

Warfare Agents Degradation on Zirconium Doped Titania

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Large efforts are currently devoted to the development of new photocatalytic materials that are able to convert light (and ultimately sunlight) into useful chemical or electrical energy. Wide band gap metal oxides belong to these classes of materials with TiO₂ being far the most studied photocatalytic material. These photocatalytic materials are interesting for pollutant degradation in new environmental clean-up technologies, where photo-induced surface reactions oxidatively decompose harmful pollutants and convert them into harmless products, and ultimately only CO₂, H₂O and mineral acids. Here we report a photo-induced degradation of two similar chemical warfare agents (CWA) for GB (DMMP) and mustard (CEES), respectively, on Zr doped anatase TiO₂ nanoparticles and evaluates their potential properties as photocatalytic materials for CWA and pesticide decontamination.

Zirconium doped TiO₂ (Zr:TiO₂) has previously been reported to yield enhanced photocatalytic activity for 2-chlorophenol decomposition [1]. Nowadays different reliable preparation methods are known to produce Zr:TiO₂ materials as, for example, inverse micro emulsion [2] and sol-gel method [1, 3] and others.

In the present study a more cost effective and environmentally more harmless method is used, where homogenous precipitation of acid aqueous solutions of TiOSO₄ with urea is applied to obtain Zr doped TiO₂ nanocrystallites with a varying Zr content between 0 – 19 wt%. The synthetic procedure has earlier been described [4]. Briefly, ZrOSO₄ was made of stoichiometric amounts of ZrCl₄ and H₂SO₄. ZrCl₄ was dissolved in 98% sulphuric acid in a crystallized dish and heated to 100 °C, letting HCl evaporate from the reaction mixture, which was further boiled till the crystallization of ZrOSO₄. The Zr⁴⁺ doped nanocrystalline titania was obtained from homogenous hydrolysis of TiOSO₄ and ZrOSO₄ aqueous solutions using urea as a precipitation agent. Typically, 100g TiOSO₄ was dissolved in 100 mL of hot distilled water acidified with 98 % H₂SO₄. The pellucid liquid was diluted into 4 L of distilled water and defined amounts of ZrOSO₄ was added and mixed with 400 g of urea. The formed precipitates were washed by distilled water with decantation, filtered off and dried. By this method five samples were prepared denoted as TiZr1 – TiZr5. An undoped sample was also synthesized, TiZr0.

The obtained samples were characterized by SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), HRTEM (High Resolution Transmission Electron Microscopy), EDX (Energy Dispersive X-ray), XRD (X-ray Powder Diffraction), Raman spectroscopy, BET (Surface Area) and BJH (Porosity).

We have shown that Zr is incorporated into the anatase lattice structure. The presence of Zr⁴⁺ ions delays the phase transformation to rutile upon annealing as well as retard grain coarsening. The thermodynamic solubility limit of Zr⁴⁺ in the anatase TiO₂ lattice is found to be ~10wt%. Particles with anatase structure forms by annealing amorphous phase Zr:TiO₂ with Zr in excess of 10wt%.

Trends of spectral Raman shifts and FWHM of the low energy E_g mode were correlated to changes of the anatase crystallite size induced by the Zr doping. All samples, except the non-crystalline TiZr5, exhibit significant photo-activity for decomposition of CEES and DMMP in synthetic air at room temperature. Urea residues are detected spectroscopically, in particular on sample TiZr0 (the sample without Zr). Photo-reaction with urea residues results in the formation of stable isocyanato complexes on the surface. Intermediate decomposition products such as sulphur complexes, phosphor complexes, carboxylates, aldehydes, acetates, carbonato, carboxyl salts can be identified on the sample after UV irradiation. They are all expected surface intermediates that have been previously reported in the literature. Photo-decomposition of intermediate hydrocarbon species occur during the whole 60 min measurement period on all the samples, except TiZr5 (the amorphous sample). The best sample for photodegradation of CEES and DMMP is TiZr2 with a fairly low Zirconium concentration (6.8 wt%). The photodegradation rate of CEES is higher on all the samples in the TiZr series (except TiZr5) compared to P25. For DMMP the TiZr0, TiZr1 and TiZr2 show degradation rates similar or higher than P25. The photodegradation of CEES is faster than DMMP under the same experimental conditions. The concentration of Zr-OH species increases with the increasing of Zr - content.

References:

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- [3] M.E. Manríquez et al., *J. Mol. Catal. A.* 220 (2004) 229-237.
- [4] V. Štengl et al., *Open Process Chemistry J.* 1 (2008) 1-7.
- [5] This work was supported by the Czech Science Foundation (project No 203/08/0335) and by the Swedish Defence Materials Administration (Project No FMV E46484)

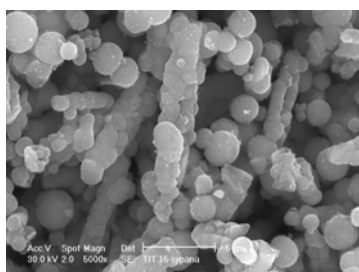


Fig. 1. SEM micrograph of TiZr0

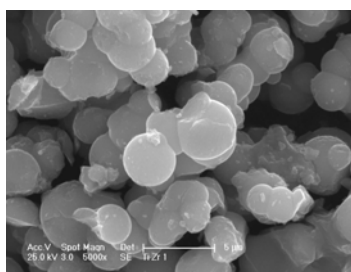


Fig. 2. SEM micrograph of TiZr1

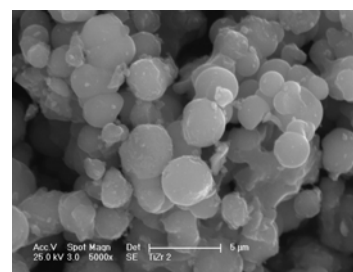


Fig. 3. SEM micrograph of TiZr2

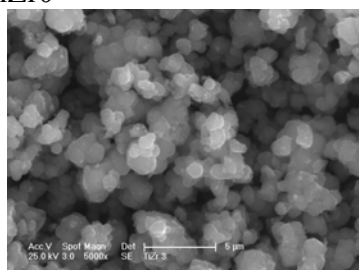


Fig. 4. SEM micrograph of TiZr3

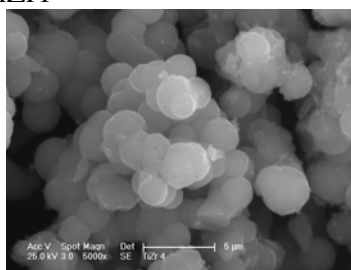


Fig. 5. SEM micrograph of TiZr4

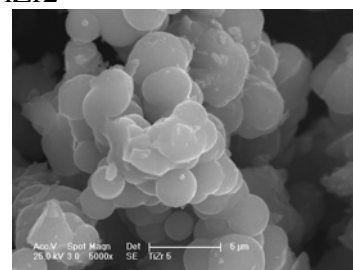


Fig. 6. SEM micrograph of TiZr5