Chemical Physics Letters 707 (2018) 31–39

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Decontamination of Chemical Warfare Agents by Zn^{2+} and Ge^{4+} co-doped TiO_2 nanocrystals at sub-zero temperatures: A solid-state NMR and GC study

Zhong Shen [a,b], Jin-Yi Zhong [a,c,*], Jin-Chao Yang [b], Yan Cui [a,c], He Zheng [a,c], Ling-Yun Wang [a], Jing-Long Wang [b]

[a] Research Institute of Chemical Defense, P.O. Box 1043, Beijing 102205, China
[b] North-western Institute of Nuclear Technology, P.O. Box 69, Xi an 710024, China
[c] State Key Lab of NBC Protection for Civilian, P.O. Box 1043, Beijing 102205, China

ARTICLE INFO

Article history:
Received 14 May 2018
In final form 14 July 2018

Keywords:
Chemical Warfare Agents
Co-doped
Titanium dioxide
Decontamination
Sub-zero temperature
SSNMR
GC

ABSTRACT

Using solid-state NMR spectroscopy (SSNMR) and gas chromatography (GC) we studied the sub-zero temperature decontamination performance of Chemical Warfare Agents (sulphur mustard (HD), soman (GD) and S-2-(diisopropylamino)ethyl O-ethyl methylphosphonothiolate (VX)) and their simulants (2-chloroethyl ethyl sulphide (2-CEES) and dimethyl methylphosphonate (DMMP)) on a novel nanoparticulate Zn^{2+} and Ge^{4+} co-doped titanium dioxide (Zn-Ge-TiO_2) material. To discover further progress toward the practice use of the powdered catalyst and improve its low-temperature disinfection, a novel suspension decontaminant was prepared successively by suspending Zn-Ge-TiO_2 in hydrofluoroether (HFE). By means of a variety of characterization methods such as XRD, BET, BJH, SEM and TEM, the evolution of structure and properties across Zn^{2+} and Ge^{4+}doping were systematically studied. Our data show that Zn (5.28 wt%)-Ge (1.48 wt%)-TiO_2 exhibited the best photocatalytic performance. Versus undoped TiO_2, the sample has unchanged crystal structure (anatase) and decreased average pore diameter (2.86 nm), accompanied with increased specific surface area (424.9 m^2/g), crystallite size (5.8 nm) and pore volume (0.29 cm^3/g). Under simulated sunlight irradiation at −30 °C, after a reaction time of 120 min, the degradation efficiency of HD, GD and VX on the suspension composed of Zn (5.28 wt%)-Ge (1.48 wt%)-TiO_2 and HFE-458 ($HCF_2CF_2CH_2OCF_2CF_2H$) were all over 99.95%. This indicated that the suspension will have a promising prospect of application in CWAs decontamination under the sub-zero environment.

1. Introduction

Decontamination of Chemical Warfare Agents (CWAs) is of significant importance not only for strategic defense, but also for anti-chemical terrorism emergency disposal. Some common CWAs include the nerve agents (soman (GD), sarin (GB), S-2-(diisopropylamino) ethyl O-ethyl methylphosphonothiolate (VX), etc.) as well as blistering agents such as sulphur mustard (HD) [1]. The decontamination process can be carried out via destruction, absorption, neutralization, oxidation or removal of CWAs from military vehicles, equipment, facilities and personnel [1]. Under consideration of safety, most work is performed using simulant compounds with similar chemical structures and properties to CWAs [2–4]. For instance, 2-chloroethyl ethyl sulphide (2-CEES, a simulant of HD) and dimethyl methylphosphonate (DMMP, a stimulant of GD, GB or VX) are two kinds of the most extensively studied stimulants in the field of CWAs decontamination.

