SOME ENVIRONMENTALLY RELEVANT REACTIONS OF CERIUM OXIDE

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Abstract: Reactive forms of cerium oxide were prepared by a thermal decomposition of various precursors, namely carbonates, oxalates and citrates, commercially available nanocrystalline cerium oxide (nanoceria) was involved in the study for comparison. Scanning electron microscopy (SEM) and x-ray diffraction analysis (XRD) were used to examine the morphology and crystallinity of the samples, respectively, whereas the Brunauer-Emmett-Teller (BET) method of nitrogen adsorption was used to determine surface areas. Interactions of cerium oxide with some phosphorus-containing compounds were investigated. Some of the examined samples, especially those prepared by annealing from carbonate precursors, exhibited an outstanding ability to destroy highly toxic organophosphates, such as pesticides (parathion methyl), or nerve agents (soman, VX). There were identified some relations between the degradation efficiency of cerium oxides and their crystallinity. It was also shown that cerium oxide is able to destroy one of widely used flame retardants – triphenyl phosphate. A phosphatase-mimetic activity of various cerium oxides was examined with the aid of a standardized phosphatase test.

Key words: cerium oxide; reactive sorbent; toxic organophosphates; chemical warfare agents

1. Introduction

Cerium oxide belongs to the most important rare earths with numerous applications in such diverse areas as electrochemistry (HRIZI *et al.*, 2014), glass polishing (JANOŠ and PETRÁK 1991) or ceramics (MARKMANN *et al.*, 2002). Specifically designed forms of cerium oxide have found widespread applications in heterogeneous catalysis (BENADDA *et al.*, 2013), mainly as a part of so-called three-way catalysts for the control of gaseous exhaust emissions. ZHAI *et al.* (2007) demonstrated a photocatalytic activity of cerium oxide and its ability to destroy synthetic dyes. In recent time, a pharmacological potential of cerium oxide has been discovered (CELARDO *et al.*, 2011) and its ability to interact with phosphate ester bonds in biological systems were studied (KUCHMA *et al.*, 2010) with the goal to find a new kind of artificial enzymes – nanozymes (WEI and WANG, 2013; XU and QU, 2014). An ability of cerium oxide to destroy highly dangerous organophosphate compounds (pesticides, nerve agents) was demonstrated in our recent papers (JANOŠ *et al.* 2014a, JANOŠ *et al.*, 2014b).

The unique properties (enhanced catalytic activity, enzyme-mimetic ability) of cerium oxide are attributed usually to its nanosized forms – nano-ceria. Various sophisticated procedures have been used to prepare the catalytically active forms of nano-ceria, including sol-gel methods (ANSARI *et al.,* 2008), thermolysis and homogeneous hydrolysis (LIU and ZHONG, 2010). It was shown that conventional precipitation/calcination methods may be also adopted to produce a highly reactive material capable to destroy toxic organophosphates; a simple and easily scalable

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procedure involves the precipitation of sparingly soluble cerium carbonate (either with an ammonium bicarbonate solution or with a gaseous mixture of CO_2 and NH_3) with subsequent calcination in the presence of oxygen (air) (JANOŠ *et al.*, 1989; JANOS *et al.*, 2014b). In this paper, three synthetic routes were used to prepare cerium oxide from: i) carbonate precursor, ii) oxalate precursor and iii) citrate precursor by annealing at 500°C. Morphology and crystalline structure of the annealed samples were studied using scanning electron microscopy (SEM) and x-ray diffraction analysis (XRD), respectively, the surface areas were determined based on nitrogen adsorption/desorption isotherms, using the Brunauer-Emmett-Teller (BET) method for evaluations. The reactivities of various cerium oxides were compared using the hydrolytic degradation of parathion methyl (organophosphate pesticide) in organic solvent as a model system. The enzyme-mimetic abilities of the cerium oxides were compared using a standardized phosphatase test. An ability to destroy other organophosphate compounds, such as highly toxic nerve agents soman and VX, as well as triphenyl phosphate (flame retardant) was also demonstrated.

2. Material and methods

2.1 Chemicals, preparation of cerium oxide samples

Cerium(III) nitrate, $Ce(NO_3)_3{\cdot}6H2O$, was obtained from Sigma-Aldrich (Steinheim, Germany) as a reagent-grade preparative with purity 99.9% (trace metal basis), ammonium bicarbonate, 99.5%, oxalic acid dihydrate, >99%, and citric acid, 99%, were obtained from the same supplier. Parathion methyl and triphenyl phosphate, as well as their degradation products 4-nitrophenol, diphenyl phosphate, phenol, were obtained from Sigma-Aldrich as chromatographic standards. If not stated otherwise, HPLC-grade organic solvents and deionized water were used for preparing the solutions including mobile phases for liquid chromatography.

