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Chemical degradation of trimethyl phosphate as surrogate for organo-phosporus pesticides on nanostructured metal oxides

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ABSTRACT

Nanostructured TiO_2 and mixed oxides of Ti and Fe, Hf, In, Mn or Zr -were prepared by homogeneous hydrolysis of aqueous solution of metal sulphates with urea. The oxides were characterised by X-ray powder diffraction (XRD), scanning electron microscopy, particle size distribution, surface area and porosity. The oxide materials consists of a few nanometre primary crystals (mainly anatase) arranged in a few micrometre regular spherical agglomerates with specific surface area 133–511 $m^2 g^{-1}$. The FTIR diffuse spectroscopy was used for monitoring chemical degradation of trimethylphosphate (TMP) as a surrogate for organo-phosphorus pesticides under ambient and higher temperatures. Undoped TiO_2 and Ti,Mn-mixed oxide were most active in cleavage (hydrolysis) of CH_3O from TMP at room temperature and 100 °C. Cleavage of CH_3O in the other studied mixed oxides was not complete until temperature exceeds the boiling point of TMP.

1. Introduction

Laboratory research on degradation of chemical warfare agents (CWAs) as sarin and soman or organophosphate-based pesticides as malathion is complicated by their high toxicity. Therefore, their surrogates, containing similar functional groups, are used [1]. Dimethylmethyl phosphate (DMMP) and trimethyl phosphate (TMP) are the most common surrogates used in this field [2]. Interactions between DMMP and metal oxides, which includes chemisorption and surface chemical decay, have been studied thoroughly, especially between DMMP and TiO_2 [2–11]. Other studies were dedicated to interactions of DMMP and aluminium oxides [12], as well as TMP sorption and decomposition on hematite, maghemite and goethite nanoparticles [13,14] and zeolites [15]. Also a computational research was conducted on DMMP and TMP interactions with CaO [16]. Apart from adsorption process, many of mentioned studies were focused on successive decomposition processes, both stoichiometric [3–14] and photo-catalytic [2,9,10,14,17]. It should be mentioned, that most of the studies used a procedure with solid oxide exposed to gaseous phosphates, while liquid-phase TMP was employed in this work.

Photocatalytic decomposition enhancement by TiO_2 doping was studied already in two last decades of the 20th century [18]. Positive effect of Au-doped TiO_2 on DMP decomposition have been proven later [5]. With regard to CWAs, TiO_2 doping by Zn, Mn, In and Ge also resulted in better decomposition rates of sulphur mustard [19–23] and soman [1,19,21,23]. Zirconium doped titania resulted in increased specific surface area, decreased particle size and enhanced surface hydroxylation leading to better sorption and decomposition of toxic compounds (or their surrogates) [19,22]. Hirakawa et al. [11] observed that decomposition rate of sarin on TiO_2 was 3.3 times higher than the DMMP. Still, bonding energies of DMMP sorbed on CaO showed to be closer to the values of adsorbed tabun bonds, that those in case of TMP [16].

1.1. TMP/DMMP adsorption on TiO_2

DMMP adsorption on TiO_2 (and iron oxides and hydroxides [13]) surface can have both molecular and reactive form. While the first mentioned occurs mainly by hydrogen bonding between oxygen atom in phosphoryl group (P=O) and surface hydroxyl group [3,4], the latter takes place on Lewis acid sites (Ti^{4+}) and active oxygen species of initial surface [3]. Higher surface concentration of OH group lead to lower TMP stability compared to dehydroxylated surface [16]. DMMP decomposition on dehydroxylated TiO_2 surface seems unlikely [7].

1.2. TMP/DMMP decomposition on TiO_2

The decomposition itself is mostly considered as a CH_3O group cleavage from DMMP/TMP molecule at low temperature such as 214 K (−59 °C) [8], room temperature [4], or after heating at 200 °C

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[3]. CH_3O group cleavage occurs at room temperature on zeolites [15] and aluminium oxides [12]. For decomposition process, surface hydroxyl groups seems to be essential, thus, it strongly depends on prior oxide treatment, especially on the annealing [10].

Main product of CH_3O group hydrolysis is methanol [4,6,15]. Other products formed on metal oxides surfaces include carboxylates, formates, formaldehyde, CO_2 and H_2O [4].

In FTIR spectrum, red shift in v(P=O) vibration band (at 1237 cm^{-1} [3] or 1234 cm^{-1}[4]) compared to gas-phase frequency is an evidence of molecule adsorption on the surface through phosphoryl group [3,13]. Its decrease is accompanied by rising of v (P—O) band at 1170–1090 cm^{-1} [4].

Evidence of CH_3O group cleavage can be observed as an intensity increase of $\nu a(Ti—(OCH_3))$ band at 2927 cm^{-1} (2942 cm^{-1} [4]) and $\nu s(Ti—(OCH_3))$ at 2827 cm^{-1} (2834 cm^{-1} [4]) and also ν(C—O) bands at 1115 cm^{-1} and 1058 cm^{-1} [8]. More distinct is a decrease of ν(P—O) band located between 1170 and 1090 cm^{-1} [4]. As CH_3O groups undergo decomposition at higher temperatures, corresponding bands $\delta(CH_3O)$ at 1459 cm-1 and ν(C—O) at 1064 cm-1 decrease in intensity [3]. Some bands may not appear in the spectrum when gaseous methanol is formed [13,24].

