

Magnetic Field-induced Increasing of the Reaction Rates Controlled by the Diffusion of Paramagnetic Gases

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The rates of some reactions are greatly limited by diffusion rates of paramagnetic gases. The idea to enhance them by means of applying a magnetic field was considered and tested in this paper. The introduction of a weak magnetic field into the oxidation reaction of aqueous suspensions of ferrous hydroxide increased the reaction rate to a considerable extent, which was attributed to magnetically induced convection for the existence of a gradient of susceptibilities and magnetic strength. The idea can be valuable in all the processes, in which diffusion rates of the paramagnetic gases control the reaction rates or at least play an important role.

1 Introduction

There are numerous processes in which gas diffusion is involved, and many of them are utilized to benefit the life of human. For example, oxygen participates in the respiration of living bodies and in chemical and metallurgical processes. And some gases are widely used to purify water with certain ions. However, in many processes it is the diffusion of gases that controls the reaction rates because of a low gas diffusion coefficient, which limits the reaction efficiency to a great extent and makes a waste of resources. Hence, how to ameliorate the status is put forward. Yet as far as we are concerned, few corresponding measures have been achieved. Considering possible behavior of the paramagnetic gases in the magnetic field, we carried out an experiment to investigate the effect of the paramagnetic gases involving reaction rates through applying a magnetic field.

In our experiments, we selected the oxidation of aqueous suspensions of ferrous hydroxide to test our idea, because of the reason that its process has been relatively clarified. In fact, many scientists [1–4] have made lots of experiments in order to elucidate reaction kinetics and achieved abundant results. They found that the oxidation rate could be expressed apparently as zero order with respect to the concentration of total ferrous species and first order with respect to the concentration of dissolved oxygen, which is characteristic of a diffusion controlled reaction [5]. This law keeps valid until the fraction of oxidation exceeds 0.9. We repeated the experiments and applied a magnetic field to the reaction system to investigate the influence of it. The magnetic field did influence the reaction in a great extent as we expected.

2 Experimental

There are many factors that would affect results of the air-oxidation experiments, which were carried out on absorption

of air into aqueous suspension of ferrous hydroxide, such as the pH values, the temperature, the stirring rates, and so on. In order to clarify the influence of the magnetic field, the experiments were carried out by applying a weak magnetic field, while all the other parameters, which were adopted in the experiments under zero field, were kept unchanged. The experimental equipment is shown in Fig. 1. The configuration of the field was the same in all the experiments with magnetic field applied and cursorily simulated in Fig. 2.

All the air-oxidation experiments were taken at 50 °C and atmospheric pressure. The suspension of ferrous hydroxide was prepared by adding a sodium hydroxide solution into a ferrous chloride solution, both of which were prepared using water free of dissolved oxygen. And the volume of the suspension was adjusted at 400 cm³ and $[NaOH]_0/[FeCl_2]_0$ was controlled to 2.0. Then, nitrogen was passed through the suspension at a rate of about 300 mL/min for 40 minutes; meanwhile the suspension was stirred at a constant rate using a beater. Subsequently air was passed through at a fixed rate in place of nitrogen. It should be notified that the air for oxidation was bubbled through washing vessels containing a

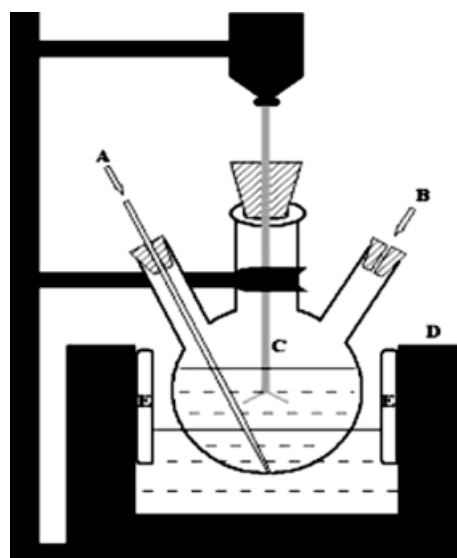


Figure 1. Equipment of the oxidation reaction: (A) gas inlet; (B) gas outlet & sampling orifice; (C) beater; (D) super water bath; (E) magnets.

