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Hydrolysis of DCNP (a Tabun mimic) catalysed by mesoporous silica nanoparticles

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ABSTRACT

The hydrolysis of diethylcyanophosphonate, DCNP (a Tabun simulant) in the presence of mesoporous silica nanoparticles (MSN) has been studied in acetonitrile:water (99.5:0.5 v/v) mixtures using ^{31}P NMR as a suitable technique to follow the DCNP hydrolysis. MSN alone was not capable to induce DCNP hydrolysis, yet MSN in combination with the presence of the bases potassium carbonate, triethylamine or DABCO enhanced DCNP degradation. When MSN was used combined with K_2CO_3, a hydrolysis of ca. 95% of the initial DCNP after 60 min was observed. In the presence of DABCO, MSN was able to induce the hydrolysis of ca. 90% of DCNP after the same time. However, the DCNP hydrolysis using MSN in the presence of Et_3N was lower (ca. 30%). In the absence of nanoparticles, DCNP hydrolysis reached only ca. 30% for K_2CO_3 and DABCO and ca. 7% for Et_3N after 60 min. Moreover, kinetic studies were also carried out with the use of solids MSN-1 and MSN-2 that were obtained by reaction of MSN with K_2CO_3 or DABCO. After the reaction the solids were isolated by centrifugation, washed with acetonitrile and dried. MSN-1 was able to hydrolyse DCNP in a similar way to that found with the MSN-K_2CO_3 mixture. However, MSN-2 nanoparticles induced a very low DCNP hydrolysis. From all these studies it was found that the main product of the DCNP hydrolysis is tetraethylpyrophosphate. The presence of diethyl phosphoric acid was also observed but at very low concentration. From kinetic data a catalytic mechanism is proposed.

1. Introduction

Chemical warfare agents (CWs) are classified in several groups; i.e. nerve agents, asphyxiant/blood agents, vesicant agents, choking/pulmonary agents, lachrymatory agents, incapacitating agents and cytotoxic proteins [1]. Among CWs, nerve gases are perhaps the most dangerous [2]. The development of nerve agents was a by-product of insecticide research and development. It was in early 1930s that German chemists first produced G-agents (Tabun (GA), Sarin (GB), Soman (GD) and Cyclosarin (GF)). Some years later further research resulted in discovery of new types of nerve agents; i.e. V-agents (VG, VM, VX, VE).

Due to its toxicity, nerve gases agents have been employed since their discovery as chemical weapons and even in the last years these poisonous compounds have been used in several terrorist acts as for instance in the subway attack in Tokyo in 1995, in the Iraq repression against Kurdish communities in 1988 and, very recently, in Syrian civil war. These compounds are strong inhibitors of the enzyme acetylcholinesterase inducing the accumulation of the neurotransmitter acetylcholine, thus, inhibiting nerve impulse [3]. The accumulation of acetylcholine produces a crisis of the nerve system characterized by convulsions, bradycardia, behavioural incapacitation, muscle weakness and respiratory failure that may

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lead to death [4]. Furthermore, the threat of these compounds as chemical weapons is enhanced by the fact they are colourless gases and their presence is not easily noticed until they have been already inhaled.

The easy fabrication of nerve gases (with severe environmental problems associated with spills and production) and their indiscriminate use by ambitious nations or by terrorist groups have boosted the efforts of the scientific community toward the detection and remediation of these deadly chemicals [5].

Dealing with their detection, a variety of instrumental methods such as surface acoustic wave (SAW) devices [6], enzymatic assays [7], electrochemical [8], interferometry [9] and gas chromatography coupled with mass spectrometry [10] have been extensively developed to detect nerve gases. More recently the design of chromo-fluorogenic chemical probes based on supramolecular concepts or in the use of hybrid silica-based organic-inorganic materials has freshly emerged in the last years [11].

However, remediation of nerve gases is still a matter of concern and active research to find safe and effective methods to detoxify without endangering human life or the environment is currently underway [12]. Certain examples of compounds able to react with nerve gases to avoid their interaction with acetylcholinesterase and several methods to reactivate the poisoned enzyme have been reported [13]. Dealing with environmental decontamination, experimental procedures such as electrolytic methods [14], oxidative degradation on active sorbents [15], catalytic [16] and biocatalytic [17] degradation methods [18], atmospheric pressure plasma [19] and photolytic procedures [20] have been explored. Moreover, very recently, highly porous multifunctional metal oxide/hydroxide micro and nanoparticles [21], clays [22], metal-organic frameworks (MOFs) [23] and porous organic polymers (POPs) [24] have been also used as destructive adsorbents against nerve gases. Among these materials, microporous and mesoporous silicas are particularly attractive for nerve gases remediation [25]. These materials could be easily synthesized in different morphologies and pore sizes and show large surface areas (up to 1200 $m^2\ g^{-1}$), are chemically inert and are easily functionalized through the use of the well-known alkoxysilane chemistries [26]. In this context, very recently, mesoporous silica materials have been used as scaffolds for the adsorption or encapsulation of decontaminant compounds or enzymes in order to prepare materials for environmental nerve gases degradation [27]. Besides, thermal decomposition of organophosphorous derivatives, previously adsorbed into zeolites, has also been reported [28]. Silica nanoparticles impregnated with reactive chemicals have been also prepared and used for the removal of sulphur mustard and the nerve gas simulant diethylchlorophosphate [29].

