# Effect of Hydrothermal Treatment of Titania-pillared Montmorillonite for Photocatalytic Degradation of Dibutyl Phthalate in Water

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Titania-pillared clay could adsorb dibutyl phthalate (DBP), one of endocrine disruptors, and degrade it photocatalytically. Hydrothermal treatment of this material, which increased the crystallinity of titania pillars, enhanced the photocatalytic activity without losing the adsorption ability and reduced the elution of titania pillars.

The organic compounds called endocrine disruptors have been spread over the environment and they influenced the generative function of some species of living thing on the earth. Although it is still discussed whether such chemicals have an influence also upon human being or not, it had better to develop the technology for elimination or decomposition of them as soon as possible. Photocatalysis over $TiO_2$ is one of the most promising system to decompose the organic compounds diluted in water.[1]

$TiO_2$-pillared clay,[2-4] one of eco-materials, has small $TiO_2$ particles as pillars between silicate layers. This material has photocatalytic activity,[2] large specific surface area and mesopores[3,4] large enough to accept huge molecules such as endocrine disruptors. In addition, pillared clays are hydrophobic in general.[5] These properties would be suitable for adsorption of organic compounds diluted in water and might accelerate of reaction rate.

In the present study, to develop an elimination system for diluted organic chemicals such as endocrine disruptors in water, we prepared $TiO_2$-pillared montmorillonite and investigated the ability of adsorption and photocatalytic decomposition for elimination of diluted dibutyl phthalate (DBP) in water. In addition, the effects of hydrothermal treatment on the properties of sample were examined.

$TiO_2$-pillared clay was prepared with the procedure reported by Yamanaka et al.[3] Titanium tetraisopropoxide was added to vigorously stirred 1 M HCl solution. The molar ratio of HCl to the alkoxide was a unity. The resulting slurry was peptized at 323 K to give clear $TiO_2$ sol. The clay used was sodium montmorillonite (Kunipia-F, Kunimine Industrial Company) with a cation exchange capacity (CEC) of 1.2 meq $g^{-1}$. The $TiO_2$ sol was mixed with a 1 wt% aqueous suspension of the clay. The molar ratio of $TiO_2$/CEC was 30. The suspension was stirred for 3 h at room temperature. The product was centrifuged and washed with water several times. The $TiO_2$-pillared clay thus obtained was dispersed in water again, and then hydrothermally treated at 473 K for 1 h. The treated product was separated and washed with water by centrifugation and dried in air at room temperature. Calcination of the products was performed at 773 K. Hydrothermally treated $TiO_2$-pillared clay sample was abbreviated as H-TPC, and non-treated one as TPC in the present paper.

The adsorption and photocatalytic decomposition test was carried out at room temperature in a stopped 50 ml Erlenmeyer flask made by borosilicate glass where is a 30 ml DBP solution of 17 ppm. After the solution was magnetically stirred in the dark for 1 h, the catalyst was introduced into the flask. Continuously being stirred well in the dark (Figure 1, period A), the sampling of the solution was sometimes carried out to monitor the variation of DBP concentration by means of GC. The amount of catalyst used was 15 mg in $TiO_2$ weight base of the sample. In case of non-pillared montmorillonite, the amount was 15 mg, which was equivalent to the amount of clay part in TPC sample. Photoirradiation from a small window (5 mm diameter) was started after the concentration of DBP achieved to adsorption equilibrium (Figure 1, period B), and the concentration was monitored in the same manner. Photoirradiation was carried out with Xe lamp through a filter made by borosilicate glass in which cooling water was passed through.

Evaluation of amount of Ti eluted in acidic solution was carried out as follows; 20 mg of the sample was dispersed in 10 ml of HCl solution (pH=2, 4) in a capped glass bottle, and then incubated at 323 K for 48 h (pH=2) or 144 h (pH=4). The Ti concentration in the solution was determined by ICP spectrometer. The amount of Ti eluted was defined as the weight ratio of Ti in the solution against Ti initially in the sample.

The results of characterization of $TiO_2$-pillared clay samples are shown in Table 1. TPC sample contained 50.8 wt% of $TiO_2$ and had a large specific surface area. A large total pore volume indicates that there is a space built by $TiO_2$ particles which should be like as pillars between silicate layers.[2-4] The pore size was 3.1 nm. This means that there is

**Table 1.** Results of characterisation of $TiO_2$-pillared montmorillonite samples

| Samples | $TiO_2$ contents[a] / wt.% | Specific BET surface area[b] /$m^2g^{-1}$ | Total pore volume[b] /$cm^3g^{-1}$ | Interlayer distance[c] /nm | Amount of eluted $TiO_2$ in acid solution[d] /% | |
|---|---|---|---|---|---|---|
| | | | | | pH=2, 48 h | pH=4, 144 h |
| TPC[e] | 50.8 | 240 | 0.212 | 3.13 | 0.067 | 0.001 |
| H-TPC[e] | 52.8 | 233 | 0.246 | 3.70 | 0.007 | 0.000 |

[a] Determined by means of XRF. [b] Calculated from $N_2$ adsorption isotherms. [c] Defined as the pore size that showed maximum value with the pore size distribution curve obtained from $N_2$ adsorption isotherm. [d] The values were of another set of samples prepared in the identical parameters. [e] See text.