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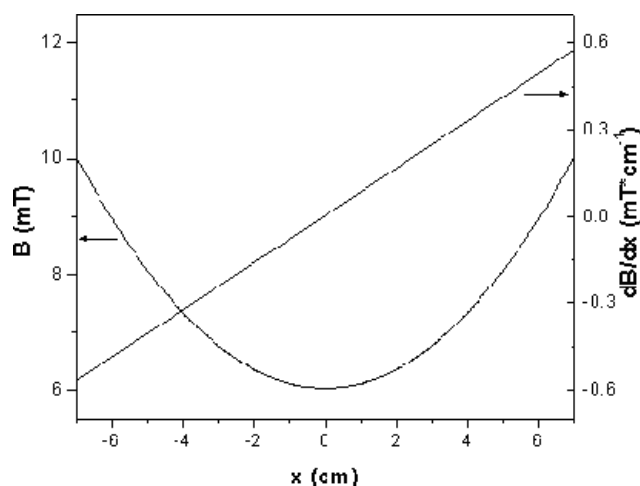


Figure 2. Distribution of the magnetic field strength and its gradient along horizontal direction, where the point $x = 0$ stands for the center of the flask.

NaOH solution first in order to remove carbon oxides and dust, or else that might influence the experimental results.

The oxidation reaction was followed by sampling a desired amount of reaction suspension repeatedly after short periods of time to determine the concentration of unreacted Fe(II) by chemical analysis. The solid samples were examined by X-ray diffraction using Cu $K\alpha_1$ radiation ($\lambda = 1.5408 \text{ \AA}$), while the morphology of the products was detected by Transmission Electron Microscopy (TEM) (Hitachi H-800). Room temperature M-H loops were measured on a Vibrating Sample Magnetometer (VSM, BHV-55) up to $H = 5 \text{ kOe}$ for magnetization measurements.

3 Results and Discussion

XRD and Mössbauer spectrum analysis of the samples collected through the oxidation experiments show that whether the magnetic field is applied or not, the magnetite nanoparticles are the only product. The Debye-Scherrer equation applied to estimate the size of the particles result in about 30 nanometers, which accords with TEM observations. Also, it is clear that the morphology does not change under the effect of applied magnetic field.

Fig. 3 shows the relationship between fractional oxidation (R) and the reaction time, where R is defined as below:

$$R = 1 - \frac{[Fe(II)]}{[Fe(II)_0]}$$

It is found that R increases in proportion to the reaction time regardless if a magnetic field was applied or not. The only difference is that the reaction rate increased when the magnetic field was applied. Meanwhile, the relations between reaction rate and concentration of dissolved oxygen as well as total ferrous species were tested. The rules are proven to keep unchanged. That is to say, under the magnetic field, the oxidation reaction rate still can be expressed

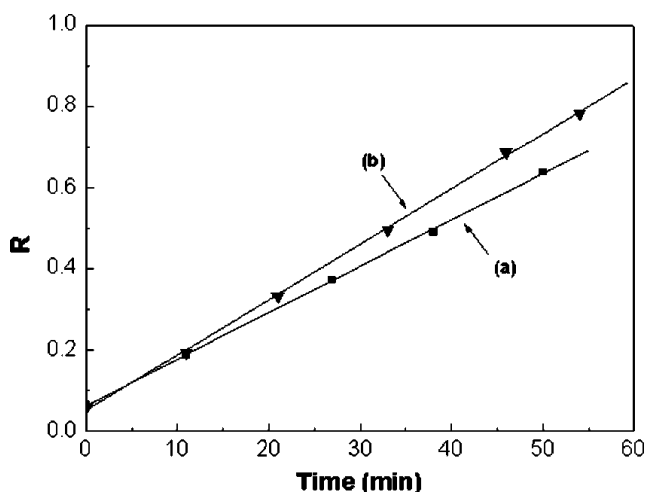


Figure 3. Relationship between fractional oxidation and reaction time in the air involved reaction, where flow rate of air is 200 mL/min : (a) without a magnetic field applied, (b) under a magnetic field.

as zero order as to the concentration of total ferrous ions and first order as to that of dissolved oxygen, as shown in Fig. 4.

Based on the experiment results above, it is clear that the rules of the oxidation reaction keep unchanged, so do morphology and phase of the products while a magnetic field is applied. Then the reaction process should also be the same to that under zero field, which has been elucidated by E. Sada [1] and can be applied in the pH range of 9 to 10. It is described as below:

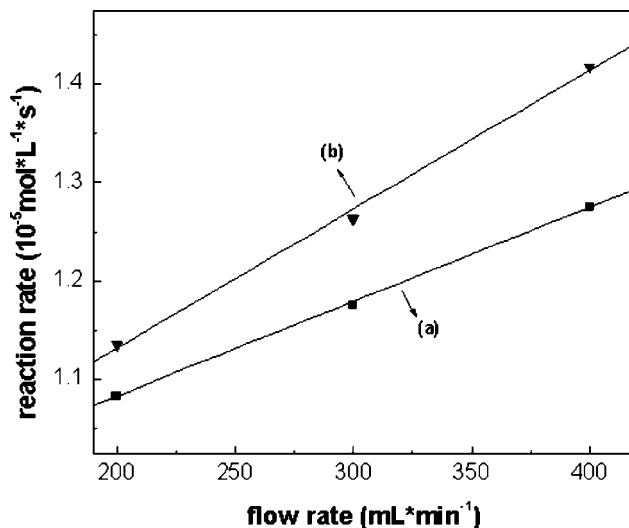
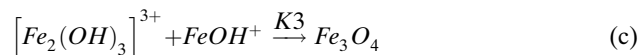
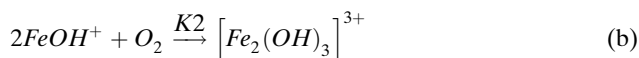
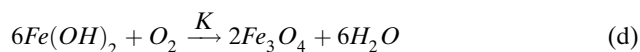


