Photocatalytic degradation of acetic acid on spinel ferrites $M\text{Fe}_2\text{O}_4$ ($M = \text{Mg}, \text{Zn},$ and Cd)

Keitaro Tezuka, Masahiro Kogure, and Yue Jin Shan

Department of Material and Environmental Chemistry, Graduate School of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya, Tochigi 321-8585, Japan

Abstract

Spinel ferrites $M\text{Fe}_2\text{O}_4$ ($M = \text{Mg}, \text{Zn},$ and Cd) with Fe(III) in a d^5 electron configuration were prepared via a conventional solid-state reaction. The amount of CO_2 generated by the photocatalytic degradation of acetic acid on these ferrites was measured under irradiation by a xenon lamp with a power of 300 W. Photocatalytic degradation was observed for all the compounds, and the results revealed that MgFe_2O_4 exhibited the highest degradation, i.e., $196 \mu\text{mol/g/h}$. The degradation in the presence of $M\text{Fe}_2\text{O}_4$ ($M = \text{Mg}, \text{Zn},$ and Cd) increased with increasing heating condition.

Keywords

Photocatalysis; Iron oxide; Spinel; Acetic acid

1. Introduction

Photocatalysis has been widely studied for its application to the decomposition of organic compounds and production of hydrogen through the decomposition of water or alcohol [1-3]. Although TiO_2 has been the most extensively investigated photocatalyst, various studies on the catalytic properties of other oxides, such as the photocatalytic degradation of acetaldehyde and toluene on Pd/WO_3 [4], have also been reported. Furthermore, CaBi_2O_4 has been reported to decompose acetaldehyde and methylene blue under visible light irradiation [5]. Likewise, methylene blue decomposition in the presence of CaIn_2O_4 under visible light has also been reported [6], and compounds such as KTaO_3 [7], $\text{Sr}_2\text{Ta}_2\text{O}_7$ [8], and $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ [9] have been well documented to exhibit photocatalytic degradation of water.

Almost all these metal oxides are diamagnetic because the transition metal ions in these oxides do not contain unpaired electrons, i.e., ions in these oxides such as Ti^{4+} , W^{6+} , and Ta^{5+} exhibit d^0 configurations, indicating that no electron occupies a d orbital. Alternatively, metal ions such as In^{3+} have d^{10} configurations, indicating that the d orbitals are completely occupied. In contrast, studies on metal oxides with electron configurations of d^n ($0 < n < 10$) having unpaired electrons have not made progress, because it seems that these metal oxides show low activity as photocatalysts. A major

reason for this assumption is that excessive transitions of the unpaired electrons seem to interrupt the photocatalytic activities of metal oxides. With respect to transition metal ions with d^n ($0 < n < 10$) configuration, we paid particular attention to the ions with d^5 electron configurations, where the d orbitals are half-filled with electrons. A half-filled electron configuration with a high-spin state is known to disturb the $d-d$ transition, which is one of the electron transitions, because of the spin-forbidden rule. Among the metal oxides with a d^5 electron configuration, we are especially interested in iron(III) complex oxides because of the high stability of the iron(III) ion. Reports of photocatalysis involving the Fe(III) complex oxides, although few in number, have nonetheless appeared in the literature. However, many of these reports are related to nanoparticles and composites with other compounds [10-14]. In contrast, not many studies have been reported with respect to the evaluation of native complex oxides as photocatalysts. Some reports of the photocatalytic activities of native oxides are mainly concerned with the decomposition of dyes such as methylene blue [15-18]. However, in these cases, problems arise due to the self-decomposition of dyes, which is influenced by pH [19]. Thus, this approach is not well suited for the evaluation of photocatalytic activity because of the instability of dyes. One of the well-known reactions used to evaluate photocatalysts is the decomposition of acetic acid via a simple and stoichiometric reaction[20-21]:

Thus, this reaction is suitable for evaluating the photocatalytic decomposition of organic materials. However, no studies on the ability of iron(III) complex oxides to catalyze this reaction have been reported. Research into photocatalytic decomposition on iron(III) complex oxides with d^5 electron configurations is essential to fully elucidate the photocatalytic properties of various metal complex oxides. Among these oxides, we are specifically interested in spinel-type complex oxides $M\text{Fe}_2\text{O}_4$ (M = metals) because of their compositional simplicity and their highly symmetric crystal structures.