Synthetic routes used for preparation of the CeO_2 samples are summarized in Table 1, more detailed description follows (if not stated otherwise, the preparation started with the solution containing 0.05 mol Ce): The carbonate precursor was prepared by precipitation of aqueous solution of cerium(III) nitrate (0.2 mol/L) with an excess of ammonium bicarbonate (0.5 mol/L) under stirring, completeness of the precipitation was checked by reaction with oxalic acid. After an addition of the last portion of ammonium bicarbonate, the agitation continued for one more hour and then the precipitate was left to stay until the next day. Then the precipitate was separated by filtration, washed with water and dried overnight at 110°C. Alternatively, cerium carbonate was precipitated from the cerium nitrate solution by gaseous mixture of CO_2 and NH_3 as follows: Under continuous stirring, gaseous NH_3 was introduced through a glass frit until pH >4, and then gaseous CO_2 was introduced along with NH_3. Absorption of CO_2 was not complete under given conditions (on contrary to the NH_3 absorption), and thus CO_2 was used in an over-stoichiometric amount – the molar ratio of $CO_2 : NH_3$ was 5 : 1. During precipitation, pH of the mixture was kept at ca. 7.2. When the precipitation of cerium carbonate was completed, the pH value raised suddenly up to 9.5. The NH_3 introduction was stopped and the mixture was saturated with CO_2 for one more hour, and then it was left to stay until the next day. The precipitate was separated by filtration, washed with water and dried at 110 °C. The oxalate precursor was prepared by precipitation of aqueous solution of cerium nitrate (0.2 mol/L) with an excess of oxalic acid solution (saturated) under stirring. After an addition of the last portion of oxalic acid, the agitation continued for one more hour and then the precipitate was left to stay until the next day. Then the precipitate was separated by filtration, washed with water and dried overnight at 110° C. The citrate precursor was prepared by the sol-gel method (ALIFANTI *et al.*, 2003) as follows: Aqueous solution of cerium nitrate (0.5mol/L) was mixed with an equal volume of aqueous solution of citric acid (0.5mol/L) and agitated at 60°Cfor 4 hours, then additional citric acid solution was added (30 mL) and agitation continued until the next day. The transparent viscous gel was placed on a Petri dish and dried at 80°C overnight. The CeO_2 samples were prepared from the above precursors by annealing at 500°C for 2 hours in an open crucible in a muffle furnace.

For comparison, a commercially available nanocrystalline cerium oxide MKN-025 (MKnano, Missisauga, USA) was involved in the study.

Table 1. CeO_2 samples used in this study – overview of synthetic routes.

Sample	Preparation route
CARB-s	Precipitation of cerous carbonate with NH_4HCO_3 solution, annealing at 500°C
CARB-g	Precipitation of cerous carbonate with gaseous CO_2 and NH_3, annealing at 500°C
OXAL	Precipitation of cerous oxalate with solution of oxalic acid, annealing at 500°C
CITR	Citrate sol-gel procedure, annealing at 500°C
MKN-025	Commercial sample, without further treatment

2.2 Methods of characterisation and chemical analyses

A Jeol JSM 6510 l scanning electron microscope (SEM) was used to examine the morphology of the CeO_2 samples. X-ray diffraction (XRD) measurements were performed using a PANalyticalXPert PRO diffractometer. The surface areas of the samples were determined based on nitrogen adsorption/desorption isotherms using a Coulter SA3100 instrument (Beckman), and the Brunauer-Emmett-Teller (BET) method was used for the surface area calculations. The pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method.

The liquid chromatographic determinations of parathion methyl and its degradation products were performed using a LaChrom HPLC system (Merck/Hitachi) equipped with a UV/Vis detector operating at 230 nm and a Luna column (Phenomenex, Torrance, CA, USA) 150 × 4.6 mm packed with 5-μm PFP stationary phase. The mobile phase consisted of an 80/20 (v/v) mixture of methanol (HPLC-grade, Labscan, Dublin, Ireland) and water. Determinations of triphenyl phosphate were performed using a Kinetex column (Phenomenex)

100 × 2.1 mm packed with 2.6-μm Biphenyl 100A stationary phase, mobile phase consisted of an 65/35 (v/v) mixture of methanol and formic acid (1%). A Varian GC 3800 gas chromatograph coupled with an ion-trap mass spectrometer (Varian 4000) and a fused-silica capillary column (VF-5; 20 m × 0.25 mm ID × 0.25 μm film thickness) was used to confirm the identities of the target analytes. An Agilent 6890 gas chromatograph with an HP-5 column (5% phenyl methyl siloxane, 30 m × 0.32 mm ID × 0.25 μm film thickness) was used to follow the degradation of the nerve agents VX and soman.

