

Synthesis of Pd/WO₃ photocatalyst by the sonochemical reduction method in a split manner

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1. Introduction

Tungsten oxide (WO₃) is a photocatalyst that absorbs visible light. The reaction mechanism of photocatalysis is that excited electrons and holes generated by light absorption act on chemical substances, causing chemical reactions such as redox reactions to proceed. However, WO₃ alone does not have high photocatalytic activity because the generated excited electrons and holes easily recombine.¹⁾ On the other hand, when an aqueous solution of noble metal containing alcohol is irradiated with high power ultrasound, the noble metal ions are reduced through the effect of cavitation, and fine metallic particles are deposited.²⁾ By temporarily trapping photo-excited electrons generated in WO₃ by the fine metallic particles during light irradiation, the recombination between excited electrons and holes can be suppressed, which is expected to improve catalytic activity. In this study, Pd/WO₃ composite particles were synthesized using a sonochemical reduction method, and their photocatalytic performance was evaluated in terms of the decomposition rate of methylene blue (hereafter referred to as MB) in aqueous solution.

2. Experimental

After adding 0.20 g of WO₃ powder of less than 100 μm to 60 mL of PdCl₂/HCl solution in a glass cylindrical vessel, Ar was bubbled into the solution for 30 minutes. Then, 2-propanol was added, and the solution was irradiated with 500 kHz ultrasound. After ultrasonic irradiation, the suspension was vacuum filtered, and the separated solids were dried at 45-60°C overnight and used as catalysts. To investigate the effect of various conditions of the sonochemical reduction method on the catalytic performance, composite particles were synthesized by changing Pd content in the solution. In addition, the number of metal additions during the sonochemical reduction and the number of ultrasonic irradiation treatments in conjunction with the metal additions were also examined. As an example of the procedure, Fig. 1 shows two synthesis steps for the preparation of 1.0 wt% Pd/WO₃ composite particles. Procedure (1) is the case in which a quantity of Pd equivalent to 1.0 wt% is prepared in a reaction vessel in a single batch and sonicated for 30 minutes, and

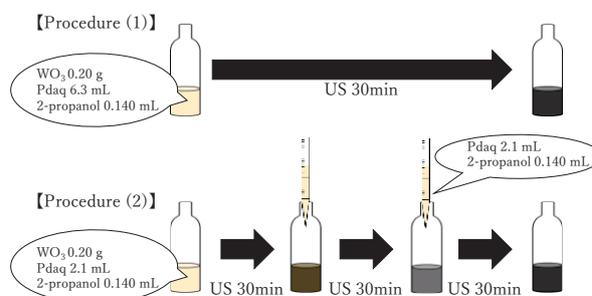


Fig. 1 Typical synthesis procedures of Pd/WO₃ composite particles by sonochemical reduction when the added total amount of Pd per weight of WO₃ is 1.0 wt%.

Table 1 Preparation conditions of catalysts in the split/no split manners.

Condition title (Catalyst title)	The number of splits of Pd solution added (N _s)	The added total amount of Pd (M _t) [wt%]*	M _t /N _s [wt%]*
Pd-0s-0.5w	0	0.50	-
Pd-3s-0.5w	3	0.50	0.17
Pd-5s-0.5w	5	0.50	0.10
Pd-7s-0.5w	7	0.50	0.071
Pd-0s-1.0w	0	1.0	-
Pd-3s-1.0w	3	1.0	0.33
Pd-5s-1.0w	5	1.0	0.20
Pd-7s-1.0w	7	1.0	0.14
Pd-0s-1.5w	0	1.5	-
Pd-3s-1.5w	3	1.5	0.50
Pd-5s-1.5w	5	1.5	0.30
Pd-7s-1.5w	7	1.5	0.21

* Weight percentage of added Pd per weight of WO₃.

the catalyst prepared according to this procedure is denoted as Pd-0s-1.0w. In procedure (2), Pd equivalent to 0.33 wt% was added to the WO₃ suspension three times in a split manner, and the suspension was subjected to ultrasonic irradiation for 30 min for each addition. The catalyst synthesized in the procedure (2) is denoted as Pd-3s-1.0w. The preparation conditions of catalysts in the other split/no split manners together with Pd-0s-1.0w and Pd-3s-1.0w are shown in Table 1.

All MB decomposition experiments using WO₃ and Pd/WO₃ catalysts prepared via sonochemical reduction were conducted by a visible light irradiation device in the dark. The maximum duration of visible light irradiation was 3 hours, and a certain amount of MB was collected from the MB solution every 30 minutes of irradiation, and the MB

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concentration was measured to examine the change over time in the MB decomposition rate.

The surface of Pd/WO₃ catalysts was observed by TEM and EDS. The amount of Pd supported on WO₃ particles was measured by ICP.