In this study, we prepared spinel-type iron(III) complex oxides $M\text{Fe}_2\text{O}_4$ (M = Mg, Zn, and Cd) via standard solid-state reaction, characterized them using powder X-ray diffraction (XRD) measurements, UV-Vis diffuse reflectance spectral measurements, and FE-SEM observations, and investigated photocatalytic degradation of acetic acid on them.

2. Experimental

$M\text{Fe}_2\text{O}_4$ ($M = \text{Mg}, \text{Zn}, \text{and Cd}$) were prepared via solid-state reactions among Fe_2O_3 , MgCO_3 , ZnO , and CdO . The starting materials were stoichiometrically mixed in an agate mortar and then heated at 1000–1200 °C. XRD patterns were measured on a RINT2200 diffractometer (Rigaku) equipped with a Cu $K\alpha$ radiation source and a graphite monochromator. The crystal structure of MgFe_2O_4 was refined with the program RIETAN-FP [22]. UV–Vis diffuse reflectance spectra were measured by a V-570 (JASCO). The morphology and particle size of the products were observed with FE-SEM images taken with an S-4500 system (Hitachi).

The photocatalytic activities of the obtained powders during the oxidative decomposition of acetic acid in suspensions were examined. The powders (150 mg) were placed in a 300-mL round flask and were suspended in 5 vol. % acetic acid aqueous solution (20 mL). The amounts of acetic acid and oxygen molecules in the flask were calculated to be 17 mmol and 12 mmol, respectively, without considering the dissolved oxygen in the aqueous solution.

The suspension was stirred using a magnetic stirring bar under an oxygen atmosphere at room temperature and was irradiated by UV–visible light using a 300-W xenon lamp (PerkinElmer, PE300BUV) for 1 h. A UV cut-off filter (Schott, GG420) was used for the irradiating visible light ($\lambda > 420 \text{ nm}$). The irradiation powers to the reaction system with and without the UV cut-off filter were calculated to be 22 W and 10 W, respectively, on the basis of the power measurements performed using a PowerMax PM3 detector (Coherent). The concentration of CO_2 generated via the photocatalytic degradation of acetic acid was measured using a gas chromatograph equipped with a TCD detector (Shimadzu, GC-2014). The pH value of all of the aqueous solutions was measured to be 2.4 before the reactions and was constant during the reactions.

3. Results and discussion

Typical XRD patterns of the obtained products are shown in Fig. 1. For all the products, spinel compounds are obtained as single phases. Two crystallographic cation sites for the spinel compound are available: the 8a tetrahedral site and the 16d octahedral site of the space group $\text{Fd}\bar{3}\text{m}$ (No. 227). All the Fe atoms occupy octahedral sites in ZnFe_2O_4 and CdFe_2O_4 , and Zn and Cd occupy the 8a tetrahedral sites. However, in the case of MgFe_2O_4 , Mg and Fe exist in a style of disorder in these two sites. The site occupancies of these cations were determined by Rietveld analysis of the XRD

patterns to account for their possible influence on the photocatalytic activity. Table 1 shows the analyzed site occupancies of the cations. From these results, it is observed that the prepared oxides do not exhibit a large difference in the cation occupancies and are found to exhibit an almost inverse spinel structure because the 8a site occupation factor of iron is almost 1. This result is consistent with previously reported results [23].

Results of the photocatalytic degradation experiments are shown in Table 2. Degradation was observed with all three types of oxides. MgFe_2O_4 clearly exhibited the highest activity toward degradation, whereas ZnFe_2O_4 exhibited the lowest activity. In the case of ZnFe_2O_4 , the photocatalytic activity increased with increasing heating temperature, and in the case of CdFe_2O_4 , the activity increased with increasing heating time. Although the heating conditions for MgFe_2O_4 were not simple to compare, the approximate tendency for the activity of these spinel compounds to increase under stronger heating conditions is evident. We expected the activity of these oxides to strongly depend on their crystallinity.

