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Photocatalytic degradation of pentachlorophenol by TiO_2 supported on mesoporous silica

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ABSTRACT

Pentachlorophenol (PCP) is a highly toxic organic pollutant. In this study, we prepared mesoporous silica containing TiO_2 with mobil crystalline material 41 (TiO_2-MCM-41) and fluoride-modified TiO_2-MCM-41 for the photocatalytic degradation of PCP. First, we examined the adsorption ability of phenols on photocatalysts. The adsorption ability on MCM-41 strongly depends on the hydrophobicity of phenols. Most hydrophobic PCP was easily adsorbed. The adsorption ability of PCP increased with an increase in fluoride content in MCM-41. The photocatalytic degradation rate of PCP with TiO_2-MCM-41 was much faster than those of PCP/TiO_2. By using more hydrophobic fluoride-modified TiO_2-MCM-41, degradation rates of PCP further increased. This behavior was caused by the difference in the adsorption ability of pollutants on photocatalysts. The degradation rate of PCP with mesoporous silica containing TiO_2 apparently obeyed the Langmuir–Hinshelwood equation and was controlled by the adsorption step of PCP on the photocatalysts.

Keywords: Phenols; Photocatalytic degradation; Mesoporous silica; Titania

1. Introduction

Pentachlorophenol (PCP) has been widely used as a biocide. It is now primarily used as a wood preservative to treat utility poles and crossarms. Uncontrolled PCP use and release has caused contamination of soil, water and ground water [1,2]. PCP is one of the persistent organic compounds and has been classified as a priority pollutant in United States and EU [3] due to its high toxicity and carcinogenic potential. Nowadays the use of PCP is severely restricted in many countries. Biological degradation of PCP is very slow and produces extremely harmful polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans [4]. The overall poor removal of PCP by conventional biological methods commonly used in wastewater treatment process led to the development of an alternative treatment approaches, such as advanced oxidation processes (AOP). A photocatalytic process, a representative AOP, employing TiO_2 is considered to be a promising method for degradation of less biodegradable and toxic organic compounds due to its ability to achieve complete oxidation of the organic pollutant and its faster degradation rate than the conventional biological methods. In previous studies, PCP degradation has been investigated by means of UV and natural solar irradiation over TiO_2 suspension [5–8]. Recently, highly active titania-based photocatalysts under visible light were developed [9,10] because TiO_2 is active under UV light. This titania-based photocatalysts exhibited the stable characteristics in wastewater treatment process.

Because the concentrations of organic pollutants including PCP in aqueous media are extremely low, the adsorption and enrichment of organic pollutants on TiO_2 is important to improve the photocatalytic performance [11]. The following factors should be considered in finding suitable support for TiO_2 [12]. First, because TiO_2 itself is not a good adsorbent for organic molecules, it is desirable that a support has adsorptive properties to enrich substrates on the surface. Second,

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the supports may be able to enhance catalytic properties. Among supports investigated, zeolite has the drawback that the pore openings are less than 2.0 nm; hence bulky molecules cannot easily access the pores and undergo facile photocatalytic reactions inside them. Thus, it became beneficial to use mesoporous materials as supports for dispersing TiO_2 [12]. The photocatalytic degradation of aromatic alcohols such as phenol and 2,4,6-trichlorophenol has been reviewed over TiO_2 supported on mesoporous silica [12]. However, photocatalytic degradation of PCP, which was hardly decomposable compared with phenol and 2,4,6-trichlorophenol, has not been reported using TiO_2 supported on mesoporous silica.

The hexagonal forms (hexagonal mesoporous silica [HMS], mobil crystalline material 41 [MCM-41]) among the mesoporous silica previously prepared have been the popular choice of support because the synthetic procedure is simple and reproducible [12]. There are two methods for loading TiO_2 onto the mesoporous silica: (1) the direct synthetic method, in which titania precursor is added along with the other precursors necessary for the formation of the mesoporous silica and (2) post-synthetic modification in which titania precursor is grafted onto the inner pores and the surface of mesoporous silica. However, the first method had the problem that the titania precursor usually undergoes hydrolysis much faster than the silica precursor [12]. TiO_2-MCM-41 prepared by post-synthetic modification has well-defined small clusters of titania at the pore walls [13].

