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Coupling effect between sonolysis and photocatalysis in dilute reactant solution

希薄溶液における超音波光触媒反応のカップリング効果

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1. Introduction

Sonophotocatalysis, that is the simultaneous irradiation of ultrasound and light in the presence of a photocatalyst, is expected to obtain the coupling effects between sonolysis and photocatalysis. There are many applications to chemical reactions. One of them is an acceleration of oxidation. We have issued report in that field of reaction. For example, the mineralization of oxalic acid was performed [1]. As you know, oxalic acid is the one of harmful compounds. Thus, sonophotocatalysis is applicable to degradation of harmful compounds in the environment [2]. Harmful materials are usually low concentration in nature. In general, the degradation rate falls down in low concentration. In this presentation, we payed attention to the behavior of sonophotocatalytic degradation in a low concentration of target material.

As model harmful materials, oxalic acid and methanol solutions were prepared. Both compounds are water soluble and they are able to be degraded by not only sonolysis but also photocatalysis.

2. Experimental procedure

Sonolysis was carried out using a ultrasonic irradiation system with a 200 kHz transducer (Kaijo, 200 W or Shinka Ind., 100 W) in the presence of TiO_2 photocatalyst (Soekawa Chem. Ind., Rutile). Argon (Ar) atmosphere was adopted and ultrasound was irradiated from bottom surface of a Pyrex glass reactor. Temperature was controlled at 25℃. Photo irradiation was carried out from one side with an Hg-lamp (USHIO, 500 W) or Xe-lamp (Ushio, 500 W). Sonophotocatalysis was performed both irradiation simultaneously in the presence of photocatalyst.

The amount of evolved gases were determined by gas chromatography (Shimadzu, GC8AT or 8AIT). Hydrogen peroxide (H_2O_2) in the solution was analyzed by colorimetry (JASCO, V530). The degradation rate was mainly evaluated via the production rate of CO_2 evolved.

3. Results and Discussion

Coupling effect of photocatalysis and sonolysis was confirmed firstly in oxalic acid solution in an Ar atmosphere. Due to the Ar atmosphere, very low activity was observed by photocatalysis. As shown in Fig. 1, blank bars, sonophotocatalyses, were higher than sum of sonolysis and photocatalysis. Figure 1 also shows dependence of the degradation rate on reactant concentrationn in Fig. 1. The

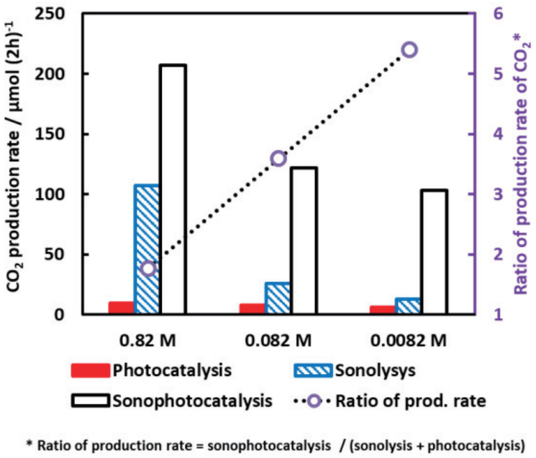

Fig. 1 Coupling effects of degradation rate on various concentrations of oxalic acid solution.

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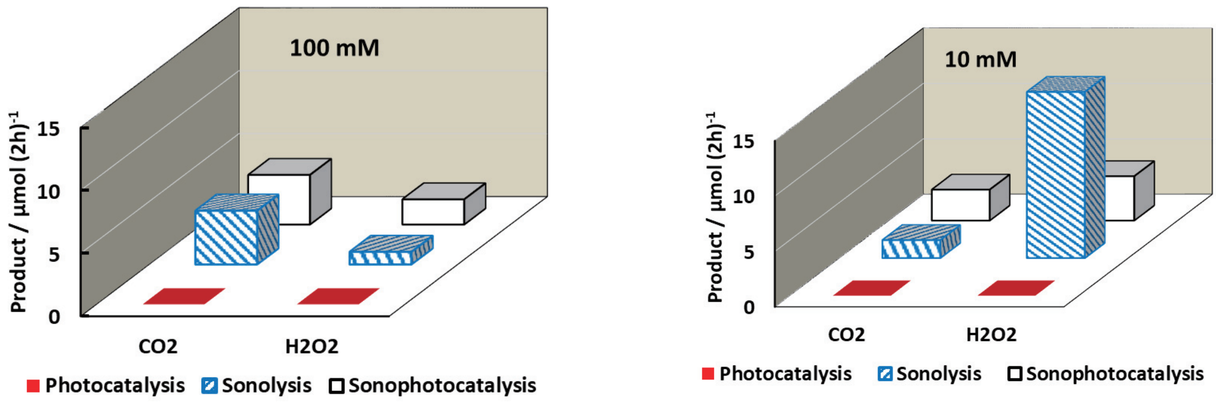

Fig. 2 Products from 100 mM (left) and 10 mM (right) methanol solutions.

higher concentration was in operation, the higher rate was observed. On the other hand, however, ratio of production rate of sonophotocatalysis to the sum of rates of sonolisis and photocatalysis increased with decreasing concentration. In other words, sonophotocatalysis is effective in the low concentration of reactant.

Figure 2 shows reaction products and those amounts from 100 mM (conc) and 10 mM (dilute) methanol solutions in an Ar atmosphere. In the case of photocatalytic system, products were below detection limit because of Ar atmosphere. Coupling effect for CO_2 production rate could not be confirmed at 100 mM. In the case of 10 mM, however, the coupling effect was confirmed. At that concentration, we noticed the amount of H_2O_2 by sonolysis. Because of presence of scavenger (methanol), we did not suppose H_2O_2 consumed in the solution. Remaining H_2O_2 might be the key for coupling effect in dilute solution.

Figure 3 shows the dependence of H_2O_2 production rate on methanol concentration. The H_2O_2 means remaining H_2O_2 after sonolysis in methanol solution. That H_2O_2 would be broken by photocatalysis and active species, such as OH radicals, were produced. Those species attack methanol and CO_2 was produced at the sonophotocatalytic system as the result. Thus, coupling effect would increase with H_2O_2 production rate. It is sure that coupling effect and H_2O_2 production rate ware similar behavior as shown in Fig. 3.

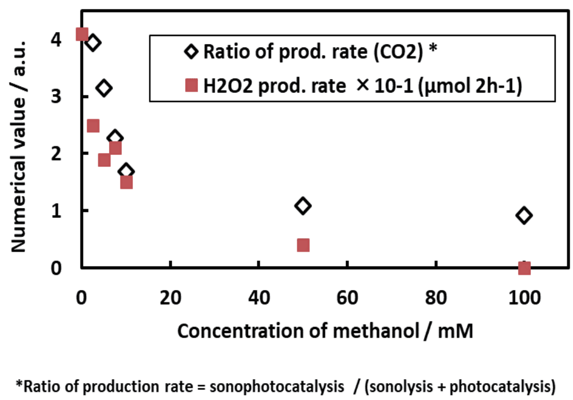

Fig. 3 Relation between coupling effect and amount of H_2O_2. Experimental conditions are same as Fig. 2.

4. Conclusion

The degradation rate increased about fourfold compared with only sonolysis at 2.5 mM methanol solution. Thus, this combined system is useful for degradation of harmful materials, especially, in the case of low concentration.

Acknowledgment

This work was supported by Meisei University.

References

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