

Photocatalysis Characteristics of Clay-Supported Fe₂O₃ on Photo-Kolbe Reaction

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The photocatalytic characteristics of the Fe₂O₃ embedded in montmorillonite for the decomposition of acetic acid into methane (called photo-Kolbe reaction) were investigated with respect to the loading amount of the oxide with a constant amount of the clay. Although there has so far been no example that the photo-Kolbe reaction was studied with the catalyst amount, the photocatalytic activity of Fe₂O₃ was found to be dependent on its loading amount; that is, when the Fe₂O₃ amount in the clay varied from 0.5 wt.% to 25 wt.% (cf., the specific surface area of Fe₂O₃ increased with the loading amount), the amount of the methane produced increased with the catalyst amount up to 2.8 wt.%, and it then decreased in the larger amount. In separate experiment, it was confirmed that the kinetics for the methane production is not controlled by the mass transfer of acetic acid. Therefore, it was most probable that the photocatalysis for photo-Kolbe reaction by a Fe₂O₃ is essentially slow, which is responsible for the downward dependence of the overall photocatalytic activity on the increasing active sites.

Key words: Iron Oxide, Photocatalysts, photo-Kolbe reaction

1. INTRODUCTION

Fe₂O₃ is one of the most promising photocatalysts responsive to visible light [1-5]. When the Fe₂O₃ embedded in clay compound (denoted as Fe₂O₃/clay) was prepared and applied to a photocatalytic reaction, the Fe₂O₃/clay has often showed a high photocatalytic activity in comparison with a neat Fe₂O₃ [6]. In earlier works, it has also been reported that Fe₂O₃ is incorporated as crystallites in the interlayer space of the clay employed [7], and such a treatment for Fe₂O₃ can prevent its aggregation [8]. Therefore, the employment of clay compound as a matrix would be essential for designing and developing an active photocatalysis system of Fe₂O₃.

The decomposition of acetic acid into methane (called photo-Kolbe reaction) has been attracting attention as a method for yielding the fuel, for which Fe₂O₃/clay has also been applied to the reaction [6,9,10]. However, the photocatalytic activity of Fe₂O₃/clay has been investigated only with the saturated amount of Fe₂O₃ in a clay compound. In the present work, the Fe₂O₃ embedded in montmorillonite (denoted as Fe₂O₃/MT) was prepared with various kinds of its loading amount in the clay, with which the photocatalysis characteristics of Fe₂O₃ for photo-Kolbe reaction are discussed on kinetic aspects.

2. EXPERIMENTAL SECTION

2.1 Preparation of photocatalyst

Bentonite (Nihon Koken, Tsugaru 2) was added into the deionized water with stirring. Montmorillonite (denoted as MT) was extracted from the water containing bentonite by means of centrifugation. In the

following step, the cation-exchange sites in the MT were replaced by Na⁺ in 1 mol dm⁻³ NaCl solution (cf., this treatment was repeated 3 times). The Na⁺-saturated MT was washed with the deionized water and dried at 100°C. The purified Na⁺-MT powder was added into the deionized water to obtain a suspension containing 1wt.% MT.

The introduction of iron (III) oxide into the clay interlayers was carried out according to the method reported by Yamanaka *et al* [11]. Firstly, trinuclear acetate hydroxo iron (III) nitrate ([Fe₃O(OCOCH₃)₇OH·2H₂O]NO₃) was prepared from iron(III) nitrate enneahydrate (Kanto Chemical) and acetic anhydride (Wako Pure Chemical). The aqueous complex solution (0.1 mol dm⁻³) was quickly dropped into a suspension of 1wt.% MT with stirring (cf., the additive amount of the complex solution changes with the loading amount of Fe₂O₃ in the resulting product of Fe₂O₃/MT), after which the mixture was stirred for 4 h at room temperature. After washing the product with the deionized water, it was dried on a glass plate at room temperature, followed by calcination at 400°C under air (for 10 h). As a reference, a neat Fe₂O₃ was also prepared by the decomposition of trinuclear acetate hydroxo iron (III) nitrate at 400°C (for 10 h) and used as available.

