



Key role of terminal hydroxyl groups and visible light in the reactive adsorption/catalytic conversion of mustard gas surrogate on zinc (hydr)oxides



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ABSTRACT

Rhombic Zn(OH)_2 and flower-like ZnO nano-particles were synthesized with a controlled precipitation rate. The materials were characterized by XRD, FTIR, potentiometric titration, nitrogen adsorption, TAMS, MS-MS, SEM and UV-vis-NIR. A commercial ZnO was used as a reference material. Hydroxyl groups were formed on the surface when a slow addition of NaOH was used. The surface area of Zn(OH)_2 was higher (350%) in comparison to that of ZnO. The presence of hydroxyl groups increased the band gap from 3.05 eV for ZnO to 3.22 eV for Zn(OH)_2 . The materials were used as reactive adsorbents of mustard gas surrogate, 2-Chloroethyl ethyl sulfide (CEES). On the surface of Zn(OH)_2 , more CEES was absorbed than of that of ZnO. Moreover, the capacity on Zn(OH)_2 significantly increased under a visible light exposure. The results indicated the paramount role of terminal —OH groups in the reactive adsorption process. The porosity was also found important since it affects the distribution of these OH active centers. Ethyl vinyl sulfide (EVS) was detected on the surfaces of both samples. At light, hydroxyethyl ethyl sulfide (HEES) was detected only on Zn(OH)_2 . Thus the absorption of photons led to the formation of the ethyl ethyl sulfide (EES) cations, which were transformed to less toxic EVS by dehydrohalogenation. With water and hydroxyl groups on the surface, the light irradiation promoted the formation of hydroxyl radicals. They reacted with the EES radicals and formed HEES via a hydrolysis pathway. No conversion of CEES was found in the dark.

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1. Introduction

Zinc (hydr)oxides are important materials for catalysis and photocatalysis fields. The size, shape, structure and morphology of zinc oxide/hydroxide crystals formed from aqueous solutions can vary considerably [1]. One of the quickest, economically feasible and green syntheses of zinc oxide/hydroxide is the addition of sodium hydroxide to a zinc salt solution. When NaOH is added to a Zn salt precursor solution, factors such as addition rate, final pH of a solution, and aging time have an effect on the crystal phase and structure [2–4]. Thus, the precipitation/formation of ZnO or Zn(OH)_2 can be promoted by controlling the addition rate of the NaOH precipitant. It was found that the properties of precipitates formed from ZnCl_2 and a base depend on the pH of the solution and mixing time a slow addition of NaOH led to the formation of $\epsilon\text{-Zn(OH)}_2$ [4,5], whereas a rapid addition yielded ZnO [6]. Nicholas

et al. reported that at temperatures less than 70°C and using a NH_4OH solution (0.03 M) as a precipitating agent, a würtzite growth from wülfingite was observed after a period of time. The latter was the initially formed stable crystalline compound in the precipitation reaction. Furthermore, by tracking the oxygen atoms via isotope labeling, they determined that the transformation occurs primarily via a solid state to a solid state path [2]. Yamabi and Imai [7] found that wülfingite Zn(OH)_2 was predominantly formed at pH 6.0–9.0, while würtzite ZnO was mainly obtained at pH 9.0–13.0 from the reaction of zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) with ammonium fluoride (NH_4F), ammonium chloride (NH_4Cl), ammonium nitrate (NH_4NO_3), and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) as complexing agents.

Whereas the adsorptive performance, as well as the photocatalytic properties of the zinc oxide are well known [8,9], the hydrated oxides have attracted less attention, even though they have been reported as superior to oxide in certain applications [10]. The latter is owing to the high reactivity of their OH groups, especially terminal ones, with specific adsorbates. For example, Mabayoje and co-workers [11] found that the efficiency of SO_2 [12], NO_2 [13],

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and H₂S [10] removal increased with an increase in the number of terminal hydroxyl groups detected on the surface. In addition, those OH groups can represent an important source of active radicals for photoactive reactions [10]. The surface chemical properties of Zn(OH)₂ also differ from those of ZnO, and a developed surface area and pore volume might promote the reactive uptake of specific target molecules.

2-Chloroethyl ethyl sulfide (CEES) is a surrogate of bis(chloroethyl) sulfide, also known as mustard gas (HD). The latter is a powerful nerve agent that has been used in the past as a chemical weapon [14]. To the best of our knowledge, the detoxification of CEES vapors has not been studied on Zn(OH)₂/ZnO materials. The presence of a particular crystal structure might change the detoxification performance of a material, promoting a reactive adsorption of CEES or influencing a mechanism pathway.

Based on the above, the objective of this paper is an evaluation of the role of the structure and chemistry of zinc hydroxide and oxide as reactive adsorbents for CEES decontamination. The target is the reactive adsorption of Chemical Warfare Agents at ambient conditions and their conversion on the surface into less toxic compounds. In order to assess the photoactivity in visible light of the materials tested, the experiments were performed in the dark and under a light irradiation with a solar simulator. Owing to the target application of these materials in ambient conditions only photoactivity under a visible light irradiation has been explored. The comparison of two different crystal phases of the zinc (hydr)oxides (including a commercial zinc oxide) will provide information about the role of –OH groups and porosity in the reactive adsorption process. We hypothesize that an increase in the number OH surface groups will enhance a detoxification extent, chemical reactivity and photocatalytic degradation/oxidation of the mustard gas surrogate, CEES.

