Heterogeneous Catalysis

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Niobium(V) Saponite Clay for the Catalytic Oxidative Abatement of Chemical Warfare Agents**

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Abstract: *A Nb^V-containing saponite clay was designed to selectively transform toxic organosulfur chemical warfare agents (CWAs) under extremely mild conditions into nontoxic products with reduced environmental impact. Thanks to the insertion of Nb^V sites within the saponite framework, a bifunctional catalyst with strong oxidizing and acid properties was obtained. Remarkable activity and high selectivity were observed for the oxidative abatement of (2-chloroethyl)ethyl sulfide (CEES), a simulant of sulfur mustard, at room temperature with aqueous hydrogen peroxide. This performance was significantly better compared to a conventional commercial decontamination powder.*

The threat of chemical weapons is back again, not only because they are used for terrorist purposes, but also for explicit warfare aims, as can be seen in the news for the current uncertain international scenarios. The development of adequate techniques for the destruction of stockpiled chemical warfare agents (CWAs) with environmentally safe methods is attracting major attention. Conventional abatement methodologies are based on the use of strong alkaline solutions, aggressive oxidants, enzymatic catalytic systems, and high-temperature treatments.[1] Standard stoichiometric oxidative abatement methods for CWAs rely on chlorine-containing oxidizing reactants such as NaOCl, $Ca(OCl)_2$, and dichloroisocyanurate salts.[2] Nevertheless, all these procedures have a strong environmental impact and are associated with high energy consumption and disposal costs. To overcome these drawbacks, many heterogeneous catalysts have been proposed for the selective oxidation of CWAs into partially or fully oxidized nontoxic products.[3]

Supported V and Mo polyoxometalates (POMs) as well as Fe-containing POMs showed very good conversion and optimal selectivities in the oxidation of organic sulfides into sulfoxides, mimicking the oxidative abatement of blistering agents.[4] Porous oxides are also promising materials, as they show noteworthy chemical, physical, and mechanical robustness and exhibit a good dispersion of catalytically active metal sites.[5] Nanostructured inorganic metal oxides such as Al_2O_3, ZnO, and TiO_2 were widely studied for CWA oxidation and/or degradation reactions.[1b] More recently, oxides with high specific surface area and an ordered array of nanometer-sized channels, mesopores, and cavities were proposed as oxidation catalysts because of their peculiar adsorption capacities toward hazardous chemical agents. However, the need for stoichiometric amounts of organic hydroperoxides or sacrificial reactants and the parallel coproduction of side products are often the major drawbacks of their practical use.[6]

Beside porous materials, layered solids such as clays can be considered as good candidates for the abatement of chemical warfare agents.[7] Advantages such as high robustness, good chemical versatility and very low production costs render these solids promising catalysts for the oxidative degradation of CWAs, although they have been poorly explored for these purposes.

Here, a class of heterogeneous-layered catalysts that are able to trigger selective oxidation reactions and to transform highly toxic agents into products with reduced environmental impact, was prepared for the first time. Particular attention was paid to the use of sustainable oxidants, such as aqueous hydrogen peroxide, under very mild experimental conditions (room temperature and atmospheric pressure). A synthetic saponite clay was selected as support for the dispersion of Nb^V ions. The conventional synthetic protocol used to obtain saponite clays[8] was modified to allow the insertion of Nb^V ions within the framework, aiming to obtain a novel solid (Nb-SAP) with both oxidizing[9,10] and Brønsted acid properties (Figure 1).

Nb-SAP was prepared by one-pot hydrothermal procedure (see the Supporting Information).[11] Niobium(V) ethoxide was used as the metal precursor. Nb-SAP was then submitted to an ion-exchange procedure in NaCl solution to replace the cations located in the interlayer space with Na^+ ions (Na/Nb-SAP). The amount of Nb species in the two solids was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and similar values of 1.32 and 1.35 wt.% for Nb-SAP and Na/Nb-SAP clays, respectively, were found. This suggests that the Nb^V metal centers