Dai et al. [14] studied photocatalytic degradation of 2,4,6-trichlorophenol using TiO_2 supported on HMS. They found that the photocatalytic activity of TiO_2–HMS was much higher than that of TiO_2 powders and that of TiO_2 on zeolite Y. The hydrophilic surface of TiO_2-MCM-41was reported to facilitate the degradation of hydrophilic pollutant [15]. Therefore, it is necessary to improve the adsorptive properties of hydrophobic compounds such as PCP on hydrophilic surface. Yamashita et al. [16] prepared hydrophobic HMS containing TiO_2 modified by fluoride. In this study, we prepared TiO_2 supported on mesoporous silica (TiO_2-MCM-41) and fluoride-modified TiO_2-MCM-41 by post-synthetic modification and investigated the degradation of hydrophobic pollutant PCP using prepared photocatalysts.

2. Experimental

2.1. Chemicals

PCP, *p*-chlorophenol and phenol were selected as model organic compounds in this study and supplied from Wako Pure Chemical Industries (Osaka, Japan). For the preparations of mesoporous silica and titania, tetraethyl orthosilicate (TEOS) and titanium(VI) isopropoxide were used, respectively, and purchased from Wako Pure Chemical Industries Hexadecyltrimethylammonium bromide (C_{16}TMABr) from Tokyo Chemical Industry (Tokyo, Japan) was used as a template surfactant. The other chemicals were obtained from Wako Pure Chemical Industries and used as received.

2.2. Preparation of mesoporous silica

Mesoporous silica was prepared by the template method [17]. C_{16}TMABr (0.875g) was dissolved in 46.8 g of water and the pH was adjusted to 12.1 by adding aqueous ammonia. The mixture was stirred vigorously until it became clear. Next, TEOS (4.17 g) was added to the solution and the mixture was stirred for 24 h. For the pore-size expansion, mesitylene was initially mixed with C_{16}TMABr in mesitylene/C_{16}TMABr with a mole ratio of 2.0. Furthermore, to obtain more hydrophobic surface, tetraethylammonium fluoride dihydrate (0.25–1.0 g) was also initially mixed with C_{16}TMABr. The thick, white precipitates obtained were filtered, washed with distilled water and dried at 60°C for 24 h. Then, they were calcined at 540°C in an electric furnace to remove the surfactant. Nitrogen gas adsorption–desorption measurements of the products (MCM-41, MCM-41(F0.25), MCM-41(F0.5) and MCM-41(F1.0)) were performed with an ASAP 2010 (Micromeritics). The Brunauer–Emmett–Teller (BET) model was employed to determine surface area and the method of Barrett–Joyner–Halenda was employed for evaluating the pore-size distribution.

2.3. Preparation of titania supported on mesoporous silica

Titanium(VI) isopropoxide (3.7 mL) and 1 mol/L nitric acid aqueous solution (15 mL) were mixed and stirred for 2 h. To adjust the pH of the solution to 3, sodium hydroxide solution (1 mol/L) was added dropwise to the solution. Mesoporous silica was added to the solution, and the mixture was stirred for 1 h. After that products were dried under vacuum and calcined at 600°C for 5 h. Photocatalysts of 51 wt% g-TiO_2/g-catalyst were prepared. The absence of rutile phase on calcinations at high temperature (>700°C) is known because the presence of silica support inhibits phase transformation from anatase to rutile by preventing the sintering of the titania particles [12].

2.4. Adsorption of phenols on mesoporous silica

Adsorption tests were conducted on various phenols (phenol, *p*-chlorophenol and PCP) dissolved in distilled water. The adsorption isotherms were measured to evaluate the maximum adsorption capacity of adsorbent (mesoporous silica) and adsorption constant. This was done by shaking and mixing 100 mg of adsorbents in 10 mL of the test solution containing 20–200 ppm of individual phenols at 100 rpm over 24 h. After attaining equilibrium, the mixtures were filtered to separate the solid adsorbent. The initial and residual concentrations of phenols in the filtrate were measured using UV–vis spectrophotometry (UV-2500PC, Shimadzu, Japan). UV detection was performed at 269, 278 and 249 nm for phenol, *p*-chlorophenol and PCP, respectively.

The amount of adsorbed phenols was calculated from the difference in the concentration of phenols between the initial solution and the filtrate, and the dry weight of the adsorbent. The amount of phenols adsorbed in the adsorbent (q_e (μmol/g--adsorbent)) was calculated using the following equation:

$$q_e = \frac{C_i - C_e}{M} \times V \tag{1}$$

where C_i and C_e are the phenol concentrations (μM) before and after adsorption, respectively, V is the volume of the test solution (L) and M is the dry mass of the adsorbent (g).