2. Experimental

2.1. Materials

All chemicals (Zinc chloride and sodium hydroxide) were reagent grade with a purity degree than 99%. Commercial NanoActive® Zinc Oxide (ZnO–C) was supplied by NanoScale Corporation. All solutions were prepared with deionized water.

The procedure for the synthesis of zinc hydroxide (ZnSA) was described previously [5]. Briefly, 1 L of a sodium hydroxide solution (0.05 M), was added to a 0.5 L of zinc chloride (0.05 M) solution, at a rate of 2.0 mL/min, using a Titronic Universal (SCHOTT) [15]. The obtained material was filtered and washed with distilled water until no trace of chloride was detected and the pH of the leachate was neutral. The solid was filtered and dried at 60 °C for 48 h. This methodology is referred to as a “slow addition” in the paper.

Zinc oxide (ZnRA) was prepared by a direct rapid addition of a 1.0 L sodium hydroxide solution (0.05 M) to a 0.5 L zinc chloride solution (0.05 M) and then aged for 2 h, which was accompanied by stirring. The obtained material was washed with distilled water until neutral pH and no traces of chloride ions were found. The filtrated phase was dried at 60 °C for 48 h. This methodology is referred to as a “rapid addition” in the paper.

2.2. Methods

2.2.1. CEES reactive adsorption

The reactive adsorption of CEES was studied in batch experiments. A glass vial containing 150 mg of a selected sample was placed in a 160 mL reaction vessel closed with a septum. The vessel was sealed hermetically and 300 μL of CEES were injected through the septum into a 5 mL beaker inside the reaction vessel. The

containers were kept under a solar light simulator (Xenon lamp, solar light Co., Inc., XPS-150™) or in the dark, at room temperature, for 24 h. Then, the containers were opened and the adsorbent samples were left to equilibrate in dry air for 1 h at the atmospheric pressure. Finally, the containers with the adsorbents were weighed, and the mass gain as a result of adsorption was recorded.

2.2.2. FT-IR spectroscopy

Fourier transform infrared (FTIR) spectroscopy was carried out on a Nicolet Magna-IR 830 spectrometer using the attenuated total reflectance (ATR) method. The spectrum was generated and collected 64 times and corrected for background noise.

2.2.3. XRD

X-ray diffraction (XRD) measurements were conducted using powder diffraction procedures. Adsorbents were ground to powder size and then analyzed by a Cu_{Kα} radiation generated in a Phillips X'Pert X-ray diffractometer.

2.2.4. Simultaneous thermal analysis-mass spectroscopy

Thermogravimetric curves (TG) were obtained using a TA Instruments Thermal Analyzer (New Castle, DE, USA). The heating rate was 10 °C/min from room temperature to 1000 °C. During the whole experiment a flow rate of 100 mL/min of ultra-purity helium was purged. The differential thermal (DTG) profiles were derived from the TG curves. Simultaneously, gases and vapors released with an increased temperature were analyzed with a ThermoStar Gas Mass Spectrometer (GSD; Pfeiffer Vacuum). The off-gas collected was scanned with a secondary electron multiplier detector and a Faraday detector. The *m/z* identified in the MS was correlated in real time with their corresponding releasing temperature and the *m/z* thermal profiles were obtained.

2.2.5. Potentiometric titration

Potentiometric titration measurements were performed with an automatic titrator (888 Titrand, Metrohm). The initial materials (~0.050 g) were added to NaNO₃ (0.01 M, 25 mL) and placed in a container maintained at 25 °C overnight for equilibrium. During the titration, the suspension was continuously saturated with N₂ to eliminate the interference of atmospheric CO₂. Volumetric standard NaOH (0.1 M) was used as a titrant starting from the initial material's pH up to pH 11. The experimental data was transformed into a proton-binding curve, *Q*, representing the total number of protonated sites [16,17]. The deconvolution of *Q*, using the SAIEUS procedure, [17] yield the *pK_a* distributions for the species present on the surface.

2.2.6. Adsorption of nitrogen

Nitrogen isotherms were measured using an ASAP 2020 (Micromeritics, Surface area and Porosity Analyzer Norcross, GA, USA) at –196 °C. The samples were outgassed at 120 °C to vacuum 10^{–4} Torr before the measurements. The surface area, *S_{BET}* (Brunauer–Emmet–Teller method was used), the micropore volume, *V_{mic}* (calculated using the Dubinin–Radushkevich approach), the mesopore volume, *V_{mes}*, and the total pore volume, *V_t* (calculated from the last point of the isotherms based on the volume of nitrogen adsorbed) were calculated from the isotherms. The volume of mesopores, *V_{mes}*, represents the difference between the total pore volume and the micropore volume.

2.2.7. SEM

Scanning electron microscopy images were obtained using a Zeiss Supra 55 VP with an accelerating voltage of 5.00 kV.

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