We examined whether these degradation reactions are dependent on the photocatalytic reaction. First, we performed the control experiment without light irradiation; as a result, carbon dioxide generation was not observed. Thus, the degradation is not due to a mechano-catalytic reaction related to the stirring energy of the magnetic stirring bar; it is instead due to the reaction that requires light irradiation. Next, to investigate the possibility of the decomposition reaction being related to the self-decomposition of the iron complex oxides, we compared the XRD patterns of the oxides obtained after the reaction with those obtained before the reaction. Because no obvious difference was detected between these XRD patterns, we surmised that no decomposition occurred. On the basis of these observations, the decomposition of acetic acid was solely due to the photocatalytic reaction. For the sake of comparison, we also performed photocatalytic degradation measurements of the acetic acid sample on native TiO_2 , which resulted in 119 $\mu\text{mol/g}$. The degradation induced by MgFe_2O_4 and CdFe_2O_4 both overwhelmed that induced by TiO_2 .

To elucidate the dependence of the catalytic activity on the wavelength of light used to irradiate the samples, we performed measurements using a cut-off filter that blocks light wavelengths of less than 420 nm, i.e., using absolutely visible light. No reaction was detected when the cut-off filter was used. From these results, it is observed that light with wavelengths less than approximately 400 nm primarily influences the photocatalytic reaction.

SEM images were obtained to observe the particle shapes of the complex oxides. The SEM images are shown in Fig. 2. In general, the particle size also influences the

photocatalytic activity, and the activity increases with decreasing particle size because of the enlargement of total surface area of the particles if there is no difference in the degree of crystallinity of particles [24]. We first verified this relationship for ZnFe_2O_4 samples prepared at different temperatures. As shown in Figs. 2(c)–(e), the particle size obtained at 1000 °C was exceedingly small in comparison with the sizes of the particles obtained at 1100 °C and 1200 °C. Furthermore, the particle size of the sample prepared at 1200 °C was slightly greater than that of the sample prepared at 1100 °C. However, the photocatalytic activity was the lowest in the case of ZnFe_2O_4 prepared at 1000 °C, which exhibited the smallest particle size and was the largest in the case of ZnFe_2O_4 prepared at 1200 °C, which exhibited the largest particle size. On the basis of these results, it is observed that the particle size only slightly influenced the photocatalytic activity of this oxide. Thus, we hypothesized that the activity is mainly dependent on the crystallinity of the oxide particles. In general, higher crystallinity of the complex oxides was attained under stronger heating conditions, and the more crystalline samples exhibited higher photocatalytic activity. In the cases of MgFe_2O_4 and CdFe_2O_4 , no dramatic differences were observed with respect to either their particle shape or their degradation properties because differences that result from different heating conditions appear to be trivial compared with the case of ZnFe_2O_4 . However, these results indicate that strong synthesis conditions tend to result in higher degradation activity of the resulting oxides; thus, crystallinity influences photocatalytic activity. However, given that ZnFe_2O_4 exhibits the highest activity even in the case of that obtained at 1200 °C, where the particle size is almost the same as that of the MgFe_2O_4 and CdFe_2O_4 , the higher activity is probably a consequence of differences in the electronic structures of these oxides.

UV–Vis diffuse reflectance spectra of these oxides are illustrated in Fig. 3. For each compound of a given composition, the spectrum shape is mostly not influenced by the preparation conditions. The spectrum of titanium oxide, which is a well-known photocatalyst, is included for comparison. Titanium oxide absorbs only in the ultraviolet region, whereas all the spinel-type iron complex oxides absorb in the visible region, probably due to the transitions of electrons in incompletely filled d orbitals. These results indicate that the optical band gaps in these spinel-type oxides are smaller than that of TiO_2 . The energies of band gaps of these oxides were determined by the Tauc plots on the assumption that the direct allowed transition ($n=1/2$) is predominant [25] (Inset of Fig. 3). The band gaps of MgFe_2O_4 , ZnFe_2O_4 , and CdFe_2O_4 were determined to be 2.1 eV, 2.1 eV, and 1.9 eV, respectively, which are almost consistent with the reported values of 2.2 eV for MgFe_2O_4 [26], 2.2 eV for ZnFe_2O_4 [26], and 1.97 eV for

CdFe₂O₄ [27]. However, as mentioned above, almost none of the light in the visible optical region was utilized for photocatalytic degradation.

