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## Influence of surface effects and crystallinity of ZnO nanoparticles in photocatalysis

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**Abstract** – ZnO nanoparticles were synthesized by chemical method and tested as catalysts in the photodegradation of Rhodamine-B (RhB). The materials were submitted to different heat treatments, and were characterized by XRD, FTIR and BET isotherm in order to observe the surface decontamination and the consequent particle change, in terms of morphology and crystallinity. RhB photo degradation in the presence of these nanoparticles was carried out by using UV-visible spectroscopy to analyze the annealing effects in photocatalytical properties. In particles submitted to thermal heating up to 300°C, surface poisoning is found to be a predominant factor in degradation. Above this temperature, a specific surface area and an increase in crystallinity are a predominant factor in degradation.

ZnO nanoparticles were synthesized by chemical method and tested as catalysts in the photodegradation of RhB. The oxides were synthesized by precipitation of zinc acetate<sup>[1]</sup>. Zinc acetate dehydrate solution was dissolved in water at pH 3. Later, ammonium hydroxide was added to suddenly change pH to 8 at room temperature to promote the hydrolysis reaction in a controlled path. The product of this reaction was isolated by centrifugation and washed with distilled water to remove residual reagents. The wet powder was lyophilized, to avoid particle agglomeration. Finally, the precursor was calcined from 100°C to 500°C (during 2h), to produce the ZnO nanoparticles. The powders were characterizes by X-ray diffraction (XRD), BET isotherm and Infrared Spectroscopy. For photocatalytic study, colloidal dispersions were prepared by mixing 3 mg of powder in 50 mL of RhB aqueous solution. Photocatalytic trials were performed in a reactor equipped with mercury lamps. The suspensions were analyzed by UV–visible spectroscopy of time to monitor the temporal color removal degradation of the dye. The RhB concentration was determined by measuring the absorbance at 554 nm.<sup>[2]</sup>

XRD revealed that as-prepared sample shows not only ZnO diffraction pattern but also other patterns, indicating the presence of metastable phases or residues from synthetic procedure. These materials should be converted into ZnO by annealing at low temperatures, as shown by the annealing at 100°C, where only ZnO is observed. By BET analysis, it was observed a reduction in specific area, with increase of particle's heat thermal. FTIR spectra confirm the presence of acetate groups in the surface, indicating possible poisoning by precursors residues. The carboxylate bands are observed in samples treated with heating up to 300°C, suggesting strong adsorption, i.e., some carboxylate groups remain attached to the surface of active groups. In this transition zone (from room temperature to 300°C) occur progressive formations of Zn-O. By annealing at 400°C, the carboxylate bands disappear and FTIR spectra show only Zn-O peaks.

The photoactivity of materials in RhB's degradation under UV radiation reveal that an increase in photoactivity with an increase in thermal heating temperature, until 300°C, is mainly related to the quantity of contaminant in particles surface, since the specific surface areas are similar until this temperature. This indicates that the presence of contaminants is a predominant factor in the difference of photoactivity until 300°C. Particles obtained at 400°C thermal heating are free of contaminant in their surface, besides presenting higher crystallinity than the particles obtained at 300°C. However, their photocatalytic activities are similar. This is justified by a reduction of specific surface area. The same behavior occurs with samples obtained at 500°C thermal heating. However, a larger catalytic activity is due to a larger crystallinity. These results lead to the conclusion that until annealing at 300°C, surface poisoning is a predominant factor in degradation kinetic. Above this temperature, specific surface area and an increase in crystallinity are a predominant factor in degradation.

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