2.2 Characterizations of photocatalyst

The basal spacing of the resulting Fe₂O₃/MT was measured by an X-ray diffraction apparatus (Shimadzu, XD-610). The thickness of Fe₂O₃ portion in the Fe₂O₃/MT was estimated by subtracting the thickness (cf., 0.97 nm for silicate layer in the MT) from the basal spacing in the absence of the oxide. The loading amount

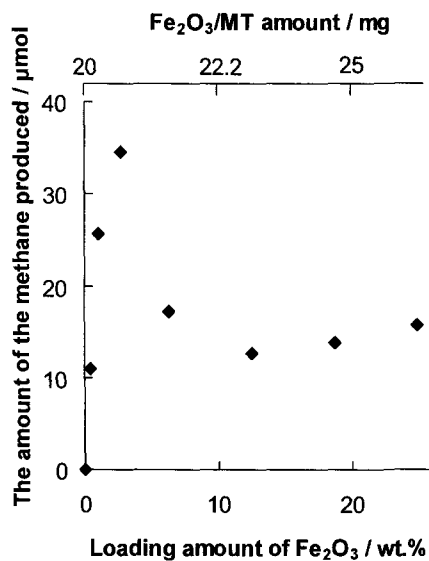


Fig. 1 Dependence of the amount of the methane produced on the loading amount of Fe_2O_3 in MT. The amount of Fe_2O_3 was controlled with the constant amount of MT (20 mg). The concentration of acetic acid was 10vol.% (pH, 2.53). Irradiation was conducted for 15h.

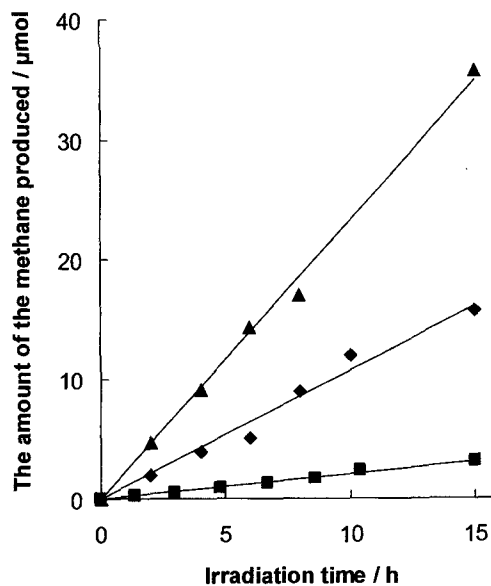


Fig. 2 The time-course of the amount of the methane produced in using 2.8wt.% Fe_2O_3 (0.6mg)/MT (20mg) (\blacktriangle), 25wt.% Fe_2O_3 (6.7mg)/MT (20mg) (\blacklozenge), and a neat Fe_2O_3 (6.7mg) (\blacksquare). The concentration of acetic acid was 10vol.% (pH, 2.53).

of Fe_2O_3 in the clay was determined by measuring TG (Rigaku, TG-8120) at 400°C under air (for 10 h). The saturated amount of Fe_2O_3 in the MT was 25 wt.%. The specific surface area of $\text{Fe}_2\text{O}_3/\text{MT}$ was determined by the B.E.T. method (Shimadzu-Micromeritics, FlowSorb II 2300). A diffuse reflectance was measured using UV-Vis spectrophotometer (JASCO, V-570) equipped with an integrating sphere (JASCO, ISN-470).

2.3 Photocatalytic experiments

The photo-Kolbe reaction was conducted in a glass vessel (volume, 20 ml) containing 10 ml of 5–20 vol.% acetic acid (cf., pH was adjusted to 2.53 by adding a conc. NaOH to the aqueous solution of acetic acid) and a known amount of $\text{Fe}_2\text{O}_3/\text{MT}$ under Ar atmosphere. The $\text{Fe}_2\text{O}_3/\text{MT}$ was washed with an acetic acid solution of pH 2.53 (*vide supra*) prior to use. A 150-W Halogen lamp (Hayashi Watch Works, LA-150TX) was used as a light source under typical conditions (light intensity, 357 mW cm^{-2}). The light intensity was measured by a power meter (Gentec, PSV-3103V2). Gaseous products were analyzed by a thermal conductivity detector (TCD) gas chromatograph (Shimadzu, GC-14B) with a packed column (Shinwa Chemical Industries, SHINCARBON ST) and Ar carrier gas.

