Magnetic field effect on heterogeneous photocatalysis

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Magnetic field effect (MFE) on heterogeneous photocatalysis is investigated, using mostly ZnO powder and methylene blue (MB) solution. Reproducibility with errors less than 2% is obtained with our newly-developed in-situ measurement system. Multiple parameters are involved in MFE phenomena. MFE magnitude depends on magnetic field intensity, while other parameters are also important, including: initial MB concentration, settling time of solution, and level/state of dissolved oxygen (DO). Short-range-order, or very-short-range-order diffusion in the Helmholtz layer just outside powder appears responsible for MFE. Accordingly, powder surface conditions, e.g. H2O, CO2 adsorption, significantly influence MFE, and magnetic adsorption appears correlated. Temperature-dependent MFE and magneto-hydrodynamic effect on photocatalytic silver reduction/deposition are also observed for the first time.

A model is proposed, whereby, in the volume in close proximate to the powder, electrostatic potential and the corresponding magnetic flux would be perturbed, resulting in the appearance of a net Lorentz force on paramagnetic DO, which is essentially responsible for various MFE phenomena (OAAN model). DO could be involved with (i) formation of DO-dye complex, (ii) modifying powder adsorption layer, (iii) scavenging rate of excited electrons, (iv) spin chemistry involving singlet-triplet conversion, and (v) manifestation of magneto-hydrodynamic effect. Simultaneous multiple mechanisms are suggested for MFE.

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1. Introduction

The first research report on magnetokinetic phenomena was the magnetic fluorescence quenching in the gas phase reaction about one hundred years ago, and in 1929 the magnetic field (MF) dependence of reaction rates was first reported [1]. The possible relationships between magnetic properties and catalytic activity were also reported in 1945, through exhaustive reviews and assessment of various oxides and the temperature dependence of their susceptibilities [2]. Thus, the ways in which chemical reactions can be affected by MFs have long been the subject of investigation. In spite of extensive research work reported, however, the early studies of magnetic field effects (MFEs) on chemical reactions were occasionally plagued by non-reproducible effects and retractions [3,4], and systematically tracing MFEs on chemical yields and kinetics is sometimes difficult. In MFE research on non-magnetic reaction systems, involving magnetokinetic chemical and related physical phenomena, the reproducibility is thus one of the major issues. There are various factors involved in the complex MFE systems and the scale of the effect is relatively small compared with the ambient thermal fluctuation and/or the reaction kinetics. The MFEs on the homogenous reaction systems have been, however, relatively well-established, through a burst era of highly reproducible results reported in the 1970s [1,4], as well as the development of MFE on various photochemical reactions [5]. In the field of electrochemistry the MF control of electrochemical reactions and precipitations has been intensively studied, especially for the last 20 years [6]. The MFEs on homogeneous reaction systems are generally explained in terms of the radical pair mechanism.

On the other hand, the MFE research on heterogeneous reaction systems, photocatalysis in particular, is rather limited [7], where there is even still becomes debate on the reproducibility of the MFE as well as elucidating the mechanism. A brief summary of the MFE research work reported on heterogeneous photocatalytic reaction systems is shown in Table 1. Kiwi reported MFEs on photosensitized electron transfer reactions in the presence of TiO2 and Cds particles (with RuO2 and Pt) [8], where H2 evolution from a suspension was decreased with MF below 0.4 T (Tesla) under oxygen-free conditions. Waka et al. studied the MFEs on photodegradation of tert-butyl alcohol, and reported that (i) with platinized TiO2 particles (<100 μm) the MFE was slightly increased under MF of 0.5 T and decreased under 1.0 T and 1.5 T [9], while
(ii) the MFE monotonically increased with ultrafine TiO₂ (~25 nm) under MF of 0–1.5 T. They claimed that magnetically induced blocking of electron-hole recombination was responsible for the MFE, and the HFCM (hyperfine coupling mechanism) was excluded as the MFE was not saturated below ~50 mT [10]. Zhang et al. reported promoted photocatalytic degradation of benzene (positive MFE) over Pt/TiO₂ [11] under MF of ~60 mT, with average particle size of 10.4 nm and specific surface area of 124 m²/g. Although there are limited numbers of other reports on MFs, the heterogeneous systems studied have been thus lopsided toward titania photocatalysis, except for our recent reports on ZnO powder [12–14]. In addition, most of the above research on MFs has been carried out during the last decade, apart from the first report by Kiiwi. Moreover, and most importantly, the mechanism of the MFE is still controversial, partially due to the complex system involving numerous parameters, where various experimental conditions and the influence on MFE are not well-controlled or at least not well-reported.

In this investigation, the MFE on heterogeneous reaction systems using ZnO powder will be discussed, extending on some of our previous work [12–14]. The major photocatalytic reaction selected is the decoloration or decomposition of methylene blue (MB) solutions, which is also utilized for previously-reported research work [12–15]. Some comparison is also made with TiO₂ powder and the photocatalytic deposition of silver from AgNO₃ solution. The MFEs are confirmed and highly reproducible in all systems. In the proceeding sections, the important parameters involved with MFE are first emphasized through experimental system alteration, and the MFE mechanism will be discussed through comparison of the effects. A model of MFE is proposed for heterogeneous photocatalysis, where the dissolved oxygen (DO) involvement is essentially responsible for various MFE phenomena. In the volume proximate to the powder, the electrostatic potential as well as the magnetic flux would be perturbed, resulting in appearance of net Lorentz force on DO with paramagnetism (OANS model). Simultaneous multiple mechanisms are suggested operative for MFE on heterogeneous photocatalysis.

2. Model systems

A commercial ZnO powder was mainly used as a photocatalyst for MFE measurements. For comparison, a commercial TiO₂ powder was used in some cases as well. According to the preliminary results, the MFE on MB degradation is rather pronounced for ZnO as compared to TiO₂, therefore in the current study the former was addressed more for investigating the heterogeneous photocatalysis. The properties of the powders are summarized in Table 2.

