Synthesis of flower-like structured $FeSi_2$ and its application to the degradation of dye molecules in water

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Abstract: Flower-like structured iron silicide (*f*-$FeSi_2$) was successfully synthesized by chemical treatment of bulk $FeSi_2$ powder under precisely controlled conditions. The crystalline structure of $FeSi_2$ and the chemical composition is almost same even after chemical treatment. Although the surface area of original $FeSi_2$ was only 3.2 m^2/g, *f*-$FeSi_2$ has high surface area (66.8 m^2/g) due to the existence of a uniform flower-like structure. The enhancement of catalytic performance in the degradation of methylene blue (Fenton's reaction) was observed on *f*-$FeSi_2$.
Keywords: Iron silicide, Flower-like structure, Fenton's reaction.

1. Introduction

Recently, morphology control of materials on a nanoscale has attracted much attentions in various research fields. A variety of morphology controlled materials with fiber, tube, core-shell, sheet, flake and other specific structures have already designed by applying various techniques. These materials have possibilities for realizing fascinating and novel functions based on their specific structures. The utilization of relatively abundant elements in the earth, which are safe and harmless, is also an important agenda in materials design. In the earth's clast, Clarke number is a famous indicator for showing the existing amount of each element, which follows the order of O > Si > Al > Fe > Ca >……. On this point, silicide is composed of silicon and abundant elements, and is thus fascinating and attracted much attentions as thermoelectric material, semiconductor and others. Among them, iron silicide ($FeSi_2$) is fascinating material and also composed of abundant elements, whereas application case of $FeSi_2$ is rare in the field of catalytic material.

On the other hand, various types of catalysts are designed for solving the environmental concerns and energy related issues. The treatment of waste water by using catalysts is also important process. The utilization of abundant elements is also strongly desired in catalytic reaction process. Water soluble dye molecules are widely used in textile industries. Dye molecules show strong color and low biodegradability, which also cause serious illnesses or cancers in some cases. Chemical method is presently available and effective for degradation of dye molecules. In the present work, we focus on the morphology control of $FeSi_2$ and investigations on the catalytic performance in Fenton's reaction, aimed at the purification of water contaminated by dye molecules.

2. Experimental

Iron silicide ($FeSi_2$) was finely crushed by a planetary ball mill. Morphology control of $FeSi_2$ was carried out by the chemical treatment in aqueous solution of sodium hydroxide at 303 K. Sample was recovered by centrifugation after washing by deionized water, and then dried in vacuum at 298 K. Characterization was carried out by various techniques such as FE-SEM, XRD, XAFS, and N_2 adsorption-desorption measurement. The catalytic performances of samples were evaluated in Fenton's reaction. Methylene blue (MB) is used as a model contaminant of water. Fe metal and Fe oxide (e.g. FeO, Fe_2O_3 and Fe_3O_4) is also used for comparative studies. The changes of solution color were monitored by UV-vis absorption measurement at certain time intervals. MB concentration in the supernatant was determined by absorption measurement at around 664 nm.

3. Results and discussion

Figure 1 shows FE-SEM image of $FeSi_2$ before and after chemical treatment. Original $FeSi_2$ is dense powder shape and has an ill-defined surface morphology (Fig. 1(a)). Clear and uniform morphology change was observed in FE-SEM image (Fig.1 (b)). $FeSi_2$ with a flower-like structure (f-$FeSi_2$) was successfully obtained after chemical treatment. Morphology of $FeSi_2$ was gradually changed to a flower-like structure depending on the chemical treatment time. Weight loss of $FeSi_2$ was scarcely observed even after chemical treatment. XRD and EDS measurements indicated that the crystalline structure and composition of $FeSi_2$ was also maintained after chemical treatment.

