Electronic supplementary information

Clarification of photocatalysis induced by iron ion species naturally

contained in a clay compound

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Characterization of Fe(III)MMT after an additional hydrogen peroxide treatment

After the preparation of Fe(III)MMT through Method A, it was additionally treated with 15% hydrogen peroxide solution. 71 cm³ of 36% hydrogen peroxide (Kanto Chemical Co., Inc.) was dropped into a 100 cm³ suspension of 1 wt% Fe(III)MMT with stirring, following which the mixture was continuously stirred for 3 h at room temperature. The product was washed with deionized water and dried at 100°C under air. The structural characteristics of the resulting sample were identified in terms of IR spectrum (Fig. S1).



Fig. S1. The IR spectrum of Fe(III)MMT after additional treatment by 15% H_2O_2 . The arrows indicate the peak positions of the species originating from structural-Fe(III) species.

Characterization of B-MMT

B-MMT was prepared through the acid treatment of Fe(III)MMT (Method B),

where the amount of HFO was varied with the concentration of HCl (Table S1).

Table S1 The amount of HFO in 20mg B-MMT with the function of the HCl concentration.

HCl concentration in acid treatment (mol dm ⁻³)	The amount of HFO (µg)
0.3	89
1.0	116
2.0	154
3.0	175

The structural and optical characteristics of B-MMT were identified in terms of

IR spectrum (Fig. S2), XRD pattern (Fig. S3), and diffuse reflectance spectrum (Fig. S4).



Fig. S2. The IR spectra of B-MMT with the changes in the concentration of HCl. The arrows indicate the peak positions of the species originating from structural-Fe(III) species.



Fig. S3. The XRD patterns of B-MMT with the changes in the concentration of HCl.



Fig. S4. The diffuse reflectance spectra of B-MMT with the changes in the concentration of HCl.

The stability of Fe(III)MMT

Fe(III)MMT was used repeatedly as the photocatalyst for acetic acid degradation; the acetic acid solution was replaced through centrifugation after every irradiation for 10 h. After each cycle, the amount of CO_2 evolved was measured (TableS2).

Table S2 The amount of CO_2 evolved after 10 hours of irradiation in repeatedly using Fe(III)MMT as the photocatalyst for the degradation of acetic acid.^a

	The amount of CO_2 / µmol
run 1	13.2
run 2	14.1
run 3	13.4

^a Concentration of acetic acid: 1 mol dm⁻³ (pH 5); light intensity: 110 mW cm⁻².

The equations in the photo-Kolbe reaction 1^{-3}

Photocatalyst + $h\nu \rightarrow$ Photocatalyst (e⁻ + h⁺) (1)

(2)

- Reduction of hydrogen: $H^+ + e^- \rightarrow \cdot H$
- Oxidation of acetic acid: $CH_3COO^- + h^+ \rightarrow CO_2 + \cdot CH_3$ (3)
- Generation of methane: $\cdot CH_3 + \cdot H \rightarrow CH_4$ (4)
- The overall reaction: $CH_3COOH \rightarrow CH_4 + CO_2$ (5)

References

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- 3. T. Sakata, T. Kawai and K. Hashimoto, J. Phys. Chem., 1984, 88, 2344-2350.