Methylene blue (MB) solution was prepared with MB granular solids (purity: 99.9%, Nacalai Tesque Inc., Japan), where the molecular structure is given in Fig. 1. A small transparent quartz cell (10 × 10 × h 45 mm) with a plastic cap was used as a reaction cell. Magnetic field (MF) was applied using static permanent magnets, with the intensity 0–0.7 Tesla (T). The homogeneity of the magnetic flux density (B) between the poles is confirmed using a gaussmeter probe (HGM-3002P, Nihon Denkei). A UV-LED (ZUV-LBV, Omron Co., Japan) was used as an excitation light source, with the center wavelength of 365 nm. It was placed at 1 cm below the bottom of a quartz cell, where the light intensity was set at 500 mW/cm² at the cell bottom. Spectroscopy was used for quantification of MB degradation according to the Lambert–Beer–Bouguer’s law. There are two spectral peaks at 610 nm and 665 nm in a visible light range for MB solution, which are identified as MB dimer and monomer, respectively. The peak absorbance of MB monomer (665 nm) was used for spectroscopic quantification of MB concentration. The MB concentration decrease after 90 min (without powder) was less than 1% without UV irradiation, and 2–3% under UV irradiation.

Dissolved oxygen (DO) values were measured by a multi-function meter equipped with a galvanic DO electrode (OE-270AA, DKK-TOA Co.). For some experiments Ar gas or O₂ gas were bubbled into the prepared MB solution to change the DO value, prior to dispersion of photocatalyst powder. The flow rate was set to 0.1 L/min and the duration was 1 h. After Ar gas bubbling, the DO value was about 0.5 mg/L, while after O₂ bubbling it was more than 20 mg/L (over the measurement limit of the DO meter; 44 mg/L estimated by Henry’s law). In order to ensure the reproducibility, every MFE measurement for each condition was carried out at least 3 times and the average value was used for MFE assessments.

3. Experimental

3.1. Previous MFE measurement system

The granular MB was dissolved into distilled water, followed by manual shaking for 5 min. After settling for another 5 min, 5 mg of photocatalyst powder was dispersed into the MB solution in the reaction cell. Hereafter, the time interval between the preparation of MB solution and the powder dispersion into the MB solution is called “settling time”. A specimen was set in the irradiation stage with a cell holder, as shown in Fig. 2. For measurement of MB concentration, the reaction cell with the sample in place was removed from the stage and placed inside the UV–vis–NIR spectrometer (Lambda 900, Perkin Elmer Co., Ltd.). The measurement

Table 1
Brief summary of MFE research work reported.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Decomposed substance</th>
<th>MF intensity (T)</th>
<th>Sign of effect</th>
<th>Ref. no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt–RuO₂/TiO₂</td>
<td>Water (H₂ generation)</td>
<td>0–0.4</td>
<td>Negative</td>
<td>[8]</td>
</tr>
<tr>
<td>Pt/TiO₂ (&lt;100 μm)</td>
<td>tert-Butyl alcohol</td>
<td>0–1.5</td>
<td>Negative (0.5 T: positive)</td>
<td>[9]</td>
</tr>
<tr>
<td>TiO₂ (20–40 nm)</td>
<td>tert-Butyl alcohol</td>
<td>0–1.5</td>
<td>Positive</td>
<td>[10]</td>
</tr>
<tr>
<td>Pt/TiO₂ (10 nm)</td>
<td>Benzene</td>
<td>0–0.06</td>
<td>Positive</td>
<td>[11]</td>
</tr>
<tr>
<td>TiO₂ thin film</td>
<td>Methylene blue</td>
<td>0–1.5</td>
<td>Positive</td>
<td>[15]</td>
</tr>
<tr>
<td>M-doped TiO₂ thin film</td>
<td>Methyl orange</td>
<td>0–0.1</td>
<td>Positive</td>
<td>[16]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Phenol</td>
<td>0–0.41</td>
<td>Positive</td>
<td>[17]</td>
</tr>
</tbody>
</table>

Table 2
Properties of photocatalysts.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Properties</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>99.9%, wurtzite structure, 3.8 m²/g, ~300 nm (from SEM &amp; particle analyzer, 5 μm in catalog)</td>
<td>Wako Pure Chemical Ind. Ltd.</td>
</tr>
<tr>
<td>TiO₂ (ST-41)</td>
<td>99.9%, anatase structure, 9.5 m²/g, 200 nm (in catalog)</td>
<td>Ishihara Sango Co., Ltd.</td>
</tr>
</tbody>
</table>

Fig. 1. Molecular structure of methylene blue (MB).
of absorbance was carried out every 10 min after UV irradiation, and the total duration of UV irradiation was 80 min. Since the ratio of MB monomer and dimer changes with solution temperature [18], temperature calibration was applied to the MB absorbance, where the value was converted to that at 25 °C.

3.2. New MFE measurement system

The new experimental system is schematically shown in Fig. 3. Temperature-controlled water was circulated by a pump (flow rate: 30 mL/min) in order to keep the reaction temperature constant during MFE experiments. With this circulation system, the temperature variation was less than ±0.2 °C from the target temperature. Since avoidance of unexpected convection due to cell movement appears to be important for accurate MFE experiments, a photonic multi-channel analyzer (PMA-12, Hamamatsu Photonics Co., Ltd.) as a detector and a white LED as a reference light source (filtered below 550 nm) were used for in-situ measurement of the absorbance of the solution. The in-situ measurement system is schematically shown in Fig. 4. The time interval of absorbance measurements was set at 1 s. In case of applying external MF, the poles of a permanent magnet were placed on two parallel opposite sides of the cell, and the in-situ measurement system was placed on the other set of parallel sides.