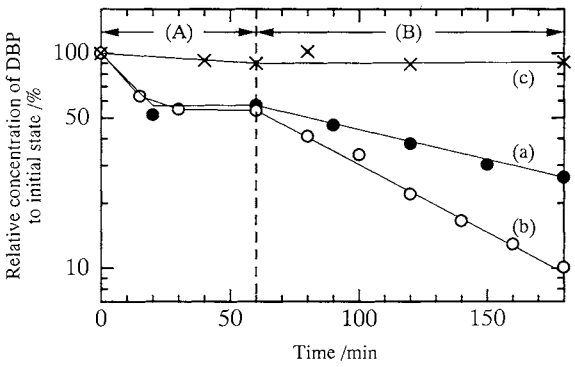


**Figure 1.** Results of adsorption and photocatalytic decomposition test for the clay samples. The concentration of DBP of the aqueous solution was monitored in the dark for 60 min (period A) and successively upon photoirradiation for 120 min (period B), in the presence of TPC sample (a), H-TPC sample (b) and non-pillared montmorillonite (c). Initial concentration of DBP in the solution was 17 ppm.

enough space for large molecules such as DBP (estimated at 1.2 nm) to enter and reach the $TiO_2$ pillars, which would function as photocatalysts, between the silicate layers.

H-TPC sample showed almost the same structure as TPC sample. However, the hydrothermal treatment slightly reduce the specific surface area, and slightly enlarge the pore volume and the interlayer distance, suggesting that the particle size of $TiO_2$ pillars became slightly larger by hydrothermal treatment.

Any $TiO_2$ phase was not detected on TPC sample by X-ray diffraction, while H-TPC sample showed some diffraction lines from $TiO_2$ anatase crystallites whose size estimated was 3.5 nm. Since the interlayer distance of the sample was only slightly changed by the treatment, appearance of the diffraction from anatase phase should be originated from the enhancement of crystallinity of $TiO_2$ pillars by hydrothermal treatment.

Figure 1 shows the results of adsorption and photocatalytic decomposition test for the $TiO_2$-pillared and non-pillared clay samples. The concentration of DBP in the presence of TPC sample (Figure 1a) decreased to 50% in 30 min even in the dark (period A). H-TPC sample (Figure 1b) showed almost the same result as TPC sample in the dark. The hydrothermal treatment seems to have no influence on the adsorption ability of the pillared clay. On the other hand, in the presence of non-pillared montmorillonite, few decrease of DBP was observed in this condition (Figure 1c). The good absorption ability of $TiO_2$-pillared clay samples would be due to their large specific surface area of the opened silicate layers and probably due to hydrophobic property of pillared clay.[5] Another possibility was that the pore size of the pillared clay sample might be suitable for the capillarity of endocrine disruptors since the size of molecules (1.2 nm) are closed to the pore size.

Upon photoirradiation after reaching adsorption equilibrium (Figure 1, period B), the concentration of DBP suddenly started to decrease in the presence of TPC (Figure 1a) and H-TPC samples (Figure 1b), although it did not decrease in the presence of non-pillared montmorillonite (Figure 1c). The decrease of concentration in the presence of TPC or H-TPC samples would be due to the photodecomposition of DBP by $TiO_2$-pillars located between the montmorillonite layers. Although some compounds as intermediates in the photodegradation of DBP by $TiO_2$ are suggested,[6] no organic product rather than DBP was observed in the solution by GC. In addition, individual experiment on H-TPC sample showed that the concentration of DBP was reduced below 0.5 $\mu g/l$ after photodegradation.[7] These results suggested that DBP would be mineralized into $CO_2$ and $H_2O$.

The most important observation in the present study is that H-TPC sample in the light showed the higher consuming rate of DBP than TPC sample, indicating that H-TPC sample exhibits higher photocatalytic activity than TPC sample. It means that crystallization of $TiO_2$ pillars by hydrothermal treatment enhanced the photocatalytic activity.

The hydrothermal treatment brought us another important effect. We measured the amount of $TiO_2$ eluted from TPC and H-TPC samples after impregnation in acidic solution.[8] After 48 h in strongly acidic solution (pH=2), while 0.067% of $TiO_2$ was eluted from TPC sample, only one tenth amount (0.007%) of $TiO_2$ was eluted from H-TPC sample. In milder acidic condition (pH=4), no elution of $TiO_2$ was detected from H-TPC sample even after 144 h, while small amount of elution (0.001%) was confirmed from TPC sample. Therefore, it was elucidated that crystallization of $TiO_2$ pillars by hydrothermal treatment is effective for the improvement of not only photocatalytic activity but also durability in acidic solution.

In conclusion, $TiO_2$-pillared montmorillonite was found to adsorb DBP molecules in water on silicate layers of pillared clay and to decompose them photocatalytically by $TiO_2$ pillars. The hydrothermal treatment enhanced the crystallinity of $TiO_2$ pillars without changing the adsorption ability of the sample. It was clarified that hydrothermally crystallized $TiO_2$ pillars in pillared clay have a higher photocatalytic activity for degradation of DBP and a higher durability in acidic solution than untreated amorphous $TiO_2$ pillars.

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7 After photoirradiation in the presence of H-TPC sample DBP in the solution was extracted by hexane, and quantitatively analysed by GC-MS spectroscopy.
8 The durability of the materials in acidic aqueous solution would be important since the solution is considered to become acidic when endocrine disruptors containing halogens are decomposed.