Figure 4. Relationship between reaction rates and flow rates of air in the air involved reaction: (a) without a magnetic field, (b) under a magnetic field.

And the process of total reaction can be expressed as:



In the reaction, ferric hydroxo-complexes are firstly formed by oxidation of the ferrous complex in the liquid film around the gas bubble, as shown in Eqs. (a) and (b). Subsequently, ferric hydroxo-complexes and ferrous complex ions coprecipitate in the thin layer adjacent to the ferrous hydroxide particles in the bulk of suspension, as shown in Eq. (c). Combining the reaction process with the laws, which relate reaction rates to concentration of dissolved oxygen and total ferrous ions, we can safely conclude that Eq. (b) is the determining step and diffusion of the oxygen controls the reaction rates.

There are two possibilities that are responsible for the obvious increase of the reaction rates under the influence of the magnetic field: One is that the average time the bubbles stay in the suspension prolongs, which leads to a longer time for the oxygen molecules in the bubbles to dissolve and react with the ferrous complexes, then cause an increase of the reaction rate. The other is that the dissolution of oxygen quickens and subsequently enhances the reaction rate. But the magnetic field is so weak that it hardly affects the bubbles in a whole, and the concentration of the suspension is so low that a change of its viscosity would not be considered. Hence the average staying time in the suspension was thought to change little. And the first possibility would not be valid.

The increase of the reaction rates, shown in Fig. 3 should be attributed to the influence of the magnetic field on the oxygen dissolution in some way. As Noriyuki Hirota [6] once stated, there are three essential steps involved in the dissolution process: (a) Diffusion of oxygen to the gas-water interface from the gas phase; (b) Oxygen dissolution at the gas-water interface; (c) Movement of dissolved oxygen molecules into the bulk of the water phase. The step, which was affected by the magnetic field and finally resulted in the increase of the dissolution rate should be clarified.

First, for the reason that diffusion in the gas phase is much quicker than that in the solution and that the time during which the gas bubbles stay in the suspension is very short, the little gradient of oxygen partial pressure in the bubbles would be neglected and concentration of oxygen at the gas-water interface is considered to be constant. Then step (a) is unlikely to be the rate-determining step and the influence of the magnetic field could not be the reason for an increase in the dissolution rate of oxygen.

Step (b) also would not determine the rate. Though the activation energy of the dissolution would be reduced by the magnetic field, in the thermodynamical point of view, the value is changed so little that it could not be the true reason.

Hence the only possibility is that step (c) controls the dissolution rate of oxygen and an applied magnetic field would increase the oxygen diffusion process in the water phase. As to the mechanism of magnetic field inducing dissolution of paramagnetic gases, there have been many reports [6–9].

The magnetically induced convection of water is considered to be responsible for the enhancing dissolution rate. In the theory's viewpoint, a gradient of the gas concentration in the water is formed during the process of dissolution, which means a gradient of magnetic susceptibility is created at the same time. Under a non-uniform magnetic field, the magnetic force acting on the water is not uniform too, which can be expressed in the following formula:

$$F = \frac{\Delta\chi}{\mu_0} * B * \frac{dB}{dr}$$

Based on the Navier-Stocks equation written as below:

$$\rho \frac{\partial v}{\partial t} + \rho(v \cdot \nabla)v = -\nabla p + F + \mu \nabla^2 v$$

where ρ is the density of the solution, v the velocity of the flow, p the pressure of the solution, F the external force and μ the coefficient of viscosity. It can be expected that convection of the water would be induced. And it is this convection that enhances the diffusion of the gases and then the dissolution rate of them.

In our experiments, it should be a similar case. The oxygen molecules diffusing into the bulk phase are quickly consumed through reacting with ferrous complexes, which results in a sharp gradient of oxygen concentration around the bubbles. Under the effect of the applied magnetic field, a considerable convection is formed and enhances the diffusion of oxygen and then the dissolution rate of it. Hence, the oxidation reaction rate is consequently increased. To test the reliability of our explanation, we also carried out a comparing experiment. Since the magnetic force has positive effects on the level of convection, as shown in the Navier-Stocks equation, and can be changed by altering magnetic susceptibility of the gases, the increasing extent of the reaction rate would be changed after altering the magnetic susceptibility of the gas. Based on this consideration, pure oxygen instead of air was used to oxidize aqueous suspensions of ferrous hydroxide, while all the parameters kept unchanged as above. The result is shown in Fig. 5. It is found that the augment of reaction rate is $5.45 \cdot 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$, while that in the air involved experiment is $1.82 \cdot 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$. The results are easy to be understood in the frame of our explanation about the increasing reaction rate, and in reverse further stand for it.