In this study we used nanostructured mixed metal oxides of Ti, Zr, Fe, In and Mn prepared by homogeneous hydrolysis for stoichiometric degradation of TMP and DMP. The methods of *operando* diffuse FTIR spectroscopy was used for degradation experiments. The aim was to compare a series of oxides and reveal chemical modifications and modes of application for enhancement of decontamination of organo-phosphorus agents. In our previous papers [1,20,21] we described the kinetics of the removal of the organophospshorus agents from solution into products, not desorbed by solvents. In this study we focused on chemical forms of those firmly sorbed products and on their fates at elevated temperatures.

2. Experimental

2.1. Preparation of nanostructured metal oxides

All used chemicals, titanium oxo-sulphate, indium(III) sulphate, zirconium chloride, iron(III) sulphate, hafnium chloride, potassium permanganate, urea and trimethylphosphate (>99,5% purity) were supplied by Aldrich. $ZrOSO_4$ and $HfSO_4$ were prepared by a reaction of stoichiometric mount of $ZrCl_4$ or $HfCl_4$ and sulphuric acid. Chlorides were dissolved in a 98% sulphuric acid solution in a porcelain crystallization dish, heated at 100 °C until HCl escaped from the reaction mixture. Then, the solution was heated to crystallization.

Stoichiometric degradation experiments were run on five different mixed oxides based on titania, included non doped TiO_2 and mixed oxides of Ti with In, Zr, Fe/Zr, Mn and Hf. All studied oxides were prepared by homogeneous hydrolysis of $TiOSO_4$ in aqueous solutions using urea as the precipitation agent as described in previous studies [20,23,25,26]. The process consisted of dissolving defined amount of $TiOSO_4$ in distilled water acidified with 10 ml of 98% H_2SO_4. Then, the specific dopant was added into solution together and then defined amount of urea was added. The mixture was heated for approximately 6 h. The formed precipitates were decanted, filtered off, dried at 105 °C and disintegrated by manual crushing in a mortar.

2.2. Characterization methods

Diffraction patterns were collected with diffractometre Bruker D2 equipped with conventional X-ray tube (CuKα radiation, 30 kV, 10 mA). The primary divergence slit module width 0.6 mm, Soller Module 2.5, Airscatter screen module 2 mm, Ni Kbeta-filter 0.5 mm, step 0.00405°, a counting time per a step 3 s and the LYNXEYE 1-dimensional detector were used. Qualitative analysis was performed with the DiffracPlus Eva software package (Bruker AXS, Germany) using the JCPDS PDF-2 database [27].

The specific surface area of samples were determined from nitrogen adsorption–desorption isotherms at liquid nitrogen temperature using a Coulter SA3100 instrument with 15 min outgas at 150 °C. The Brunauer–Emmett–Teller (B–E–T) method was used for surface area calculation [28], the pore size distribution (pore diameter, pore volume and micropore surface area of the samples) was determined by the Barrett–Joyner–Halenda (B–J–H) method [29].

The particle size distribution was determined by laser scattering using ZEN 1600 equipment (Malvern Co.). The sample was tested in a square glass cuvette with round aperture (PCS8501) filled with ethylene glycol.

Scanning electron microscopy (SEM) studies were performed using a Philips XL30CP microscope equipped with EDX (energy dispersive X-ray), Robinson, SE (secondary electron), and BSE (backscattered electron) detectors. The sample was placed on adhesive C slice and coated with 10 nm thick Au–Pd alloy layer.

2.3. Stoichiometric degradation of methyl phosphate

Degradation process has been studied on FTIR Spectrometer Nicolet Impact 400D equipped with the Praying MantisTM (Harrick) for diffuse reflection measurement (DRIFTS). Heating of the cell was controlled by ATC-024-3 equipment (Harrick).

The amount of each oxide inserted into the cell was different as the cell had to be completely filled and the oxide specimens had different densities. One drop of TMP (approximately 9.23 µl ~ 78.9 µmol) was dosed onto the oxide surface using a syringe. It resulted in different TMP concentration in the oxide. Also, different specific surface area and weight of the samples lead to different surface area available for adsorption process. It is clear, that higher specific surface area leads to lower coverage of TMP on the oxide surface (in the case of equal dosage of the phosphates) and conversely.

TMP dosage was probably higher than the amount of organophosphate which could be sorbed and hydrolysed on the oxide surface. In case of DMMP, 0.68 µmol/mg of TiO_2 (with

Table 1
Properties of the prepared samples.

Sample	Cryst. size [nm]	Specific surface area [$m^2 g^{-1}$]	Total pore volume [$cm^3 g^{-1}$]	Average agglomerate size [nm]	Average weight of oxide [mg]	Average surface area of oxide [m^2]	Average TMP amount per 1 mg of oxide [µmol]	Average TMP amount per 1 m^2 of oxide [µmol]
TiO_2	3.9	133.1	0.0834	2188	73.7	9.8	1,071	8,051
TiIn	8.9	262.6	0.2343	1501	64.2	16.86	1,229	4,680
TiZr	5.6	510.7	0.2908	1497	47.6	24.31	1,658	3,246
TiFeZr	–	375.4	0.3558	1218	44.2	16.59	1,785	4,756
TiMn	7.7	224.9	0.3005	689	86.3	19.41	0,914	4,065
TiHf	5.5	356,8	0,2555	660	72,5	25,868	1,088	3,050