

NĚKTERÉ NOVÉ TYPY REAKTIVNÍCH SORBENTŮ PRO ROZKLAD VYSOCE TOXICKÝCH CHEMICKÝCH LÁTEK

SOME NEW KINDS OF REACTIVE SORBENTS FOR DESTRUCTION OF HIGHLY TOXIC CHEMICAL SUBSTANCES

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Abstract

On contrary to conventional sorbents, which retain toxic substances on their surface without altering their chemical structure and thus preserve their toxicity, the reactive sorbents are capable to destroy the toxic substances or to convert them into less toxic residuals. Most of the reactive sorbents are derived from the nanocrystalline metal oxides and their effectiveness depends on their chemical and phase composition as well as on their physical characteristics, which may be governed by a proper selection of the synthetic route. The Ti and Mg oxides belong to the most promising reactive sorbents for the destruction of nerve gases as well as blistering agents, although the nanocrystalline ceria provides some advantages in the destruction of toxic organophosphates. Recently, some new kinds of reactive sorbents were introduced, namely the materials derived from metal-organic frameworks (MOFs), which were applied successfully for the degradation of toxic substances including chemical warfare agents.

Key words: *reactive sorbents, nanocrystalline metal oxides, metal-organic frameworks (MOFs), toxic compounds, decontamination*

1 INTRODUCTION

A persistent threat of terrorist attacks and continuing risks of industrial accidents stimulate the development of new decontamination equipment and technologies [1]. So-called “reactive sorbents” or “stoichiometric reagents” belong to the most promising decontamination agents because of their ability not only to retain a wide range of chemical compounds by a physical sorption, but also to destroy them chemically or convert them to less toxic residuals [2]. Based on the works of Klabunde et al. [3-5], the first nanocrystalline metal oxide-based reactive sorbents were developed and applied for the destruction of dangerous compounds in industry and also for the degradation of highly toxic organophosphates including nerve gases (sarin, soman, VX) and some other kinds of chemical warfare agents (mustard gas). FAST-ACT (First Applied Sorbent Treatment Against Chemical Threats) [6] introduced by NanoScale Corp. represents probably the most famous commercially available reactive sorbent widely used in industry as well as in rescue and armed forces. The family of the metal oxide-based reactive sorbents was extended substantially by Štengl and his group, who developed a series of nano-structured reactive sorbents consisting of a single metal oxide (MgO) [7] or doped metal oxides (Ti and Fe oxides doped with Zr) [8] prepared by a simple and easily scalable “wet” methods, e.g. by homogeneous hydrolysis. In recent time, the research activities are focused on the examination of the mechanism(s) effective during the degradation of main kinds of toxic

compounds (organophosphates in the first place) on various reactive sorbents with the goal to develop alternative decontamination strategies utilizable e.g. in the soil remediation or for the destruction of toxic pesticides; the findings are summarized briefly in this article. New kinds of reactive sorbents (not belonging to the metal-oxide group) are mentioned as well.

2 DEVELOPMENT OF NEW REACTIVE SORBENTS

2.1. Metal oxide reactive sorbents

The mechanisms of the degradation of chemical substances were studied extensively by Klabunde et al. [4, 9], who proposed that the nucleophilic substitution S_N2 is effective in the degradation of toxic organophosphates on the surface of metal oxides. It follows from the theory of chemical reactions that the S_N2 substitution is favoured in the aprotic solvents (e.g. acetone, acetonitrile and all non-polar solvents), but it is inhibited in polar protic solvents including water, as was shown for the degradation of organophosphate pesticides in the presence of cerium oxide [10]. This fact represents a serious limitation for the environmental applications of the reactive sorbents. To overcome these limitations, the reactive sorbents often contains more than one component with different degradation capabilities. FAST-ACT, for example, contains titanium oxide together with MgO and thus it exhibits a strongly alkaline reaction in aqueous medium (pH of the aqueous suspension is 9 or even higher). Thanks to this combination, FAST-ACT has found wider applications in industry serving here as a neutralizing agent for the treatment of the mineral acids spills. As a result, however, it adsorbs an air humidity and carbon dioxide and loses its activity when improperly stored. On the other hand, cerium oxide as one of the recently introduced reactive sorbents exhibits a low hydrophilicity and a low tendency to react with carbon oxide. Despite its virtually inert nature, cerium oxide was able to degrade the organophosphate pesticide parathion methyl even faster than FAST-ACT.

