

MESOPOROUS ORDERED OR DISORDERED SILICA FOR ZnO IMMOBILIZATION AND WASTEWATER TREATMENT

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ABSTRACT

Different types of supported ZnO nanoparticles have been reported as efficient photocatalysts for removal of organic dyes in wastewater at different pH values and conditions. Herein, we evaluate for the first time ordered and disordered mesoporous silica supported ZnO photocatalysts at neutral pH and equal conditions in terms of adsorption and degradation. Anionic RB19 dye was adsorbed onto silica supported ZnO nanoparticles at neutral pH in high manner. This was ascribed to the strong positive zeta potential of pure ZnO nanoparticles at neutral pH value (ca. +37 mV) and consequently to more mixed oxide (spinel-like) ZnO/silica composite behaviour. Interaction between SiO₂ and ZnO resulted in increased resistance to photocorrosion of ZnO, which was proven to be an issue in pure ZnO nanoparticles. It turned out that ZnO composites exhibited higher adsorption and faster degradation kinetics when grafted onto disordered KIL-2 silica than on ordered SBA-15. The most active materials were the ones with Zn/Si molar ratio of 1:1.

Keywords: wastewater photocatalysis, ZnO photocorrosion, mesoporous SiO₂.

INTRODUCTION

It is estimated that worldwide production of dyes is reaching 7×10^5 tons per year. However, during dyeing process, 10–50 % of these are lost in effluent,^[1] which is creating a great burden on the aquatic environments. The remediation is commonly done by adsorption, flocculation and neutralisation. However, for complete removal of the dyes and their degradation products advanced oxidation processes can be employed. Among these photocatalysis offers compelling options of being run at room temperature and pressure and possibly operating under visible light. Zinc oxide (ZnO) has been identified as potential photocatalyst due to its similar band structure to TiO₂, structural versatility, high photosensitivity and low cost.^[2] However, several drawbacks have to be overcome, before major application of this material will take place, such as fast recombination of photogenerated charge carriers, relatively high toxicity of released ZnO nanoparticles^[3] and low resistance to UV-photocorrosion.^[4]

The main emphasis of this work is the evaluation of ZnO nanoparticles loaded onto ordered or disordered mesoporous silica supports for photocatalytic removal of dyes via adsorption and/or degradation in wastewater carried out at neutral pH value.

EXPERIMENTAL

First, 0.1 M solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was prepared in 500 ml of absolute ethanol.^[5] The solution was heated in a distillation flask for 3 h at 80 °C to evaporate 300 ml of condensate. The remainder of the solution was cooled and then diluted with the absolute ethanol to 500 ml. After that LiOH was added and the distillation flask was placed to ultrasonic bath to help dissolve LiOH. Finally the colloidal solution of well dispersed ZnO nanoparticles was obtained. Pure ZnO nanoparticles in the form of powder were prepared via drying at room temperature.

Mesoporous silicas were made according to literature for disordered KIL-2^[6] and ordered SBA-15.^[7]

ZnO/SBA-15 and ZnO/KIL-2 composites were prepared by first outgassing the mesoporous supports on a Schlenk line 2 h at 110 °C, to ensure good immobilization. Then, onto 1 g of well outgassed support different amounts of ZnO colloidal solutions were added depending on the ZnO/SiO₂ molar ratios.

Photocatalytic experiments were performed at atmospheric pressure in a 250 ml three-phase glass batch slurry reactor at pH=7.0. Anionic dye Reactive Blue 19 (RB19) ($C_0 = 25 \text{ mg/l}$) was used and 800 mg of catalyst was added to the solution. The suspension was thermostated at $T=25 \text{ °C}$ under continuous stirring (320 rpm) and with pure N₂ (6 l/h) bubbling through the solution to stimulate oxidation of the model organic compound by $\cdot\text{OH}$ rather than reduction by $\cdot\text{O}_2^-$, which could be formed when purging with O₂. Illumination was provided via an UV high-pressure mercury lamp (150 W, emission in the 300–400 nm region with a maximum at ~365 nm) laid in a water-cooling jacket immersed vertically in the slurry. Temporal concentration of RB19 dye in withdrawn and filtered (0.45 µm filter) samples was determined by measuring the absorbance peak at 592 nm in a Lambda 45 UV-VIS spectrophotometer (Perkin Elmer).

RESULTS AND DISCUSSION

After the photocatalytic test, the wurtzite ZnO structure was lost and transformed partially into lithium zinc oxide borate (ICDD #00-036-0637) and partially into lithium acetate hydrate (ICDD #00-023-1171). The former could arrive from partial dissolution of glass due to one week exposure of glassware to basic ZnO suspension, hence the presence of Si and even B in the transformed composite. This phenomenon was not observed at XRD patterns of ZnO-SiO₂ composites after reaction, where decrease in intensities can be seen, but positions of peaks remain the same. Therefore we can convincingly say that wurtzite structure of ZnO nanoparticles was stabilized by impregnation on the mesoporous supports (KIL-2 and SBA-15).

Measurements of surface charge showed large positive charge of ZnO at pH 7, which could attract negatively charged dye molecules. However, even small addition of SiO₂, i.e. ordered or disordered shifted the isoelectric point to the value close to that of pure SiO₂, i.e. ~2.6. This implies on strong interaction between the two phases and supports the observed reinforcement of UV-stability as proven by XRD.