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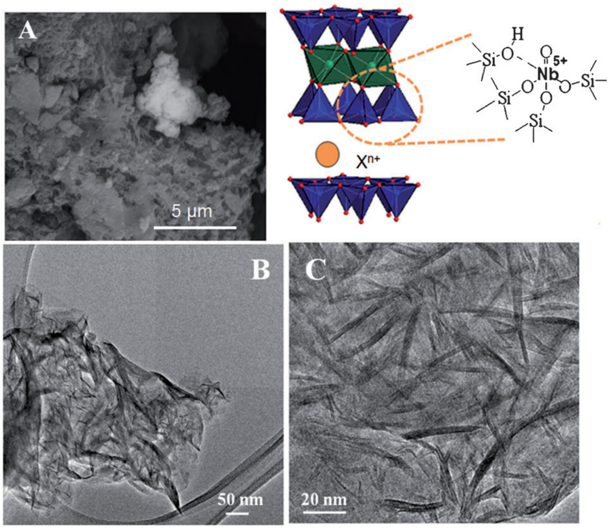


Figure 1. Schematic view of the structure of Nb-SAP catalyst ($X^{n+}=H^+$, Na^+) as well as SEM (A) and TEM (B, C) micrographs of the Nb-SAP catalyst.

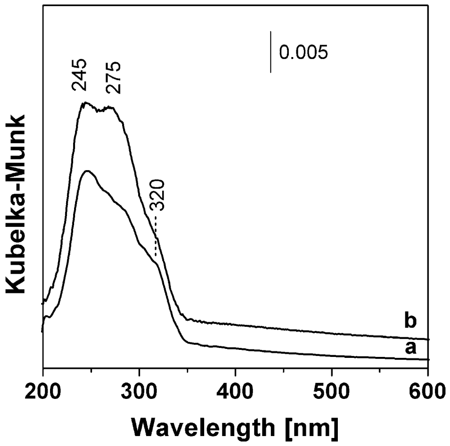


Figure 2. DR-UV/Vis spectra of Nb-SAP (a) and Na/Nb-SAP (b) diluted in a $BaSO_4$ matrix (20 wt%) in air and at room temperature.

are mainly located within the framework of the inorganic clay rather than in exchangeable sites in the interlayer space.

Structural and morphological properties of Nb-SAP and Na/Nb-SAP clays were investigated by X-ray diffraction (XRD) as well as scanning and transmission electron microscopy (SEM and TEM). The XRD pattern of both samples (Figure S1) showed reflections typical of tri-octahedral clays, indicating that the introduction of Nb^V ions did not affect the layered structure.[12] The interlayer space of the two clays was estimated to be 1.3 nm (Figure S1). The basal plane of the Nb-SAP catalyst appeared well-defined, thus suggesting a more ordered stacking of the clay layers. Sheet aggregates are well-identified in the SEM images of Nb-SAP sample (Figure 1 A). In addition, the TEM micrographs indicated that the sample is composed of sheet-like crystals with nanometer size in width and length (Figure 1 B)[13] and lattice fringes of the basal planes, showing an interlayer space of ca. 1.3 nm (Figure 1 C).

The coordination state of the Nb^V species in Nb-SAP and Na/Nb-SAP was investigated by diffuse reflectance UV/Vis (DR-UV/Vis) spectroscopy (Figure 2). In both cases, no absorption bands typical for Nb_2O_5 large domains were observed.[10] Both samples showed two absorption maxima at 245 nm (assigned to a charge-transfer transition between oxygen and the Nb^V centers in tetrahedral coordination) and at 275 nm. The latter signal can either be due to the presence of structural octahedral Nb^V species or to the expansion of the metal geometry promoted by coordination of water (Figure 2 and S2).[14] A shoulder at ca. 320 nm, ascribed to the presence of Nb^V oligomeric sites, was also observed.[10]

The spectrum at the Nb K-edge of Nb-SAP in the X-ray adsorption near edge structure (XANES) region is mainly consistent with the presence of Nb^V species with tetrahedral coordination (Figure S3). The relevant pre-edge feature observed for Nb-SAP and associated with 1s–*n*d transitions is an indication of Nb sites having tetrahedral geometry.

