

Reduction of MnO_4^- and formation of MnO_2 nanoparticles in an ultrasonic field: the effects of organic additives

超音波場における MnO_4^- の還元と MnO_2 ナノ粒子の生成: 有機添加剤の影響

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1. Introduction

There are a number of reports concerning the sonochemical synthesis of functional nanoparticles. However, the formation mechanism under ultrasonic irradiation has not yet been investigated sufficiently. It is important to understand the reduction mechanism of metal ions under ultrasonic irradiation, because the reduction reactions are often applied to the synthesis of various types of nanoparticles [1-3].

In this study, we have investigated the sonochemical reduction of MnO_4^- to MnO_2 in the presence of organic additives under Ar atmosphere. It is well known that MnO_2 is one of the useful materials for the application to Li-batteries, sensors, catalysts, etc. Although MnO_2 nanoparticles have been synthesized by the sonochemical reduction of MnO_4^- [4-7], the reduction mechanism in the presence of organic additives has not yet been investigated sufficiently. Here, we have reported the effects of organic additives on the reduction of MnO_4^- to MnO_2 during ultrasonic irradiation.

2. Experiment

Ultrasonic irradiation was performed using a 65 mm ϕ oscillator (Kaijo) and a 200 kHz ultrasonic generator (Kaijo 4021 type, 200 W). The details of the irradiation set-up and the characteristics of the reaction vessel are described elsewhere [1]. A 60 mL argon saturated aqueous solution containing KMnO_4 was irradiated in the water bath, which was maintained at 20 °C by a cold water circulation system. The vessel was mounted at a constant position (4 mm from the oscillator). The reaction vessel was closed from air during irradiation. When the effects of alcohols on the sonochemical

reduction of MnO_4^- are investigated, alcohols were injected into the solution with a microsyringe through a silicon rubber septum after Ar bubbling. After irradiation, the solution was taken by a syringe through the septum and then placed in a vial. The absorption spectra of the irradiated solutions were measured by an UV-visible spectrophotometer. The concentration of MnO_4^- in the irradiated solution was determined by a spectrophotometric method. The concentration of H_2O_2 formed in the sonolysis of pure water and aqueous solution was measured by a KI colorimetric method.

3. Results and Discussion

It was observed that the color of the sample solution of MnO_4^- was gradually changed by ultrasonic irradiation from purple to pale yellow. After long time irradiation, the color of the sample solution turned to colorless. The changes in the absorption spectra of 0.1 mM MnO_4^- aqueous solution in the presence of 1-butanol by ultrasonic irradiation were measured. The obtained results

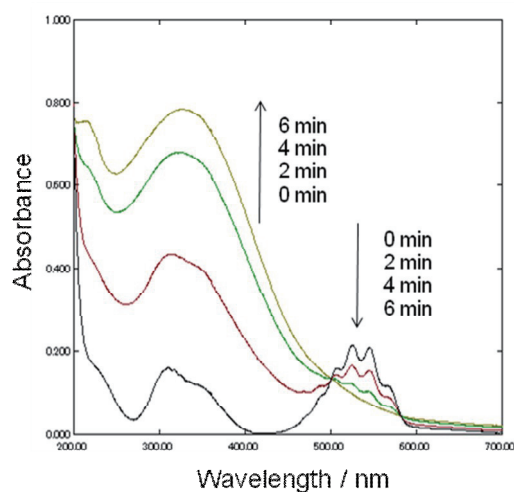
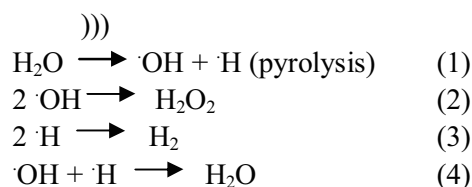


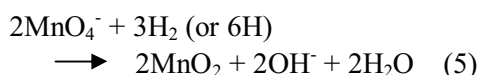
Fig. 1 Absorption spectra of sample solution in the presence of 1-butanol before and after ultrasonic irradiation.

are shown in Fig. 1. It was found that the absorption peaks corresponding to MnO_4^- at around 530 nm gradually disappear and a new broad peak at around 330 nm emerges. Based on previous reports [8], this new peak can be attributed to colloidal MnO_2 nanoparticles. In addition, it can be seen that the absorption intensity corresponding to colloidal MnO_2 nanoparticles gradually increases with increasing irradiation time. This would be due to the progress of MnO_4^- reduction to MnO_2 , taking into account previous papers [7,8].

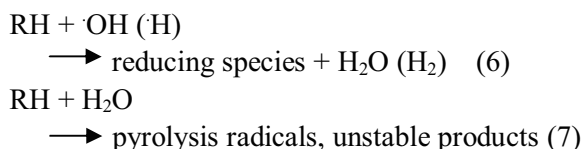
It has been reported that the following reactions occur, when an aqueous solution is irradiated under Ar atmosphere:



where the symbol))) corresponds to the ultrasonic irradiation. The pyrolysis of water molecules occurs due to high temperature cavitation bubbles [9]. In pure water, OH radicals and H atoms that are formed rapidly recombine to form H_2O_2 , H_2 and H_2O , where H atoms and H_2 molecules are well-known to act as reducing species for the reduction of noble metal ions [1,2]. Therefore, in the case of MnO_4^- reduction, the following reaction would occur:



On the other hand, in the presence of organic additives, some reducing radicals and unstable products are also formed from the sonolysis of organic compounds [1,2]:



where RH corresponds to organic additives. Reactions (6) and (7) indicate the sonochemical formation of reductants: (1) reducing species and H_2 are formed from the abstraction reaction of RH with $\cdot\text{OH}$ or $\cdot\text{H}$, and (2) pyrolysis radicals and

unstable products are formed via pyrolysis of RH and water. Therefore, the following reaction takes place:



where M corresponds to various reducing species, pyrolysis radicals and unstable products. Previously, it was reported that H_2O_2 formed in the sonolysis of aqueous solutions acts as the reductant for MnO_4^- [7]. The concentration of organic additives in solution was found to affect the yield of H_2O_2 and other reducing species. Therefore, it was clear that the concentrations and types of added organic compounds are the important parameters to control the rate of MnO_4^- reduction.

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