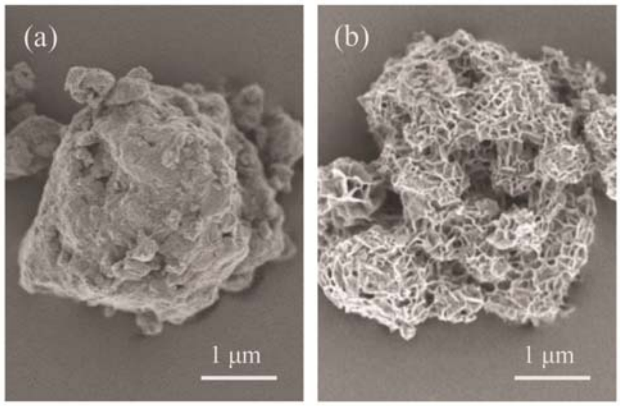

Figure 1. FE-SEM image of (a) $FeSi_2$ and (b) f-$FeSi_2$.

The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method. Although the surface area of original $FeSi_2$ was only 3.2 m^2/g, f-$FeSi_2$ has high surface area (66.8 m^2/g) due to the existence of a flower-like structure. Hysteresis was only observed in the nitrogen adsorption-desorption isotherms of f-$FeSi_2$, indicating the formation of uniform space in a flower-like structure.

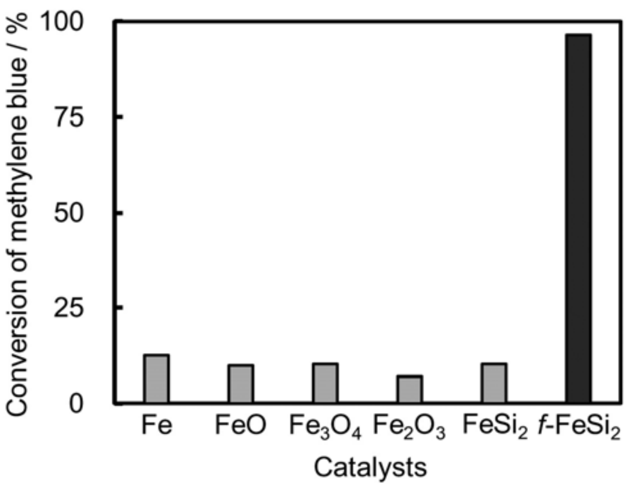

Figure 2. Conversion of methylene blue in the Fenton's reaction (Reaction conditions: catalyst (20 mg), methylene blue (0.3 μmol), water (9.0 mL), 30 wt.% H_2O_2 (1.0 mL), temp. (303 K), time (60 min)).

Figure 2 shows the conversion of methylene blue (MB) in heterogeneous Fenton's reaction on original $FeSi_2$, f-$FeSi_2$, Fe metal, and Fe oxides (FeO, Fe_2O_3 and Fe_3O_4). The particle size of reference samples was almost same or smaller than that of original $FeSi_2$ and f-$FeSi_2$. The time profiles of degradation reaction was monitored by measurement of UV-vis spectrum. The concentration changes of MB were proportional to the reaction time. The catalytic performance of f-$FeSi_2$ was higher than that on other samples. Blue color of MB solution was almost completely disappeared on f-$FeSi_2$. These results indicate that the chemical treatment enhances the catalytic activity of $FeSi_2$. A flower-like structure of f-$FeSi_2$ enables the efficient transport of reactants to the catalytically active sites, which realizes the significant enhancement of catalytic performances of f-$FeSi_2$. The detailed results of characterization and unique properties will be presented.

4. Conclusions

Morphology control of $FeSi_2$ was carried out by the chemical treatment in aqueous solution of sodium hydroxide at 303 K. The formation of a flower-like structured iron silicide (f-$FeSi_2$) was confirmed by FE-SEM investigations. Crystalline structure and chemical composition of $FeSi_2$ was maintained even after chemical treatment. Chemical treatment induced the structural change of $FeSi_2$ powder. As compared to the original $FeSi_2$, f-$FeSi_2$ has ca. 20 times higher specific surface area. The advantageous structure of f-$FeSi_2$ realizes the efficient transport of reactants to the catalytically active sites, leading to the enhanced catalytic performance in the degradation of methylene blue (Fenton's reaction) for water purification.