

## **Nb(V)-Containing Saponite Clay: a Catalyst for the Oxidative Abatement of Blistering Chemical Warfare Agents**

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### **Abstract**

The abatement of toxic chemical warfare agents (CWA) is conventionally achieved via stoichiometric reactions using strong oxidants with high environmental impact and/or via thermal degradation. In this work a class of heterogeneous catalysts is designed to transform selectively and under mild conditions toxic organosulfur chemical agents in non-noxious products with reduced environmental impact. Nb(V)-containing saponite clay was identified as an optimal catalyst for the CWA oxidative abatement. The conventional synthetic protocol used to obtain saponite materials was modified to allow the insertion of Nb(V) ions within the inorganic framework of the clay, thus obtaining a bi-functional catalyst with strong oxidizing and acid properties. The catalytic performance of these clays was evaluated in the oxidation reaction of (2-chloroethyl)ethylsulfide (CEES), simulant of sulfur mustard (blistering CWA), with aqueous hydrogen peroxide. Remarkable activity and outstanding selectivity were obtained, at room temperature and ambient pressure, with respect to a conventional commercial decontamination powder mixture.

### **Introduction**

Destruction of chemical and biological warfare agents is required on the field (*i.e.* for ground decontamination after warfare or terrorist use) as well as in laboratories, pilot plants and chemical agent destruction sites devoted to the systematic abatement of residual stockpiled non-conventional chemical, biological, radio-logical and nuclear (CBRN) weapons. Nerve and blistering chemical warfare agents (CWA) are considered among the most deadly tools humankind has ever invented deliberately [1]. Actually, the threat of use of chemical weapons is back again, not only for terrorist purposes, but also for explicit warfare aims, due to the current uncertain international scenario [2]. The development of innovative detection, protection, decontamination and abatement capabilities can help to improve global security in terms of: 1) reduced risks of illegal uses, 2) reduced vulnerability for the civilian population and, 3) improved risk management. Among conventional abatement methodologies, it is worth mentioning degradation approaches based on the use of strong alkaline solutions, strong oxidants or enzymatic catalytic systems [3]. However, the oxidation of CWA over heterogeneous catalysts is particularly promising, since it usually finds a broader spectrum of application (for both chemical and biological agents) than other approaches [4].

The standard stoichiometric oxidative abatement of pollutants and toxic chemical agents relies on strong oxidizing reactants, such NaOCl, Ca(OCl)<sub>2</sub>, KMnO<sub>4</sub> or on thermal degradation at high temperatures [5]. Nevertheless, both these procedures have a heavy environmental impact and are associated to high energy consumption and disposal costs. To overcome these drawbacks, many heterogeneous catalysts have thus been proposed for the selective oxidation of CWA into partially or fully oxidized non-toxic products [6].

The addition or insertion of catalytically active sites into/onto an inorganic support with high specific surface area is one of the most convenient strategies to obtain materials with marked adsorption properties together with abatement and decontamination capabilities. Porous inorganic oxides are optimal materials for these purposes: they show noteworthy chemical,

physical and mechanical robustness and are suitable supports for obtaining good dispersions of active metal sites (e.g. V, Ag, W, Mo) [7]. Nanostructured inorganic metal oxides such as  $\text{Al}_2\text{O}_3$ , ZnO and  $\text{TiO}_2$  were widely proposed and studied in the literature for CWA oxidation and/or degradation reactions [3c,8]. More recently, oxides with high specific surface area and with an ordered array of nanometer-sized channels, pores or cavities were proposed as oxidation catalysts because of their peculiar adsorption capacities towards hazardous chemical agents. For instance, the enhanced degradation of dimethylmethylphosphonate (DMMP; a nerve agent simulant) to methylphosphonate over sodium X zeolite (Na-FAU) was attributed to the marked nucleophilic character of oxygen atoms in the Na-FAU framework and to a peculiar confinement effect within its supercages [9]. However, the practical applicability of these systems is restricted due to diffusion limitations of the reactants towards the active sites and, in general to size limitations. To overcome these limitations, mesoporous solids were used in the preparation of catalysts for CWA decomposition. Vanadium oxide supported on mesoporous silica supports, for instance, is an effective catalyst for the oxidation of sulfur mustard analogue ((2-chloroethyl)ethylsulfide, CEES) at room temperature and using *tert*-butylhydroperoxide [10] or molecular oxygen in the presence of a sacrificial aldehyde [11]. The material acts as a stable heterogeneous catalyst and, in fact, no leaching of vanadium ions was observed during the reaction.

