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PAPER

The reactivity of quaternary ammonium- *versus* potassium- fluorides supported on metal oxides: paving the way to an instantaneous detoxification of chemical warfare agents†

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The reactions of the chemical warfare agents (CWAs) 2,2′-dichloroethyl sulfide (HD), *O*-ethyl *S*-2-(diisopropylamino)-ethyl methylphosphonothioate (VX) and isopropyl methylphosphonofluoridate (GB) with various metal oxide-supported quaternary ammonium fluorides (QAF) and/or potassium fluoride (KF) reagents are described. These active sorbents, which were prepared by a modified procedure, include alumina, silica and titania, enriched with "available" (not bound to the surface) fluoride ions. Alumina-based fluoride reagents were found to be more active than their silica or titania counterparts. QAF/Al_2O_3 reagents, compared to KF/Al_2O_3, exhibit an exceptional reactivity toward HD, as demonstrated both in reaction rates and product identity. For example, with TBAF, $t_{1/2}$ is 15 min for the formation of the elimination product divinyl sulfide (DVS), while with KF, $t_{1/2}$ is 10 h for the formation of the hydrolysis product thiodiglycol (TDG). On the other hand, both sorbents reacted similarly against the nerve agents GB or VX. In order to increase the "available" fluoride content on the solid surface, the mixed active sorbent TBAF/KF/Al_2O_3 (20/20/60) was developed. On this powder, all three CWAs were degraded instantaneously at the low loading of 1 wt% ($t_{1/2} < 2$ min) and rapidly at the higher loadings of 5–10 wt% ($t_{1/2}$ of minutes scale). We assume that the relatively large amount of inorganic fluoride (KF) acts synergistically as a reservoir for the more reactive organic fluorides (TBAF). Moreover, the alumina surface hydroxyl groups may also operate as a water reservoir for the hydrolysis of VX or GB. Therefore, TBAF/KF/Al_2O_3 might be considered as a promising destructive sorbent for CWAs.

Introduction

Detoxification of the chemical warfare agents (CWAs) HD (2,2′-dichloroethyl sulfide, or mustard gas), GB (isopropyl methylphosphonofluoridate, or sarin) and VX (*O*-ethyl *S*-2-(diisopropylamino)-ethyl methylphosphonothioate) is a current concern, not only in view of the obvious military scenario but also due to the fact that chemical terror has become relevant more than ever.[1] One approach to decontaminate these extremely toxic agents is to use reactive sorbents that can adsorb and chemically destroy them to non-toxic products. These active sorbents should be characterized by a capability to neutralize CWAs in a rapid and safe manner, and by their ease of handling, stability, availability and environmental compatibility. An important goal is to find an active sorbent that, beside these requirements, can effectively destroy both nerve agents, such as VX and GB, and blister agents such as HD. In the past decade, various powders, for instance, nanosize particles of MgO,[2] CaO,[3] NaY and AgY zeolite,[4] Al_2O_3[5] and TiO_2,[6–8] as well as various types of KF/Al_2O_3,[9,10] have been proved to act as destructive sorbents for the degradation of these CWAs. However, in spite of their reactivity, they suffer from two main drawbacks: (1) lack of generality in terms of degradation kinetics and product toxicity of both types of CWAs, and (2) loading dependent degradation rate (high loading of CWA causes slow diffusion toward the active sites[5,10]). For example, some of the sorbents react rapidly with HD but slowly with VX[2] and *vice versa*,[9,10] or produce toxic products such as dimeric/trimeric sulfonium salts[4,6] or desethyl-VX (*S*-2-(diisopropylamino)ethyl *O*-hydrogen methylphosphonothioic acid).[9] In addition, most of the above-mentioned metal oxides sorbents are unstable in the presence of air or moisture,[6] and consequently, their reactivity might be reduced in a real decontamination scenario.

In the course of our study on the detoxification of the CWAs VX, GB and HD upon reaction with various types of KF/Al_2O_3, we realized that the main drawback of these active sorbents is a slow

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† Electronic supplementary information (ESI) available: Fig. S2–S19, MAS NMR spectra and reaction profiles of adsorbed CWAs onto selected MF/Al_2O_3 powders; Fig. S20, GC-MS chromatogram of the extraction mixture of HD* on KF/TiO_2. See DOI: 10.1039/c1ob06136d

degradation rate of HD.[9,10] For instance, wet (5 wt%) KF/Al_2O_3 (20, EtOH, 160) reacts rapidly with GB (5 wt%, $t_{1/2} < 10$ min) and VX (5 wt%, $t_{1/2}$ 13 min)[9] but rather slowly with HD (6.5 wt%, $t_{1/2}$ 2660 min).[10] Moreover, this rate is most likely faster (*ca.* 3-fold) than that of the real-life scenario of HD detoxification, due to the high spinning rate of the sample over the course of the MAS NMR measurement.[10,11] The expression KF/Al_2O_3 (20, EtOH, 160) refers to KF/Al_2O_3 that contains 20 wt% of KF, prepared in ethanol, and finally dried overnight at 160 °C.[9]