3. Results and discussion

To investigate the effect of Pd loaded on WO₃ on the photocatalytic performance of WO₃, the MB degradation rate ($= [1 - C/C_0] \times 100 \%$) after 3 hours of visible light irradiation was compared between WO₃ particles with no addition of Pd and Pd-os-1.0w, where C_0 [mol/L] the initial concentration of MB solution and C [mol/L] is the concentration of MB solution after visible light irradiation time, 3 hours. The MB degradation rate for WO₃ particles and Pd-0s-1.0w were about 22.2 and 63.6%, respectively. This improvement in photocatalytic performance may be attributed to the fact that photoexcited electrons are trapped by Pd on the WO₃ surface, and Pd acts as a reduction site.

Fig. 2 shows the results of MB decomposition experiments using Pd/WO₃ composite catalysts. The figure compares the MB degradation rate after 3 hours of visible light irradiation. The results in the figure show that Pd-3s to Pd-7s, which underwent multiple step treatments, showed higher MB degradation rates than Pd-0s. This suggests that the catalytic performance can be improved by controlling the concentration of the Pd solution in the preparation of Pd/WO₃ composite particles in a stepwise manner during the synthesis of the Pd/WO₃ composite particles as the ultrasonic reduction process proceeds.

The effect of the total amount of Pd added (M_t) on the amount of Pd loaded on the catalyst particles synthesized by Pd-0s-@w (@=0.5, 1.0, 1.5), i.e., one-step treatment, is shown in Table 2(a). On the other hand, Table 2(b) shows the amount of Pd loaded on the catalyst particles of Pd-0s-1.0w, Pd-3s-1.0w, Pd-5s-1.0w, and Pd-7s-1.0w prepared in split manners. The results in Table 2(a) demonstrate that the amount of Pd loaded on the catalyst particles increased with the M_t . However, as shown in Fig. 2, for Pd-0s-@w (@=0.5, 1.0, 1.5), the photocatalytic activity decreased with the M_t . On the other hand, the results in Table 2(a) showed that the amount of Pd loaded on the catalyst particles increased when the N_s was increased to three compared to no splits, but when the N_s was increased to five or seven, the amount of Pd loaded was not much different from that of three splits ($N_s=3$). On the other hand, as shown in Fig. 2, the photocatalytic activity increased with the N_s . Therefore, the results in Fig. 3 and Table 2 suggest that the degree of photocatalytic activity is not determined solely by the amount of Pd loaded on WO₃ particles.

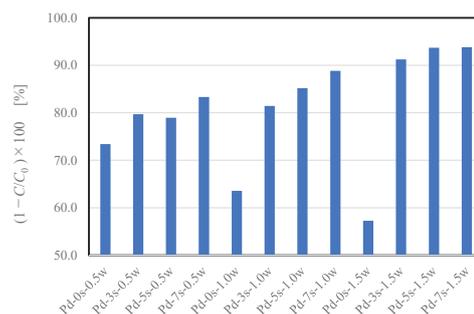


Fig.2 Effects of the amount of Pd added and split manner on photocatalytic activity.

Table2 The amount of Pd loaded on WO₃ particles measured by ICP.

(a)Effect of total amount of Pd added without splitting

Condition title (Catalyst title)	Pd-0s-0.5w	Pd-0s-1.0w	Pd-0s-1.5w
Amount of Pd loaded on the WO ₃ [mg-Pd/g-WO ₃]	5.55	7.2	7.5

(b)Effect of split manner when the total amount of Pd added is 1.0 wt%

Condition title (Catalyst title)	Pd-0s-1.0w	Pd-3s-1.0w	Pd-5s-1.0w	Pd-7s-1.0w
Amount of Pd loaded on the WO ₃ [mg-Pd/g-WO ₃]	7.20	9.35	8.70	9.10

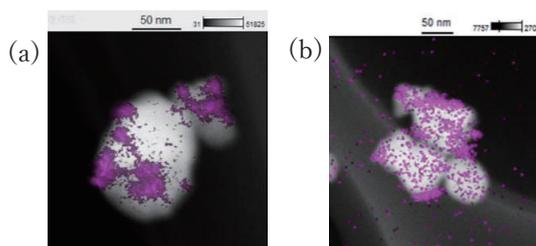


Fig.3. EDS mapping of Pd for Pd/WO₃ particles. (a) Pd-0s-1.0w, (b) Pd-7s-1.0w.

The results of EDS mappings for the samples of Pd-0s-1.0w and Pd-7s-1.0w are shown in Fig. 3. From Fig. 3, it can be seen that Pd nanoparticles were supported on WO₃ particles in a wider and more uniform dispersion in Pd-7s-1.0w compared to Pd-0s-1.0w. As a result, it is inferred that ultrasonic reduction in a split manner improves the dispersibility of Pd nanoparticles supported on WO₃ particles, leading to an increase in photocatalytic activity.

Acknowledgment

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