Magnetic field effect on heterogeneous photocatalytic reaction

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Introduction

Magnetic field effect (MFE) on photocatalytic reactions is one of the most interesting topics in terms of science and applications. The MFE on homogeneous reactions, especially on photochemical reactions, had been studied experimentally and theoretically [1], however, the reports regarding MFE on heterogeneous reactions, particularly on photocatalytic reactions, are few [2,3]. In addition, magnetic field may affect not only the reactions but also the interfaces [4,5], and the MFE reproducibility often becomes controversy due to the complex system involved. This work aims to unambiguously reproduce MFE on photocatalytic reactions and investigate the various parameters involved. Especially, the reaction temperature is focused since, despite an important factor for photocatalysis, there is no report regarding the dependency on MFE. Methylene blue (MB) solution and ZnO powder are, as model systems, selected for decomposed substance and photocatalyst, respectively.

Materials and Methods

Powdery ZnO (purity: 99.9%, average particle size: 300 nm. BET surface area: 3.8m²/g) was dried in an electric thermo-constant furnace (120°C) in air for more than 24 hours and cooled in Ar (4N). Ultra-pure water (Millipore) for the MB solution was, at



Figure 1. Schematics of experimental apparatus

least for 48 hours, kept in a water bath at 20°C to make the dissolved oxygen (DO) concentration saturated (8.8 mg/L) in air. The MB solution was made in air from powdery MB (> 99.9%) dissolved into the water, stirred for 5min, and diluted to adjust its concentration as 0.02 mmol/L, followed by another 5 min stirring. The MB solution (3 mL) was poured into a quartz cell, followed by inserting 1.0 mg of ZnO powder, and the cell was set to the light irradiation stage with water circulation system as Figure 1. Eight reaction temperatures were selected in the range of 6°C~45°C by altering the water temperature. The UV-LED (wavelength center: 365 nm, intensity: 500 mW/cm²) was placed at 1 cm below the cell bottom, where temperature-controlled water was circulated around the cell to keep the solution temperature constant. A permanent magnet (0.7 T) was placed along one set of cell sides, while a photonic multi-channel analyzer and a white LED were set along another to measure *in-situ* the absorbance (A) of MB solution, evaluated at 665 nm, with 1 sec measurement interval. After 5 min of pre-measurement, UV irradiation was started. The experiment was conducted 4 times for each condition and the average was used for MFE evaluation.

Results and Discussion

The degradation curves of MB at 20°C with and without magnetic field are shown in **Figure 2**, where A_0 denotes A at the start of UV irradiation. The results are highly reproducible (errors < 2%), and the degradation rate is clearly reduced upon applying magnetic field. According to the time-derivative analysis on the curves, the MFE is maximal just after the UV irradiation, decreased gradually with time, and finally disappeared around 40 min.

Figure 3 shows, for the first time, MFE temperature dependence on heterogeneous photocatalytic systems, where η_m $(=1-A_{85min}/A_0)$ signifies the MB degradation ratio under magnetic field (m: 0T, 0.7T) after 85 min UV irradiation. The MFE is negative $(n_m/n_0 < 1)$ when the reaction temperature is below 30°C and the effect is more significant at lower temperatures. The dependency is not linear,



field, especially at lower temperatures, magnetic adsorption could be one of the factors responsible for MFE [3]. This is consistent with the report that adsorbed laver thickness is affected by magnetic field [5]. In addition, when the MB solution is bubbled with O₂ gas for 1h prior to the reaction, the MFE at 20°C is largely increased (1.7 times after 85 min), as shown in Figure 4. It is known that the behavior of paramagnetic DO molecules is influenced by gradient magnetic



field [6]. For our heterogeneous system the field gradient may exist in the vicinity of powder surface through potential variations with many species. Hence, effective force may act on DO molecules. MFE on photocatalytic reactions might be caused by simultaneous multiple mechanisms. The mechanism of novel phenomena will be discussed.

Significance

MFE on photocatalytic reactions is clearly observed, reproducible, and the temperature dependence is observed for the first time. The MFE is maximal just after the reaction begins, followed by gradual decrease, and eliminated around 40 min, which appears involved with DO.

References

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