3. RESULTS AND DISCUSSIONS

As for the photocatalyst prepared in the present study, the amount of Fe_2O_3 was controlled with the constant amount of MT (20 mg), where the loading amount of the oxide was varied from 0.5wt.% to 25wt.%. The specific

surface area of the $\text{Fe}_2\text{O}_3/\text{MT}$ was found to increase with its loading amount from $159 \text{ m}^2 \text{ g}^{-1}$ (0.5wt.%) to $329 \text{ m}^2 \text{ g}^{-1}$ (25wt.%). The relative intensity on absorbance in the visible regions increased with the increase of the loading amount; however, there was no change with the wavelength ($\sim 650 \text{ nm}$) of the absorption edge.

The amount of the methane produced at $\text{Fe}_2\text{O}_3/\text{MT}$ was investigated using 0.5–25wt.% $\text{Fe}_2\text{O}_3/\text{MT}$, and the result is shown in Fig. 1 (cf., the amount of the MT employed was constant (20 mg) in Fig. 1, whereby 0wt.% on the lower x-axis represents no loading of Fe_2O_3). The methane amount increased with the catalyst amount up to 2.8wt.%, and it then decreased in the larger amount. In a separate experiment, the photocatalytic methane production was also studied with a neat Fe_2O_3 , where the Fe_2O_3 amount corresponding to 25wt.% $\text{Fe}_2\text{O}_3/\text{MT}$ was used as photocatalyst. The produced amount of methane was one-third lower than that in the 25wt.% $\text{Fe}_2\text{O}_3/\text{MT}$ system, which evidently shows that the use of the clay as Fe_2O_3 supporter is effective. It has previously been known that the methane production at $\text{Fe}_2\text{O}_3/\text{clay}$ is dependent on pH [12]; however, it was confirmed that no change of pH in the water phase occurs after the photocatalytic reaction. The details for Fig. 1 will be discussed later.

The time-course of the amount of the methane produced at both 2.8wt.% and 25wt.% $\text{Fe}_2\text{O}_3/\text{MT}$ exhibited a linear dependence on irradiation time (Fig. 2). The turnover numbers of a Fe_2O_3 for the methane production were estimated to be $\sim 10/(15\text{h})$ and $0.4/(15\text{h})$ at 2.8wt.% and 25wt.% $\text{Fe}_2\text{O}_3/\text{MT}$, respectively. A

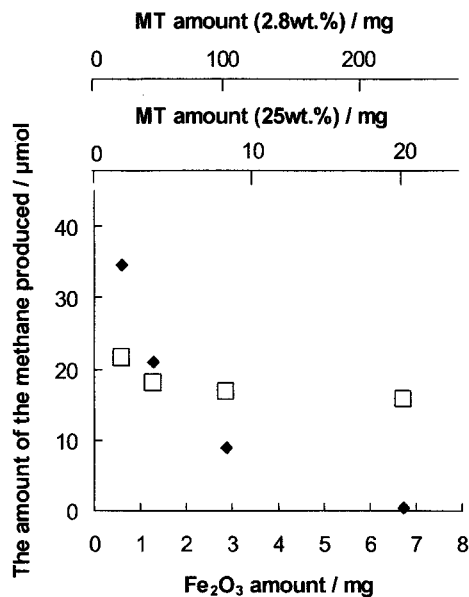


Fig. 3 Dependence of the methane production on the Fe₂O₃ amount in using 2.8wt.% (◆) and 25wt.% (□) Fe₂O₃/MT. The concentration of acetic acid was 10vol.% (pH, 2.53). Irradiation was conducted for 15h.

stable photocatalysis was found to take place, in spite of the low turnover numbers of 25wt.% Fe₂O₃/MT.