Some CWAs such as VX, GD and GB can still flow below 0 °C. The freezing point of the VX, GD and GB are −39 °C, −42 °C and −56 °C, respectively. Even in winter or cold regions, these CWAs can still play a good role in toxicity. In addition, changes in physical properties such as the viscosity and evaporation rate of CWAs at sub-zero temperature will lead to changes in kinetics and mechanism of disinfection reaction. These complicated situations highlight the research needs and reflect the technical short board of the sub-zero temperature decontaminants in the development of CWAs' decontamination. Therefore, it is necessary to carry out research on the decontamination in sub-zero temperature environment.

Conventional methods of decontamination that on one hand are wet-type chemical reactions by using liquid decontaminants (aqueous or solvent systems) which contain hypochlorite, organic

* Corresponding author at: Research Institute of Chemical Defense, P.O. Box 1043, Beijing 102205, China
E-mail address: linfzjy@163.com (J.-Y. Zhong).

https://doi.org/10.1016/j.cplett.2018.07.033
0009-2614/

chloramines, caustic alkali as well as organic super alkaline decontaminants, and on the other hand is physical adsorption by solid adsorbents such as active clay and active carbon [1]. According to the effect of disinfection, the water-based decontaminants can basically meet the requirements of decontamination. But in practical application, there are some problems in terms of metal corrosion, environmental pollution, logistics burden and sub-zero temperature freezing, *etc*. Some non-aqueous solvent decontaminants are suitable for sub-zero temperature conditions and unable to corrode most metals, while, there are also some severe problems for these decontaminants such as solvent flammability, skin irritation, paint layer soften and so on. Solid adsorbents have obvious advantages in environmental security, non-corrosion and low skin irritation. But in fact, solid adsorbents can only produce physical adsorption, and the desorption may cause secondary pollution. Therefore, it is urgent to develop alternative decontaminants that are high efficiency, broad spectrum, environmental security, low corrosion, *etc*.

Nowadays, large efforts have been continuously pursuing breakthroughs from new materials and new technologies. Reactive sorbents have gradually come to the fore, especially TiO_2 nano-

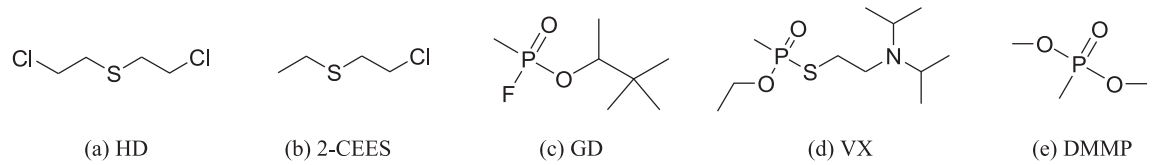

Fig. 1. Three CWAs and their stimulants.