2.3 Testing the reactivity of cerium oxides

An ability to destroy toxic organophosphates was examined using the testing procedure derived from previously used procedures for assessing the degradation of chemical warfare agents, as described in our previous work (JANOS *et al.*, 2014a): Equal amounts (50 mg) of cerium oxide were placed into a series of glass vials (Supelco, 4 mL), and exact volumes (150 μL) of the pesticide solution (6660 mg/L) were added to each vial (corresponding to a dosage of 1 mg of pesticide per 50 mg of CeO_2). The vials were sealed with caps and covered with aluminium foil to shield the reaction mixture from ambient light. At pre-determined time intervals, the reaction was terminated by the addition of 2-propanol, and solid phase was immediately separated by centrifugation. The supernatant was decanted into a 50 mL volumetric flask, and solid phase was re-dispersed in 4 mL of methanol and centrifuged again. The extraction with methanol was repeated three times. All the supernatants were combined in the same volumetric flask, brought to volume with methanol, and analysed immediately by liquid chromatography and gas chromatography. All of the degradation experiments were performed at a laboratory temperature of 22±1°C in an air-conditioned box. The degradation of soman and VX agents was assessed using essentially the same procedure: gas chromatography was used to follow the course of degradation. If not stated otherwise, heptane served as the solvent and as a reaction medium in the degradation of parathion methyl, and nonane was used in the degradation tests for soman and VX.

Degradation of triphenyl phosphate was examined in a batch arrangement using acetonitrile as reaction medium: 200 mg of cerium oxide was suspended in 1 mL of acetonitrile and mixed with 3 mL of solution containing 5000 mg/L of triphenyl phosphate; the reaction mixture was agitated using a horizontal shaker. At pre-determined time intervals, small amounts of mixture were withdrawn and diluted immediately with mobile phase acidified with formic acid. Solid phase was separated by centrifugation and the supernatant was decanted into a 25 mL volumetric flask. Then the solid phase was extracted with methanol repeatedly in a similar way as described above, the combined extracts/supernatants were analysed by liquid chromatography.

The phosphatase-mimetic activity was assessed using the commercially available ALP-MEG L-500 (ErbaLachema, Brno, Czech Republic) phosphatase test, in which the reaction with 4-nitrophenyl phosphate in an aqueous buffer solution was used to compare the activities of the samples.

3. Results and discussion

3.1 Characterization of the samples

It was shown in our previous work that the reactivity of cerium oxide is governed mainly by the calcination temperature – it was also found that the samples annealed at temperatures below ca. 600°C exhibit the highest degradation efficiency towards organophosphate compounds (JANOS *et al.*, 2014a). Therefore, all the CeO_2 samples were prepared by calcination at the same temperature 500°C. As follows from thermogravimetric analyses (Fig. 1), this temperature is sufficient for a conversion of the respective precursors to cerium oxides.

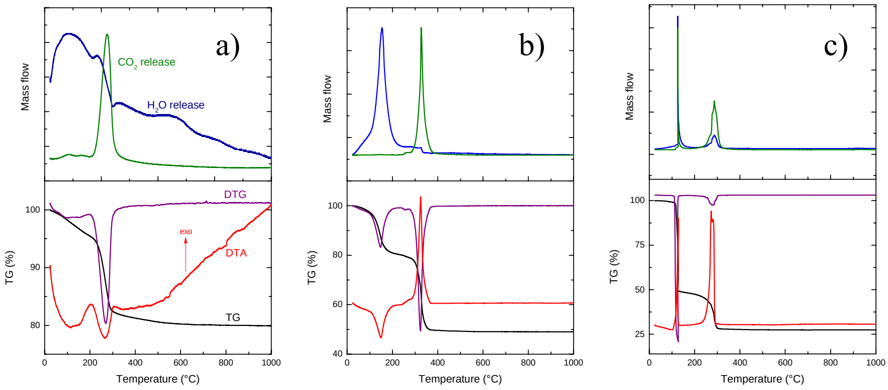

Fig. 1. Thermogravimetric analyses of precursors used for preparation of cerium oxides. Upper row: MS detection of released gases. a) cerium carbonate prepared by precipitation with aqueous NH_4HCO_3 (cerium carbonate precipitated by CO_2(g) and NH_3(g) exhibited almost identical behaviour); b) cerium oxalate; c) cerium citrate.

