

Degradation of Trimethyl Phosphate on TiZrCe Mixed Oxides

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Abstract. The nanostructured mixed oxides of Ti, Zr and Ce were prepared by homogeneous hydrolysis of aqueous solution of metal sulphates with urea. This method proceeds at low temperatures (≤ 100 °C) in water environment without utilizing organometallic compounds. The prepared samples were characterized by XRD, XRF, Raman spectroscopy, SEM and BET and BJH methods. The FTIR diffuse spectroscopy was used for monitoring chemical decay of trimethyl phosphate (TMP) as a surrogate for organophosphorus pesticides under ambient temperature. The samples possessed high surface area ~ 500 m²g⁻¹ thanks to addition of zirconium and cerium. All the samples proved to degrade TMP at room temperature; the CH₃O group hydrolysis and (P=O) group cleavage are leading ways of TMP decomposition.

Keywords: homogeneous hydrolysis, urea, TMP, mixed oxides

1. Introduction

The toxicity and difficult handling of chemical warfare agents (CWAs) considerably limit their laboratory research. Thus, various surrogates containing similar functional groups are used instead. Trimethylphosphate (TMP) and dimethylmethylphosphate (DMMP) are the most common surrogates for organophosphate-based CWA (such as sarin or soman) and pesticides (malathion, etc.) [1], [2]. Several studies on the interactions of DMMP with TiO₂ [2], [3], aluminium oxides [4] and TMP with hematite, maghemite, goethite [5] were published. Recently, cerium dioxide has been proven to be an effective reactive sorbent for the degradation of parathion methyl and some other organophosphates [6]. Besides adsorption, both the photocatalytic [2]-[7] and stoichiometric [1]-[6] degradation of gaseous phosphates were described. However liquid-phase phosphates did not **receive** such attention, therefore liquid TMP was used in this work.

Nanostructured metal oxides are popular materials for the degradation of toxic and hazardous chemicals. The homogeneous hydrolysis with urea as a precipitation agent has been proven to be effective way to produce various metal oxides (Ti, Fe, Zr, Ce, Mn, etc.) [1]-[11] with the ability to degrade stoichiometrically CWAs [1]-[11] or photocatalytically other compounds such as azo dyes [9]. This method utilizes water as a solvent, proceed at low temperature (≤ 100 °C) and does not use organometallic precursors, which demands non-aqueous solvents and an annealing step. Thus, this method has the potential to deal with environmental issues and therefore was used in this study.

2. Experimental

2.1. Synthesis

The four samples of mixed oxides consisting of TiO₂ with zirconia and various cerium content (Table 1) were prepared by homogeneous hydrolysis of aqueous solution of metal salts with urea as a precipitation agent. The process consists of dissolving defined amount of TiOSO₄ (100g) and ZrOSO₄ (15g) in distilled

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water acidified with 10 ml of 98% H_2SO_4 . Then, a specific amount of $\text{Ce}_2(\text{SO}_4)_3$ (1g, 5g, 10g, 15g) was added into solution and 250g of urea was added. The mixture was heated at 80 °C for approximately 6 hours. The formed precipitates were decanted, filtered off, dried at 100 °C and disintegrated by manual crushing in a mortar.

2.2. Methods

Diffraction patterns were collected with a diffractometer Bruker D2 equipped with a conventional X-ray tube (Cu $\text{K}\alpha$ radiation, 30 kV, 10 mA). A 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 1s and a 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.

Raman spectra were obtained using a DXR Raman microscope (Thermo Fisher Scientific, Waltham, Massachusetts, USA). A 532 nm laser was used at a power of 3 mW.

Scanning electron microscopy (SEM) analysis was conducted on a FEI Nova NanoSEM microscope equipped with an Everhart-Thornley detector (ETD) using accelerating voltage 4-30 kV. Samples on the carbon holder were coated with a thin gold layer using vacuum sputtering.

The specific surface areas (BET) and pore-size distribution (BJH) of the samples were determined from nitrogen adsorption–desorption isotherms at a liquid-nitrogen temperature using a Coulter SA3100 instrument with 15 min of outgas at 150 °C.

Elemental analysis was performed by an energy-dispersive X-ray fluorescence spectrometer (MiniPal 4.0; PANalytical, Almelo, The Netherlands), using “standardless” measurements and a calculation procedure based on the first principles of XRF using the software MiniPal and MiniMate version 6.0.B. (6.00) (PANalytical, Almelo, Netherlands).