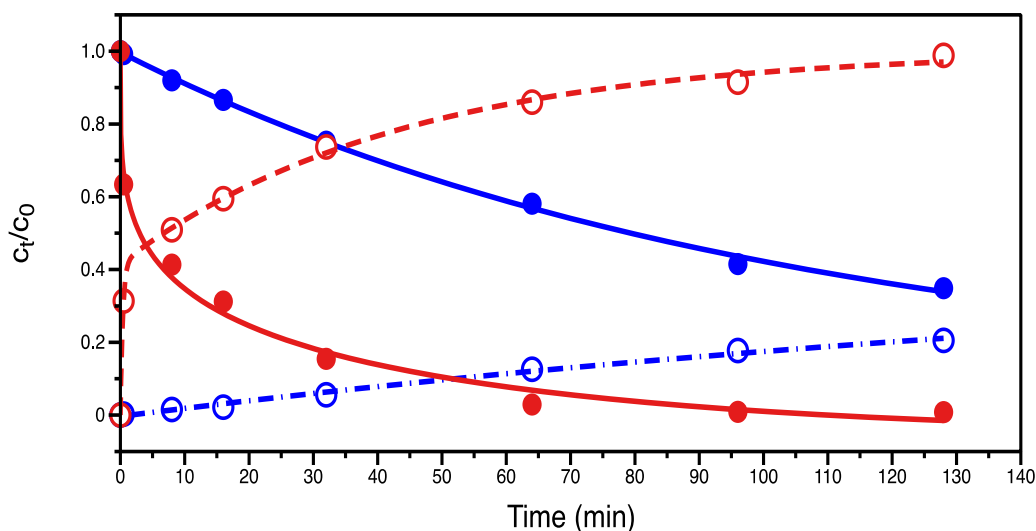


Figure 1 Degradation of parathion methyl in the presence of cerium oxide (in red) and in the presence of FAST-ACT (in blue). Full lines – decrease of the parathion methyl concentration, dashed lines – creation of 4-nitrophenol. Reaction medium: acetonitrile

The effectiveness of the reactive sorbent is governed by the activity of surface functional groups, which is, however, strongly related to the main physical characteristics, such as crystallinity and surface area. It was shown that various synthetic routes are utilizable for the

production of cerium oxide capable to destroy the nerve agents [11] soman and VX. Interestingly, the cerium oxides prepared by homogeneous hydrolysis and by the precipitation/calcination method differ markedly in their morphology, but their decontamination efficiencies were almost identical. The cleavage of the phosphoester bonds is facilitated by the presence of the metal cations on the sorbent surface (acting as the Lewis acid centre) and also by the presence of the hydroxyl groups or molecules of strongly adsorbed water (acting as nucleophilic agents). A suitable spatial arrangement of these active sites on the sorbent surface may be achieved by a proper selection of the synthetic conditions, e.g. by a proper adjustment of the annealing temperature. An alternative approach consists in a modification of crystallite parameters with the aid of suitable dopants. Mixed-metal oxides (titania/ceria) were also used for the degradation of organophosphate pesticides and CWAs simulants [12].