XRD analyses confirmed the presence a single crystalline phase in all the examined samples, corresponding to cerium oxide with its characteristic fluorite-like structure (space group Fm-3m). The cell unit parameters were nearly identical in the examined samples (Table 2). However, the shapes of the XRD patterns differed markedly.

Table 2. Physico-chemical characteristics of the CeO_2 samples.

Sample	**Cell parameter a (nm)**	**Crystallite size (nm)**	**Surface area (m^2/g)**	**Micropore area (m^2/g)**	**Total pore volume (mL/g)**	**Micropore volume (mL/g)**
CARB-s	0.5413	9.8	57.4	6.35	0.074	0.00234
CARB-g	0.5414	9.7	116	21.0	0.114	0.00829
OXAL	0.5423	5.6	138	14.8	0.174	0.00516
CITR	0.5413	19.4.	19.4	0	0.094	0
MKN-025	0.5412	62.6	9.8	0	0.079	0

As can be seen from Fig. 2, the most developed crystalline structure was detected in the commercial cerium oxide MKN-025.The narrow and sharp diffraction peaks indicate the presence of a more organised crystal structure in this sample, which may be related to the crystallite sizes as calculated from the peak broadening using the Scherrer formula (JOHNSON, 1987) - see Table 2.

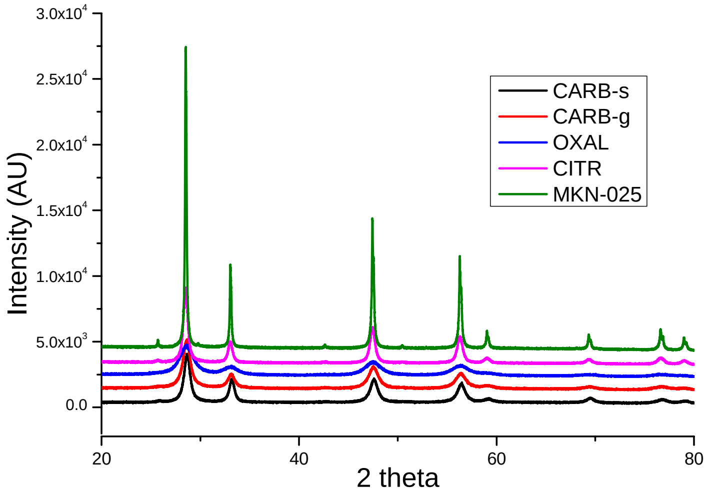

Fig. 2. XRD patterns of cerium oxides.

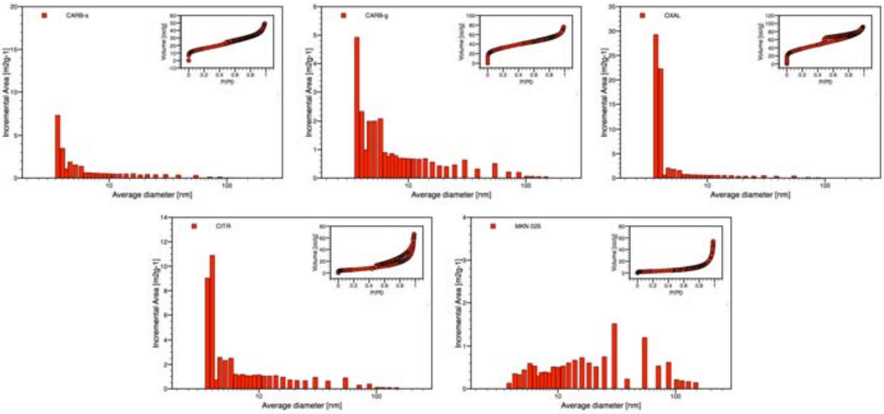

Fig. 3. Pore size distribution of the examined cerium oxides.