The ZnO powder was dried in an electric thermo-constant furnace at 120 °C in air atmosphere for more than 24 h. Ultrapure (ρ ≥ 18.2 MΩ cm, Direct-Q, Millipore Co.) water as a solvent was kept in a water bath at 20 °C for more than 48 h to maintain the same water conditions, especially the dissolved oxygen (DO) and CO₂ concentration (DO: ~8.8 mg/L at 20 °C in ambient air atmosphere [19]). The granular MB solid was dissolved in the water and the concentration was adjusted by water dilution and vigorous stirring. After 2 min settling time, 1.0 mg of ZnO powder was dispersed in 3 mL of MB solution in the reaction cell. After the dispersion of ZnO powder, the cell with MB solution containing powder was placed in a water bath at 20 °C for 3 min. It was then set to in the irradiation stage, as shown in Fig. 3. After 5 min pre-measurement of absorbance of the MB solution, UV irradiation was started, and was continued for 85 min. The adsorption time was: 3 min without MF, followed by 5 min under MF.

More attention is paid to the surface state of the ZnO powder, as the powder used for the previous experiments has been kept

Fig. 3. New system for MFE measurement.
in an ambient atmosphere for an extended period of time. The ZnO powder dried for more than 48 h is intentionally put into a humid atmosphere (~90%RH) at room temperature for 24 h. The FT-IR (Spectrum 100, Perkin Elmer Co., Ltd.) measurement on the ZnO powder is carried out with an ATR attachment to investigate the surface state.

4. Results and discussion

4.1. From Section 3.1 (previous MFE system)

Fig. 5 shows, as a function of UV irradiation time, the photodegradation of MB solution with 5 min settling time. A positive MFE exists on the photodegradation of the MB solution, and the MFE is monotonically increased with MF intensity. When the settling time is varied from 5 min to 1 h, 3 h and 24 h, the MB photodegradation curves under 0 and 0.7 T change, as shown in Fig. 6(a)–(d), respectively. The MFE is clearly decreased with increasing settling time. Also, the total photodegradation ability without MF is decreased with increasing the setting time. The settling time may be involved with [12–14]: (i) the state and amount of DO in MB solution, (ii) other factors, such as complex formation between MB-dye and DO molecules, or MB dimer/trimer formations.

When the settling time is fixed at 5 min and the MB initial concentration is varied, the MFE is clearly changed under static MF of 0.7 T. The MFE magnitude becomes higher for lower initial concentration, as shown in Fig. 7. The dependence of MFE on initial concentration suggests the rate determining step of the MFE phenomena to be diffusion of the involved species in the solution. One possibility is the DO diffusion in the MB solution. The existence of DO in the solution is known to play an important role for MFE on MB photodegradation [12–14]. To further clarify the role of DO, the MB solutions with different DO levels are investigated. When different gases (Ar, air, or O2) are bubbled into the MB solution of 24 h settling time, the DO value becomes ~0.5 mg/L for Ar gas,
~8.2 mg/L for air gas, and more than 20 mg/L (~44 mg/L by Henry's law) for O₂ gas, respectively. Fig. 8 shows photodegradation of gas-bubbled MB solutions using ZnO particles. The MFE is exhibited for O₂-bubbled or air-bubbled solution, where the former is large negative compared with the latter (Fig. 8c and d). No MFE is observed for Ar-bubbling and no bubbling.

When MB solid is mixed with water, oxygen molecules (in water or from air bubbles produced during the shaking process) may adhere or attach to the MB dye molecules. The bonding interaction similar to that for chemical adsorption may have been produced between DO and the MB dye, which may block the reactive site(s) of the dye molecule. In addition, since the MB dye molecule is much larger than DO in size (molecular weight of 320 versus 32), where formation of dimers and trimers is even possible for the MB dye, more DO molecules can be attached to the MB molecules, possibly forming not only simple MB-DO complexes but also complicated multiple MB-DO complexes. For an aqueous photochemical system, the excited-state interactions between molecular oxygen (O₂)
and organic molecules (M) in solution can be considered in term of charge–transfer (C–T) state [20,21]. The weak-bonded complex or the encountered pair between M and O2 is the so-called M–O2 complex [22]. The number of O2 molecules in the 4 mL of solution for 24 h settling time (DO ~8 mg/L) is estimated to be ~6.0 × 10^20 molecules, which is larger than that of MB molecules by ~13 times (4 mL at 0.02 mmol/L: 4.8 × 10^9 molecules). There are enough DO molecules in solution to form M–O2 complexes with all MB molecules at this concentration.

For short settling time periods, the formation of the M–O2 complex may be less complete, and an appropriate amount of DOs and photogenerated–electrons may efficiently react to produce the superoxide radicals to decompose the rather “bare” organic dye, resulting in the higher photodegradation rate. While, for the longer settling time, it appears that the key bonding of the MB molecule for decoloration is blocked by the existence of oxygen molecules, possibly due to formation of M–O2 complex. The reaction on the photocatalyst surface would then be one between photogenerated-electrons or superoxide radicals and the M–O2 complex. Although many superoxide radicals would be generated on the powder surface, they could not easily decompose the M–O2 complex due to the blocked bonding. In addition, it is also proposed that cleavage may start with electronic reorganization [23] during the passage of MB to the sulfoxide form. If the oxygen molecules (DOs) form a complex with the MB dye deactivating the above cleavage process through blocking the electronic reorganization, the decomposition of the MB dye would be suppressed due to the “stabilized MB-dye”.

Fig. 9 shows, as a function of UV irradiation time, the influence of the applied MF on the photodegradation of the MB solution (5 min settling time) for TiO2 particles (ST-41). Negative MFE is exhibited, where the magnitude is increased with MF intensity. This tendency is opposite to the ZnO case. In order to examine the negative MFE exhibited for TiO2, the disincentive factor for the reaction is further considered, where the magnetic adsorption – the MFE on the acceleration or deceleration of MB adsorption on powder surface – is addressed. Fig. 10(a) and (b) show the decrease in MB concentration for ZnO and TiO2, respectively, where each powder is dispersed into the solution in the dark. In the case of ZnO, the MB concentration under 0.7 T is decreased faster than without MF (0 T), indicating acceleration of MB adsorption, while slight deceleration is observed for TiO2. It has been reported elsewhere [24] that the thickness of the adsorption layer on a mica plate is increased under MF and the magnitude is reduced with temperature. This may be similar to the above acceleration of adsorption under MF. There is a possibility that, although DO adsorption is not measured, a change could be caused on or near the powder surface due to the DO molecules because magnetic adsorptions of gases, especially vapor, have been reported [25]. The network of structured water molecules, such as clusters with hydrogen-bonded networks, could also be disturbed due to the DO molecules involved with the magnetic adsorption, leading to the MFE on the reaction.