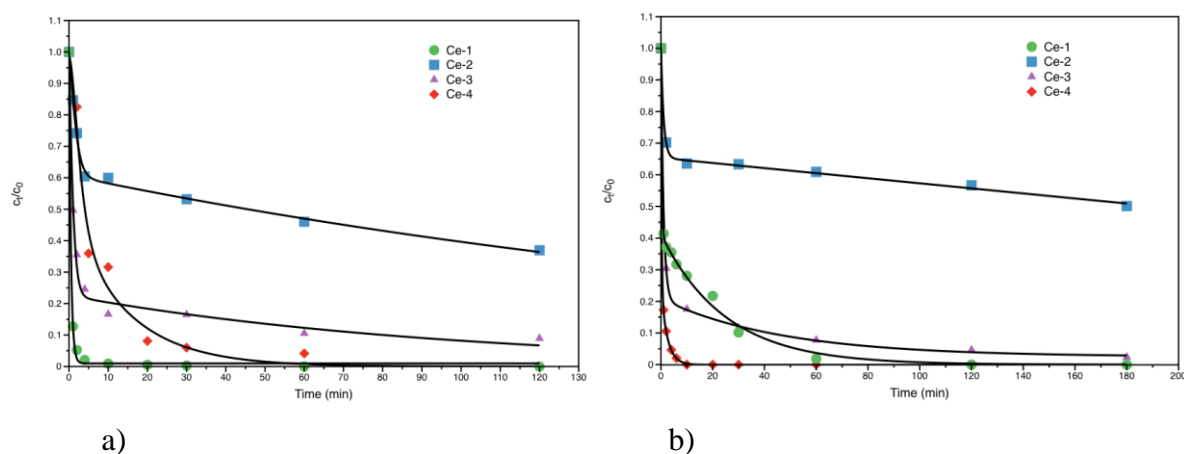


Figure 2 Degradation of nerve agents VX (a) and soman (b) on various cerium oxides. Ce-1 – cerium oxide prepared by homogeneous hydrolysis; Ce-2 – cerium oxide prepared by sol-gel method; Ce-3 cerium oxide prepared from oxalate precursor, Ce-4 cerium oxide prepared from oxalate precursor [11]

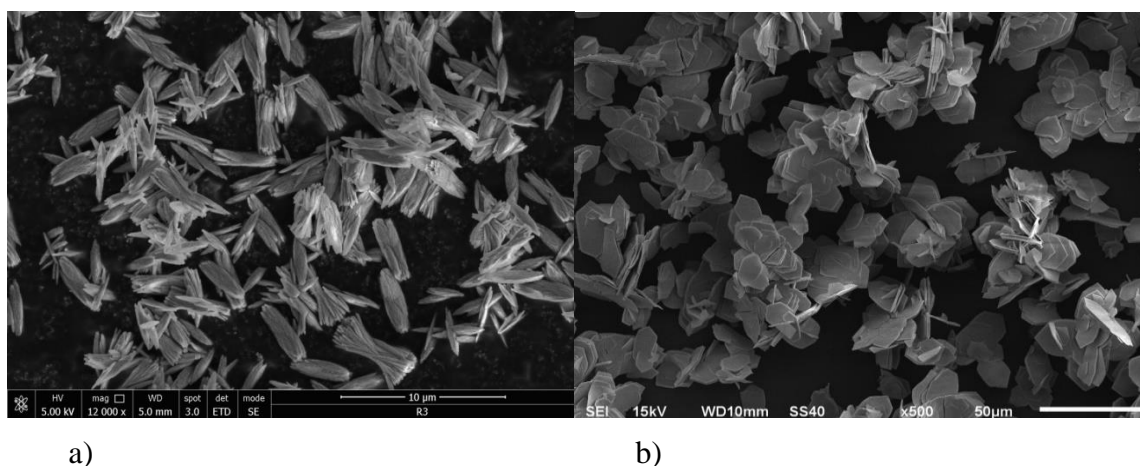


Figure 3 SEM images of the cerium oxides prepared by homogeneous hydrolysis (a) and precipitation/calcination method (b)

2.2. Metal-organic frameworks (MOFs) as reactive sorbents

MOFs are crystalline metallo-organic compounds with a well-defined geometric structure consisting of metal ions or clusters coordinated to organic ligands. Some of them, especially those containing the Zr clusters ($\text{Zr}_6\text{O}_8^{8+}$), are highly effective in the degradation of nerve gases and their simulants, as well as the blistering agents. Some of the Zr-based MOFs and their rare earths analogues were prepared by the Lang's group at IIC CAS Řež and tested in our laboratory for the degradation of organophosphate pesticides. A great progress has been made towards the practical applicability of MOFs in the decontamination technologies during the last years in several laboratories around the world (Germany, Spain, USA, Saudi Arabia); the Zr-based MOFs (UiO-66, NO-1000, MOF-808) were incorporated into a textile matrix, and this composite material was used as an active filter capable to destroy the main kinds of CWAs [13-15].