However, the need for stoichiometric amounts of organic hydroperoxides or aldehydes and the parallel co-production of alcohol are the major drawbacks to practical use.

Beside porous materials, layered solids such as clays can be considered good candidates for the abatement of chemical warfare agents [12]. Advantages such as high robustness [13], good chemical versatility [14] and very low production costs render these solids, actually poorly explored for these purposes, promising catalysts for the oxidation of CWA substrates.

In this work, a class of heterogeneous layered catalysts, that are able to trigger selectively oxidation reactions and transform highly toxic agents into products with reduced environmental impact, was prepared for the first time and optimized. Particular attention was paid to the use of sustainable oxidants, such as aqueous hydrogen peroxide, under mild experimental conditions (room temperature and atmospheric pressure).

## Methods and Scope

A synthetic saponite clay, belonging to the class of smectites, was selected as support for the dispersion of Nb(V) ions. The conventional synthetic protocol used to obtain saponite clays [15] was modified to allow the insertion of Nb(V) ions within the inorganic framework of the clay, aiming to obtain a novel solid (niobium-saponite; Nb-SAP) with both oxidizing properties (due to the presence of Nb(V) centers [16]) and Brønsted acid character. This solid was compared to a Na exchanged niobium-saponite material that does not contain Brønsted acid sites (Na/Nb-SAP). The catalytic properties of these solids were evaluated at room temperature in the oxidative degradation, with hydrogen peroxide, of (2-chloroethyl)ethylsulfide (CEES) whose chemical structure and reactivity is similar to that of sulfur mustard (blistering HD agent), but with reduced toxicity ( $\text{LD}_{50}$  values for rat subcutaneous are 566 and 3.4 mg  $\text{kg}^{-1}$ , for CEES and HD, respectively) [17].

## Synthesis and Characterization of the Catalyst

Nb(V)-containing saponite clay (Nb-SAP) was prepared by hydrothermal synthetic procedure optimized in our laboratories to introduce, through a one-pot reaction, transition metal species inside the inorganic framework [18]. Niobium(V) ethoxide was used as metal precursor. Nb-SAP was then submitted to ionic-exchange procedure in NaCl solution in order to replace the various cations located in the interlayer space and deriving from the synthesis (typically  $\text{H}^+$  along with traces of unreacted  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ ) with sodium ions (Na/Nb-SAP samples; Fig. 1) [13]. As from ICP-AES elemental analysis, the amount of Nb ions in the two solids resulted similar: 1.32 and 1.35 wt.% for Nb-SAP and Na/Nb-SAP clays, respectively. This suggests that the Nb(V) metal centers are mainly located in framework position of inorganic clay rather than in exchangeable sites in the interlayer space. Such Nb content proved to be ideal for other classes of selective oxidations [16,19].

