
Thesis points of Ph.D. dissertation

Structural and Photooxidation Properties of Layered Silicate Stabilized ZnO and SnO₂ Nanoparticles

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Introduction and aims of the work

In the course of the different industrial processes large amounts of toxic pollutants having harmful effects on living organisms get out into our natural environment. It is important to remove and make harmless these pollutants to protect the living environment and human health.

The first goal of the work was the preparation of such ZnO and SnO₂ catalysts with grain size in the nanometer range, which are able to degrade these harmful pollutants in photooxidative processes with the highest possible degradation efficiency. The second goal was to develop an environmentally friendly synthesis process for the preparation of the nanoparticles avoiding the use of the large amount of organic solvents and surfactants. Therefore, principally synthesis methods in aqueous medium were worked out, applying clay minerals as stabilizing agents which are themselves also nanostructured materials.

The third main goal of the work was to explore the effect of the structural properties of the nanocomposites on the photocatalytic efficiency. For this purpose photooxidation of organic model molecules was investigated. This way the optimization of the conditions of catalyst preparation and the improvement of the photooxidation efficiency was carried out. The final aim of the work was to develop the suitable conditions for the application of the catalysts in industrial environment. To accomplish this purpose, nanofilms were prepared containing ZnO nanoparticles and these ultrathin layers were applied in a flow photoreactor.

Experimental methods

The semiconductor content of the prepared nanocomposites was determined by chemical analysis. The structural properties of the nanomaterials were examined by X-ray diffraction (XRD), nitrogen gas adsorption, transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), Mössbauer spectroscopy, and thermal analysis (DTA-TG). The optical properties of the nanoparticles without layered silicate were examined by UV-VIS absorption spectrophotometry, the streaming potential of the nanocrystallites was measured by a particle charge detector.

Nanocomposites were selected to study the interaction between the salicylic acid model pollutant and the catalyst surface by titration microcalorimetry investigations. The photooxidation process of the model pollutants was followed by UV-VIS absorption spectrophotometry.

New scientific results

1. Preparation of nanoparticles and nanocomposites

- 1.1. New synthesis methods were worked out employing homogeneous nucleation in aqueous medium in order to prepare ZnO nanoparticles from zinc acetate precursor applying photolysis, alkaline and thermal hydrolysis. Nearly monodisperse nanoparticles in the 5-9 nm diameter range were produced by these synthesis methods.
- 1.2. New synthesis methods were worked out employing homogeneous and heterogeneous nucleation in dimethyl sulfoxide medium in order to prepare ZnO nanoparticles. In the presence of clay minerals the concentration of the nanoparticles can be increased without the increase of their size. This phenomenon indicates that the clay minerals – growing the crystallites on their surface – are able to stabilize the size of the nanoparticles.
- 1.3. In the case of the nanocomposites prepared by the heterocoagulation method an intercalated composite structure was formed as the result of the electrostatic attraction between the components having oppositely charged surfaces (between the positively charged nanoparticles and the negatively charged layered silicate lamellae).
- 1.4. The structural parameters (basal distance, specific surface area, porosity) of the ZnO/layered silicate nanocomposites prepared by heterogeneous nucleation can be controlled by the appropriate regulation of pH, the concentration of the precursor ions and layered silicates. pH has a strong effect on the formation of the composite structure. As pH was increased, more zinc ions hydrolyzed, therefore increasing basal distances, decreasing specific surface areas and wider particle size distribution functions were obtained.
- 1.5. The basal distance of the catalysts shows a maximum as the function of the calcination temperature, however, the specific surface area continuously decreases according to the experiments investigating the structure of SnO₂/layered silicate nanocomposites. Appropriate heat treatment plays a basic role in the formation of the composite structure.

- 1.6. Self-assembled ZnO/hectorite nanofilms were prepared applying negatively charged synthetic hectorite and positively charged ZnO nanoparticles synthesized by the photolysis method. The nanofilms were formed in a two dimensional heterocoagulation process and showed intercalated structure according to XRD.
- 1.7. A model was worked out in order to characterize the pillared structure of the nanocomposites. The specific surface area and particle size predicted by the calculations based on the model are in accordance with the experimentally obtained values. It was established that the intercalation of the nanoparticles does not unfold the complete interlamellar space of the layered silicates, but a significant part of the lamellae remains in aggregated state.

2. Photooxidation experiments

- 2.1. In the case of the nanocrystalline ZnO intercalated in layered silicates the specific degradation rate of salicylic acid test molecule was 0,6 – 5,4 times higher than in the case of the macrocrystalline ZnO sample. Higher degradation rate was observed for the catalysts having higher specific surface area, indicating the direct surface oxidation mechanism of the salicylic acid. When ZnO content of two nanocomposites was equivalent, we experienced higher photooxidation activity when the nanocomposite contained a layered silicate with higher transmittance (hectorite).
- 2.2. In the case of the nanocrystalline SnO₂ intercalated in layered silicates the specific degradation rate of salicylic acid test molecule was 6,6 – 20,5 times higher than in the case of the macrocrystalline SnO₂ sample. Higher degradation rate was observed when nanocomposites with higher specific surface areas were applied in the test reactions.
- 2.3. The photooxidation efficiency of the powder catalysts showed a maximum as the function of the catalyst concentration. This phenomenon can be explained by the self-shielding effect of the catalyst particles when high concentrations were applied. The efficiency also showed a maximum as the function of the calcination temperature, what can be explained by the not entirely developed metal oxide lattice structure at low temperatures and the significant increase of the particle size at high temperatures.

2.4. Applying nanofilm catalysts in the course of the experiments investigating the photooxidation of kerosene, we experienced higher degradation rate when calcinated films were used. The calcinated ZnO/hectorite films removed 39,2 % of the pollutant after 3h of the irradiation time.

Publications

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