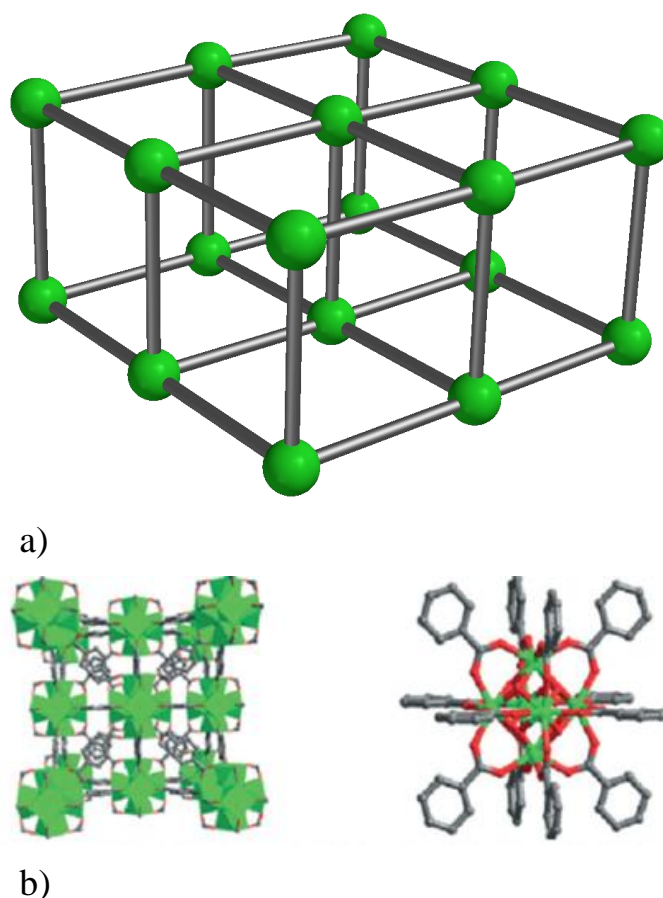


Figure 4 a) Schematic representation of MOF; b) UiO-66 (Universitetet i Oslo) – one of the most frequently used MOFs [15]

2.3. “Soft” reactive sorbents

Numerous studies have been published on the degradation of toxic organophosphates using various organocatalysts, i.e. organic compounds with a special arrangement of functional groups in their molecule. The study of Barba-Bon et al. [16], who examined a series of different amines, aminoalcohols and glycols as potential organocatalysts for DCNP (diethylcyanophosphate) degradation, may serve as an example. Taking inspiration from

the solution chemistry we introduced some functional groups into the macroporous bead cellulose matrix and tested a degradation efficiency of the functionalized sorbents towards the organophosphate pesticide parathion methyl. It was found that some of the functionalized sorbents are capable to destroy parathion methyl and convert it to 4-nitrophenol in a similar way as the metal oxide-based reactive sorbents. On contrary to the metal oxide-based reactive sorbents, the degradation proceeds in aqueous solutions, although the rate of degradation is lower – see *Fig. 5*.

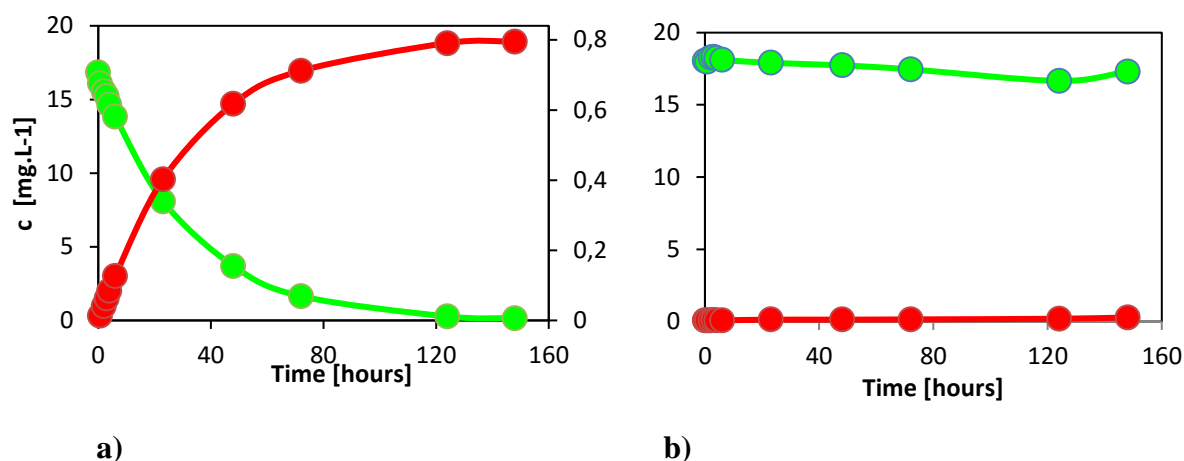


Figure 5 a) Degradation of parathion methyl in the presence of the sorbent Iontosorb PaO in an aqueous solution (TRIS buffer with pH 7); b) blank experiment (TRIS buffer without sorbent)

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