4. Conclusions

Spinel-type iron complex oxides MgFe₂O₄, ZnFe₂O₄, and CdFe₂O₄ were prepared via conventional solid-state reactions, and the photocatalytic degradation of acetic acid on these oxides under irradiation by a 300-W xenon lamp was examined. All the compounds were active for the photocatalytic degradation of acetic acid. MgFe₂O₄ exhibited the highest activity toward degradation and was found to be more active than TiO₂. Among samples of a given composition, stronger preparation conditions tended to result in higher degradation activity. Despite the fact that the diffuse reflectance spectra show the spinel-type oxides considerably absorbing visible light, degradation was not observed when visible light with wavelengths longer than 420 nm was exclusively used to irradiate the samples. Therefore, we concluded that almost none of the visible light absorbed was utilized for photocatalytic degradation.

Acknowledgements

This work was partially supported by Saneyoshi Scholarship Foundation, Yazaki Memorial Foundation for Science and Technology, JST, and JSPS KAKENHI Grant Number 23760631.

References

- [1] M. R. Hoffman, S. T. Martin, W. Choi, and D. W. Bahnemann, *Chem. Rev.* 95 (1995) 69-96.
- [2] A. Fujishima, T. N. Rao, and D. A. Tryk, *J. Photochem. Photobiol. C* 1 (2000) 1-21.
- [3] T. Takata, A. Tanaka, M. Hara, J. N. Kondo, K. Domen, *Catal. Today* 44 (1998) 17-26.
- [4] T. Arai, M. Horiguchi, M. Yanagida, T. Gunji, H. Sugihara, and K. Sayama, *Chem. Commun.* 43 (2008) 5565-5567.
- [5] J. Tang, Z. Zou, and J. Ye, *Angew. Chem. Int. Ed.* 43 (2004) 4463-4466.
- [6] J. Tang, Z. Zou, J. Yin, and J. Ye, *Chem. Phys. Lett.* 382 (2003) 175-179.
- [7] H. Kato and A. Kudo, *J. Phys. Chem. B* 105 (2001) 4285-4292.

- [8] A. Kudo, H. Kato, and S. Nakagawa, *J. Phys. Chem. B* 104 (2000) 571-575.
- [9] S. Ikeda, M. Hara, J. N. Kondo, K. Domen, H. Takahashi, T. Okubo, and M. Kakihana, *Chem. Mater.* 10 (1998) 72-77.
- [10] J. Luo and P. A. Maggard, *Advanced Materials* 18 (2006) 514-517.
- [11] Z. Liu, Z.-G. Zhao, M. Miyauchi, *J. Phys. Chem. C* 113 (2009) 17132-17137.
- [12] S. Chen, Wei Zhao, Wei Liu, Huaye Zhang, Xiaoling Yu, *Chem. Eng. J.* 155 (2009) 466-473.
- [13] H. Lv, L. Ma, P. Zeng, D. Ke, T. Peng, *J. Mater. Chem.* 20 (2010) 3665-3672.
- [14] K. M. Parida, K. H. Reddy, S. Martha, D. P. Das, N. Biswal, *Int. J. Hydrogen Energ.* 35 (2010) 12161-12168.
- [15] L. Wu, J. C. Yu, L. Zhang, X. Wang, and S. Li, *J. Solid State Chem.* 177 (2004) 3666-3674.
- [16] Q.-J. Ruan, W.-D. Zhang, *J. Phys. Chem. C* 113 (2009) 4168-4173.
- [17] Y. Huo, Y. Jin, Y. Zhang, *J. Mol. Catal. A: Chemical* 331 (2010) 15-20.
- [18] M. Zhang, H. Yang, T. Xian, Z. Q. Wei, J. L. Jiang, Y. C. Feng, X. Q. Liu, *J. Alloy. Compd.* 509 (2010) 809-812.
- [19] X. Yan, T. Ohno, K. Nishijima, R. Abe, B. Ohtani, *Chem. Phys. Lett.* 429 (2006) 606-610.
- [20] S. Ikeda, N. Sugiyama, B. Pal, G. Marci, L. Palmisano, H. Noguchi, K. Uosaki, B. Ohtani, *Phys. Chem. Chem. Phys.* 3 (2001) 267-273.
- [21] T. Torimoto, N. Nakamura, S. Ikeda, B. Ohtani, *Phys. Chem. Chem. Phys.* 4 (2002) 5910-5914.
- [22] F. Izumi and K. Momma, *Solid State Phenom.* 130 (2007) 15-20.
- [23] G. E. Bacon and F. F. Roberts, *Acta Cryst.* 6 (1953) 57-62.
- [24] H. Kominami, S. Murakami, J. Kato, Y. Kera, B. Ohtani, *J. Phys. Chem. B.* 106 (2002) 10501-10507.
- [25] J. Tauc, R. Grigorovici, A. Vancu, *Phys. Stat. Sol.* 15 (1966) 627-637.
- [26] L. G. J. De Haart and G. Blasse, *Solid State Ionics* 16 (1985) 137-140.
- [27] F. Miao, Z. Deng, X. Lv, G. Gu, S. Wan, X. Fang, Q. Zhang, S. Yin, *Solid State Commun.* 150 (2010) 2036-2039.