In order to overcome the challenging aspects of these solid-state reactions, both the active site reactivity and the reactants diffusion inside the inorganic matrix should be improved. Based on our recent results on the improved synthesis of so-called Enriched Coordinatively Unsaturated Fluorides-KF/Al_2O_3 (ECUF-KF/Al_2O_3),[9] we hypothesized that quaternary ammonium fluorides (QAF) as an organic source of "naked" (unsolvated) or "available" (not bound to the surface) fluorides, may act as powerful active sites and at the same time may facilitate the diffusion of the CWAs. The difference between ECUF-KF/Al_2O_3 (prepared in dry MeOH or EtOH) and standard KF/Al_2O_3 (prepared in water) is that the former contains large amounts of "available" fluorides, which may react as strong base, while the latter sorbent mainly contains K_3AlF_6 (nonreactive) and KOH, as previously observed by ^{19}F Solid-State (SS) MAS NMR.[9]

The use of quaternary ammonium fluorides (QAF) in various organic reactions such as desilylations, eliminations and substitutions is well reviewed and documented.[12] Compounds, such as tetrabutylammonium fluoride (TBAF), when carefully dried,[13] synthesized in anhydrous conditions[14,15] or coordinated with *t*-BuOH,[16] may be considered as convenient organic-soluble sources of "naked" fluorides, which have been proved to be strong bases or nucleophiles.[12–16] The high availability and reactivity of the fluoride ion were found to be strongly dependent on its hydrated state. In fact, the idea to impregnate KF onto the surface of alumina, was originally based on the hypothesis that, when well dried, such a fluoride will act as a reactive "naked" fluoride.[17,18] However, it was found by others[17,18] and by us,[9,10] that such "naked" or even "available" fluorides could be obtained only in cases in which the impregnation occurred under appropriate conditions. In order to distinguish between standard KF/Al_2O_3 that mainly contains KOH and K_3AlF_6 (non-reactive fluorides) and "real" KF/Al_2O_3 that contains "available" reactive fluorides, we chose to term the latter as ECUF-KF/Al_2O_3. In fact, in the numerous reported synthetic applications in the literature, the standard KF/Al_2O_3 was used, which in many cases might be equivalent to KOH/Al_2O_3 in the total absence of fluoride.[19] As far as we are aware, our recent publication on this subject was the first to directly compare standard KF/Al_2O_3 with KOH/Al_2O_3 and ECUF-KF/Al_2O_3.[9,10] In the elimination or hydrolysis reactions studied, the latter reagent was much more reactive than the two former ones that were also found to be of similar activity.

QAF impregnated onto the surface of silica or alumina were proved to be non-hygroscopic sources of fluoride ions.[20] $TBAF/Al_2O_3$ is commercially available, but its usage is limited, as far as we know, to the simple removal of protecting groups in multi step processes.[21] In this reagent, the fluoride ions were never confirmed as "naked" or even "available" fluorides, as actually is spectroscopically proved by us in the present work (*vide infra*). Therefore, the synthesis of ECUF-QAF/MO (metal oxides) supports and their reactivity in various organic reactions are still a potential interesting research area.

Herein, we wish to disclose our findings on the reactions of HD, VX and GB with various metal-oxide-supported QAF and/or KF reagents that were synthesized by a modified procedure. A comparison study of these organic *versus* inorganic impregnants has been carried out by SS MAS NMR. The unique effects of the organic fluorides on the surface reactivity of the metal oxides, which enabled us to overcome the above-mentioned drawbacks, will be described.

