



Magnetic Field Effect (MFE) on Heterogeneous Photocatalysis and the Role of Oxygen

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Abstract

Heterogeneous photocatalysis involves multiple elementary steps at the interphase interface. Although magnetic fields are known to influence photocatalytic reactions, the mechanism is still not clearly understood or agreed-upon. In this short article, the significant roles of oxygen will be discussed, including the involvement of water.

Heterogeneous photocatalysis is a light (photon)-driven reaction process with multiple elementary steps or phenomena at the interphase interface, involving, simultaneously or in succession, generation and transport of electrons, radicals, atoms and/or molecules. It has already found various applications, particularly in the field of environmental remediation. If a key (rate-determining) step is controlled under a magnetic field, wider environmental applications, as well as energy harvesting, might become possible.

The magnetic field effect (MFE) or magnetokinetic phenomenon was discovered in the gas phase reaction for magnetic fluorescence quenching about one hundred years ago, and magnetic field (MF) dependence of reaction rates was first reported in 1929 [1]. The possible relationships between magnetic properties and catalytic activity were reported in 1945 through exhaustive reviews on various oxides and the temperature dependence of susceptibilities [2]. Thus, the MFEs on chemical reactions have long been the subject of investigation. These early studies were, however, occasionally plagued by non-reproducible effects and retractions [3], and the establishment of MFE as a recognized research field had to wait till the 1970s or 1980s when many reproducible data were reported in homogeneous reaction systems. The MFEs on homogeneous systems are generally explained in terms of the radical pair mechanism [1].

On the other hand, MFE research on heterogeneous reaction systems, in particular photocatalysis, is relatively new, and still rather limited. The first such report was on the MF-dependence of hydrogen production from a suspension, by Kiwi in 1983 [4], using TiO_2 and CdS particles (both Pt-RuO₂ loaded) under UV-light irradiation, where the MF-dependence is only exhibited in the presence of $\text{Ru}(\text{bpy})_3^{2+}$. Although the MFE seems to exist in photocatalytic phenomena, the field has not developed (there has been a paucity of MFE research) for almost 20 years, probably due to the difficulty in reproducing the results leading to skepticism over the scientific credibility, or due to the seemingly weak influence relative to thermal fluctuation. Thus, there is only a decade-long history of MFE research on photocatalysis [5].

Although several parameters have been found responsible, it should be emphasized here in particular the significant roles of oxygen on photocatalytic MFE in conditions where the surface state is otherwise the same. Oxygen is typically involved with photocatalysis through ROS (reactive oxygen species) generation and reactions. It is thus rather surprising that, even for common photocatalytic degradation of dye solutions, the dissolved oxygen (DO) involvement with the MFE has never been discussed in detail.

On considering the MHD (magneto-hydrodynamic) effect in a solution, the Lorentz force is generally expected to act upon the charged ions. Since there is no net charge on DO molecules, the general MHD mechanism is not expected for DO. Besides, according to the equation describing the force term in the modified Navier-Stokes equation [5], the DO is not expected to involve the MFE under static magnetic field application, as a magnetic field (flux density) gradient is required for a net Lorentz force to be exerted on the DO molecules. It is therefore natural to neglect the DO as the major contributor to MFE, as appears to have been the prevailing perspective in this research field. This could be one of the major reasons for difficulty in obtaining reproducible data in the MFE research on photocatalysis.

The DO content (and state) is clearly involved with the MFE even under static magnetic configurations [5]. Or, to put it differently, the DO could be one of the main contributors to photocatalytic MFE phenomena. This is associated with the very special features of a heterogeneous system. At the interphase interface, the local fluctuation of various physical (and chemical) properties — electric charge density, viscosity, conductivity, and so on — must exist within the narrow volume in the vicinity of solid (e.g. powder) surface, mostly ascribed to the concentration changes in various species. In addition, any state variation at the surface (e.g. the number, kind, and distribution of adsorbed molecules, vacancies, and dangling bonds) would interact with surrounding molecules/atoms in the vicinity volume. Both would contribute to the electrostatic potential variation in the narrow volume at the interface.

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Molecular oxygen exhibits large susceptibility as a paramagnetic species, where the magnitude is generally at least two orders larger than other non-magnetic ionic species. If the Brownian motion is considered for each DO molecule, the net Lorentz force could be exerted on DO even under the static magnetic field application, due to the presence of perturbed electrostatic potential. The situation is equivalent to various local gradients in the electrostatic potential and the corresponding (effective) magnetic flux density in the narrow volume near the surface, resulting in the appearance of a net Lorentz force on paramagnetic DO. It is noted that this could happen even without a DO concentration gradient or a charge on a DO molecule, though the superoxide produced at the photocatalyst surface could also modify the DO transport. The net force would then induce magnetic convection in the solution through kinetic forces such as form drag and friction drag [5].

According to our limited data as well as some results in the literature regarding the photocatalytic MFE, a semi-quadratic relation is occasionally reported as a function of applied MF intensity, which appears to support this notion. In such cases, the above model based on oxygen acceleration or deceleration near surface (OANS model) [5] would be worth considering for the heterogeneous MFE phenomena.

The significant role of oxygen for MFE could also be extended to water. When a water molecule is attached to the surface, the oxygen atom in the molecule would often be captured by an oxygen vacancy site on the oxide surface. This would lead to weaker hydrogen bonding and restricted degree of freedom, possibly activating a quantum effect under MF, i.e. an ortho-para conversion of hydrogen atoms [6]. The situation could be similar for DO molecules, in that the trapped DO molecules might exhibit charge imbalance and weaker bonding with restricted degree of freedom. The activated DO might interact with the surrounding molecules, possibly leading to intersystem crossing (S-T conversion) under MF for the diradical DO system [5]. Besides, the photo-excited electrons/holes might assist (or deter) both quantum effects through charge transfer. Furthermore,

various clathrate states of water appear to be modified under MF application, only in the presence of DO [6,7]. Thus, the hybrid state of water and DO molecules seems important for MFE, especially near the interface, as magnetic adsorption/desorption of water is known, which is modified with light irradiation.

Finally, it is noted that some non-magnetic oxides exhibit weak ferromagnetism around oxygen vacancies, particularly for small particles. This should have various influences on molecular transport in the narrow volume at the surface. In addition, the dissolved CO₂ and the corresponding change of pH value also influence the MFE on heterogeneous photocatalysis, as well as the adsorbed CO₂ on the surface [5]. Since CO₂ easily dissolves into water, MFE research requires special care. Both points are, however, beyond the scope of this article. Although further research must be continued to elucidate the MFE mechanism, an analysis on DO involvement with MFE photocatalysis would clarify the path, or at least, extend one step further toward elucidation of this complex mechanism.

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