The localization of Nb centres in Nb-SAP sample was monitored by infrared spectroscopy of CO adsorbed on both oxidized and reduced material at 100 K. A positive absorption at 3250 cm^{-1} appeared in the difference spectrum of oxidized sample upon CO admission (Figure S4). This band can be assigned to the stretching mode of hydroxy groups that are generated in the presence of both $Si(OH)Nb^{5+}$ and Al(OH)Si acid species, interacting with CO probe molecules.[11] As a consequence of the transformation of Nb^{5+} into Nb^{4+} ions, this band is completely absent in the IR spectrum of reduced Nb-SAP sample (Figure S4). The replacement of the interlayer cations with Na^+ allows the complete elimination of Brønsted acid sites (see Figure S5).

The catalytic properties of Nb-SAP and Na/Nb-SAP samples were evaluated in the oxidative abatement of the blistering agent simulant (2-chloroethyl)ethyl sulfide (CEES), whose chemical reactivity is similar to sulfur mustard (blistering HD agent), but has a reduced toxicity.[15] The tests were performed at 298 K in the presence of 30 wt% aqueous H_2O_2 (70 mM) dispersed in *n*-heptane and 20 mg of catalyst. The decomposition reaction of CEES (14 mM) was followed by monitoring the characteristic UV/Vis absorption at 206 nm (Figure S6). In the presence of hydrogen peroxide alone without catalyst (blank test), CEES showed a negligible self-decomposition (a maximum of 3 mol% degradation after 24 h; Figure 3). 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 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. Conversely, a remarkable degradation capability was observed over Nb-containing saponite (Figure 3). A virtually complete disappearance of the UV absorption band at 206 nm was recorded in reasonable times (8 h) for Nb-SAP catalyst.

The cooperative effect of Nb centers and acid sites in the catalyst is evident by comparing the abatement profiles for

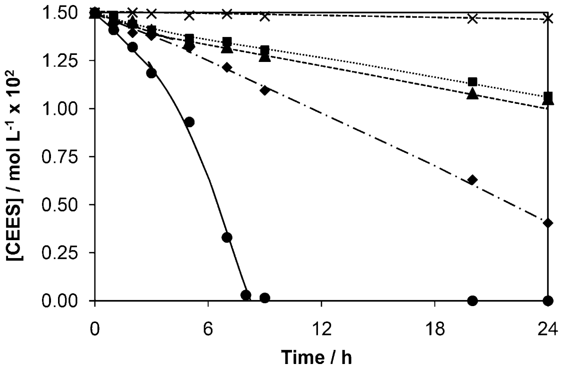
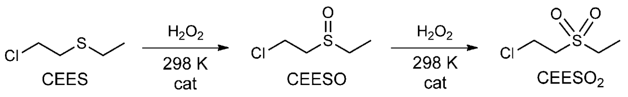


Figure 3. Oxidative abatement of CEES with hydrogen peroxide over Nb-SAP (●), Na/Nb-SAP (◆), H-SAP (▲), Na-SAP (■) and without catalyst (×). Reaction conditions: 14 mM CEES; 70 mM 30% aq. H_2O_2; *n*-heptane; 20 mg catalyst; 298 K.

Na/Nb-SAP and Nb-SAP. In fact, niobium centers provide the clay with oxidizing properties in the presence of H_2O_2 that are peculiar for Nb^V sites evenly dispersed in inorganic oxide matrices.[9,10] Then, the presence of protonic sites in the interlayer sites of the saponite helps to increase the abatement activity through acid-catalyzed degradation pathways.[16,17] In fact, when the protonic sites were replaced by Na^+, the abatement capability was largely reduced (cf. half-life times, 16 h versus 5.5 h, for Na/Nb-SAP and Nb-SAP, respectively). In addition, protonic sites may also take part, in a synergistic way, in the formation of niobium η^1-hydroperoxo species (in the presence of H^+ species and H_2O_2), which are the active sites over which the selective heterolytic oxygen transfer from H_2O_2 to the sulfide occurs. A fully comparable proton-promoted activation of transition metal peroxo complexes has been thoroughly studied and explained with model polyoxometalates (in particular, Ti- and Zr-POMs).[18]

In terms of selectivity, the sulfoxide (CEESO) and the sulfone ($CEESO_2$; Scheme 1) were the two main direct products of CEES oxidation. It is worth mentioning that the sulfoxide of sulfur mustard blistering CWA possesses a significantly reduced toxicity, whereas the related sulfone is almost as toxic as the CWA itself.[15]



Scheme 1. Oxidative abatement of (2-chloroethyl)ethyl sulfide (CEES) to the corresponding sulfoxide CEESO and further reaction to the toxic sulfone $CEESO_2$.