Results and discussion

Preparation of ECUF-QAF/Al_2O_3 and reactions with HD

Following our original procedure for the preparation of ECUF-KF/Al_2O_3, we firstly tried to impregnate TBAF onto an alumina surface, using a dry ethanolic solution and an 80 °C drying temperature under reduced pressure. It was found that even at this relatively low temperature the organic salt slowly decomposed to volatile products, presumably by Hoffman elimination.[13] In this powder no "available" fluoride was detected by ^{19}F NMR. Therefore, for the drying process, the temperature was reduced (to 60 °C for 45 min and then to 25 °C for additional 24 h under reduced pressure). No indication of a decomposition process was observed by weight analysis and NMR spectroscopy, and therefore, this procedure was chosen for the impregnation of other QAF (tetraethyl-, tetramethyl-, decyltrimethyl-, and benzyltrimethyl ammonium fluoride- TEAF, TMAF, DTMAF and BTMAF, respectively). ^{13}C and ^{19}F MAS NMR analyses of the QAF/Al_2O_3 supports (Fig. 1) show the appropriate signals of the tetraalkylammonium cations (^{13}C NMR) and clearly confirm the presence of a significant amount of "available" fluorides in the region of −115 ± 6 ppm (^{19}F NMR). These chemical shifts indicate that the fluoride ions are present in their hydrated form; however, in this configuration they are still available to react. In some cases we also observed surface bound fluorides (K_3AlF_6) in the region of −155 ± 5 ppm (^{19}F NMR). These unreactive fluorides are formed as a result of a reaction between QAF and a proton source (water, ethanol *etc.*) during the preparation procedure.[9] Interestingly, in the commercial $TBAF/Al_2O_3$ (15% wt) no signals were observed

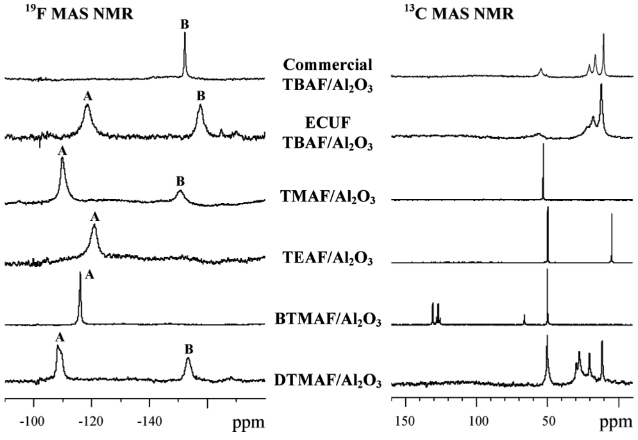


Fig. 1 ^{19}F and ^{13}C MAS NMR spectra of tetraalkylammonium fluorides. **A**: "available" fluoride ion signal. **B**: surface-bound fluoride signal.

in the region of −115 ppm, indicating, as will be shown later, that there are no "available" fluorides in this sorbent (Fig. 1, top).

These fluoride reagents were initially tested as active sorbents for the adsorption and degradation of HD* (^{13}C labeled sulfur mustard)[10] at ambient conditions (25 °C). For effective comparison, they were loaded with equivalent amounts of fluorides, *i.e.* 1 mmol g^{-1}, and reacted with 1 wt% of HD*. In a typical experiment, the appropriate amount of the CWA was carefully added to the examined powder (*ca.* 100 mg, placed in a rotor). The results of the real time kinetics, using solid-state MAS NMR, are graphically shown in Fig. 2. Inspection of the data revealed that QAF salts have a significant impact on both the degradation rates and products. For instance, when subjected to TBAF/Al_2O_3, HD (1 wt%) rapidly ($t_{1/2}$ 15 min) decomposes only to divinyl sulfide (DVS), while onto the surface of KF/Al_2O_3 in the same conditions it was slowly degraded ($t_{1/2}$ 10 h) to thiodiglycol (TDG) as a major product. It is reasonable to assume that gentle heating to 60 °C for only 45 min during the drying process of the sorbents leaves a sufficient amount of water to initiate hydrolysis reactions. These fluoride-promoted reactions themselves cause a simultaneous release of water by the reaction of HF with Al–OH group.[9,10,17] These results were reproduced with all QAF/Al_2O_3 sorbents. Only a negligible effect was observed when the organic fluoride loading was doubled, for instance, 1 or 2 mmol TMAF gave similar results ($t_{1/2}$ 34 *versus* 25 min, ESI Fig. S3–S4†). As expected, the commercial reagent TBAF/Al_2O_3, which didn't contain "available" fluorides, was found to be much less reactive toward HD (37% degradation after 18 h). This result strongly emphasizes the essential role of our mild procedure in the preparation of ECUF-QAF/Al_2O_3 reagents.

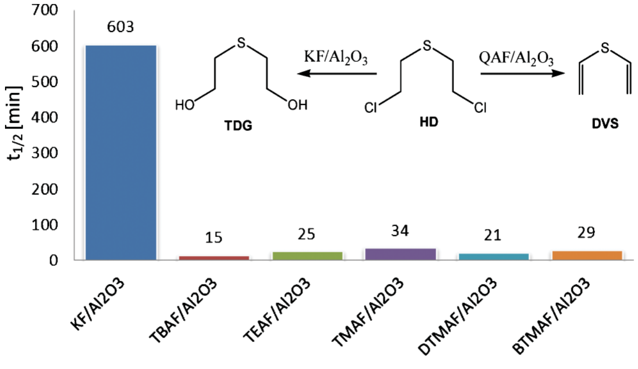


Fig. 2 Degradation half-life times ($t_{1/2}$) and products of HD* adsorbed onto the surface of alumina supported QA and potassium fluoride reagents (1 mmol g^{-1}).

