Correlation between Preparation Procedure of Fe_2O_3 Embedded in Clay and Its Photocatalytic Activity

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The preparation of ferric oxide in montmorillonite (denoted as MT) was conducted with two kinds of methods: one is that a trinuclear iron complex (precursor) is loaded into the clay, followed by its calcination (denoted as Fe_2O_3/MT), and the other is the hydrolysis of ferric ion into hydrous ferric oxide (*i.e.*, an amorphous ferric oxide) (denoted as HFO/MT). Both of the samples were prepared with a low loading of ferric oxide into the supporter. The polymorph of 5wt.% Fe_2O_3/MT was assigned to the amorphous phase, similar to that of 5wt.% HFO/MT; moreover, the specific surface areas of ferric oxide were almost constant in each case. When those photocatalysts of ferric oxide were applied to the photo-Kolbe reaction (*i.e.*, methane formation from acetic acid), it was noted that the photocatalytic activity of amorphous ferric oxide for the methane formation is independent of the preparation procedures of the photocatalyst part.
Key words: Ferric Oxide, Photocatalysts, photo-Kolbe reaction

1. INTRODUCTION

Fe_2O_3 is in itself an old material but currently one of the promising photocatalysts under visible-light irradiation. Various kinds of studies have been conducted to establish an efficient photocatalysis system of Fe_2O_3 [1-5]. For example, it has been known that the photocatalytic activity of Fe_2O_3 can be improved by embedding it in a clay compound (denoted as Fe_2O_3/clay), in comparison with that of a neat Fe_2O_3 [6]. The typical merit of the use of clay compound as a supporter is that the aggregation of Fe_2O_3 particles can be suppressed to involve an increase in the specific surface area of the particles [7-9].

Photocatalysis by Fe_2O_3/clay has often been studied under the condition where the saturated amount of Fe_2O_3 is loaded into a clay compound (*cf.*, when employing montmorillonite (denoted as MT) as the supporter, the maximum loading amount was ca. 25wt.% of Fe_2O_3 to MT [10]). However, the authors have recently reported that the photocatalytic activity of Fe_2O_3/MT depends on the loading amount of Fe_2O_3 into a MT supporter, in which a Fe_2O_3 in 2.8wt.% Fe_2O_3/MT shows the most active and efficient photocatalysis for the methane formation from acetic acid (called the photo-Kolbe reaction (see Fig. 1)) [10]; moreover, it also appeared that the photocatalysis for the photo-Kolbe reaction by a Fe_2O_3 is kinetically slow [10]. Therefore, it was probable that the higher loading of Fe_2O_3 causes the interspersion of the active sites, thus leading to a
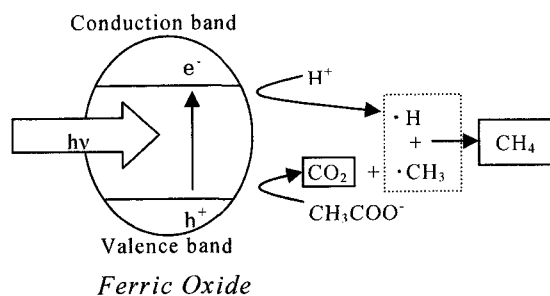

Fig.1 Schematic illustration of the decomposition of acetic acid into methane (the photo-Kolbe reaction) at ferric oxide embedded in clay.

decrease in the overall photocatalysis activity.

In the present work, the photo-Kolbe reaction was investigated particularly in terms of the preparation procedures of the photocatalyst part, for which a low loading of ferric oxide in MT supporter was conducted with two kinds of methods.

2. EXPERIMENTAL

2.1 Purification of MT, and preparation of Na^+-type MT

20 g of bentonite (Nihon Koken, Tsugaru 2) was introduced into 900 ml of deionized water, and subsequently, 3% hydrogen peroxide solution (100 ml) was added into the suspension for

removing organic matters from soil. Continuous stirring of the suspension was conducted for 5 h, after which MT was isolated from bentonite by means of centrifugation. The resulting MT was soaked in 1000 ml of 1 mol dm^{-3} NaCl solution, through which the entire cation-exchange sites in the MT were replaced by Na$^+$ (*cf.*, this treatment was repeated 3 times). The Na$^+$-type MT was washed with deionized water and dried at 100 ℃. As a result, *ca.* 7 g of Na$^+$-type MT was obtained.

2.2 Preparation of photocatalyst embedded in clay

The loading of ferric oxide into MT was conducted with two kinds of methods.

Method (a): 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), according to the previous procedure [11]. A 2.3 ml portion of the aqueous complex solution (0.1 mol dm^{-3}) was quickly dropped into 100 ml of 10.0 g dm^{-3} Na$^+$-type MT suspension with stirring, and the mixture was then stirred for 4 h at room temperature. After washing the Fe^{III}-type MT with deionized water, it was dried on a glass plate at room temperature, followed by calcination at 400℃ under air (for 10 h). The resulting 5wt.% Fe₂O₃/MT was stored in a glass vessel under air.