Figure Captions

- Figure 1 Typical XRD patterns of (a) MgFe_2O_4 heated at 1150 °C for 5 h and at 850 °C for 10 h, (b) reported pattern for MgFe_2O_4 (ICSD No. 9939), (c) ZnFe_2O_4 heated at 1200 °C for 5 h, (d) reported pattern for ZnFe_2O_4 (ICSD No. 37430), (e) CdFe_2O_4 heated at 1000 °C for 6 h, and (f) reported pattern for CdFe_2O_4 (ICSD No. 619857).
- Figure 2 SEM images of (a) MgFe_2O_4 heated at 1200 °C for 5 h, (b) MgFe_2O_4 heated at 1150 °C for 5 h and at 850 °C for 10 h, (c) ZnFe_2O_4 heated at 1000 °C for 5 h, (d) ZnFe_2O_4 heated at 1100 °C for 5 h, (e) ZnFe_2O_4 heated at 1200 °C for 5 h, (f) CdFe_2O_4 heated at 1000 °C for 5 h, and (g) CdFe_2O_4 heated at 1000 °C for 6 h.
- Figure 3 Diffuse reflectance spectra of (a) MgFe_2O_4 heated at 1200 °C for 5 h, (b) MgFe_2O_4 heated at 1150 °C for 5 h and at 850 °C for 10 h, (c) ZnFe_2O_4 heated at 1000 °C for 5 h, (d) ZnFe_2O_4 heated at 1100 °C for 5 h, (e) ZnFe_2O_4 heated at 1200 °C for 5 h, (f) CdFe_2O_4 heated at 1000 °C for 5 h, (g) CdFe_2O_4 heated at 1000 °C for 6 h, and (h) TiO_2 .

Table of Contents

Table 1 Site occupancies of Mg and Fe in MgFe_2O_4 .

Heating conditions	Atom	Site	Occupancy
1200 °C, 5 h	Mg/Fe	8a	0.087/0.913
	Mg/Fe	16d	0.456/0.544
1150 °C, 5 h $\rightarrow$ 850 °C, 10 h	Mg/Fe	8a	0.093/0.907
	Mg/Fe	16d	0.454/0.546

Table 2 Results for the photocatalytic degradation of acetic acid on spinel ferrites $M\text{Fe}_2\text{O}_4$ ($M = \text{Mg}, \text{Zn}, \text{and Cd}$).

Oxide	Heating conditions	Concentration of CO_2 [$\mu\text{mol/g}$]
MgFe_2O_4	1200 °C, 5 h	167
MgFe_2O_4	1150 °C, 5 h $\rightarrow$ 850 °C, 10 h	196
ZnFe_2O_4	1000 °C, 5 h	30
ZnFe_2O_4	1100 °C, 5 h	62
ZnFe_2O_4	1200 °C, 5 h	67
CdFe_2O_4	1000 °C, 5 h	132
CdFe_2O_4	1000 °C, 6 h	148

Figure 1

Figure 2

Figure 3