A typical profile for the degradation of HD under the action of QAF/Al_2O_3 is presented in Fig. 3. The ^{13}C MAS NMR spectra gave the characteristic peaks for HD (33.3, 44.0 ppm) and its final degradation product DVS (112.8, 129.0 ppm). As in other studies,[2–10] the profiles of HD degradation processes (as well as VX and GB, *vide infra*) were found to be compatible with a pseudo-first-order reaction (see also ESI Fig. S2–S7†).

The reactions of HD with TBAF/Al_2O_3 were found to be strongly dependent on the loading of the substrate. For instance, the reaction rate was slowed down when a higher concentration of HD (5 wt%) was used (ESI Fig. S8†). In this sorbent, the fluoride content was limited to 1 mmol g^{-1}, and therefore, the degradation rate of a higher loading of HD is affected not only by the relatively slow diffusion of the reactant toward the active sites, but also by their limited quantity/availability. Hence, it is not surprising that this reaction was actually divided into two processes, the first, a relatively rapid dehydrohalogenation of HD promoted by fluoride ions ($t_{1/2}$(1), 6.6 h) and the second, a slower hydrolysis by water or hydroxyl groups ($t_{1/2}$(2), 100 h). This issue is addressed in the following discussion.

Interestingly, the degradation rates of HD by the other active QAF/Al_2O_3 sorbents (*i.e.* TEAF, DTMAF and BTMAF) were fairly close to each other, indicating a minor influence of the nature of the alkyl moiety. However, in all cases that were studied here, these alumina supported organic fluorides exhibited superior reactivity toward HD (*ca.* 20–30-fold faster) compared to the inorganic KF/Al_2O_3 support. At first glance, there are two possible explanations for the enhanced reactivity: 1) as mentioned above, QAF in which the fluoride ions are less ion-paired, are consequently more reactive than their inorganic MF counterparts,[12] and therefore, may enhance the basicity of the active sites onto the alumina surface. This might be the reason for the fact that only the corresponding elimination product (DVS) was observed when HD reacted with QAF/Al_2O_3. In the absence of water these vinylic products should be obtained *via* an E2 mechanism, which requires the presence of a strong base. 2) QAF is able to transform the inorganic alumina support into an organophilic sorbent, facilitating the diffusion and the dispersion

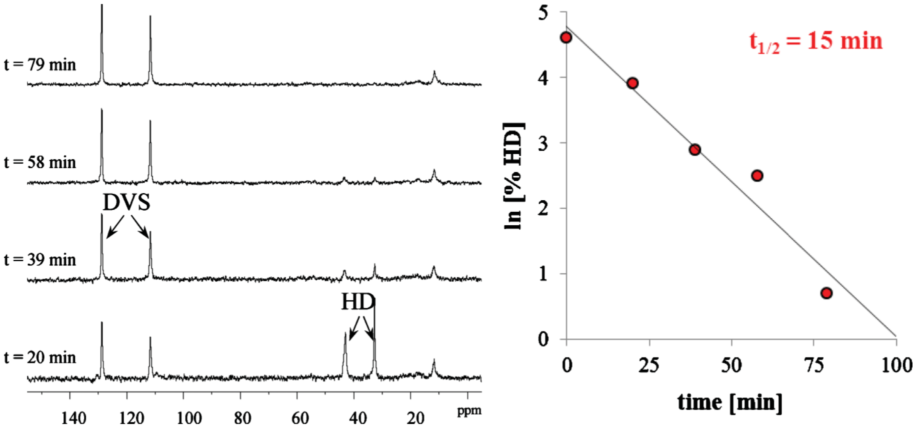


Fig. 3 Selected ^{13}C MAS NMR spectra of adsorbed HD* (1 wt%) on TBAF/Al_2O_3 (1 mmol g^{-1}) and its degradation profile onto this sorbent.

of the hydrophobic reactant HD. Replacing the inorganic cations of mineral clays by quaternary ammonium salts was found to be a useful tool to convert them to so-called organophilic organoclays.[22] Such clays can effectively remove, and in some cases destroy, organic pollutants from water. The organic nature of these sorbents makes them more compatible for the adsorption of hydrophobic compounds. In view of the fact that a relatively minor influence of the alkyl group in the QAF was observed (*ca.* factor 2 between TMAF and TBAF), it seems that the effect described in the first explanation is more dominant.