The cerium oxides prepared from the carbonate and oxalate precursors exhibited the highest surface area (Table 2) with certain amounts of micropores (Fig. 3). As can be seen from SEM images (Fig. 4), the CeO_2 samples prepared by annealing from carbonate and oxalate precursors consist of relatively large clusters with layered structure, which is clearly visible in a more detailed view in Fig. 4b. Aggregates of the CeO_2 crystals obtained from the citrate precursor (Fig. 4e) exhibit an even finer structure resembling a crumpled silk scarf, whereas the commercial nanocrystalline cerium oxide consists of small sub-micron particles forming aggregates with a complex structure (Fig. 4f).

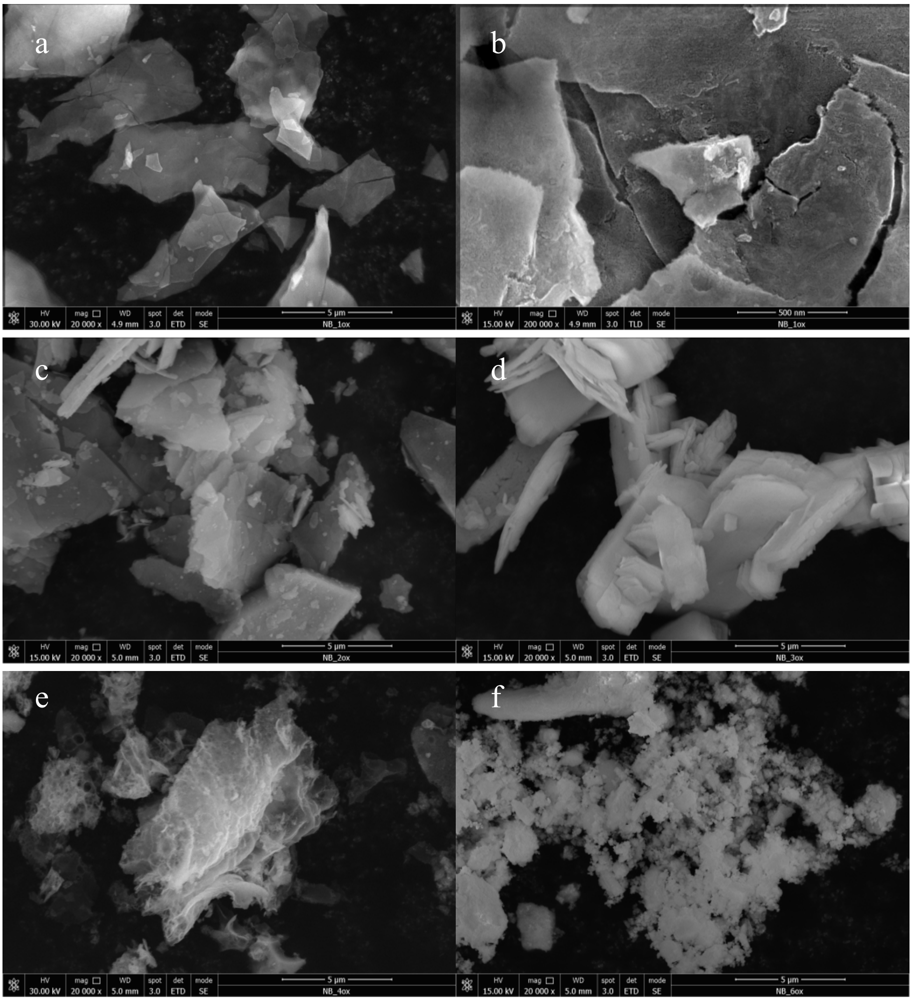

Fig. 4. SEM images of CeO_2. a, b) CARB-S; c) CARB-g; d) OXAL; e) CITR; f) MKN-025.

3.2 Degradation of parathion methyl

Degradation of parathion methyl was examined in organic solvent heptane using all the examined samples of CeO_2; the respective kinetic dependencies are shown in

Fig. 5. Experimental data for the parathion methyl degradation were fitted to the pseudo-first order kinetic equation in the form:

$$q_t = q_1 \exp(-k_1 t) + q_\infty \tag{1}$$

Generally, a variable q indicates a dimensionless fraction of the reactant with respect to its initial amount. Specifically, q_t represents the residual quantity of parathion methyl at time t, q_1 is the fraction of parathion methyl degraded during the experiment, q_∞ is the residual fraction of parathion methyl at the end of the reaction in the event that the destructive capacity of the reactive sorbent is insufficient for complete degradation, and k_1 is the degradation rate constant. The model parameters obtained by non-linear regression are listed in Table 3.