As shown above, the MFEs are certainly reproducible, however, the responsible factors are not yet determined. To determine this would require extraction of essential MFE phenomena as a function of involved parameters. For example, the following factors should be at least considered: (i) well-controlled temperature during photocatalytic reactions, (ii) in-situ DO and CO2 concentrations in MB solutions, (iii) detailed surface state including adsorption of gas molecules, (iv) time lag between MB photodegradation and measurement of MB concentration by spectroscopy, and, (v) unavoidable cell movement that causes convection in the dye solution. The parameters or the conditions must be controlled or improved to extract the MFE phenomena. Since simultaneous multiple mechanisms are suggested to be operative, or to switch from one to another, depending on MF intensity or on other parameters, the responsible factors must be separated and well–controlled to elucidate the novel MFE phenomena on heterogeneous photocatalysis.

![Fig. 9. MF dependence of MB photodegradation under MF (0–0.7 T), using TiO2 (ST-41) particles.](image1)

![Fig. 10. Adsorption of MB on ZnO and TiO2 (ST-41) in the dark under MF of 0 and 0.7 T.](image2)
4.2. From Section 3.2 (new MFE system)

The degradation curves of MB solution at 20 °C with and without MF are shown in Fig. 11. The normalized concentration is determined by comparison between the initial peak absorbance \((A_0)\) of MB solution at 665 nm and the absorbance after UV irradiation \((A_{\text{min}}): t=0–85 \text{ min}\). The results are highly reproducible (errors < ±2%), and the degradation rate is clearly suppressed under MF. In addition, the magnitude of suppression is dependent on the MF intensity, i.e. the degradation rate is more suppressed under stronger MF in the range from 0 to 0.7 T. The magnitude of MFE is evaluated by following equations:

\[
\eta_m = 1 - A_{\text{85 min}} / A_0 \tag{1}
\]

\[
\text{MFE} = (\eta_m - \eta_{0T}) / \eta_{0T} \tag{2}
\]

where, in Eq. (1), \(\eta_m\) is the MB degradation rate (\(\eta\)) under MF intensity \(m\) (0–0.7 T) after 85 min UV irradiation. The positive value of MFE in Eq. (2) indicates promotion of dye degradation under MF. As illustrated in Fig. 12, the MF dependence exhibits a non-linear curve, where the absolute value is increased with MF. This tendency is similar to the results obtained with the previous experimental system (Sections 3.1 and 4.1).

Fig. 13 shows the influence of reaction temperature on MFE, where the measurements are carried out at 6, 20 and 30 °C. At 6 °C, more pronounced MFE, i.e. clear suppression of MB photodegradation, is observed, as compared to that at 30 °C. The clear MFE at 6 °C is similar to that at 20 °C, while the MFE almost disappears at 30 °C. The temperature influence on MFE will be discussed later.

When the concentration of MB is varied from 0.01 to 0.03 mmol/L, the MFE is more distinguished for lower concentration of MB, as shown in Fig. 14. This suggests that adsorption and/or diffusion is involved with the rate-determining step of the MFE phenomena. The MB adsorption test is then carried out at low (6 °C) and high (30 °C) temperatures, as shown in Fig. 15. At low temperature, adsorption is suppressed under MF of 0.7 T (Fig. 15(a)), while, at higher temperature, there is no significant change (Fig. 15(b)). The suppression tendencies of magnetic adsorption are similar to those observed for MB photodegradation. In addition, this is consistent with the report that adsorbed layer thickness is affected by MF [26]. The PZC (point of zero charge) of ZnO is about 9 [27], while the pH of MB solution is about 6. The surface of ZnO powder should be then positively charged. The MB becomes a cation in the solution, whereas the chlorine becomes an anion (Cl⁻), which would preferentially adsorb on the ZnO surface due to the Coulombic force. Besides, there would be other dissolved anions such as carbonate (CO₃²⁻) or hydrogen carbonate (HCO₃⁻). If the adsorbed layer is increased by MF, less adsorption of MB would result, leading to suppressed MB degradation. It is also reported that the magnetic adsorption is affected by temperature, where it is more distinguished at lower temperatures and the magnitude decreases with temperature [24]. The destruction of adsorbed layer may be caused by thermal disturbance, which is consistent with the above MFE results.

![Fig. 11. MB photodegradation curves at 20 °C under MF of 0–0.7 T.](image1)

![Fig. 12. MF dependence of MFE at 20 °C.](image2)

![Fig. 13. MB photodegradation curves under MF (0, 0.7 T) at temperatures of: (a) 6 °C, (b) 20 °C, (c) 30 °C.](image3)
When the settling time period is varied for the new MFE measurement system, the influence on the MFE is clearly observed with dried ZnO powder, as also found for the previous system. The results for MB solutions (0.01 mmol/L) with two different periods (10 min and 24 h) of settling time are shown in Fig. 16. The magnitude of MFE decreases with an increase of settling time. The tendency similar to the previous experiments strongly suggests that some microscopic MB state change at the molecular or electronic level is ongoing in the macroscopically still MB solution during the settling time. Possible formation of MB–DO complex is suggested as well. The influence of DO concentration on MFE with dried ZnO powder is summarized in Fig. 17. The MFE is more distinguished (a < b < c for the MFE magnitude) for higher DO concentrations (0.5, 8.8, 44 (estimated) mg/L for a, b, c), where the degree of suppression in MB degradation is more significant for the O₂ bubbled solution under MF (0.7 T). The MFE is almost eliminated for the Ar-bubbled
solution with the lowest DO concentration. It is known that the behavior of the paramagnetic DO molecules in water is influenced by gradient MF [28]. For our heterogeneous system the field gradient may exist in the vicinity of the powder surface through potential variations with many species involved (This point will be discussed later). Hence, effective force may act on DO molecules, which may contribute to revealing the workings of MFE with further examination. It is also possible that simultaneous multiple mechanisms are involved with the MFE in photocatalytic reactions.