Method (b): A 6.7 ml portion of iron (III) nitrate enneahydrate aqueous solution (0.1 mol dm^{-3}) was dropped into 100 ml of 10.0 g dm^{-3} Na$^+$-type MT suspension with stirring, followed by continuous stirring of the mixture for 4 h at room temperature. In order to remove nitrate, the resulting Fe^{III}-type MT was washed with deionized water by means of centrifugation, after which it was put back into deionized water. The formation of hydrous ferric oxide (*i.e.*, ferric hydroxide) in the MT was conducted by means of hydrolysis, where 100 ml of aqueous NaOH solution (1 mol dm^{-3}) was added into 100 ml of Fe^{III}-type MT suspension. The resulting suspension (conc., 10.5 g dm^{-3}) of 5wt.% hydrous ferric oxide to MT (denoted as HFO/MT) was washed with deionized water by means of centrifugation, and stored at room temperature.

2.3 Characterization of photocatalyst

The loading amount of ferric oxide in MT was determined by measuring TG (Rigaku, TG-8120) at 400 ℃ under air (for 10 h). The specific surface areas of Fe₂O₃/MT and HFO/MT were determined by the B.E.T. method (Shimadzu-Micromeritics, FlowSorb II 2300). The polymorph of the photocatalyst part embedded in MT was identified by electron diffraction. A transmission electron microscope (Hitachi, H-8000) operated at 200 kV was applied to obtain the sample image. For the observation of TEM image with Fe₂O₃/MT (or HFO/MT), *ca.* 0.1 g dm^{-3} of the suspension of Fe₂O₃/MT (or HFO/MT)

was prepared. A 10 μl portion of the suspension was dropped onto a micro grid supported on a copper grid mesh (Nisshin EM, MJD02A), and it was then dried at room temperature.

2.4 Photocatalytic experiment

The photo-Kolbe reaction was conducted in a glass vessel (vessel volume, 20 ml) containing 10 ml of 10 vol.% acetic acid (*cf.*, pH was adjusted by adding a conc. NaOH to the aqueous solution of acetic acid) and 21.1 mg of 5wt.% Fe₂O₃/MT (or 5wt.% HFO/MT) under Ar atmosphere. The photocatalyst samples were washed with an acetic acid solution (pH = 5.0) prior to use. A 150-W Halogen lamp (Hayashi Watch Works, LA-150TX) was used as a light source (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

The polymorph of ferric oxide was investigated by means of TEM. Fig. 2 shows the TEM image of 5wt.% Fe₂O₃/MT and the electron diffraction pattern (inset). The size of Fe₂O₃ particles in 5wt.% Fe₂O₃/MT was at most ca. 20 nm (Fig. 2a), but there was no presence of the diffraction spot from crystalline Fe₂O₃. Therefore, in 5wt.% Fe₂O₃/MT, the polymorph of Fe₂O₃ is assignable to the amorphous phase.

Hydrous ferric oxide, identified with an amorphous ferric oxide [12, 13], was separately prepared (*vide supra*). The method (b) for HFO/MT is very simple in comparison with the method (a) for Fe₂O₃/MT: in the former, an amorphous ferric oxide can be prepared without the use of iron complex (such as trinuclear acetate hydroxo iron (III) nitrate) as a precursor and its calcination. As depicted in Fig. 2b, the polymorph of hydrous ferric oxide in 5wt.% HFO/MT was confirmed to be an amorphous phase through the TEM image, where the diffraction ring only from MT was observed similar to the 5wt.% Fe₂O₃/MT (cf., the size of ferric oxide particles in 5wt.% HFO/MT was also ca. 20nm). In summary, it appeared that the polymorph of ferric oxide is independent of the preparation procedures in the case of its low loading.