The degradation process has been studied on FTIR Spectrometer Nicolet Impact 400D equipped with the Praying Mantis™ (Harrick) for diffuse reflection measurement (DRIFTS). One drop of TMP (approximately ~ 70 μl) was dosed onto the powder samples using a syringe. Spectra were acquired in determined time intervals (0-70 min) with a resolution of 4 cm^{-1} , without further modification (smoothing, background editing).

3. Results and Discussion

3.1. Materials characterization

As can be seen in the diffractograms (Fig. 1a) the samples consisted of a mixture of TiO_2 in anatase form and cerium zirconium oxide. The peaks were broad and low in intensity with a noticeably elevated background, which points out to poorly crystallized or very small particles with the content of an amorphous phase. This is consistent with earlier studies [11], where the addition of zirconia caused the amorphisation of TiO_2 , whereas without zirconia good crystallised titania is produced [12]. With the increasing addition of cerium, the peaks of anatase continuously lower in intensity. Thus, cerium caused further amorphisation or the increasing content of emerging cerium zirconium oxide phase covers the titania particles.

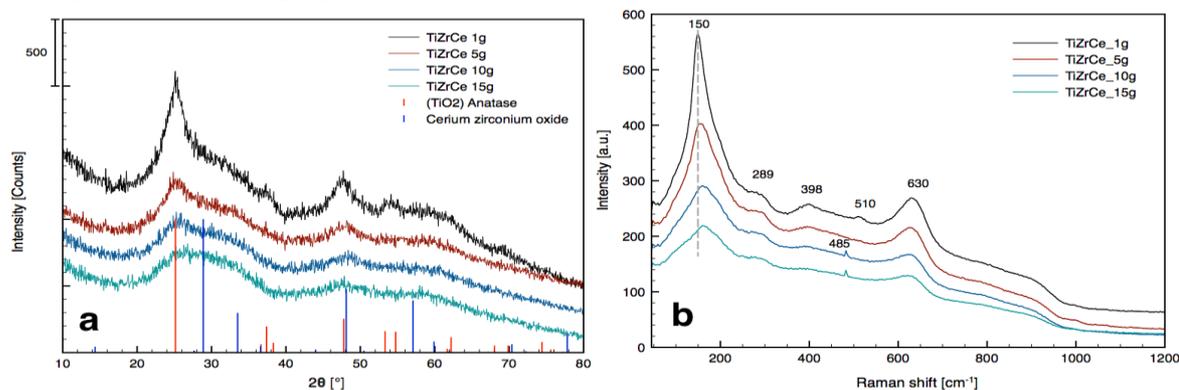


Fig. 1: a) Diffractograms and b) Raman spectra of prepared samples.

Raman spectroscopy confirmed the formation of titanium dioxide with characteristic bands at positions 150 cm^{-1} (E_g), 398 cm^{-1} (B_{1g}), 510 cm^{-1} ($B_{1g} + A_{1g}$), 630 cm^{-1} (E_g). The background is also significantly elevated as a result of the amorphous phase.

As described elsewhere [12], homogeneous hydrolysis of TiOSO_4 provides regular spherical agglomerates which consisted of a few nanometre primary particles. On the SEM (fig. 2) micrographs the formation of spherical agglomerates of anatase is clearly visible. Nevertheless they are not smooth but overlaid by the coating of another phase and with a higher amount of added cerium they are substantially defective with poorly crystallized domains.