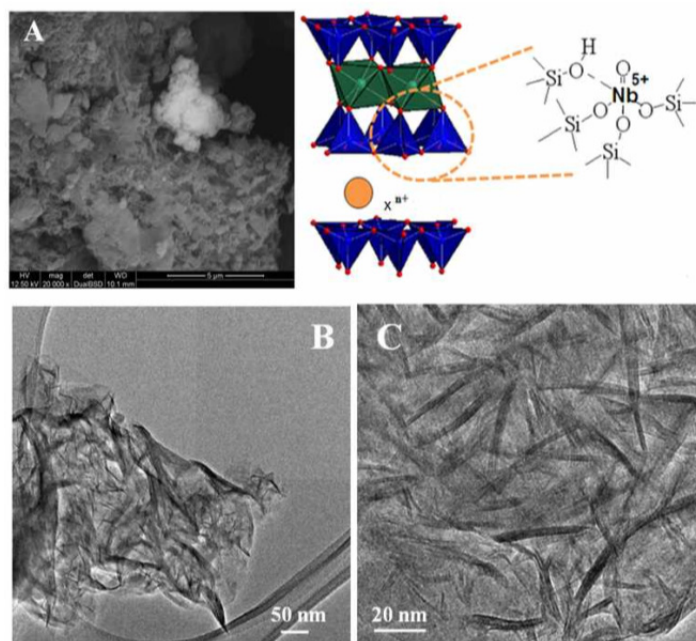


Figure 1. Schematic view of the structure of Nb-SAP catalyst ( $X^{n+} = H^+, Na^+$ ) and SEM (A) and TEM (B, C) micrographs of Nb-SAP catalyst.

The structural and morphological properties of Nb-SAP and Na/Nb-SAP clays were investigated by X-ray diffraction (XRD) and electron microscopy (SEM and TEM). The XRD pattern of both samples showed the reflections typical of trioctahedral clays, indicating that the introduction of Nb(V) centers into the synthesis gel did not affect the layered structure [20]. The interlayer space of the two clays was estimated to be 1.3 nm, larger than that reported for the typical Na-containing saponite clay, Na-SAP (ca. 1.1 nm). The basal plane of the Nb-SAP catalyst appeared well-defined with respect to the Na-SAP sample, thus suggesting a more ordered stacking of the clay layers [20]. The ionic exchange procedure did not alter significantly the Nb-SAP structure.

Sheet aggregates are well identified in the SEM images of Nb-SAP sample (Fig. 1A). TEM micrographs indicated that the sample is composed of sheet-like crystals with nanometer size in width and length (Fig. 1B) [21]. TEM images collected at higher magnifications led to the observation of lattice fringes of the basal planes, showing an interlayer space of ca. 1.3 nm in agreement with X-ray analysis (Fig. 1C).

Nitrogen physisorption analyses have been carried out to verify how the introduction of Nb(V) ions influences the textural features of the saponite material. The adsorption isotherm for Nb-SAP sample is type IV (IUPAC classification), indicating the presence of both micro- and mesoporosity in the material [21]. Moreover, while traditional Na-SAP sample showed a hysteresis loop of H4 type [22], indicating the presence of slit-pores, the isotherm of Nb-SAP is characterized by loops of H3 type, related to the formation of aggregates of plate-like particles giving rise to mesopores formation. This reflects the presence of disordered and smaller aggregates in Nb-containing sample [21]. BET algorithm has been used to estimate the specific surface area (SSA) of the solids: Na-SAP shows a SSA of  $226 \text{ m}^2 \text{ g}^{-1}$ , whereas a significant increase of the surface area is observed for Nb-SAP sample (SSA of  $361 \text{ m}^2 \text{ g}^{-1}$ ).

The coordination state of the niobium species in Nb-SAP and Na/Nb-SAP was investigated by DR-UV/Vis spectroscopy (Fig. 2).

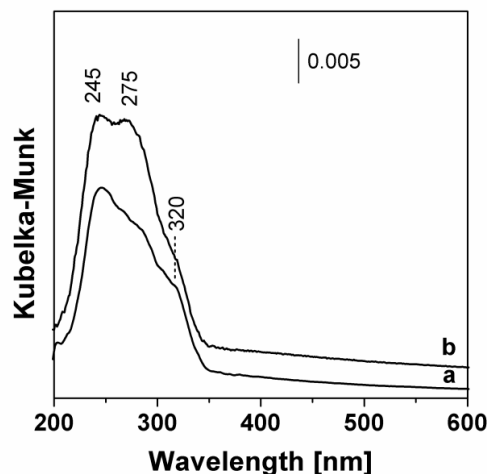


Figure 2. DR-UV/Vis spectra of Nb-SAP (a) and Na/Nb-SAP (b) diluted in a  $\text{BaSO}_4$ , in air and at room temperature.