From a chemical point of view, nerve gases are characterized by the presence of an electrophilic central phosphorus atom that is prone to suffer nucleophilic addition reactions with nucleophiles. In fact it is the reaction of the P atom with hydroxyl anions one of the paths of the degradation of nerve gases in the environment [30].

Based in these concepts we were interested in testing the potential use of silica-based nanoparticles for the degradation of nerve gases. We envisioned that by using certain bases it would be possible to transform the silanol groups at the surface of silica on silanolate nucleophiles [31] that could react with these chemicals yielding non-toxic degradation products. With this idea in our aim, we report herein the use of mesoporous silica nanoparticles (MSN) treated with different bases (i.e. potassium carbonate, triethylamine and DABCO) as potential new easy to prepare materials for the degradation of nerve gases. For our study we have selected diethylcyanophosphonate (DCNP) as a suitable nerve agent simulant. DCNP has been typically used as model compound as it has similar reactivity but reduced toxicity when compared with the corresponding chemical warfare agent Tabun. The aim of the present study is to contribute to the design of simple remediation materials that could be of potential use in decontamination devices and filtration systems to remove toxic nerve gases from contaminated environments.

2. Results and discussion

2.1. Design of the materials

Nerve agent simulants are, from a chemically point of view, organic phosphates and phosphonates bearing good leaving groups. One of most remarkable chemical feature of these compounds is related with the presence of an electrophilic phosphorus atom that is prone to suffer nucleophilic attacks. In this work we have used MCM-41 mesoporous (MSN) silica nanoparticles as catalysts for the hydrolysis of the nerve agent Tabun simulant DCNP. The reactivity of the solids was enhanced via deprotonation of the silanol groups by using the bases K_2CO_3, DABCO and Et_3N.

MCM-41 mesoporous nanoparticles were prepared, via well-known procedures, from tetraethyl orthosilicate (TEOS) as inorganic precursor and *n*-cetyltrimethylammonium bromide (CTABr) as a porogen species [32]. The removing of the surfactant by calcination yielded the final MCM-41 mesoporous nanoparticles (MSN).

In a first step the hydrolysis of DCNP was carried out in acetonitrile:water (99.5:0.5 v/v) mixtures containing the silica nanoparticles (MSN), the base (K_2CO_3, DABCO and Et_3N) and the simulant. An illustrative picture of the hydrolysis procedure is shown in Scheme 1.

The above mentioned hydrolysis procedure required the suspension of the silica nanoparticles and the corresponding base in an organic solvent. Moreover, in order to simplify the procedure and, taking into account a possible application of the approach in remediation processes, we also prepared the materials MSN-1 and MSN-2 by treatment of MSN with K_2CO_3 and DABCO. For the preparation of these materials the MSN nanoparticles were treated with an aqueous solution of K_2CO_3 (for MSN-1) or with an acetonitrile solution of DABCO (for MSN-2). The suspensions were stirred at room temperature for 1 h and then the solids were then centrifuged, washed with acetonitrile and dried at 60 °C.

2.2. Characterization of the materials

The prepared nanoparticles (MSN, MSN-1, and MSN-2) were characterized by standard solid state techniques. Fig. 1 shows the PXRD patterns of the MCM-41 as synthesized, calcined MCM-41 nanoparticles (MSN), MSN-1 and MSN-2.

The PXRD of the mesoporous MCM-41 material as-synthesized (Fig. 1, curve i) displayed the expected four peaks of a hexagonal ordered array indexed as (100), (110), (200), and (210) Bragg reflections. From the PXRD data, an a_0 cell parameter of 47 Å (d_{100} spacing of 40.78 Å) was calculated. In curve ii, corresponding to the MCM-41 calcined sample (MSN), a significant shift of the (100) reflection in the PXRD is clearly observed. This displacement, together with the broadening of the (110) and (200) reflections, corresponds to an approximate cell contraction of 6–8 Å due to the condensation of silanol groups in the calcination step. Fig. 1 also depicts the PXRD patterns for solids MSN-1 and MSN-2. For these materials, reflections (110) and (200) were lost, most likely due to partially order loss induced by the basic treatment. In case of MSN-1 the treatment with K_2CO_3 induced the formation of amorphous inorganic silica and/or potassium silicate that is deposited on the mesoporous surface, thus, blocking the pores (*vide infra*) and