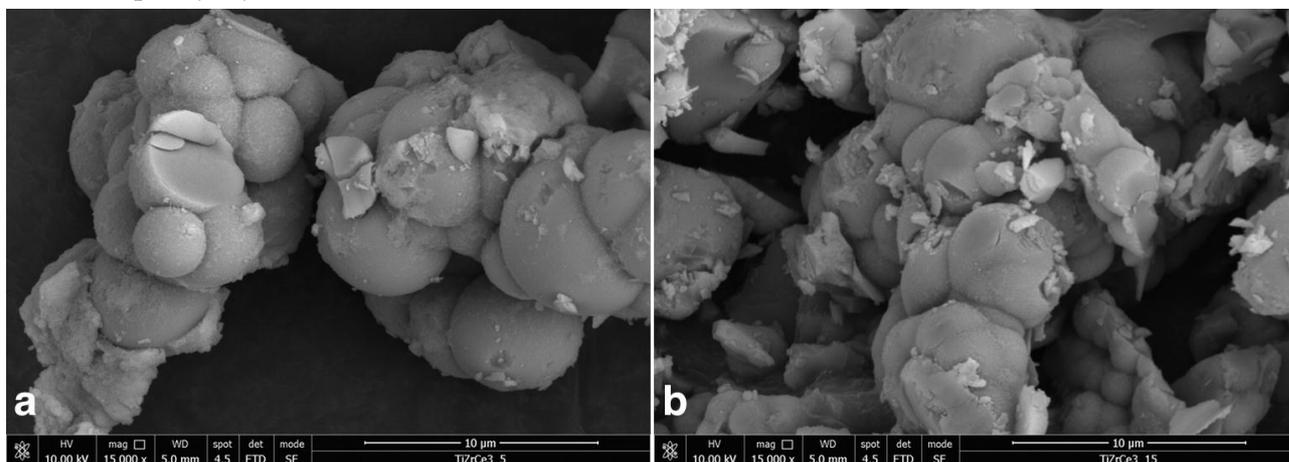


Fig. 2: SEM micrographs of the samples a) TiZrCe_5g, and b) TiZrCe_15g

The samples possessed considerably high surface areas (Table 1). Titania prepared by homogeneous hydrolysis has a surface area commonly of $< 300\text{ m}^2\text{g}^{-1}$ [12]. The samples with the addition of zirconium and cerium had significantly higher values reaching $< 500\text{ m}^2\text{g}^{-1}$, which was caused by the amorphous phase. Such a high surface area should contribute to good adsorption ability of prepared materials and allows their potential use as sorbents and reactive sorbents for the degradation of the toxic chemicals, pesticides, etc.

Table 1: Surface areas, pore volumes and composition of the samples (from XRF spectroscopy)

Sample	Surface area [m^2g^{-1}]	Total pore volume [mlg^{-1}]	Ti (XRF) [at. %]	Zr (XRF) [at. %]	Ce (XRF) [at. %]
TiZrCe_1g	504	0,31	46.5	16.0	0.7
TiZrCe_5g	485	0,29	44.0	16.1	4.0
TiZrCe_10g	485	0,32	42.1	15.3	7.5
TiZrCe_15g	521	0,23	39.9	14.1	11.8

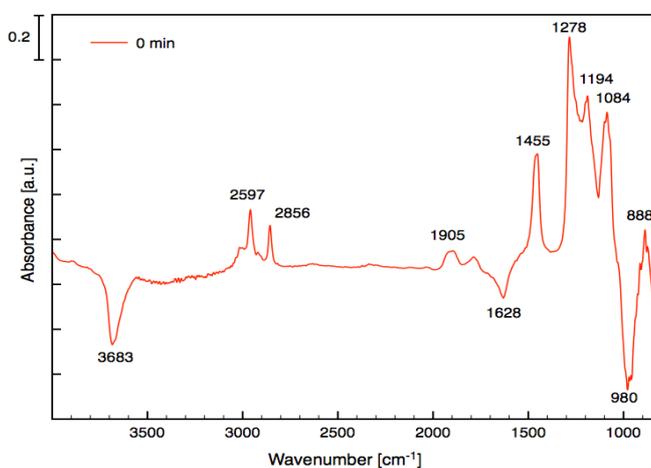


Fig. 3: DRIFT spectra of TMP adsorption on sample TiZrCe_10g

3.2. TMP adsorption and degradation

The representative DRIFT spectra of the TMP adsorption on sample TiZrCe_10g is presented in Fig. 3. The adsorption of organophosphorous compounds (TMP, DMMP, etc.) can have both a molecular and reactive form. The former mentioned results mainly from hydrogen bonding between the surface hydroxyl group and oxygen atoms in the phosphoryl group (P=O) [3], while the latter takes place on Lewis acid sites and active oxygen species of initial TiO₂ surface [3]-[13]. The negative bands at 3683 cm⁻¹ and 1628 cm⁻¹ were due to the disappearance of the -OH groups and adsorbed water caused by H-bonding with TMP. The bands 2597 cm⁻¹ and 2856 cm⁻¹ in CH region were assigned to methyl bands. In the lower frequency region (> 1600 cm⁻¹) CH₃O group vibrations are represented by bands centred at <1455 cm⁻¹. A Phosphoryl group (P=O) was identified in all samples around 1280 cm⁻¹. Band <1194 cm⁻¹ is probably associated with a P-O bond. The Combination band at 1084 cm⁻¹ is most likely associated with C-O vibrations [3].