2.5. Photocatalytic degradation of phenols

Sodium pentachlorophenolate (20 ppm, 10 mL) aqueous solution was prepared in a vial tube with Mininert® *valves*. Titania supported on mesoporous silica (TiO_2 concentration = 1.0 g/L) was added to the solution and a mixture was stirred for 24 h to reach adsorption equilibrium. After that, the valve was opened and the head space of the vial tube was filled with fresh air. Just before the valve was closed again and the light was turned on, both liquid and head space gas samples were taken in order to determine the initial concentrations of phenols in the solution and the CO_2 in the air. A low-pressure mercury lamp emitted UV light at a wavelength of 254 nm with an intensity of 300 mW/cm^2. The head space sample in the vial tube was taken at specific time intervals for analysis. Concentration of CO_2 in the head space sample was monitored by gas chromatography (GC14B with TCD, Shimadzu, Japan).

All experiments were duplicated and reproducible within 15%.

3. Results and discussion

3.1. Preparation of mesoporous silica containing TiO_2

Table 1 shows the mean pore diameters and BET surface area in mesoporous silica (MCM-41) and TiO_2 supported on mesoporous silica (TiO_2-MCM-41) in the absence and presence of mesitylene. Mesitylene is added as a pore-swelling agent in the preparation of the mesoporous silica [17] to relieve the intraparticle diffusion limitation. The total surface area of the supported catalysts was found to decrease with TiO_2 loading as reported previously [15], suggesting that the pores were partially blocked by the TiO_2 particle. The effect of mesitylene on pore-size expansion of TiO_2-MCM-41 was relatively small probably due to the two calcinations in the preparations of mesoporous silica and mesoporous silica-supported TiO_2. The mean pore diameters and BET surface areas of fluoride-modified TiO_2-MCM-41 catalysts were determined as shown in Table 1. The surface area decreased with an increase in the content of fluorine, as those of TiO_2 supported on HMS reported by Yamashita et al. [16]. Excessive fluoride-modification leads to the deterioration of mesopores, resulting in decreases in mean pore diameters and surface area [18].

Table 1
Mean pore diameters and BET surface area in mesoporous silica (MCM-41) and TiO_2 supported on mesoporous silica (TiO_2-MCM-41)

Mesoporous silica	Pore diameter (nm)	BET surface area (m^2/g)
MCM-41	3.31	943.0
MCM-41 (TMB/C_{16}TMABr = 0.5)	3.34	905.1
MCM-41 (TMB/C_{16}TMABr = 1.0)	3.36	873.6
MCM-41 (TMB/C_{16}TMABr = 2.0)	3.93	874.9
MCM-41 (TMB/C_{16}TMABr = 3.0)	5.24	659.9
TiO_2-MCM-41	3.34	690.1
TiO_2-MCM-41 (TMB/C_{16}TMABr = 0.5)	3.32	697.4
TiO_2-MCM-41 (TMB/C_{16}TMABr = 1.0)	3.38	649.3
TiO_2-MCM-41 (TMB/C_{16}TMABr = 2.0)	3.96	639.6
TiO_2-MCM-41(F0.25)	3.02	679.8
TiO_2-MCM-41(F0.50)	3.02	622.5
TiO_2-MCM-41(F0.1)	2.95	600.3

Note: TMB denotes mesitylene.

3.2. Adsorption of phenols on mesoporous silica containing TiO_2

Aqueous organic pollutants adsorb on the catalysts, and then the photocatalytic reaction proceeds with the UV irradiation. First, we examined the adsorption properties on the MCM-41 prepared. Fig. 1 shows the adsorption isotherms of phenols on MCM-41. Evidently, the adsorption ability on MCM-41 strongly depends on the hydrophobicity of phenols. Most hydrophobic PCP was easily adsorbed and most hydrophilic phenol was not adsorbed at all. This was inconsistent with the previous result that the TiO_2-MCM-41 depressed the degradation of hydrophobic pollutant [15]. There is a difference in the preparation methods of MCM-41. In the previous paper [15], MCM-41 was synthesized without calcinations. Because free hydroxyl groups of the surfaces were removed at calcination temperature above 450°C [19], the surfaces of MCM-41 prepared in the present study became more hydrophobic. This may cause the high PCP adsorption.