Real time ^{19}F MAS NMR monitoring of the reaction of TMAF/Al_2O_3 with HD (5 wt%) reveals a gradual decrease in the "available" fluoride signal (−110 ppm) and a simultaneous increase in the intensity of the surface-bound fluoride peak (−150 ppm) (Fig. 4). Namely, the "available" fluorides fully participate in the elimination reaction as a strong base, after which, they immediately react as HF with the alumina surface to give K_3AlF_6.[9,10,17] These results imply that, in spite of the partial formation of bound fluorides during the sorbent preparation, the QAF salts still exhibit high reactivity onto the solid surface.

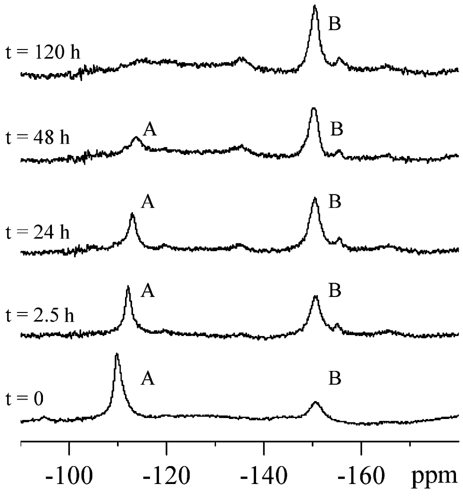
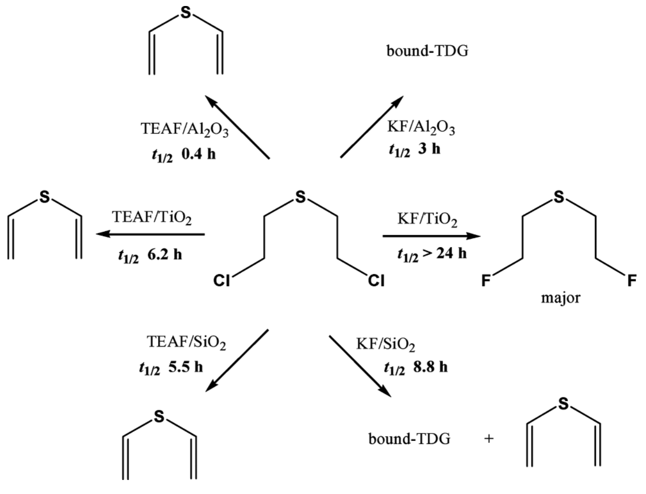


Fig. 4 Selected ^{19}F MAS NMR spectra of TMAF/Al_2O_3 (20, EtOH, 60) with adsorbed HD* (5 wt%). **A**: free fluoride ion signal of TMAF. **B**: surface-bound fluoride signal.

Reactivity of other metal oxides-supported QAF *versus* KF

Encouraged by these results we proceeded to investigate the reactivity of other metal oxide-supported fluorides, such as TEAF/SiO_2 *versus* KF/SiO_2, and TEAF/TiO_2 *versus* KF/TiO_2. For convenience, this specific QAF (TEAF) was chosen here because of its relatively low molecular weight and higher "available" fluoride content on the alumina sorbent (Fig. 1). The results are summarized in Scheme 1. It was found that silica-supported potassium fluoride (KF/SiO_2) reacts with HD similarly to its alumina counterpart to give bound-TDG and DVS but at a slower rate (Fig. S9†). With TEAF, all sorbents gave exclusively DVS but the reaction of HD with TEAF/Al_2O_3 was found to be much faster than that of TEAF/SiO_2 or TEAF/TiO_2 (ESI Fig. S10–S11†). It can be concluded that solid supports, such as ECUF-TEAF/MO, react as strong bases to give the elimination product exclusively, and that alumina is superior to the other metal oxides investigated.

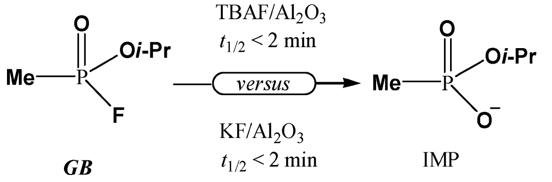


Scheme 1

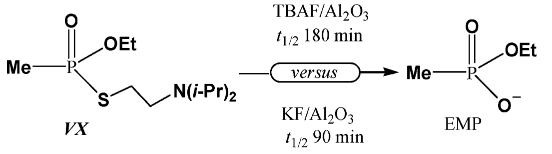
Interestingly, we were quite surprised to find that titania supported potassium fluoride (KF/TiO_2) reacts with HD to furnish slowly the fluorinated sulfur mustard (bis(2-fluoroethyl) sulfide) as a major product (Scheme 1 and ESI Fig. S12†).[23] This product was barely extracted from the titania sorbent (trace amount), however the analytical data (^{13}C NMR and GC-MS spectra) confirmed the structure assignment (ESI Fig. S20†). As far as we are aware, it is the first time that such a fluoride ion reacts as a nucleophile with a carbon electrophile in metal oxide supported potassium fluoride reagents, when usually these fluorides react as bases.