5. Comparison of experimental systems

In this section, the MFE with the previous system and the new system are compared. The brief summary is shown in the following Table 3.

As shown in Fig. 18, the MF dependences for both systems are similar, exhibiting non-linear increase of the MFE magnitude, though the sign or direction of MFE is opposite. The other variables involving MB solution, such as initial concentration, settling time, and DO concentration, also exhibit similar influences on MFEs for both systems, though the signs of MFE are opposite for the effects of initial concentration and settling time. One of the possible factors influencing the sign of MFE is the powder surface state. The ZnO powder used in previous experiments has been kept in ambient atmosphere for an extended period, whereas it is dried for the new system experiments. A comparison of the surface state of ZnO powder, prior to powder immersion into the MB solution, therefore needs to be addressed.

Fig. 19 shows the FT-IR spectra of dried and moistened ZnO powders (see Section 3.2 for detailed conditions). Increased intensities of some spectral peaks are clearly observed for the latter powder (i) 1620–1590, (ii) 1520–1490, (iii) 1410–1380, (iv) 840–810 cm⁻¹. The peaks are identified as H₂O- and CO₂-related species [29,30], suggesting that adsorption of H₂O and CO₂ gas molecules on the powder surface is increased after the damp treatment. When MFE measurement on MB photodegradation (MB concentration of 0.01 mmol/L) is carried out using the moistened powder, the magnitude of MFE is significantly decreased, with the sign of MFE even reversed, compared with the dried powder (Fig. 20). This result strongly indicates that the surface condition of powder, especially CO₂ and H₂O adsorption and powder agglomeration, prior to the powder immersion into the MB solution, is important for MFE.

6. Mechanism of MFE

According to our highly reproducible MFE results, it is clear that the MF does alter photocatalytic behavior of ZnO photocatalyst as a whole, in terms of decomposing methylene blue (MB) dye solution. From the gas-bubbling experiments the MFE magnitude is larger with higher dissolved oxygen (DO) levels. Possible complex formation of DO with dyes is also suggested from the settling time variation, where the reactive site(s) of a dye may become blocked with DO molecules. Although many parameters and conditions are
involved, it is thus confirmed that the state and amount of DO is one of the key parameters for revelation of the MFE phenomena. It is then quite important to examine the special role(s) of the DO, particularly since the DO is also required for oxidative decomposition of dye molecules. The oxygen molecules and the dye molecules must meet on or near the ZnO powder surface, whether the photodecomposition is through other involved radical species or not. This is the special feature of the heterogeneous photocatalysis.

6.1. MHD effect and OANS model

In order to further elucidate the role of DO, photocatalytic Ag⁺ reduction under MF is also performed using a solution of AgNO₃ (0.01 mol/L). The reason for the system choice is that there are some metal ions with higher oxidation-reduction potentials than oxygen, so that the DO is not expected to be involved in the photocatalytic reaction:

\[
\text{Ag}^+ + e^- \rightarrow \text{Ag} (+0.799 \text{V : Standard electrode potential vs SHE})
\]  

(3)

\[
\text{O}_2 + e^- \rightarrow \text{O}_2^- \text{ (potential : } -0.284 \text{V})
\]  

(4)

where the amount of ZnO photocatalyst powder used is 5 mg, and UV-LED is utilized, with the central wavelength of 365 nm, intensity of 500 mW/cm², and irradiation duration of 1 h. To quantify the precipitated Ag, titration of NaCl (0.01 mol/L) is carried out. Compared with 0 T (without MF) the reduction rate is clearly increased under 0.7 T, and the morphology of deposited Ag metal becomes more flat or plate-like compared with no MF. Similar phenomenon has been reported for the electroless Ag deposition under MF, where the growth pattern of Ag metal deposition from AgNO₃ solution through ion exchange is changed under MF, suggesting that Ag⁺ drifts spiral to the MF under the influence of Lorentz force (the so-called “MHD (magneto-hydrodynamic) effect”) [31,32]. Therefore, the MHD effect appears to exist for the ZnO photocatalytic reaction. Under high MF, the Ag⁺ ions would be effectively transported away to the region with active photocatalysis due to stronger light intensity through the MHD effect. The detail of this novel phenomenon, including the MF dependence, will be presented in the forthcoming publication.

It should be mentioned here that the MHD effect is generally explained in terms of the Brownian motion, where the MFs can induce microscopic currents in a moving conductive fluid. Infinite-mal modification of each step or motion of ions can contribute to the summation of the partial fluctuations, and the Navier–Stokes equations of fluid dynamics can be applied. In terms of the MHD mechanism, however, the magnetic convection ascribed to the effective Lorentz force on DO should be also considered. The oxygen molecule is paramagnetic, and the molecular transport may cause “drag force” on the solution species based on Stokes’ law. Increased DO and the diffusion in water under MF have been reported without altering the equilibrium [28], as well as the magnetic convection due to DO [33]. The force term in the modified Navier–Stokes equation can be written as [28,34–36]:

\[
F = \frac{\chi}{\mu_0} \frac{\partial B}{\partial z} \quad \text{or} \quad F = \frac{\Delta \chi}{\mu_0} \frac{\partial B}{\partial z}
\]  