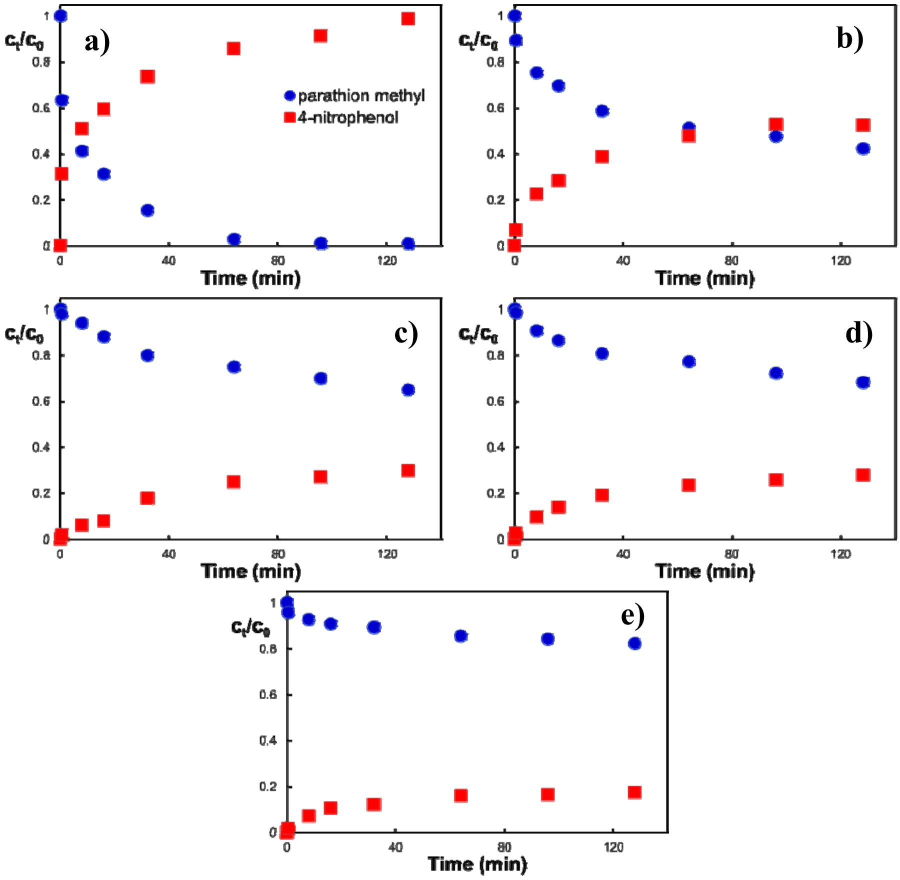

Fig. 5. Kinetic dependencies for degradation of parathion methyl on various CeO_2.a) CARB-s; b) CARB-g; c) OXAL; d) CITR; e) MKN-025.

Table 3. Model parameters describing kinetics of the parathion methyl degradation on various CeO_2 samples

Sample	y_∞ [a)]	k_1 (min^{-1}) [a)]	$t_{1/2}$	R^2
CARB-s	0.026 (0.065)	0.073 (0.026)	9.50	0.896
CARB-g	0.458 (0.029)	0.045 (0.010)	15.4	0.958
OXAL	0.645 (0.023)	0.021 (0.003)	33.0	0.985
CITR	0.699 (0.020)	0.025 (0.005)	27.7	0.969
MKN-025	0.831 (0.015)	0.031 (0.008)	22.4	0.920

[a)] standard errors given in parentheses

As can be seen from the degradation curves, the CeO_2 sample prepared from carbonate precursor CARB-s exhibited the superior degradation efficiency with the degree of conversion approaching 100% whereas the efficiency of the commercial nanocrystalline cerium oxide MKN-025 was rather poor, with the degree of conversion of about 20%. Different efficiencies of these samples may be related to the differences in their surface areas, the presence (absence) of micropores and mainly to the differences in their crystallinity. The differences in the degradation efficiency between the samples CARB-s and CARB-g may be attributed to the differences in their surface area and porosity. It should be noted that the high surface area by itself does not guarantee high degradation efficiency – note a relatively low efficiency of the sample CITR.