In Fig. 4 the DRIFT spectra of the selected region of all samples in determined time intervals are presented. The continuous decrease of the combination band with two components centered at <1464 cm⁻¹ and <1452 cm⁻¹ was clearly visible on all samples. Thus, cleavage of the CH₃O is achieved. Some authors described that decomposition of organophosphorous compounds (DMMP) on TiO₂ takes place even at low [14] and room temperatures [13], while Kim *et al.* reported that decomposition requires heating at 200 °C [3]. In our cause, the decomposition was observed on as-prepared samples without any modification. The surface hydroxyl groups seems to have a crucial role for decomposition [15], thus prior oxide treatment (such as annealing) is essential for degradation. The low temperature (≤100°C) water-based preparation route results in the abundance of the surface hydroxyls, which has been proven by XPS analysis in prior studies [16], [17].

The decrease of the bands <1287 cm⁻¹ and <1270 cm⁻¹ caused by the cleavage of the (P=O) group, is accompanied with the simultaneous increase of the band centered approximately at 1194 cm⁻¹ associated to ν(P-O); which again points out to the reactivity of the surface of the prepared samples.

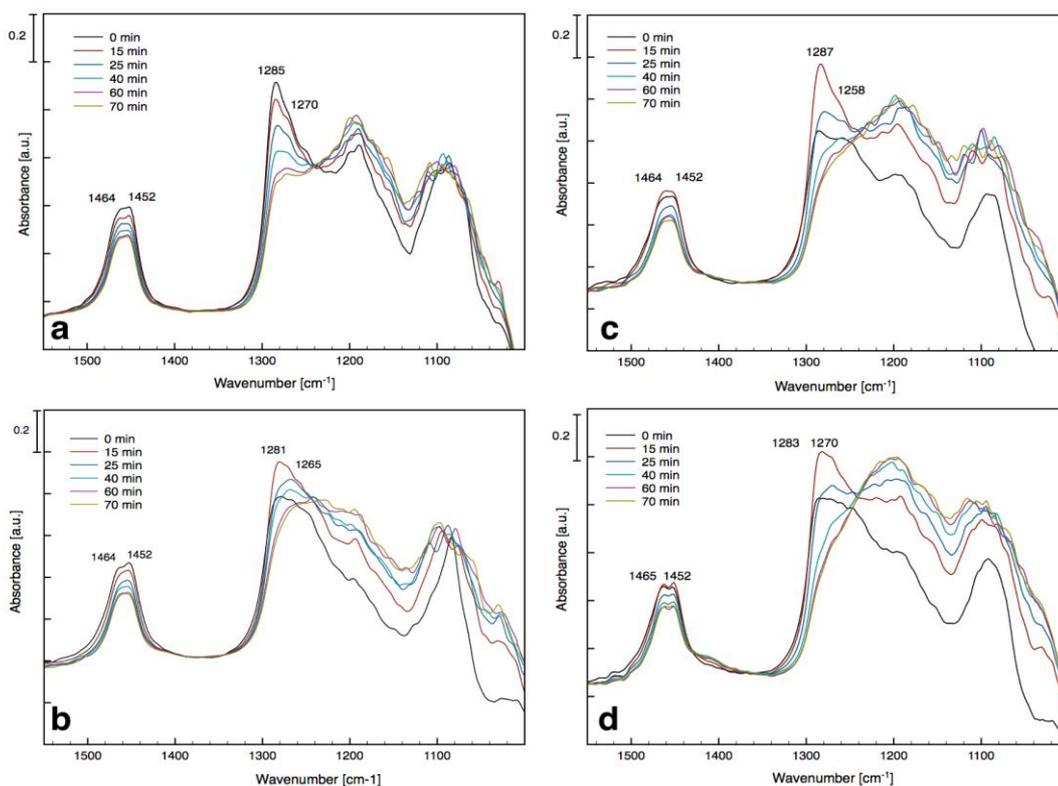


Fig. 4: DRIFT spectra of TMP degradation on samples a) TiZrCe_1g, b) TiZrCe_5g, c) TiZrCe_10g, d) TiZrCe_15g

4. Conclusions

TiZrCe mixed oxides were prepared by an environmentally benign low temperature method using water as a solvent and excluding organometallic precursors. The samples had a large surface area reaching < 500 m²g⁻¹ and were tested for degradation of TMP. The cleavage of the CH₃O and (P=O) groups were the main

decomposition ways. The disappearance of the (P=O) band on the most active sample (TiZrCe_10g) was achieved within 60 min.

5. Acknowledgements

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6. References

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