(5)

where \(\Delta \chi\) is the difference of the magnetic susceptibilities (\(\chi\)) between the surface and bottom of the water phase (for the case of magnetic convection), \(\mu_0\) is the magnetic permeability of a vacuum, and \(B\) is the magnetic flux density. The equation essentially states that, on considering the maximal Stokes’ terminal velocity relative to the solution flow, the force acting on a magnetic species is proportional to \(\Delta \chi\) (difference in \(\chi\) of the species and the solution), \(B\) and \(\partial B/\partial z\) (spatial variation of \(B\)), although the expression macroscopically describes the force acting on a “homogeneous” fluid with different susceptibilities. The DO molecule is a paramagnetic species, where the volume susceptibility under 1 atm, 293 K, is \(+0.1447 \times 10^{-6}\) [37], the magnitude of which is generally two orders of magnitude larger than other molecules. The equation is then approximated as the first one with \(\chi\). The MF dependence of MFE in Fig. 18, which appears to exhibit semi-quadratic curves, is supportive of Eq. (5) expression, in that the force acting on DO

![Fig. 20. Influence of powder surface state on MFE: (a) dried, (b) moistened.](image-url)
would be proportional to the product of the magnetic flux density \((B)\) and its gradient.

There are some fundamental reports regarding the MFE on the DO behavior. It is known [28] that the dissolution of the oxygen molecules into water is promoted by a strong gradient static MF. As mentioned, the DO is paramagnetic and magnetic convection is also possible [33]. Besides, faster diffusion of DO under MF is reported elsewhere [28]. In this case, the issue would be to evaluate the magnitude of \(\partial B/\partial z\) since static magnets are utilized in our experimental system. Without any gradient or flux variation the force should not act on the paramagnetic DO. We therefore proposed a model, the so-called OANS (oxygen-acceleration-near-surface) model, based on the idea that the state of the (mother) fluid such as MB solution just outside the ZnO powder surface or in the vicinity volume exhibits a special character with varying potentials, as illustrated in Fig. 21. On considering our heterogeneous photocatalytic system with large powder/solution interphase interface area, a non-negligible amount of local fluctuation on various chemical and physical properties – viscosity, conductivity, electric charge density, and concentrations of various species adsorbed on powder or in the buffer layer of the solution – should exist within the narrow volume in the vicinity of the powder. Any state variation at the powder surface including various dangling bonds and their distribution should intricately interact with the surrounding molecules or atoms of the fluid (e.g. MB solution) in the vicinity volume, which must also contribute to the potential variation. It is then natural to assume that, though the detail of the fluctuation is not known, various local gradients in the electrostatic potential and the corresponding magnetic flux density exist in the narrow volume. This is a special feature of the heterogeneous system, wherever, near the powder surface, the potential is significantly altered compared with the bulk solution.

If the maximal possible force acting on the DO molecule in solution is assumed to be proportional to the terminal velocity of the molecule, according to Stokes’ law, the assumed maximal velocity of a DO molecule acted on by the MF can be estimated. According to the given parameters below for the reported conditions [28]:

(i) Representative distance of the experimental setting: \(z = 100–200\) mm.
(ii) Magnetic susceptibilities \((\chi)\): \(\approx +1.45 \times 10^{-7}\) (as maximal difference: 1 atm, 293 K).
(iii) Magnetic flux density: \(B = 0–10\) T.
(iv) Estimated \(\partial B/\partial z\): \(0–1000\) T/m.
(v) Estimated max. DO velocity: \(v \approx 50\) mm/s (min. 0.16 mm/s).

Noting that this is merely an order of magnitude calculation, and not even intended to estimate the approximate values. The real DO velocity, even as a maximal value, must be much smaller than the value in (iv) due to the counter kinetic force comprised of the form drag and friction drag. In addition, there must be much cancellation or averaging out of the potential fluctuations caused in the solution. However, since the magnetic susceptibility of water is about \(-0.53 \times 10^{-9}\) (at 1 atm, 293 K: diamagnetic), the estimated value should be larger than 0.16 mm/s.

On the other hand, in the heterogeneous system, the representative distance in (i) above would be largely modified. The fluctuation or variation of the potential addressed here is just outside the powder surface. In order to suggest an order of magnitude of the maximal possible force and the maximal assumed velocity, the rough estimation is shown below:

(I) Representative perturbed distance near powder: \(z \approx 10–100\) nm.

(II) \(\approx +1.45 \times 10^{-7}\) (as maximal difference).

(III) \(B = 0–0.7\) T.

(IV) Estimated \(\partial B/\partial z\): \(10^2–10^5\) T/m.

(V) Estimated max. DO velocity: \(v < 5000\) mm/s (min. 16 mm/s).

Again, in the real solution, counter kinetic forces exist, and the perturbation is averaged, where the potential variation must be limited. The maximal possible DO velocity must be much smaller than the estimate in (v).

Although the estimates above are rough, it is natural that, for the heterogeneous powder surface or in the vicinity volume, the order of the velocity is larger than that in the bulk fluid or the bulk motion itself, provided that there is an adequate potential fluctuation for MFE revelation, influencing the reaction. It is also suggested that the product of B and its gradient be at least comparable or even larger than those reported [28], causing non-negligible magnetic force on the DO molecules around the photocatalyst. Three levels of MFE may then exist near the powder surface (Fig. 21): LRO (long-range-order), SRO (short-range-order), and VSRO (very-short-range-order). The LRO effect could be exhibited in the Gouy–Chapman layer at several tens of nanometers or more, while for the SRO effect the representative distance is several nanometers, which may include the VSRO effect in the Helmholtz layer just around the powder surface. The observed MFE is usually significant at the early stage of the MB photodegradation, indicating the importance of the VSRO. The shorter the representative distance \((z)\) is, the stronger the magnetic force would be, according to Eq. (5), and it is easily understood that magnetic adsorption is the phenomenon involved with this model, particularly with the VSRO effect. This is essential for the special characteristics of the heterogeneous system, as a speculative hypothesis, with various molecules (\(O_2, H_2O, MB\)-monomer, MB-dimer) and ions (\(Cl^-\), \(MB^+\), \(CO_3^{2-}\), \(HCO_3^-\)) near the powder surface comprising the electrostatic potential and the corresponding magnetic flux density \((B)\) variation.