During the degradation experiments, an increase in the concentration of 4-nitrophenol was measured simultaneously with the decrease in the parathion methyl concentration (Fig. 5). It follows from a mass balance that an amount of 4-nitrophenol liberated is almost identical to an amount of parathion methyl disappeared. No other reaction products were identified by GC-MS. It was hypothesized that nucleophilic substitution (S_N2) is the main mechanism responsible for cleavage of the P-O-aryl bond in the pesticide molecule (JANOS *et al.*, 2014a). The –OH groups on the surface of the sorbent play a crucial role in the degradation process, acting as a very strong nucleophile toward P atom. Analogously to hydrolytic reactions in aqueous solutions (KHARE *et al*,. 2012), the possible reaction pathway involve the nucleophilic attack to the central phosphorus atom with a subsequent liberation of 4-nitrophenol (leaving group). It is assumed that metal ions are involved in the degradation process as well. Possible intermediate and transition states are depicted in Fig. 6.

3.3 Degradation of nerve agents

Based on the measurements presented above, the CARB-s sample prepared from carbonate precursor was selected to examine its efficiency in degrading the extremely dangerous nerve agents VX (*O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate) and soman (GD, *O*-Pinacolylmethylphosphonofluoridate). The experimental procedure was essentially the same as that described in the previous section, except that the reactions were performed in nonane.

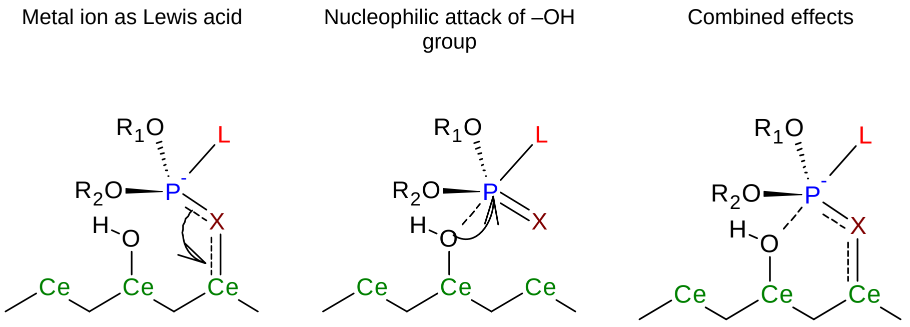

Fig. 6. Modes of interaction of cerium oxide with organophosphates. Based on an analogy with hydrolysis of organophosphates in the presence of metal complexes and metalloenzymes: (KHARE et al. 2012, ZHAO et al. 2012, NAIK and SHINDE 2013). X=S (alternatively O), L – leaving group (4-nitrophenolate in the case of parathion methyl).

As can be seen from Fig. 7, cerium oxide was very effective in the degradation of these organophosphorus nerve agents: it was capable of destroying VX agent nearly completely in less than one hour, and a substantial degree of conversion was achieved within the first ten minutes. A total degree of conversion about 80% was achieved also for soman.

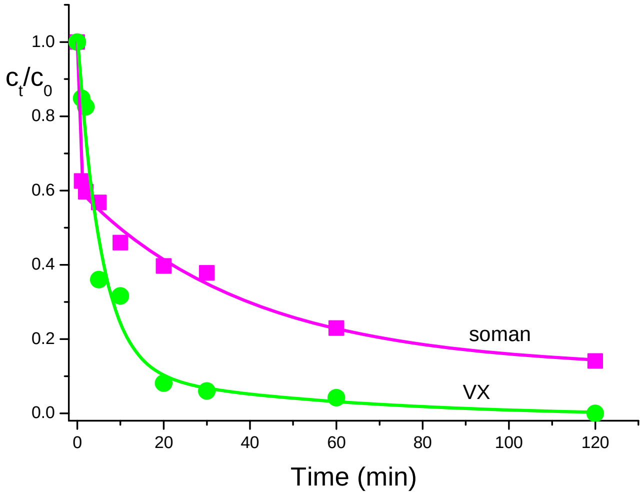

Fig. 7. Degradation of soman and VX using cerium oxide CARB-s.

3.4 Degradation of triphenyl phosphate

Phosphorus flame retardants were introduced as an alternative to brominated flame retardants with (supposedly) less negative impacts to the environment and human health (van der VEEN and de BOER, 2012). Some of them, however, exhibit toxic effects to living organisms (WAAIJERS *et al.*, 2013) and allergic effects to humans (CAMARASA and SERRA-BALDRICH, 1992). The degradation of triphenyl phosphate, as a representative of halogen-free phosphorus flame retardants, was investigated in a batch arrangement using the CARB-s sample as a reactive sorbent. It was found that triphenyl phosphate was destroyed relatively quickly in organic aprotic solvent (acetonitrile) - phenolic groups are gradually released by the mechanism of nucleophilic substitution to form diphenyl phosphate and subsequently phenol – Fig. 8.