From Fig. 1, adsorption isotherms of PCP and *p*-chlorophenol approximately obey the Langmuir equation, and Table 2 lists parameters, maximum adsorption capacity (q_m) and adsorption constant (K) calculated. We also

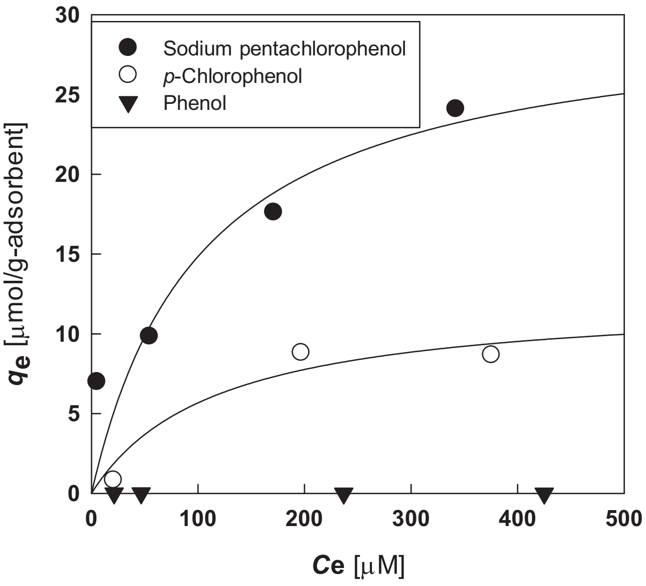

Fig. 1. Adsorption isotherm of phenols on mesoporous silica. Solid lines were calculated by Langmuir equation.

examined the adsorption isotherms of PCP on TiO_2-MCM-41 and fluoride-modified TiO_2-MCM-41. As expected, both values of q_m and K of PCP increased with an increase in fluoride content. On the other hand, addition of mesitylene had no significant impact on the adsorption characteristics. Values of q_m on TiO_2-MCM-41 are halved compared than that of MCM-41. This is because phenols adsorbed not titania but silica and TiO_2-MCM-41 contains the 51 wt% TiO_2.

3.3. Degradation of PCP on mesoporous silica containing TiO_2

Fig. 2 shows the time courses of CO_2 production by photocatalytic degradation of PCP. The stoichiometric production of CO_2 for a complete degradation of 20 ppm of PCP is 4.5 μmol. The degradation rate of PCP with TiO_2-MCM-41 was much faster than that of TiO_2 particles, probably due to a decrease in effective surface area because of aggregation of TiO_2 particles. Production of CO_2 was found to be approximately proportional to the reaction time during the initial period and then the rate was gradually decreased. Wu and Chern [20] studied the kinetics of photocatalytic decomposition of methylene blue. According to their discussion, the decomposition rate of PCP, $-r_{PCP}$, and production rate of CO_2, r_{CO2}, were apparently expressed as the following equation of the Langmuir–Hinshelwood type:

$$r_{CO_2} = -6r_{PCP} = \frac{6k_a\left[PCP\right]}{1+k_b\{PCP]} = \frac{k_a'(4.5-[CO_2\})}{1+k_b'(4.5-[CO_2\})} \qquad (2)$$

where k_a, k_a', k_b and k_b' are lumped parameters. In Fig. 2, solid lines were calculated based on Eq. (2), and calculated lines were well explained in experimental results. Table 3 lists values of the apparent kinetic constants, k_a' and k_b', obtained from the integrated form of Eq. (2) by the nonlinear regression method included in SigmaPlot. Table 3 also shows no effect of mesitylene on photodegradation of PCP with TiO_2-MCM-41.

As expected from the results of adsorption abilities, degradation rates of phenol and *p*-chlorophenol were much lower than that of PCP, and rates with fluoride-modified TiO_2-MCM-41 increased with an increase in fluoride content. Fig. 3 shows the relationship between the apparent kinetic constant k_a' and adsorption constant K for fluoride-modified

Table 2
Adsorption parameters, maximum adsorption capacity q_m and adsorption constants K, of phenols

Mesoporous silica	Phenols	q_m (μmol/g-sorbent)	K (L/μmol)
MCM-41	Phenol	0	0
MCM-41	*p*-Chlorophenol	12.3	85.6
MCM-41	PCP	30.4	96.3
TiO_2-MCM-41	PCP	16.0	64.5
TiO_2-MCM-41 (TMB/C_{16}TMABr = 2.0)	PCP	15.3	70.3
TiO_2-MCM-41(F0.5)	PCP	16.5	70.4
TiO_2-MCM-41(F1.0)	PCP	18.0	74.1

