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Influence of preparation method of bismuth silicates/oxides materials on photocatalytic performance

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Different approaches are in use for removal of the dyes in wastewater. Photocatalysis is an attractive method for dye degradation since it requires only presence of the photocatalyst and light. Unlikely, other oxidation methods occur at high temperatures or pressures or additional oxidizing agent [1]. Bismuth metasilicate Bi_2SiO_5 has layer perovskite-type structure that promotes a spatial separation of the charge carries that ameliorates photocatalytic properties.

The report is focused on influence of preparation method of bismuth silicate/oxide materials on their phase composition, structure, optical and photocatalytic properties.

Photocatalysts were synthesized via 3 methods: mechanochemical activation (MA), solvothermal treatment (+ post-processing with impulse laser ablation (ILA)), and sol-gel. The atomic ration of Bi to Si in samples was mainly 2 to 1. When sol-gel technique was used, the ratio Bi/Si varied as following: 2.09/1, 2/1, 2/1.5.

Characterization of the samples were implemented with the use of XRD (and *in situ*), XRF, IR and Raman spectroscopies, SEM, UV-Vis DRS, TG-DSC. The features of the processes at the semiconductor/liquid interface were studied by electrochemical methods. Moreover, quantum-chemical simulation in OpenMX software package made it possible to predict structure of composite materials as well as its effect on optical properties. Photocatalytic performance was estimated in photodegradation of Rhodamine B (RhB) solution under Xe arc lamp irradiation.

Sample prepared via MA and subsequent thermal treatment at 600 °C for 2 h consisted of Bi_2SiO_5 and $Bi_{12}SiO_{20}$ phases identified by IR spectroscopy. The sample demonstrated 29% conversion of RhB degradation for 4 h. Despite the advantages of the method such as absence of solvents, more low temperature of phase formation compared to conventional solid-state approach, the material showed low photocatalytic activity due to poor value of S_{BET} (1 m^2/g).

Hydro/solvo-thermal treatment with following calcination allows preparing the samples with specific surface area up to 10 m^2/g. The sample prepared via solvothermal treatment absorbed the visible light up to 550 nm due to the presence of bismuth beta-oxide. The multiphase composition of the sample, namely, Bi_2SiO_5, $Bi_{12}SiO_{20}$, α-Bi_2O_3, β-Bi_2O_3, led to the highest photocatalytic activity in these series: 75% conversion of RhB through deethylation mechanism. Further post-processing of the photocatalyst by ILA increased the S_{BET} to 34 m^2/g but decreased the activity to 25% conversion. It is caused by high defectiveness of the composite structure that enhanced the recombination process but worsened the photocatalytic activity. The most active photocatalyst was synthesized via sol-gel technique in the study. Composite materials prepared with varying of synthetic conditions were characterized with S_{BET}=10-100 m^2/g. It was important to notice that the key role in the activity was played by the phase composition, and not by S_{BET}. Thus, the sample consisted of Bi_2SiO_5, α-Bi_2O_3, $Bi_{12}SiO_{20}$, β-Bi_2O_3 (35 m^2/g) showed higher photocatalytic performance that β-Bi_2O_3/Bi_2SiO_5 sample (100 m^2/g) or the sample prepared by solvothermal treatment. Additionally, this sample with the highest photoactivity is characterized with higher current intensity in dye solution compared to the sample synthesized with solvothermal treatment.

The comparison of activity for prepared samples with ones from literature as well as the details on phase formation common for each of the approaches will be also discussed. Additional measurements concerning conduction and valence bands positions for prepared photocatalyst, as well as detailed results of photoelectrochemical measurement (EIS, CVC) in different media will be discussed in report.

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References

1. Das, M.; Bhattacharyya, K. G. *J. Mo.l Catal. A Chem.* **2014**, *391*, 121–129.