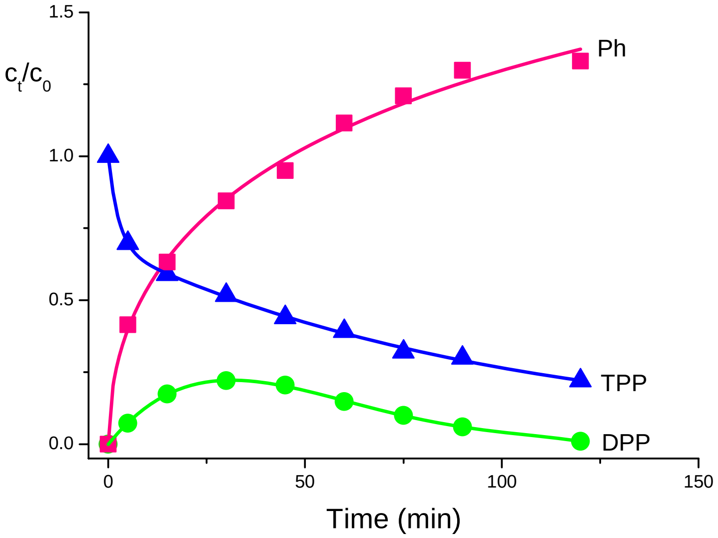

Fig. 8. Degradation of triphenyl phosphate using cerium oxide CARB-s. TPP – triphenyl phosphate; DPP – diphenyl phosphate; Ph .phenol.

3.5Phosphatase-mimetic activity of cerium oxide

An ability of cerium oxide to interact with biologically relevant molecules may show promise in new applications in medicine, but it may also pose a threat of damage to important chemical bonds in biological systems. The enzyme-like ability of various CeO_2 samples to hydrolyse (accelerate hydrolysis) the organophosphate compounds was examined in aqueous solutions using a standardised phosphatase test (ALP-MEG L 500); 4-nitrophenyl phosphate was used as the substrate. As shown in Fig. 9, the commercial nanoceria MKN-025 exhibited the lowest activity again, but the differences between examined samples were not so pronounced. It is supposed that this activity belongs to unique properties of certain forms of cerium oxide, as other metal oxides, such as magnetite, maghemite or photocatalytically active TiO_2 gave a significantly lower response (JANOŠ *et al.*, 2015).

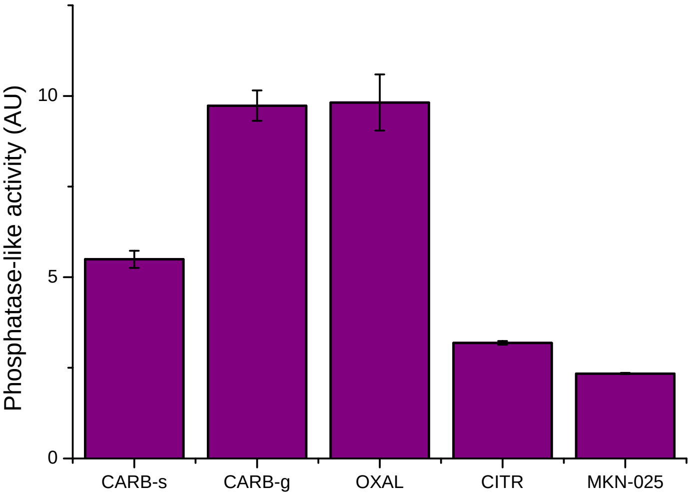

Fig. 9. Phosphatase-mimetic activity of various CeO_2 samples.

4. Conclusions

It was shown that cerium oxide exhibits a remarkable ability to interact with important phosphorus-containing compounds. The reactivity of cerium oxide depends strongly on its physicochemical characteristics, such crystallinity, surface area, surface chemistry (presence of functional groups). These characteristics may be adjusted by a proper selection of the preparation route. It was proven that relatively simple procedures, such as a precipitation/calcination route, or sol-gel process, can be used to obtain highly reactive kinds of cerium oxide. However, much more must be done to establish simple relations between a synthetic route, physicochemical characteristics and reactivity in the given system. Interactions of cerium oxide (and engineered nanoparticles in general) are important not only for technical applications of these materials, but also for their (potential) ability to interact with many compounds having vital functions in living organisms.

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