Reactivity of alumina-supported TBAF *versus* KF toward VX and GB

In order to evaluate the effectiveness of these QAF/Al_2O_3 sorbents against other CWAs, we proceeded to investigate their reactivity toward the nerve agents VX and GB. In our recent report on the hydrolysis-based detoxification of VX and GB on some ECUF-KF/Al_2O_3 supports,[9] the reactions rates and the product nature were found to be strongly dependent on the water content of the sorbents. For instance, the degradation of VX onto KF/Al_2O_3 (40, MeOH, 160) with small amounts of water (0–2 wt%) slowly gives bound-EMP (ethyl methylphosphonate), while more water in the sorbent (5–10 wt%) furnishes EMP at a higher rate. As mentioned above, TBAF/Al_2O_3 was found to be the most reactive sorbent toward HD (DVS product, $t_{1/2}$ 15 min). Hence, we chose this sorbent as a prototype for further development. The preparation procedure included impregnation of 20 wt% of fluoride onto the alumina surface. Again, we assumed that after the partial drying of the above-mentioned alumina supported fluoride, enough water molecules were left on the surface of the sorbent to initialize the hydrolysis process. As expected, the degradations of the more labile nerve agent GB (1 wt%), onto the surface of both sorbents KF/Al_2O_3 and TBAF/Al_2O_3 were apparently instantaneous ($t_{1/2}$ < 2 min) and gave IMP (Scheme 2). However, the reactions of these sorbents with VX, without any addition of water, yielded EMP at a much slower rate (Scheme 3 and ESI Fig. S13–S14†). Concerning the degradation rates, only a little difference between these two sorbents was observed, since KF/Al_2O_3 reacts with VX (1 wt%) slightly faster than TBAF/Al_2O_3. The degradation rate of VX onto the surface of



Scheme 2



Scheme 3

TBAF/Al_2O_3 is *ca.* 10-fold slower than that of HD. It seems that fluoride ions play different roles in the degradation mechanism of various CWAs. For VX, because no "GB-analogue" (replacement of the thiolate group by fluoride) was detected, the hydrolysis should occur due to the presence of water and hydroxyl groups on the alumina surface, and catalyzed by fluoride ions.[9] For HD, the organic fluoride behaves as a strong base and reacts directly with the alkyl halide substrate in the elimination process.[10]

Loading effect on the chemical destruction of HD and VX onto the surface of alumina supported fluorides

In our previous work we have found that the hydrolysis-based destruction of VX on the wet (5 wt%) surface of KF/Al_2O_3 is not affected by its loading extent.[9] We deduced that this process is only slightly limited by the diffusion of the reactant toward the active sites. Therefore, it is not surprising that both inorganic (KF/Al_2O_3) and organic (TBAF/Al_2O_3) sorbents react with similar rates with VX (Table 1, runs 3, 4 and 9, respectively). On the other hand, in similar conditions (5 wt% H_2O, KF/Al_2O_3)[10] the degradation rate of HD was found to be strongly dependent on its loading concentration, implying that the diffusion of the reactant toward the active sites plays a crucial role in the process. This trend was found to be relevant in the present work, when a higher loading concentration of HD was reacted with both KF/Al_2O_3 and TBAF/Al_2O_3. For instance, the degradation rate of 1 wt% of HD *versus* 10 wt% onto the surface of the former sorbent is much faster, *i.e.*, $t_{1/2}$ 181 min *versus* $t_{1/2}$ >1.15×10^4 min (Table 1, runs 1 and 2, respectively). Even with TBAF/Al_2O_3 (20, EtOH, 60) the degradation process of HD (1 wt%) is much faster than that of 5 wt% HD (runs 7 and 8, respectively). The latter seems to be strongly limited by the quantity of organic fluoride ions that are available for the elimination process. This is the reason why in the case of 5 wt% of HD the degradation process began with the formation of the elimination product DVS (by fluoride ions) and ended with the production of the hydrolysis product TDG (by water molecules or hydroxyl groups, see also ESI Fig. S8†). If larger amounts of CWAs have to be decontaminated, the heterogeneous mixture will be characterized by a gradient of concentrations. Thus, in spite of the high ratio of decontaminant/CWA (>100 : 1), the effective ratio will be lower. Therefore, we focused our efforts to develop an active sorbent that can rapidly and efficiently destroy the CWAs HD, VX and GB at higher loading concentrations (5–10 wt%).