In both samples no absorption bands were detected above 400 nm, indicating the absence of large extraphase domains of  $\text{Nb}_2\text{O}_5$  [19]. As a general feature, both samples showed two absorption maxima: the first one at 245 nm can be assigned to charge-transfer transition between oxygen atoms and the Nb(V) centers in tetrahedral coordination. The second one at 275 nm was attributed to the presence of Nb(V) centers with penta/hexacoordinated geometry, induced by the coordination of water molecules to the metal ions (Fig. 2) [23]. In addition, a shoulder at ca. 320 nm is ascribed to the formation of low amount of Nb(V) oligomeric sites [19].

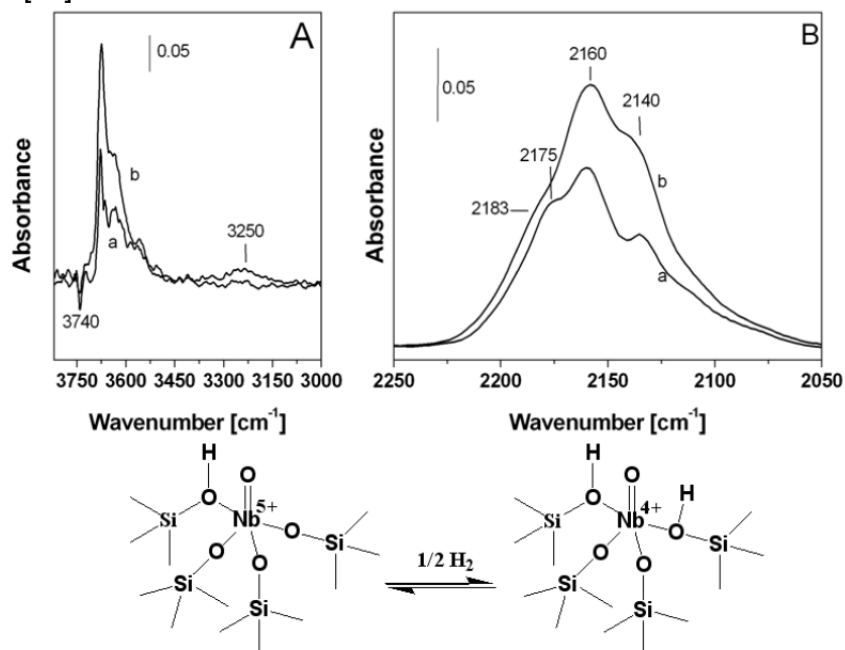


Figure 3: Difference IR spectra of CO adsorbed at 100 K (50 mbar) on Nb-SAP after oxidation in  $\text{O}_2$  at 853 K (a) and reduction under  $\text{H}_2$  at 773 K (b). The spectra are reported in the 3800–3000 (A) and 2250–2050  $\text{cm}^{-1}$  (B) range after subtracting the spectrum of the material before CO interaction. A scheme of the conversion of structural  $\text{Nb}^{5+}$  to  $\text{Nb}^{4+}$  sites after reduction procedure is reported below.