The catalytic properties of composites and pure ZnO in RB19 oxidation under UVA-irradiation is shown in Figure 1. All samples showed complete decolourisation under 180 min apart from Zn-Si molar ratio 0.2. Generally, the addition of SiO₂ decreased adsorption of the anionic dye as well as its degradation kinetics. At high SiO₂ addition (low Zn-Si ratio, e.g. 0.2) the adsorption reached cca. 8%, compared to 91 % adsorption in pure ZnO sample. Also, composites with SBA-15 showed higher percentage of dye decrease due to catalysis, while the combined removal was higher in KIL-2 disordered silica composites. These effects can partially be explained by the decrease in surface charge, thus diminishing the electrostatic attractions between the dye and ZnO particles, due to the presence of SiO₂ phase. It must be noted that the surface area of SiO₂ was severely decreased upon impregnation, due to instability of SiO₂ under basic pH, which was the pH of the mother solution of ZnO nanoparticles. This is one of the reasons why disordered KIL-2 generally performed better than SBA-15 (Figure 1b) in terms of kinetics.

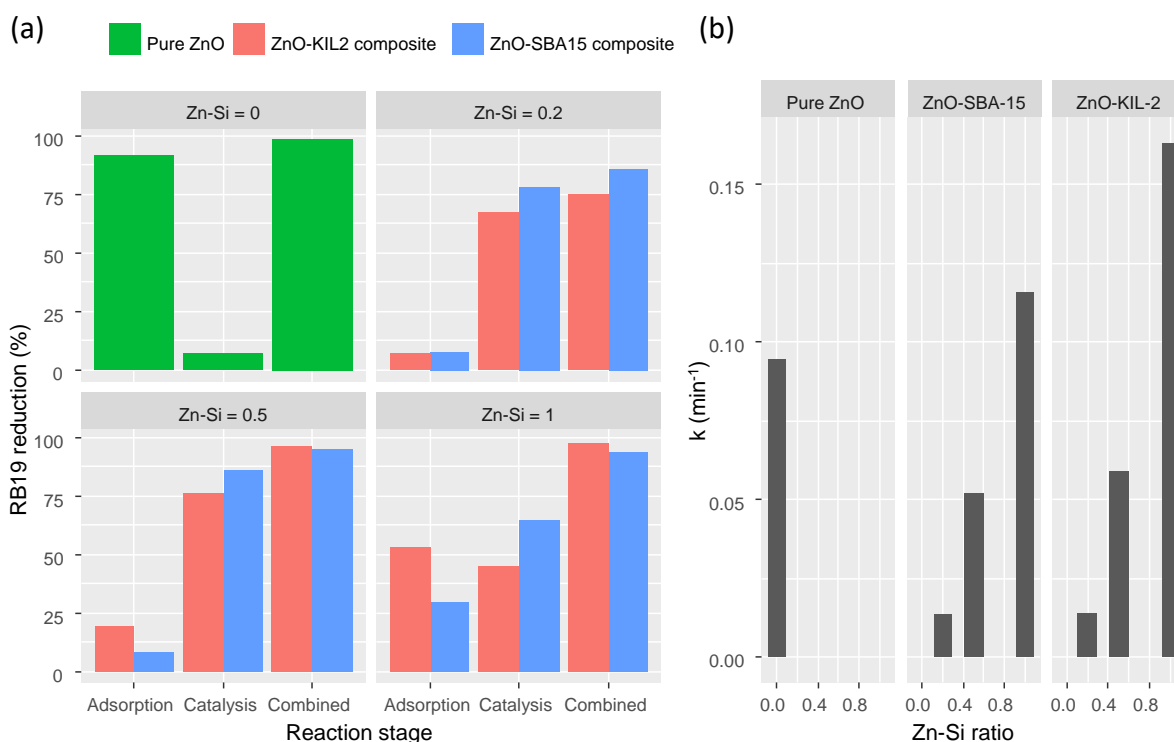


Figure 1. Effect of SiO₂ (dis)ordered structure and Zn-Si molar ratio on extent of adsorption and catalysis of ZnO-SiO₂ composites (a) and effect of the same factors on reaction rate constant of RB19 oxidation (b). Adsorption numbers were obtained after 45 min of dark phase while extent of combined reduction of RB19 was collected at the end of illumination period. To attain catalysis value, adsorption was subtracted from combined value.

CONCLUSION

ZnO nanoparticles were immobilized into SiO₂ and tested for dye degradation at neutral pH. Photocorrosion of ZnO was successfully hindered with facile incipient wet impregnation of ZnO nanoparticles into mesoporous silica. High affinity of ZnO nanoparticles to SiO₂ surface resulted in large shifts of zeta potentials to lower values even at low weight fraction of SiO₂. The highly positive ZnO particles resulted in high adsorption of the anionic RB19 at neutral pH. The extent of adsorption was lowered monotonically with the addition of SiO₂, regardless

of its ordered structure, due to high affinity of ZnO to SiO₂ surface. Composites with disordered KIL-2 mesoporous SiO₂ generally showed faster kinetics, due to higher adsorption of RBA19 dye to the composites.

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