Table 3
Apparent kinetic constants for photocatalytic degradation of phenols

Photocatalysts	Phenols	k_a'	k_b'
TiO_2	PCP	7.09×10^{-4}	≈0
TiO_2-MCM-41	PCP	1.37×10^{-2}	9.09×10^{-2}
TiO_2-MCM-41 (TMB/C_{16}TMABr = 2.0)	PCP	8.13×10^{-3}	≈0
TiO_2-MCM-41	Phenol	1.18×10^{-4}	≈0
TiO_2-MCM-41	*p*-Chlorophenol	1.19×10^{-3}	2.62×10^{-2}
TiO_2-MCM-41(F0.5)	PCP	1.53×10^{-2}	≈0
TiO_2-MCM-41(F1.0)	PCP	1.64×10^{-2}	≈0

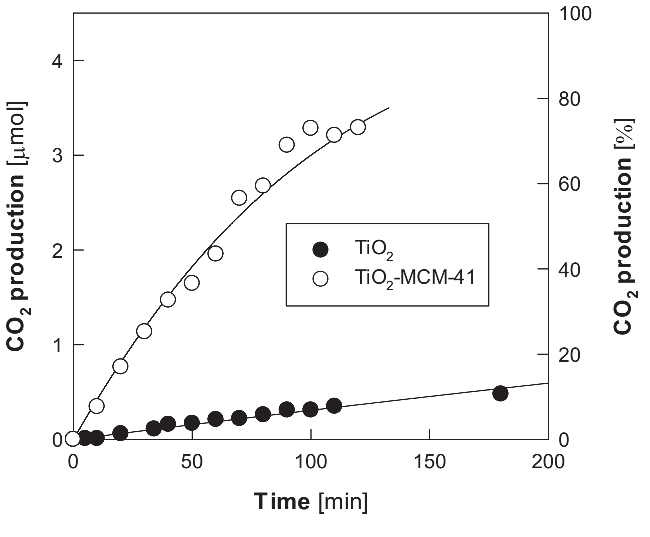

Fig. 2. Time courses of CO_2 production by photocatalytic degradation. Solid lines were calculated based on Eq. (2). Initial concentrations of phenols were 20 ppm.

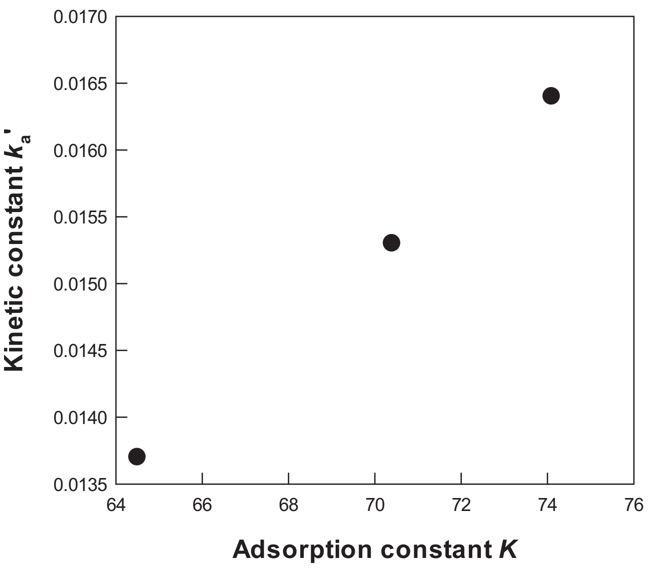

Fig. 3. Relationship between kinetic constant k_a' and adsorption equilibrium constant K.

TiO_2-MCM-41. This linear relationship suggests that the degradation process controlled the adsorption step of PCP.

4. Conclusion

In this paper, we prepared TiO_2-MCM-41 and fluoride-modified TiO_2-MCM-41 calcinated by post-synthetic modification and investigated the degradation of hydrophobic pollutant PCP using prepared photocatalysts. First, we examined the adsorption ability of phenols. The adsorption ability on calcinated MCM-41 strongly depends on the hydrophobicity of phenols. Most hydrophobic PCP was easily adsorbed, and most hydrophilic phenol was not adsorbed at all. The adsorption ability of PCP increased with an increase in fluoride content in MCM-41. On the other hand, the addition of mesitylene as a pore-expanding agent had no significant effect on the adsorption.

The photocatalytic degradation rate of PCP with TiO_2-MCM-41 was much faster than those of PCP/TiO_2, phenol/TiO_2-MCM-41 and *p*-chlorophenol/TiO_2-MCM-41. This behavior was caused by the difference in adsorption ability of pollutants on photocatalysts. By using fluoride-modified TiO_2-MCM-41 as a more hydrophobic photocatalyst, degradation rates of PCP further increased. It was found that the degradation rate apparently obeyed the Langmuir–Hinshelwood equation and was controlled by the adsorption step of PCP on the photocatalysts.

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