The localization of the Nb centers in Nb-SAP sample was monitored by infrared spectroscopy of CO adsorbed at 100 K on both oxidized and reduced material. A positive

absorption at  $3250\text{ cm}^{-1}$  appear in the difference spectrum of oxidized sample upon CO admission on oxidized Nb-SAP sample (Fig. 3). In agreement to the literature [24], this band can be assigned to the stretching mode of hydroxyl groups that are generated by the presence of both  $\text{Si(OH)Nb}^{5+}$  and  $\text{Al(OH)Si}$  species, interacting with CO probe molecules ( $\Delta\nu_{\text{OH}}$  shift of ca.  $300\text{ cm}^{-1}$ ). The large shift in frequency upon CO absorption indicated that these sites have a strong acidity, comparable to that of acid zeolites or acid saponite samples [25]. The band at  $3250\text{ cm}^{-1}$  is completely absent in the IR spectrum of reduced Nb-SAP sample (Fig. S3), as a consequence of the transformation of Nb(V) into Nb(IV) ions. This is a clear indication that the Brønsted acidity of Nb-SAP sample is promoted by the isomorphous substitution of Si(IV) by Nb(V) centers in the tetrahedral framework of the saponite (see scheme in Fig. 1) [18]. The replacement of the interlayer cations with  $\text{Na}^+$  allows then a complete elimination of the Brønsted acid sites, as can be observed in the IR spectrum of oxidized Na/Nb-SAP upon CO admission [13].

### Evaluation of the Oxidative Abatement Capability

The catalytic properties of Nb-SAP and Na/Nb-SAP samples were evaluated in the oxidative abatement of the blistering agent simulant (2-chloroethyl)ethylsulfide (CEES). The tests were performed at room temperature (298 K) in the presence of  $\text{H}_2\text{O}_2$  (70 mM) dispersed in *n*-heptane and 20 mg of solid catalyst. The decomposition reaction of CEES (14 mM) was followed by monitoring the characteristic UV-Vis absorption maximum at 206 nm [18b]. In the presence of hydrogen peroxide alone, with no catalyst (blank test), CEES showed a negligible self-decomposition (3 mol% degradation max. after 24 h; Fig. 4). When Nb-free saponite samples, namely Na-SAP (sodium-containing saponite) and H-SAP (proton-containing saponite), were added, some CEES abatement was observed (20 mol% after 24 h), showing that the clay itself does possess sulfide degradation capability, especially when some Brønsted acid sites are present. In addition, such tests demonstrate that the physical adsorption capabilities of the saponite itself are limited and cannot account for a complete removal of the sulfide. However, remarkable degradation values and short half-life values were observed over Nb-containing saponites only (Fig. 4). A virtually complete disappearance of the 206 nm UV absorption band was recorded in reasonable times ( $< 9\text{ h}$ ) for Nb-SAP catalysts.

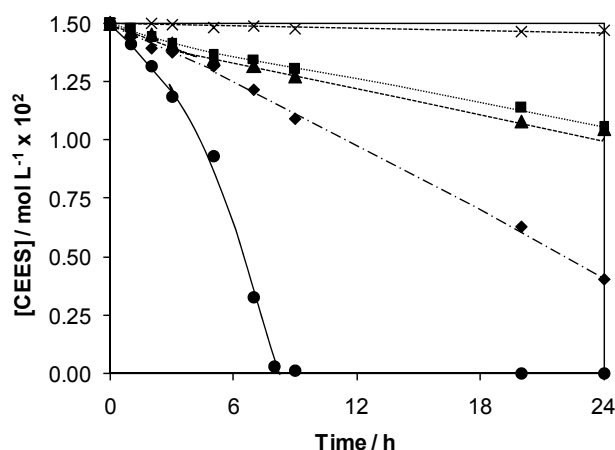
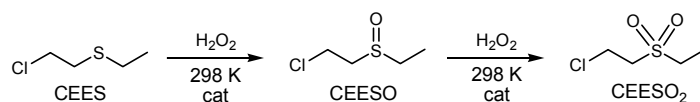


Figure 4. Oxidative abatement of CEES with hydrogen peroxide over Nb-SAP (●), Na/Nb-SAP (◆), H-SAP (▲), Na-SAP (■) and with no catalyst (×). Reaction conditions: CEES (14 mM),  $\text{H}_2\text{O}_2$  (70 mM), catalyst (20 mg), *n*-heptane, 298 K.