During the first 7 h of the reaction, CEESO was formed preferentially as long as CEES substrate was still present. After 8 h, at a CEES conversion of more than 98%, the selectivity to CEESO was 73%. When the sulfide was almost completely consumed, further oxidation of CEESO to $CEESO_2$ occurred and, after longer reaction times (>8 h) the hazardous sulfone was the major product (Figure 4). In addition, no significant amount of polymerized sulfur-containing by-products was observed.[16] This is a noteworthy point, because many conventional abatement approaches suffer from the coproduction of large amounts of side products, which are often as toxic and dangerous as the pristine organosulfur blistering CWA.

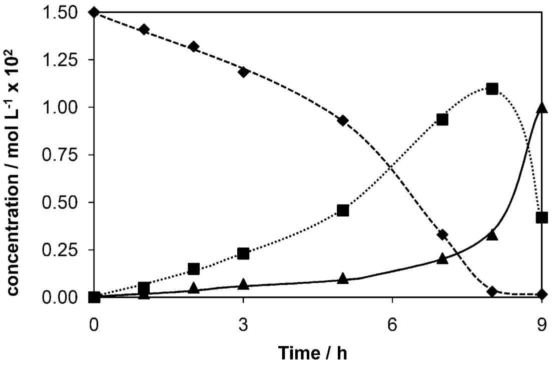


Figure 4. Concentration profiles of CEES (◆), CEESO (■), and $CEESO_2$ (▲) versus reaction time over Nb-SAP.

Considering the sigmoidal shape of the CEES conversion profiles in Figures 3 and 4, the contribution of radical species, which need an induction period to trigger the formation of products through radical homolytic oxidation pathways, cannot be fully excluded.[19] Indeed, products such as disulfides or aldehydes (derived from the oxidative cleavage of the S−C bonds) are detected only for longer reaction times (after ca. 5 h) in a minor amount (below 5 mol% overall).

The large oxidant to sulfide molar ratio was due to the fact that a test with a 2:1 ratio showed a lower initial activity (CEES half-life was 8 h instead of 5.5 h, with 2:1 and 5:1 ratio, respectively) and the conversion of CEES was incomplete even after 24 h (Figure S7). The efficiency of H_2O_2 utilization was around 60% in these tests. Finally, a conventional commercial 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 multigram 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. Nb-SAP catalyst showed thus a superior behavior, because it 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 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). To assess the heterogeneous nature of the Nb-SAP catalyst, hot-separation tests were performed, but no Nb species were detected by ICP-AES analysis of the filtrate, indicating that no leaching occurred (see the Supporting Information; Figure S8).

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.

Experimental Section

Synthesis of Nb-SAP and Na/Nb-SAP: Niobium-containing saponite clay (gel composition: $(Na)_{0.81}Mg_6(OH)_4(Al_{0.81}Nb_{0.07}Si_{7.11})O_{20}\cdot n\,H_2O$, H_2O:Si ratio = 20:1) was prepared by modifying a method proposed in the literature for parent systems.[20] In a typical synthesis, 8.52 g of amorphous silica were gradually dispersed in 50 mL of water containing 0.63 g of NaOH. After 1 h, 3.20 g of aluminum isopropoxide and 24.86 g of magnesium acetate tetrahydrate were added and the gel was stirred for another 2 h. 0.44 g of $Nb(EtO)_5$ was then added. The gel was poured into a Teflon cup of a sealed autoclave and heated in an oven for 72 h at 513 K.

Na/Nb-SAP was prepared by submitting Nb-SAP to an ion-exchange process in a saturated solution of NaCl for 36 h at RT.

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