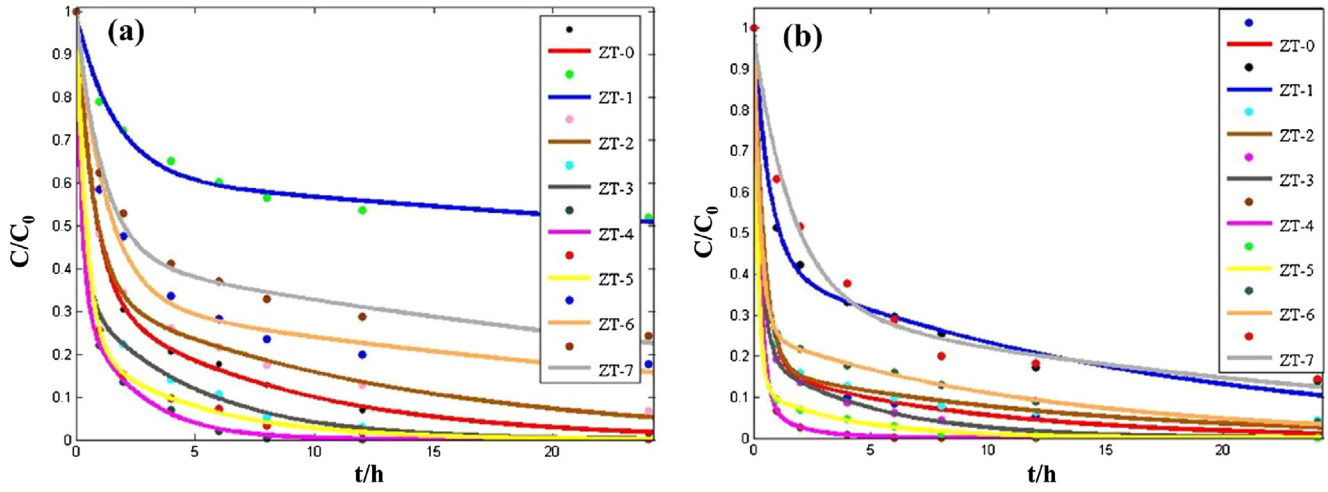

Fig. 2. Degradation kinetic curves of (a) 2-CEES and (b) DMMP on the Zn-Ge-TiO_2 under simulated sunlight irradiation.

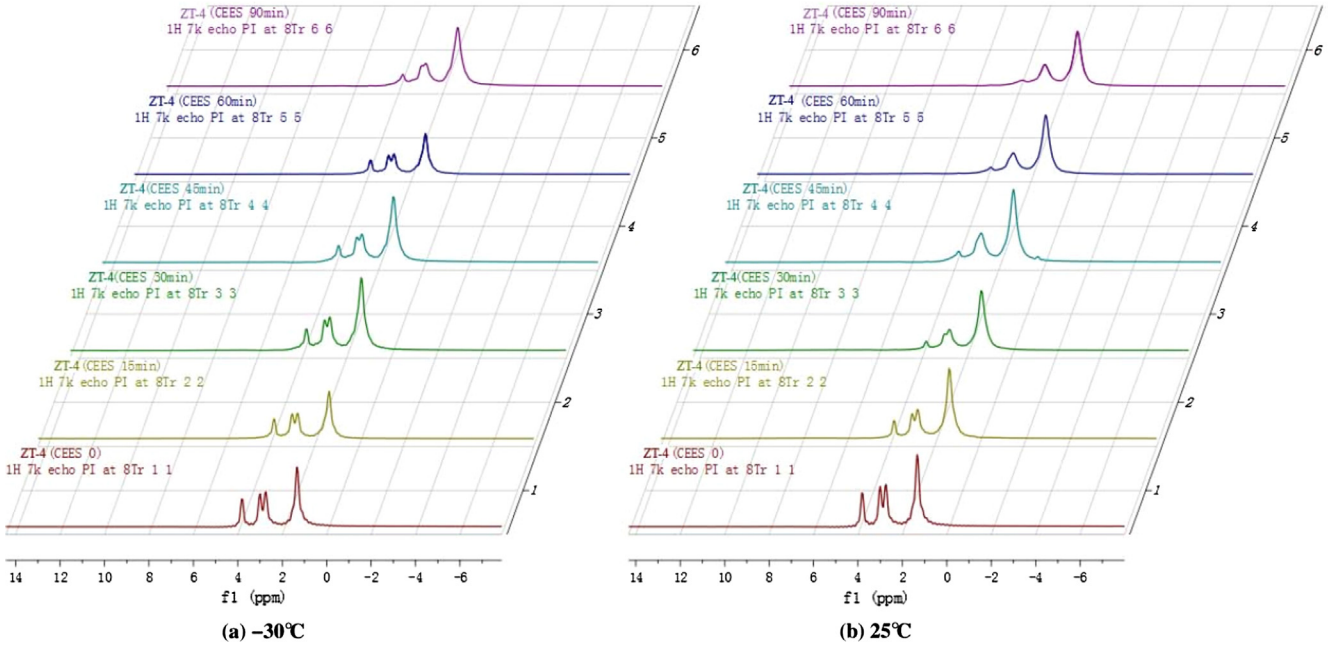

Fig. 3. ^{1}H MAS NMR spectra obtained for 2-CEES photocatalytic reacted with the ZT-4 sample at different temperature.