Since the increase of the reaction rate under a non-uniform magnetic field is mainly for the reason that the magnetic force acting on the paramagnetic gases induces convection of the water, the idea that enhancing the reaction rates through applying a non-uniform magnetic field can be fit for all the processes, in which the diffusion of paramagnetic gases controls the reaction rates or plays an important role.

The effect of the magnetic field on the reaction can also be revealed through magnetic properties variation of the products formed under a magnetic field. As shown in Fig. 6 the saturated magnetization (Ms) of the sample prepared under zero magnetic field is about 60 emu g^{-1} , while the val-

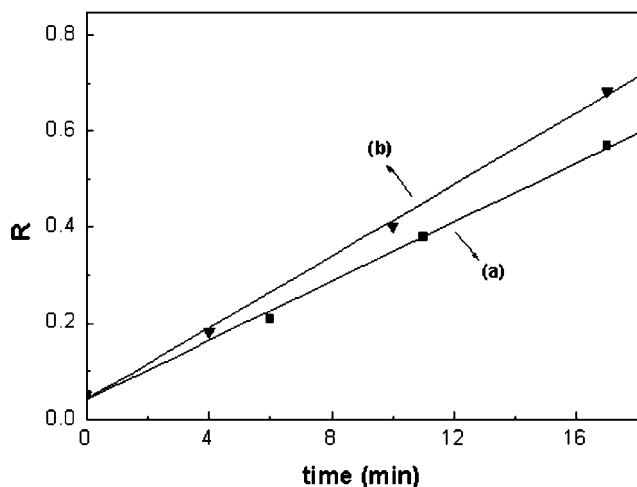


Figure 5. Relationship between fractional oxidation and oxidation time in the pure oxygen involved reaction, where flow rate of oxygen is 200 mL/min: (a) without a magnetic field, (b) under a magnetic field.

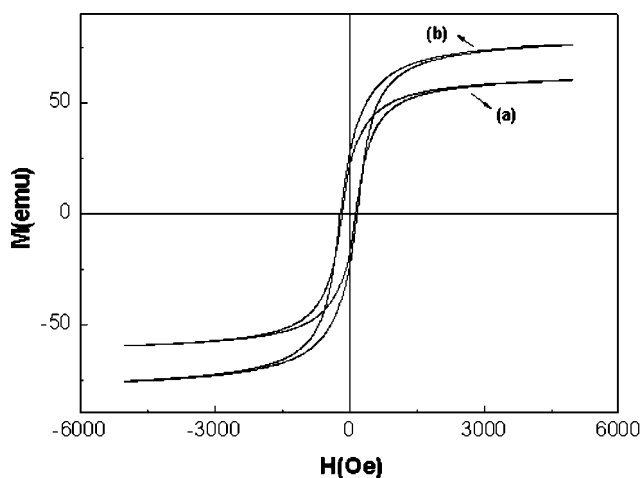


Figure 6. Magnetic properties of Fe_3O_4 products formed after 50 minutes of oxidation by air, where flow rate of air is 200 mL/min: (a) without a magnetic field, (b) under a magnetic field.

ue of that prepared under the magnetic field is 76 emu g^{-1} . It shows that the M_s is enhanced greatly under the effect of a magnetic field. It has been suggested that the magnetic properties of magnetite is correlated with its microstructure

[10–12]. According to the results discussed above, it is reasonable to suggest that the samples formed under an applied magnetic field could have less oxygen defects, which might result in strengthened superexchange interaction of Fe-O-Fe, and finally increase the saturated magnetization.

4 Conclusions

During the oxidation of aqueous suspensions of ferrous hydroxide, a magnetic field was applied. It was found that the reaction rate was significantly increased, while the laws of the reaction kept unchanged compared with those without a magnetic field applied. The magnetic field would induce a convection of the water due to an existed gradient of magnetic susceptibility, which enhances the diffusion of gases and then the dissolution rate of them. As a result, the oxidation reaction rate was increased. The improved magnetic properties due to strengthened superexchange interaction of Fe-O-Fe in the yielded products also provide an evidence that the magnetic field increased the diffusion of O_2 and decreased the density of oxygen defects. The phenomenon is considered to appear in all the processes, in which the diffusion of the paramagnetic gases controls or influences on the reaction rates.

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