The specific surface areas of 5wt.% Fe₂O₃/MT, 5wt.% HFO/MT, and MT determined by the B. E. T method were 213 m^{2}g^{-1}, 239 m^{2}g^{-1}, and 163 m^{2}g^{-1}, respectively. The loading of ferric oxide resulted in the increase in the specific surface area. Moreover, it should be noted that the value for HFO/MT was almost consistent with that for Fe₂O₃/MT, showing the independence on the preparation procedures of amorphous ferric oxide.
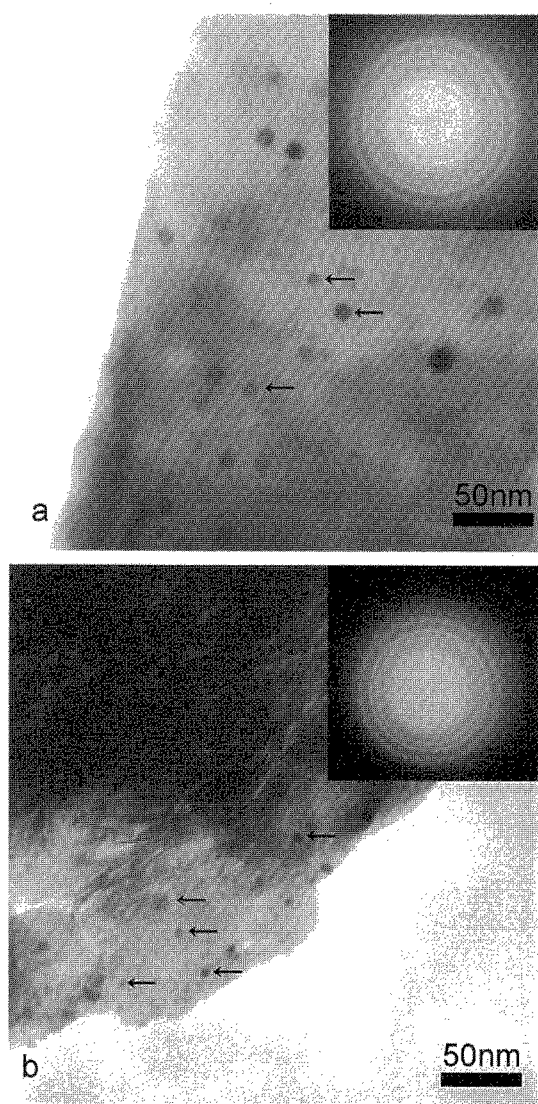
Fig. 2 Transmission electron micrographs (bright-field images) of ferric oxide particles in MT (arrows indicate the particles) and electron diffraction pattern (inset): (a), 5wt.% Fe₂O₃/MT; and (b), 5wt.% HFO/MT.

Fig. 3 Time-course of the amount of the methane produced in 5wt.% Fe₂O₃/MT (21.1mg) (□) and 5wt.% HFO/MT (21.1mg) (●). The concentration of acetic acid was 10vol.% (pH = 5.0).

The photo-Kolbe reaction was conducted using 5wt.% HFO/MT and 5wt.% Fe₂O₃/MT as photocatalyst, and the results are summarized in Table I. Note that the amount of the methane produced in 5wt.% Fe₂O₃/MT was as much as that in 5wt.% HFO/MT, which evidently exhibits that the photocatalytic activity of amorphous ferric oxide for the photo-Kolbe reaction is independent of the preparation procedures of the photocatalyst part (*cf.*, for both 5wt.% HFO/MT and 5wt.% Fe₂O₃/MT systems, the turnover numbers (TON) of a photocatalyst for the methane production were estimated to be ca. 3.3 for 15 hours). In addition, in both systems of amorphous ferric oxide, the time-course of the amount of the methane produced exhibited the linear dependence on irradiation time (Fig. 3), which also reveals that an amorphous ferric oxide acts as a stable photocatalyst.

Table I The amount of the methane produced in each photocatalyst system

Sample [a]	The amount of the methane produced [b] / μmol
5wt.% Fe₂O₃/MT	22.5
5wt.% HFO/MT	21.8

a: The amount of the ferric oxide (Fe₂O₃, or HFO) employed was constant (1.1mg) in each case.
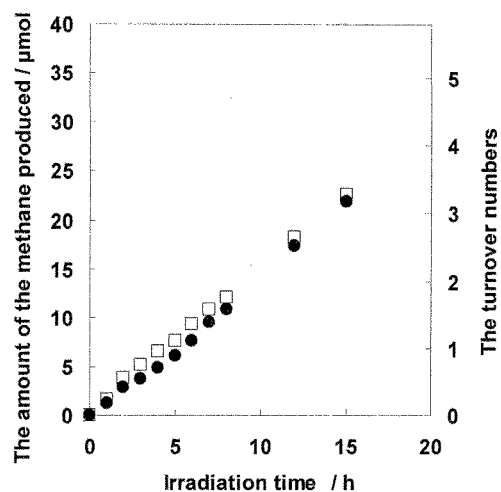b: The concentration of acetic acid was 10vol.% (pH=5.0), and the irradiation was conducted for 15h.

4. CONCLUSION

The present study showed that an amorphous ferric oxide can lead to an efficient and stable photocatalysis particularly for the photoproduction of methane from acetic acid, irrespective of the preparation procedures of the photocatalyst part. This involved the first example of the photo-Kolbe reaction by hydrous ferric oxide. The preparation of amorphous ferric oxide through hydrolysis (i.e., method (b)) is of simple in comparison with another methods, and moreover, the way is also reasonable in terms of the conservation of the global environment. Hydrous ferric oxide should be passively used as a photocatalyst coming up to the concept of green chemistry.

5. REFERENCES

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