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Nanosized inorganic metal oxides as heterogeneous catalysts for the degradation of chemical warfare agents

Chiara Bisio^{a,b,*}, Fabio Carniato^a, Chiara Palumbo^b, Sergey L. Safronyuk^d,
Mykola F. Starodub^c, Andrew M. Katsev^d, Leonardo Marchese^a, Matteo Guidotti^{b,**}

^a Dipartimento di Scienze e Innovazione Tecnologica and Nano-SiTeMI Interdisciplinary Centre, Università del Piemonte Orientale "A. Avogadro", Viale T. Michel 11, 15121 Alessandria, Italy

^b CNR-Istituto di Scienze e Tecnologie Molecolari, via C. Golgi 19, 20133 Milano, Italy

^c National University of Life and Environmental Sciences of Ukraine, Kyiv, Ukraine

^d V.I. Vernadsky Crimean Federal University, Medical Academy, Simferopol

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ABSTRACT

Nanosized inorganic metal oxides, such as TiO₂, ZnO, γ -Al₂O₃, are proposed as heterogeneous catalysts for the oxidative degradation of chemical warfare agents (CWA), particularly of organosulfur toxic agents, into oxidised products with reduced toxicity. The morphology, structural and textural properties of the catalysts were investigated. Furthermore, their catalytic properties were evaluated in the oxidative abatement of (2-chloroethyl)ethylsulfide, CEES, a simulant of sulfur mustard (blistering CWA). Their performance was also compared to a conventional decontamination powder and a commercial Nb₂O₅ sample. The metal oxides powders were then employed in the active oxidative decontamination of CEES from a cotton textile substrate, mimicking a real contamination occurrence. Remarkable results in terms of abatement and degradation into desired products were recorded, achieving good conversions and decontamination efficiency with Nb₂O₅, TiO₂ and γ -Al₂O₃, under very mild conditions, with hydrogen peroxide (as aqueous solution or as urea-hydrogen peroxide adduct), at room temperature and ambient pressure. In the aim of a real on-field use, the potential environmental impact of these solids was also evaluated by bioluminescence toxicity tests on reference bacteria (*Photobacterium leiognathi* Sh1), showing a negligible negative impact for TiO₂, γ -Al₂O₃, and Nb₂O₅. A major biotoxic effect was only found for ZnO.

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1. Introduction

Chemical warfare agents (CWAs) have been considered among the most deadly tools humankind has ever invented deliberately. The oxidative abatement of pollutants and toxic chemical warfare agents is conventionally achieved via stoichiometric reactions based on the use of strong oxidants (mainly, sources of active chlorine, such as NaOCl, Ca(OCl)₂ or dichloroisocyanurate salts) with high environmental impact and/or via thermal degradation [1,2]. These procedures are often associated with high energy consumption, large over-stoichiometric amounts of reactants and high costs.

As an alternative to these well-established conventional chemical abatement strategies, and aiming to overcome their limits,

many heterogeneous catalysts have been proposed for the selective oxidation of CWAs into partially or fully oxidized non-toxic products [3,4]. For instance, polyoxometalates activated with transition metal centres (i.e. V, Fe, W, Mo) [5,6] and porous oxides, such as zeolite and metal-containing mesoporous silica [7–11], have been studied for these purposes. Typically, these catalysts have shown good conversion and high selectivity values in the oxidation of organic sulfides into sulfoxides, in particular of those compounds that mimic the oxidative abatement of blistering agents. Furthermore, these inorganic solids are characterized by a remarkable chemical, physical and mechanical robustness and, thanks to their high surface area, display a good dispersion of the catalytically active sites.

More recently, phyllosilicate clay materials have also been tested in the abatement of CWA [12,13]. The good chemical versatility and the low production costs render these solids promising candidates for the oxidative degradation of CWAs. A novel Nb(V)-containing saponite clay (Nb-SAP) was prepared by some of us (at

* Corresponding author. Fax: +39 0131 360250.

** Corresponding author. Fax: +39 02 50314405.

E-mail addresses: chiara.bisio@mfn.unipmn.it (C. Bisio), m.guidotti@istm.cnr.it (M. Guidotti).

the University of Eastern Piedmont, Italy) and identified as an efficient catalyst for the oxidative abatement of blistering agents [14]. The synthesis method used to obtain metal-substituted saponite material was modified to allow the insertion of Nb(V) ions within the inorganic framework of the clay: a bifunctional redox/acid catalyst with strong oxidizing properties, due to the presence of Nb(V) centres [15] and Brønsted acid character, due to aluminium ions embedded into the tetrahedral silica sheets of the saponite clay, was thus obtained [16]. The cooperative effect of the metal centres and the acid sites was crucial to promote the oxidative abatement of organosulfur blistering agents with hydrogen peroxide under very mild conditions and, in particular, with no use of chlorine-containing oxidising reagents. In detail, (2-chloroethyl) ethylsulfide (CEES), an organic compound whose structure and reactivity is similar to sulfur mustard (the blistering agent yperite, used for the first time during World War I), was selectively oxidized to the non-toxic (2-chloroethyl) ethylsulfoxide. The Nb-saponite catalyst was able to convert more than 98% of CEES, with a 73% selectivity to the related sulfoxide in 8 h [14]. Notably, this performance was significantly better than the one obtained over a conventional commercial decontamination powder, based on alumina and calcium hypochlorite.