The dependence of the amount of the methane produced on Fe₂O₃ amount was studied using 2.8wt.% and 25wt.% Fe₂O₃/MT (cf., the MT amount is always ca. 10-fold larger in 2.8wt.% Fe₂O₃/MT than in 25wt.% Fe₂O₃/MT even though the same amount as Fe₂O₃ is employed in both systems). The methane amount decreased with the increase of the Fe₂O₃ amount in each system, where the decreasing magnitude was found to be remarkable in the case of 2.8wt.% Fe₂O₃/MT (Fig. 3). This may indicate that the amount of the methane produced decreases with the decrease of the total number of the photons absorbed by Fe₂O₃, due to a large excess of the MT (i.e., the optical filter effect by the MT itself). Fig. 4 shows the dependence of the amount of the methane produced on light intensity. The methane amount increased with the light intensity. Fig. 4 indicates that the larger absorption by Fe₂O₃ leads to the higher amount of the methane produced, which also supports the result of Fig. 3.

In Fig. 1, the photo-Kolbe reaction was conducted under the constant conditions of both MT amount and light intensity, where the absorption by Fe₂O₃ can be expected to increase with the oxide amount, which may result in a linear enhancement of the methane production; however, Fig. 1 is not the case. Different from Fig. 4, Fig. 1 could imply that the increase of the number of the active sites depending on specific surface area causes the decreasing photocatalysis by a Fe₂O₃ especially in the higher loading. In Fig. 5, the relationship between the produced amount of methane and the concentration of acetic acid was studied using

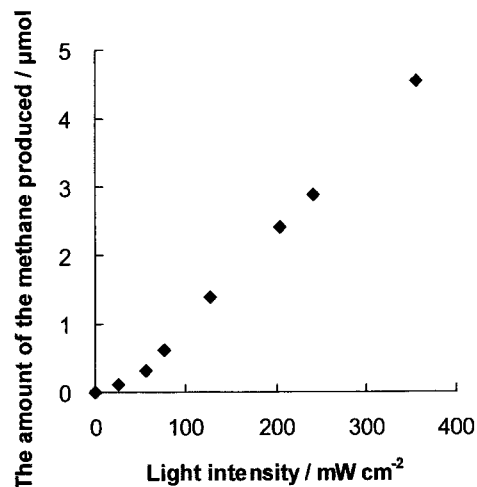


Fig. 4 Dependence of the amount of the methane produced on light intensity in using 2.8wt.% Fe₂O₃/MT. The concentration of acetic acid was 10vol.% (pH, 2.53). Irradiation was conducted for 2h.

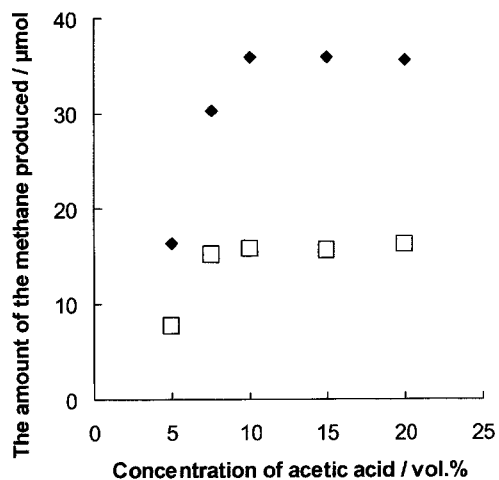


Fig. 5 Relationship between the produced amount of methane and the concentration of acetic acid in 2.8wt.% (20.6mg, ◆) and 25wt.% (26.7mg, □) Fe₂O₃/MT (cf. the amount of the MT employed was constant (20 mg)). The pH value was adjusted to 2.53 in both systems. Irradiation was conducted for 15h.

2.8wt.% and 25wt.% Fe₂O₃/MT. In both systems the amount of the methane produced was saturated at ca. 10vol.%. This means that the rate-determining stage is affected by the photocatalysis involving the charge-transfer rather than the mass-transfer of acetic acid (i.e., diffusion). Therefore, as for Fig. 1, it is most probable that the interspersions of the active sites with

the increasing loading amount causes the decreasing activity because of the slow photocatalysis by Fe₂O₃.

It has so far been reported that the photo-Kolbe reaction efficiently takes place under a high loading condition (~36%) of Fe₂O₃ in Fe₂O₃/clay [6]. Although the employment of a clay as supporter is essential when fabricating the photocatalyst system of Fe₂O₃, the present work shows the importance of the detailed investigations to bring in an efficient photocatalysis by Fe₂O₃/clay.

4. REFERENCES

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