Table 1 Degradation rates of HD, VX and GB adsorbed on alumina supported KF, TBAF and mixed TBAF/KF

Run	Destructive sorbent[a]	CWA	Loading (%)	$t_{1/2}$ (min)
1	KF/Al_2O_3	HD	1	181
2			10	>1.15×10^4
3		VX	1	90
4			5	85
5		GB	1	<2
6			5	7
7	TBAF/Al_2O_3	HD	1	13
8			5	400 (6×10^3)[b]
9		VX	1	180
10	**TBAF/KF/Al_2O_3**	**HD**	**1**	**<2**
11			5	6
12			10	32 (620)[b]
13	**TBAF/KF/Al_2O_3**	**VX**	**1**	**<2**
14			5	5
15			10	15
16	**TBAF/KF/Al_2O_3**	**GB**	**1**	**<2**
17			5	11

[a] The sorbents contain 20 wt% of each fluoride type and are used without addition of water. [b] Second steady state $t_{1/2}$ (in parenthesis) observed in the reaction profile.

Mixed sorbent TBAF/KF/Al_2O_3

With the above-mentioned insights, we hypothesized that mixed organic/inorganic alumina supported fluorides such as TBAF/KF/Al_2O_3 (20 wt% each fluoride) would be both sufficiently reactive and highly enriched with "available" fluorides. Theoretically, 1 g of this sorbent may contain 0.63 mmol of fluoride ions from TBAF and 3.44 mmol fluoride from KF. Taking into account that every HD molecule requires two fluorides to complete the double elimination process (resulting in DVS), there is a sufficient number of active sites to destroy at least 2 mmol of HD (*ca.* 25 wt% loading) onto the surface of 1 g sorbent. Indeed, we have found that the mixed powder TBAF/KF/Al_2O_3 is a very effective active sorbent for the adsorption and destruction of both nerve gases VX and GB and blister agent HD, even at high loadings of 5–10 wt% (Table 1). This sorbent, as clearly demonstrated by Fig. 5, almost immediately destroys all three CWAs at a relatively low loading of 1 wt% (Table 1, runs 10, 13, 16). It is important to point out that the toxic desethyl-VX was not observed as a product. The signal at 29 ppm in spectrum 5B (Fig. 5) is attributed to diethyl methylphosphonate due to a trace amount of ethanol originated from sorbent preparation. Moreover, with higher concentrations, 5 and even 10 wt%, the degradation processes are still completed in minutes scale (runs 11, 14, 17 and 12, 15, respectively). The loading effect is remarkable when one compares the degradation rates of 10 wt% of the hydrophobic HD onto the surfaces of TBAF/KF/Al_2O_3 *versus* KF/Al_2O_3 (runs 1, 2 and 10, 12, respectively). Despite the fact that the latter sorbent contains similar amounts of fluoride ions, it is much less effective than the former. The degradation rates of VX onto the mixed powder TBAF/KF/Al_2O_3 are much faster than those observed with KF/Al_2O_3 and TBAF/Al_2O_3, as shown in runs 13–15, *versus* 3, 4 and 9, respectively.

Both from reaction kinetics and products points of view, these findings have situated the mixed powder TBAF/KF/Al_2O_3 at a similar position to that of the excellent liquid decontaminant, the

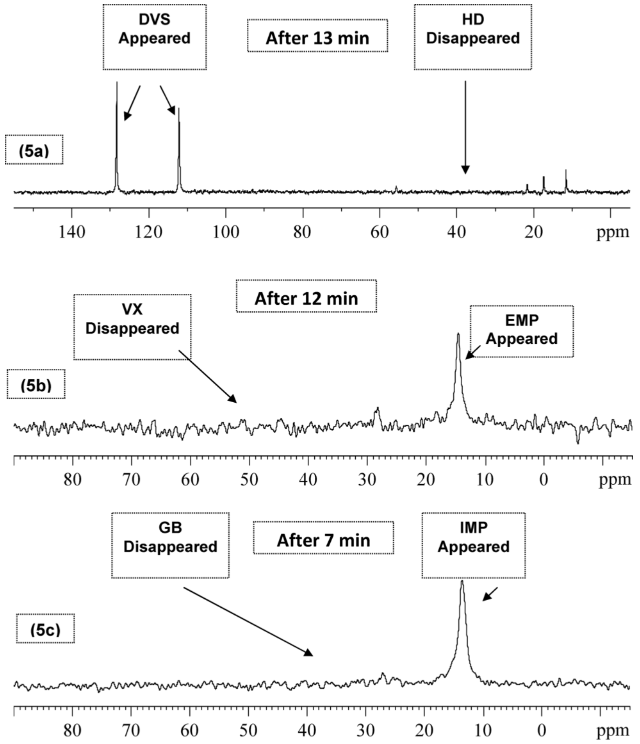


Fig. 5 MAS NMR spectrum of the adsorbed CWA (1 wt%) on TBAF/KF/Al_2O_3 (20, 20, EtOH, 60): (5a) ^{13}C, HD*, after 15 min; (5b) ^{31}P, VX, after 12 min; (5c) ^{31}P, GB, after 7 min.

