

氏名	コブズィ バラージュ Kobzi Balazs
所属	理工学研究科 分子物質化学専攻
学位の種類	博士(理学)
学位記番号	理工博 第276号
学位授与の日付	平成30年9月30日
課程・論文の別	学位規則第4条第1項該当
学位論文題名	Synthesis and characteristics of silica-based composite materials including nanostructured tin and iron oxides for visible light-activated photocatalytic degradation 酸化スズまたは酸化鉄ナノ粒子を含むシリカをベースとした複合体の合成と可視光応答型光触媒としての特性 (英文)
論文審査委員	主査 准教授 久富木 志郎 委員 教授 杉浦 健一 委員 教授 山添 誠司 委員 准教授 野村 貴美

【論文の内容の要旨】

Focusing on the organic pollutants and toxic materials in wastewater, the application of photocatalytic materials that mineralize and decompose these elements have drawn a lot of interest. Our main purpose was to investigate the possibilities of preparing tin silicate ($\text{SnO}_x \cdot \text{SiO}_2$) and iron silicate ($\text{FeO}_x \cdot \text{SiO}_2$) composite materials that have a visible light-activated photocatalytic property. Using ^{119}Sn and ^{57}Fe Mössbauer spectroscopy, the key components within the composite materials that are responsible for the photocatalytic effect were identified. Additional data was acquired by X-ray diffractometry, Scanning and Transmission Electron Microscopy (SEM and TEM). For the dye degradation, we used visible light irradiation with methylene blue (MB) or rhodamine B (RhB) organic dyes.

The first part of the thesis introduced the possibilities of a preparation method for $\text{SnO}_x \cdot \text{SiO}_2$ composite material that is capable of MB degradation. The key component, which makes the material photocatalytically active with visible light is the Sn^{II} content. With this knowledge, we selected the most convenient initial material, SnCl_2 , and the initial ratio of $\text{SnO}:\text{SiO}_2$ for the best photocatalytic activity. This sample was the 50Sn50Si (50 mass% of initial SnO) heat treated at 300°C . We made efforts to further enhance the photocatalytic degradation properties by modifying the structure of the $\text{SnO}_x \cdot \text{SiO}_2$ system. By doing so we introduced a novel sol-gel preparation for

SnO_x nanoparticles (SnNP). We synthesized three types of silica composite samples. For comparison SnSiO_x a bulk silicate sample, almost identical to 50Sn50Si was made. One of the other two samples incorporating SnNP, namely SiO₂•SnNP, and finally, the SnSiO_x•SnNP where the Sn content came from both SnNP and simple SnCl₂. The best photocatalytic degradation properties were acquired using the SnSiO_x•SnNP sample, with the first-order rate of $(1.8\pm 0.2)\cdot 10^{-2} \text{ min}^{-1}$. The ¹¹⁹Sn Mössbauer revealed that the major part of the Sn content was oxidized to Sn^{IV} leaving just a small amount of Sn^{II} preserved. Regardless of the type of silica composite, the Sn^{IV} content was in a distorted, amorphous SnO₂ state, and the Sn^{II} was in the form of oxy-hydroxychloride. This indicates that is no chemical connection between the silica matrix and the Sn content. The reusability of the silica composite samples was examined by using the same sample powder over 4 times repeatedly. We observed a rapid decrease in the efficiency for SnSiO_x, however, the samples that contained SnNP, namely SiO₂•SnNP and SnSiO_x•SnNP, showed only a slow drop in the degradation rate in each circle. The Mössbauer revealed that after the 4 circles most of the Sn^{II} content of the samples disappeared, leaving only Sn^{IV} within the composites.

For the second part of this thesis using a similar synthesis route to SnO_x•SiO₂ preparation, we made Fe₂O₃ nanoparticles (FeNP), a bulk Fe₂O₃ sample (FeGEL) and FeO_x•SiO₂ silicate-based composite samples, namely FeSiO_x, SiO₂•FeNP and FeSiO_x•FeNP. The MB dye degradation results showed poor performance compared to SnO_x•SiO₂ where the highest first-order rate constant was $(1.26\pm 0.03)\cdot 10^{-3} \text{ min}^{-1}$ with FeGEL heat treated at 1000 °C. This sample also had one of the largest amounts of hematite in its structure according to the Mössbauer spectrum, which is the key component in the photocatalytic activity concerning Fe₂O₃ materials. The silica-based samples are quite different from each other, the FeSiO_x contained mostly Fe^{II} in the form of Fe₂SiO₄ which is not photocatalytically active. The SiO₂•FeNP composite was made out of hematite, and the FeSiO_x•FeNP contained both phases. This large amount of Fe^{II} was caused by the remaining organic component of the initial silica base, which reduced the Fe^{III} through the synthesis to Fe^{II} forming Fe₂SiO₄ nanoprecipitations.

We made efforts to utilize this large amount of Fe^{II} by applying photo-Fenton reaction. Adding H₂O₂ to the system, the dye degradation ability increased significantly. With the largest amount of Fe^{II}, the best performing sample was FeSiO_x. The first-order rate constants for MB and RhB were $(1.57\pm 0.04)\cdot 10^{-2} \text{ min}^{-1}$ and $(2.09\pm 0.05)\cdot 10^{-2} \text{ min}^{-1}$, respectively. With some decrease in the degradation rate, the materials can be reused after the dye degradation at least seven times.

Both main silica systems have their advantages and disadvantages; the best performing silica composite was FeSiO_x, which showed a slightly better first-order rate constant than the SnSiO_x•SnNP. The Sn^{II} content was sensitive to oxidation, which caused a decrease in the photocatalytic effect after a few circles of reusing the material. The FeSiO_x could be used repeatedly at least seven times, with no sensitivity to oxidation. However, the disadvantage of the photo-Fenton

reaction is that it always needs additional H_2O_2 to work.