As shown in Figs. 7 and 14, the degree of MFE on MB photodegradation is dependent on the initial MB concentration. Although the sign of the MFE is opposite, the absolute value is more distinguished for lower MB concentrations for both experimental systems. In general, when a certain phenomenon involving chemical reactions is dependent on the concentration of the reactant chemical species, the rate determining step of the reaction is often the diffusion of a certain chemical species involved. For example, in case of the first order reaction kinetics (degradation):

\[
-d[Cl]/dt = k[C]
\]

(6)

\[
C(t) = C_0 \times \exp(-kt)
\]

(7)

where \([C(t)]\) represents a concentration of certain chemical species in a solution, as a function of the reaction time \((t)\). \(C_0\) is the initial concentration, and \(k\) is a constant. The degradation rate \((-d[C]/dt)\) is proportional to \([C]\) in this case, which in turn is proportional to the initial concentration \(C_0\), and the assumed rate–determining step is diffusion of the involved species in the solution [38]. Although the MFE phenomenon itself is different from the general chemical reaction, it is reasonable to consider that the diffusion is the key factor responsible for the MFE. Since, for complete oxidation (chemical reactions) for dye degradation, the oxygen (DO) molecules and the dye molecules must collide on/near the ZnO powder surface, the diffusion of both species toward the surface is prerequisite for the photodegradation reaction to occur. This is consistent with the OANS model, and the MFE appears to be diffusion-controlled.

6.2. Radical pair mechanism and intersystem crossing

As already shown in Figs. 5, 11, 12 and 18, the MFE is more significant under larger MF, and the dependence is not linear. The
MB photodegradation kinetics is only slightly altered under low MF, however, the MFE appears progressively larger under high MF. Another possible explanation for the non-linear MF dependence other than that described in Section 6.1 (Eq. (5)) would be a simultaneous (at least) dual operative MFE mechanism [39], or switching from one to another depending on the MF applied. In a homogeneous system, the MFE is generally explained in terms of the radical pair mechanism [1,4], where the HFCM (hyperfine coupling mechanism) is operative at smaller MFs, often less than 0.1 T, while the ΔgM (delta-g mechanism) is effective at larger MFs. Both effects are ascribed to disturbance in the Larmor precession of electrons, and the Larmor frequency ω is proportional to the g-value and the magnetic flux density B. The former hyperfine coupling is originated from interaction between nuclear spins and electron spins, which varies for different elements and depends on the dwell time of unpaired electrons on its nucleus. On the other hand, the latter ΔgM depends on the difference in the g-values of the involved radicals. The non-linear MFE behavior observed in the MB photodegradation could be thus related to the simultaneous hybrid mechanism of the HFCM and the ΔgM.

A radical can be considered for an atom, a molecule, or an ion that has unpaired electrons, having one or more dangling bonds. Through spin–orbital coupling of the unpaired electrons, the intersystem crossing of singlet–triplet state (S–T conversion) may be possible for the radicals involved, where the MFE may be exhibited on the triplet state. As for the HFCM, the S–T conversion rate is known to attain saturation at low MF, while, for the ΔgM, the rate is known to increase with MF. On considering the magnitude of the magnetic susceptibility, the DO radical could be involved with the intersystem crossing, where a diradical mechanism is possible, having both excited singlet oxygen (1O2) and ground state triplet oxygen (3O2) produced. Since the spin states of the diradical are analogous to those of a radical pair [40], the diradical could be influenced by MF. This could be the reason for small MFE under low MF, as the yield of singlet oxygen (1O2) may be relatively small at low MF and increased with MF through Δg mechanism.

But, the question then arises: Is the general mechanism of MFE on homogeneous chemical reactions applicable to heterogeneous systems? It is known that, unlike a solid or gas phase, a fluid as a condensed phase is appropriate for radicals to meet with each other. In a gas phase the collision probability of reactive species is rather low, while in a solid the bonding is too strong for effective MFE. Thus, the liquid is appropriate to manifest the so-called “cage effect” for MFE as well as the “escape” phenomenon to be exhibited. Near the powder surface the reactant radicals would be produced in the MB solution, or some of MB dyes would be directly photodecomposed by excited electrons and holes through adsorption of the dye on the powder. The photogenerated radicals would survive near the heterogeneous interface (surface), for a certain period of time, where the radical pair model for a homogeneous system could be plausible and applicable for some of the heterogeneous photocatalytic systems.

Another point that should be noted is the photosensitization of the MB dye. Since the MB dye is known to photosensitize oxygen with visible light irradiation [41], it is quite possible that the singlet DO is produced through photosensitization of MB, as shown below (Fig. 22):

\[ \text{MB} (S_0) + h\nu \rightarrow \text{MB} (S_1) \]  \hspace{1cm} (8)

\[ \text{MB} (S_1) \rightarrow \text{MB} (T_1) \]  \hspace{1cm} (9)

\[ \text{O}_2 (\Sigma_g^+) + \text{MB} (T_1) \rightarrow \text{O}_2 (\Delta g) + \text{MB} (S_0) \]  \hspace{1cm} (10)

Fig. 21. Schematic illustration of OANS model.

Fig. 22. Generation of singlet oxygen through photosensitization of MB.
where the singlet dye (MB\(S\)) at the ground state is excited by light irradiation to the singlet excited state (\(\text{MB}\left(S\right)\)), which decays to the triplet \(\text{MB}\left(T_1\right)\) through intersystem crossing. And, finally, the \(\text{MB}\left(T_1\right)\) triplet state may excite the DO from the ground state biradical oxygen \(\text{O}_2^\left(\downarrow \downarrow \right)\) to the singlet oxygen \(\text{O}_2^\left(\uparrow \uparrow \right)\) state \([42]\), as the energy difference between the singlet \(\text{MB}\left(T_1\right)\) state and the ground state \(\text{MB}\left(S\right)\) is comparable with the energy difference between the two states \(\text{O}_2^\left(\uparrow \downarrow \right)\) and \(\text{O}_2^\left(\downarrow \uparrow \right)\). If one of the \(S-T\) conversions in the whole process is somehow affected by MF \([43]\), the degradation rate might be changed as well. Since the MB photodecomposition is only a few percent without ZnO powder, the MFE could be exhibited near the powder surface through promotion or suppression of the intersystem crossing acted upon by the applied MF.