'Decon green' solution.[24] As far as we are aware, our powder is the most effective active sorbent yet observed for chemical destruction of HD, VX and GB. Using controlled experiments, no spinning effect[9–11] (by MAS NMR) was observed in the degradation of HD onto this sorbent, and therefore, in a real decontamination scenario it would effectively decontaminate CWA with the above-mentioned rates and efficacy.

Conclusions

The results described herein highlight two important aspects of the differences in reactivity between QAF and KF. The first one is more general and clearly illustrates that QAF are much more reactive bases than KF, when supported onto the surface of alumina. The effect is more significant on the surface of Al_2O_3 as compared to TiO_2 or SiO_2. The second valuable aspect of this comparative research is the ability of the mixed solid-support TBAF/KF/Al_2O_3 to degrade all the above-mentioned CWAs in a very rapid manner to non-toxic products (practically instantaneous for 1 wt% and in minutes scale for 5–10 wt%). These results show that the presence of a substoichiometric amount of quaternary ammonium ions is sufficient to increase the catalytic activity of a balance of fluoride ions onto the alumina surface. We assume that in this highly reactive sorbent, the relatively large amount of inorganic fluorides (KF) acts synergistically as a reservoir for the more reactive organic fluorides (TBAF). Moreover, the alumina surface hydroxyl groups may also operate as a water reservoir for the hydrolysis of VX or GB. The presence of "available" fluorides is critical to rapid decontamination of CWAs; however, the nature of these species and the mechanism of which they catalyze the decontamination of the CWAs still have to be studied.

Experimental

Materials

^{13}C-labeled HD (HD*) was prepared according to a literature procedure.[25] KF/Al_2O_3, QAF/Al_2O_3 and QAF/KF/Al_2O_3 reagents were prepared by impregnation of KF and/or QAF onto dry γ-Al_2O_3 from dry ethanolic solution, and dried at 60 °C. For example, TBAF/KF/Al_2O_3 (20 wt% each fluoride) was prepared by dissolving 1.0 g of KF and 1.0 g of TBAF in ethanol (30 ml), then 3.0 g of γ-Al_2O_3 (dried at 160 °C for 24 h) was added, and organic solvent was removed by evaporation at 60 °C for 45 min. The powder was further dried at room temperature under vacuum (oil pump) for 24 h.

NMR

^{31}P, ^{13}C and ^{19}F MAS NMR spectra were obtained at 202, 125, and 471 MHz, respectively, on a 11.7 T (500 MHz) spectrometer, equipped with a 0.4 cm standard CP-MAS probe, using direct polarization (*i.e.* no cross polarization (CP) was used). Typical spinning rates were 5–7 kHz. Chemical shifts for ^{31}P, ^{13}C and ^{19}F were referenced to external trimethyl phosphate (TMP), TMS and $CFCl_3$, respectively, as 0 ppm. For ^{31}P spectra the pulse delay was 2 s, which is considered sufficient for relaxation in OP esters on solid matrices. The number of transients per spectrum was 200. For ^{13}C spectra the pulse delay was 15 s, and the number of transients per spectrum varied between 20 and 100. For ^{19}F spectra the pulse delay was 2 s, and the number of transients per spectrum varied between 100 and 2000. For comparison purposes, spectra were recorded under identical conditions. The half-life time values are based on the relative amplitudes of the NMR integrations of both products and starting materials. Typical estimation of the reliability of an integral in NMR spectrum are 3–5%, and even with relatively poor s/n, random errors are quite small.[26]

Sample preparation

Caution: *These experiments should only be performed by trained personnel using applicable safety procedures.* Samples of the appropriate powder (40–100 mg) were added to the 0.4 cm ZrO_2 rotor, and 0.8–8 µL of the CWA (VX, GB or HD*) was applied *via* syringe to the center of the sample. The rotor was sealed with a fitted Kel-F cap. ^{31}P, ^{13}C and ^{19}F MAS NMR spectra were measured periodically to determine remaining starting material and identify degradation products.

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