption on various surfaces.

Metal oxides, remarkably known for their industrial use as adsorbents, catalysts and catalyst supports, have several potential decontamination applications, such as environment friendly hasty decontamination on the battlefield, protective filtration systems for vehicles, aircraft, and buildings and demilitarization of CWA munitions and stockpiles. Another advantage of these metal oxides lies in their capability to neutralize CWA in a rapid and safe manner, ease of handling, stability in long-term storage, environment friendliness, availability, and easy disposal. The metal oxide nanoparticles currently employed for CWA decomposition purpose are MgO [10,11], CaO [12,13], Al_2O_3 [14–16], TiO_2 [17,18], ZnO [19–21], *etc*. For sarin adsorption on metal oxide nanomaterials, studies [15,17,19] have shown its degradation to the non-toxic isopropyl methylphosphonic acid accompanied by elimination of fluorine.

Amongst the various metal oxides, it is the nanoparticles of MgO that have been most widely employed for adsorption and decomposition of numerous toxic compounds. Several new forms of nano-MgO, such as MgO nanotube bundles [22], single-walled carbon nanotube reinforced magnesia films [23], as well as Ga filled MgO nanotubes for use as nanothermometers [24] have been reported. In addition, numerous different structures, such as nanorods [25,26], nanobelts [27], nanowires [28], aligned crys-

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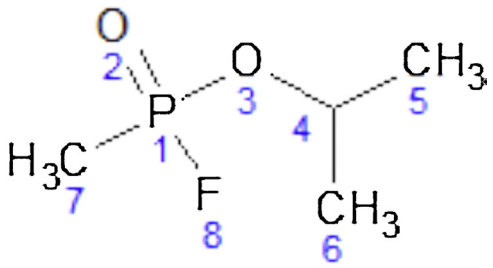

Scheme 1. Structure of sarin.

talline nanoporous films [29], three-dimensional nanostructures [30] and fishbone fractal nano-structures [31] have been fabricated [32].

Experimental observations [33–36] have indicated that small stable clusters of stacked hexagonal rings of MgO exist in the gas phase. In recent years, there have been several theoretical studies on structural, electronic and adsorption properties of the MgO nanotube [37–44]. In our previous work [45,46], we had observed that the reactive $(MgO)_{12}$ species is not a cubic bulk-like structure, but a nanotube. We had also seen that even if the input geometry for MgO is taken to be bulk-like, it readily distorts to a nanotube upon formaldehyde adsorption. Moreover, dissociation of the carbonyl compound was found to take place relatively easily on these MgO nanotubes, as all the ions are at the surface and have low coordination numbers [47]. According to other theoretical studies [48,49], the stability of tube-like $(MgO)_{12}$ has been established by the fact that its ground state energy is only 0.12–0.66 eV higher than the cage and cubic isomers.

Moreover, incorporation of second element into oxide matrices is a very useful method to modify the physical and chemical properties of oxides. The idea is to elucidate whether the properties of oxides can be controlled and, therefore, altered by appropriate doping. For example, Valero et al. and Yang et al. [50,51] studied adsorption of CO on transition metal doped MgO nanotubes, providing evidence for potential adsorption properties of doped MgO nanotube. Similarly, many researchers have reported studies on Mg–Ti–O systems [52–57].

Considering these studies, in our work, MgO in its nanotube form (both perfect and Ti-doped) is taken as an adsorbent for the sarin molecule. The aim is to examine if doping has a positive effect on the adsorption properties of the MgO nanotube. The work further deals with investigation of surface defect sites arising from atom, ion, and MgO vacancies. The adsorption of sarin at different defect sites is then considered.

2. Computational details

First-principles density functional calculations were performed using the DMol^3 code [58,59] available from Accelrys Inc., in the Materials Studio 5.5 package. The exchange–correlation contribution to the total electronic energy was treated in a spin-polarized generalized-gradient corrected (GGA) form of the local density approximation (LDA) [60] with the Perdew–Burke–Ernzerhof (PBE) correlation [61]. The calculations employed numerical basis sets

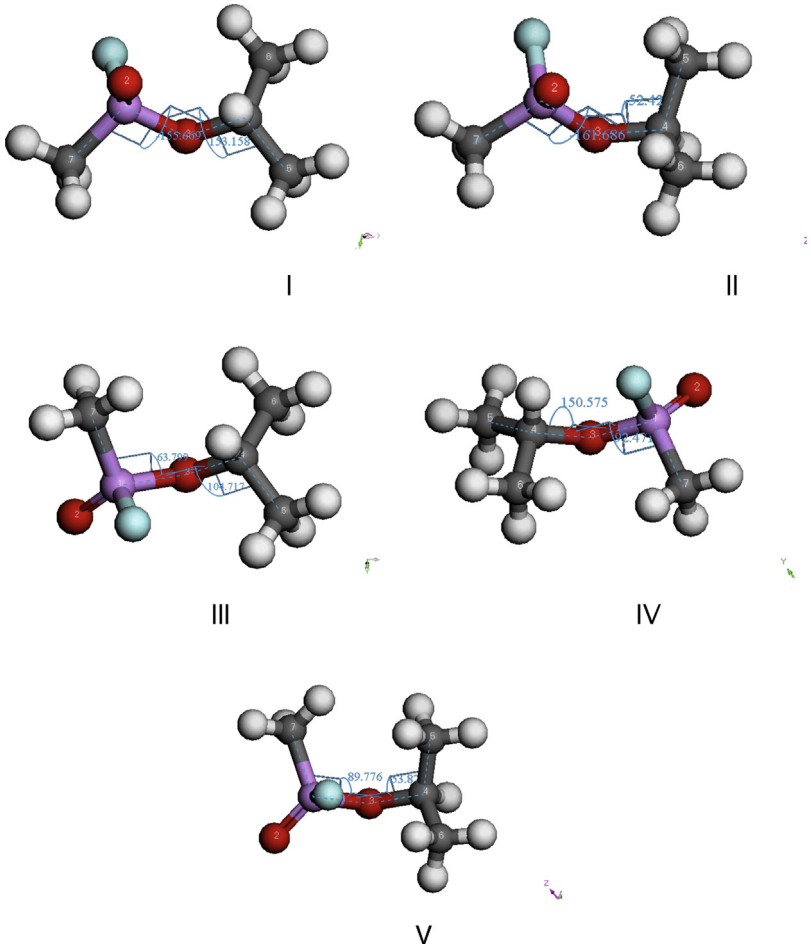

Fig. 1. Low energy conformations of sarin. Color codes: O, red; P, pink; F, cyan; C, gray; H, white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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