### 6.3. Various models and DO roles for MFE mechanism

Dissolved oxygen (DO), as above, appears to have various important roles, not only for heterogeneous ZnO photocatalysis on MB photodecomposition but also for the novel phenomena of MFE manifestation. Paramagnetism exhibited by DO may be acted upon by the applied MF, where the DO molecular diffusion could be accelerated or decelerated depending on the surrounding conditions, ascribed to the potential fluctuations in the vicinity volume just outside photocatalytic powder surface (hypothetical OANS model proposed). Along with the diffusive motion of DO molecules, other molecules in the fluid could be dragged with them due to the “drag force” of fluid dynamics. This could also be responsible for the observed magneto-hydrodynamic (MHD) effect for silver photoreduction, the effect of which is often reported in the literature.

It is also suggested that the MFE is correlated to magnetic adsorption (MA) phenomenon. It is quite natural that this adsorption phenomenon is related to photocatalysis as the decomposition event should occur on or near the powder surface. The powder surface potential as well as the distribution of PZC (point of zero charge) would be perturbed through possible DO-involved stacking of various adsorbing ions/molecules. This could be one of the reasons for the reported increase in adsorbed layer thickness containing ions with unlike charge under MF \([28]\).

The DO may exhibit another role for the MFE through spin chemistry. The diradical system of oxygen could be involved with the singlet–triplet intersystem crossing (\(S-T\) conversion), which could be perturbed under MF. Both positive MFE (promoted photocatalysis) and negative MFE (suppressed photocatalysis) are possible, depending on the rate of different \(S-T\) conversions. Also, the dye as well as the excited electrons at the powder surface could be involved with the intersystem crossing, where the selection of \(S-T\) conversion and the relative decay rate would determine whether the MFE is exhibited or not under MF.

The surface condition and the agglomeration of powder are extremely important for MFE on photocatalytic reactions (MB degradation). Adsorption of CO\(_2\) and H\(_2\)O molecules on powder even before powder immersion into the MB solution is important for the heterogeneous MFE, as revealed in Fig. 19, where the MFE could even change the sign (Fig. 20). For CO\(_2\) concentration of 400 ppm in air, the equilibrium solubility in water at 298 K is \(0.526 \times 10^{-5}\) mol/L, while for O\(_2\) the equilibrium solubility at 298 K is \(25.3 \times 10^{-5}\) mol/L. Although there is a large difference of about 50 times, the effect on the MFE could be significantly different, besides the CO\(_2\) concentration in buildings and cities is generally much higher. This point would be important for the MFE mechanism, however, the details are not investigated in this work or in the literature. Further detailed investigation is thus required to elucidate the mechanism of these novel phenomena.

### 7. Summary

Magnetic field effect (MFE) exists on heterogeneous photocatalysis, where ZnO powder and methylene blue (MB) solution are mainly used for MFE evaluation. The reproducibility of MFE is quite high, with error less than 2% utilizing our newly-developed in-situ measurement system. In addition, the magneto-hydrodynamic (MHD) effect is observed for the first time on photocatalytic reduction and deposition of Ag using ZnO powder.

Various parameters involved with heterogeneous MFE are examined. The magnitude of MFE is dependent on MF intensity, with a non-linear relationship. The MFE is also dependent on (i) initial MB concentration, (ii) settling time period of MB solution, and (iii) the level and state of dissolved oxygen (DO), where the solution state intrinsically affects MFE phenomena. Diffusion of short-range-order (SRO), particularly very-short-range-order (VSRO) in the Helmholtz layer just outside the powder, is suggested to be responsible for MFE. Accordingly, the powder surface condition including adsorption of H\(_2\)O and CO\(_2\) molecules, even before powder immersion into the solution, significantly influences MFE, and magnetic adsorption (MA) appears correlated with MFE on the MB dye photodegradation. Temperature dependence of MFE is also exhibited for the first time.

A model for MFE is proposed for heterogeneous photocatalysis, where the DO involvement is essentially responsible for various MFE phenomena. In the vicinity volume surrounding the ZnO powder, the electrostatic potential as well as the magnetic flux would be perturbed with various ions, radicals and adsorbed molecules, resulting in the appearance of a net Lorentz force on DO with paramagnetism (OANS model). The DO could also be related to MFE through (i) formation of DO-dye complex, (ii) modifying powder adsorption layer, (iii) changing the scavenging rate of excited electrons, (iv) spin chemistry involving \(S-T\) (singlet–triplet) conversion, and (v) manifestation of magneto-hydrodynamic (MHD) effect.

The findings on MFE in this article have various potential applications and much significance. Environmental remediation, which has become more and more urgent in this century, would be promoted through simple configuration or appropriate arrangement of magnets. The DSSC (dye-sensitized solar cell) as the promising future technology generally utilizes photocatalytic material as scaffolding for an electrode, where the capacity could be enhanced with MFEs. Furthermore, the MFEs can be applied in the medical field through efficient control of the oxygen state. The singlet oxygen generated in the human body is often claimed as one of the most important causal species for damaging DNAs, where the alterations caused can change gene function or regulation of gene expression, possibly leading to cancer progression in human body. Thus, controlled MFEs may have various potentials in the fields of environmental, energy, and even medical applications. Accordingly, the MFE can be said to be one of the important topics that would not only provide us academic or scientific stimulation but also benefit us through multifaceted applications, which would require a multidisciplinary or interdisciplinary approach.

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