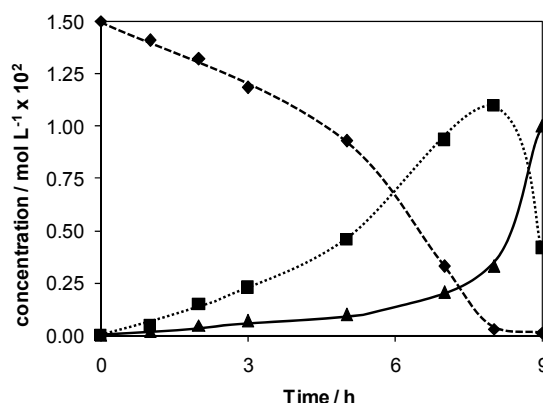
The cooperative effect of Nb centers and acid sites in the catalyst is evident by comparing the abatement profiles for Na-SAP, Na/Nb-SAP and Nb-SAP. Niobium centers provide the clay with the oxidizing properties in the presence of  $\text{H}_2\text{O}_2$ , that are peculiar of Nb(V) sites evenly dispersed in inorganic oxide matrices [16]. Conversely, the presence of protonic sites

in the interlayer sites of the saponite helps the abatement activity via acid-catalyzed degradation pathways [3c,26]. In fact, when the protonic sites were removed by ionic exchange with NaCl aqueous solutions, the abatement capability was largely reduced (*cf.* half-life times, 16 h vs. 5.5 h, for Na/Nb-SAP and Nb-SAP, respectively).



*Scheme 1*

In terms of selectivity, the sulfoxide (CEESO) and the sulfone (CEESO<sub>2</sub>; Scheme 1) are the two main direct products of CEES oxidation. It is worth mentioning that the sulfoxide of sulfur mustard blistering CWA possesses a far reduced toxicity, whereas the related sulfone is almost as toxic as the CWA itself [27]. It is therefore important to monitor the evolution of the oxidized species with respect to time and to select the optimal reaction time to maximize the production of non-noxious (or far less toxic) degradation products.



*Figure 5. Concentration profiles of CEES (◆), CEESO (■) and CEESO<sub>2</sub> (▲) vs. reaction time over Nb-SAP.*

The formation of CEESO was preferential during the first 7 h of reaction, as long as some CEES substrate was present. After the sulfide was almost completely consumed, the further oxidation of CEESO into CEESO<sub>2</sub> occurred and, after longer reaction times (>8 h) the hazardous sulfone was the major product (Fig. 5). In addition, no remarkable amount of polymerized sulfur-containing by-products was observed [27]. This is a noteworthy point, since many conventional abatement approaches suffer from the co-production of large amounts of such side compounds, that are often as toxic and dangerous as the pristine organosulfur blistering CWA.

Finally, a conventional commercial CBRN decontamination powder mixture, M75, currently in use within the Italian Armed Forces has been tested and compared to the proposed catalysts. M75 powder contains bentonite, alumina and calcium hypochlorite and was often used in multi-gram amounts, as a total-loss reactant, for the oxidative degradation of residual CWA stocks. Under the same reaction conditions, with M75 powder, a maximum CEES abatement of 13% after 24 h was obtained, likely thanks to the physical adsorption capability of bentonite. The Nb-SAP catalyst showed thus a superior behavior with respect to this kind of current commercial decontamination product.

Nb-SAP can be easily recovered by filtration, rinsed with solvent (methanol and fresh *n*-heptane) and reused as catalyst in a new reaction batch. The abatement capacity was slightly affected by some deactivation and the CEES half-life times shifted from 5.5 h for the fresh Nb-SAP catalyst to 7.5 h after the third catalytic run (second recycle).

## Concluding Remarks

Nb(V)-containing saponite clay was thus identified as a promising effective catalyst for the chlorine-free oxidative abatement of organosulfur blistering chemical warfare agents with hydrogen peroxide under very mild conditions.

## Acknowledgements

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