Besides porous and layered materials, inorganic metal oxides, such as Al_2O_3 , TiO_2 and MgO have been also studied for their positive effects on the CWA oxidation and/or degradation reactions [1,17,18]. Often, these solids have been merely used as supports to disperse catalytically active metals, rather than as directly involved catalysts [19–21]. The catalytic decontamination performance of such inorganic oxides is moderate when they are in the form of bulk aggregates or micrometric dispersions, since they are able to remove quite efficiently by physical adsorption the hazardous agent, but then they can degrade it only partially [22–25]. On the contrary, when they are dispersed at nanometric level, their intrinsic acid/base properties and hence their hydrolytic capabilities, which are related to both the chemical nature of the metal oxide and to the surface properties, can be directly exploited for a successful CWA abatement [26–30].

Finally, considering the ever-growing concern about the potential detrimental effects of nanostructured inorganic oxides on living organisms [31,32], it is also necessary to pay a constant attention to the potential risks connected to the use of catalytically-active nanosized solids at large scale. Since the use of nanostructured decontamination powders is envisaged, in the present case, not only for the abatement of CWAs in closed and confined environments, but also in on-field total-loss situations, it is necessary to carry out an estimation of the potential detrimental effects on both living organisms and the environment [33–35].

In this respect, a series of nanostructured inorganic oxides, namely, ZnO with layered morphology, TiO_2 with anatase structure and $\gamma\text{-Al}_2\text{O}_3$, were synthesized and tested in the oxidative degradation of the chemical warfare blistering agent simulant (2-chloroethyl) ethyl sulfide. The first set of reactions was conducted in a batch reactor, under controlled conditions (room temperature), and in the presence of aqueous hydrogen peroxide as an oxidant. A critical comparison of their catalytic properties in relation to their physico-chemical characteristics was also carried out. The second series of reactions was performed on a textile substrate, mimicking a real contamination occurrence, at room temperature, with the urea hydrogen peroxide (UHP) adduct as an oxidant. A difference in reactivity of the catalysts within the two series was registered and is herein described.

In the aim of a real on-field use, the potential environmental impact of these solids was finally evaluated by bioluminescence tests, using reference marine bioluminescent bacteria (*Photobacterium leiognathi* Sh1) as a target.

2. Experimental details

2.1. Materials

Commercial M75CBRN (chemical, biological, radiological and nuclear agent) decontamination powder, packed in sealed batches, was obtained at the local Military Hospital in Milan (Italy) and used as received, as a reference material.

Bulk hexagonal-phase Nb_2O_5 (Aldrich, 99.99%) was used as reference for the catalytic comparison.

2.2. Catalyst preparation

ZnO with nanosheet morphology was prepared by thermal decomposition of the $\text{Zn}_4\text{CO}_3(\text{OH})_6\cdot\text{H}_2\text{O}$ precursor obtained by chemical bath deposition (CBD), adapting a methodology reported in the literature [36]. 0.55 g of hydrated zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, Sigma–Aldrich) were added to 3.00 g of urea (Sigma–Aldrich) in 50 mL of deionized water, and the pH value of the solution was adjusted to 4.5 with diluted acetic acid. The solution was transferred in an autoclave and kept at 353 K for 12 h. $\text{Zn}_4\text{CO}_3(\text{OH})_6\cdot\text{H}_2\text{O}$ in powder form was obtained. The sample was finally heated under air at 673 K to promote the decomposition of $\text{Zn}_4\text{CO}_3(\text{OH})_6\cdot\text{H}_2\text{O}$ into ZnO .

$\gamma\text{-Al}_2\text{O}_3$ was synthesized by modifying the classical sol–gel procedure that is normally used to produce boehmite phase [37]. In this method, the sol–gel procedure is assisted by sonication in order to reduce the synthesis time. Urea (0.22 g, NH_2CONH_2 , Sigma–Aldrich) was dissolved in 30 mL of deionized water. Then, aluminum isopropoxide (3.18 g, $\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$, Sigma) was added to the solution. The obtained gel was stirred at room temperature for 1 h. After this time, the gel was dried at 363 K for 12 h, in order to obtain boehmite precursor, and submitted to a thermal treatment, under oxygen flow (100 mL min^{-1}) at 773 K for 4 h, to promote the phase transition to $\gamma\text{-Al}_2\text{O}_3$.

TiO_2 was prepared as follows. 3.5 mL of titanium(IV) isopropoxide (Sigma–Aldrich) were mixed to 3.5 mL of 2-propanol (Sigma–Aldrich) and the solution was submitted to sonication for 15 min. 8 mL of pure water were added drop-by-drop to the previous solution under slow stirring. The final suspension was sonicated for other 15 min and dried at 353 K overnight. The sample, in form of white powder, was calcined under air flow (100 mL min^{-1}) at 573 K for 2 h.

2.3. Catalyst characterization

X-ray powder diffraction (XRPD) of unoriented ground powders was collected with a Thermo ARL 'XTRA-048 diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.54\text{ \AA}$) radiation. Diffractograms were recorded at room temperature with a step size of 0.02° and a rate of $1^\circ 2\theta\text{ min}^{-1}$. The particle size for the different samples was estimated by using the Debye–Scherrer equation.

Transmission electron microscopy (TEM) images were obtained using a JEOL 3010-UHR instrument operating at 300 kV and a FEI Tecnai F20ST operating at 200 kV. Samples were ultrasonically dispersed in isopropanol and a drop of the suspension was deposited on a copper grid covered with a lacey carbon film.

N_2 physisorption measurements were carried out at 77 K in the relative pressure range from 1×10^{-6} to 1 P/P_0 by using a Quantachrome Autosorb1MP/TCD instrument. Prior to analysis, the samples were outgassed at 100°C for 3 h (residual pressure lower than 10^{-6} Torr). Apparent surface areas were determined by using Brunauer–Emmett–Teller equation (BET), in the relative pressure range from 0.01 to 0.1 P/P_0 . Pore size distributions were obtained by applying the Non Local Density Functional Theory (NLDFT) method.

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