

## Photodecomposition of 4-Chlorophenol Catalyzed by Titanium Silicalite-2

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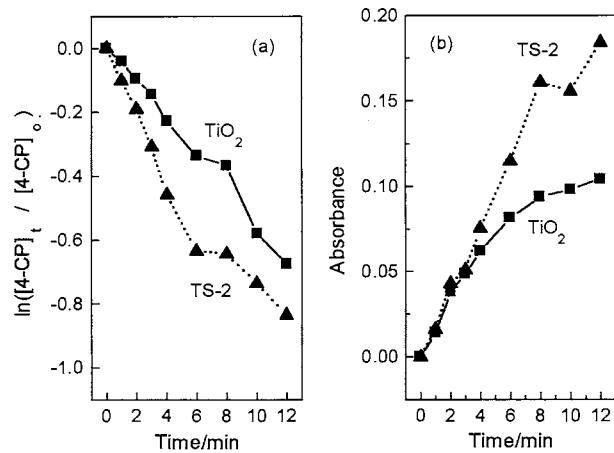
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The photodegradation reaction rate of 4-chlorophenol (4-CP) with a titanium silicalite-2 (TS-2) catalyst is found to be faster in the initial stage than with  $\text{TiO}_2$ . This is primarily due to the stronger adsorption of 4-CP on the hydrophobic surface of the TS-2 catalyst. The hydrophobicity is evaluated by determining the distribution coefficients (D) between TS-2 and aqueous medium using a variety of aromatic hydrocarbons. The larger the D, the faster the initial reaction rate. The D correlates with solubility in water and partition coefficient,  $\log P_{\text{oct}}$ .

$\text{TiO}_2$  is one of the most efficient photocatalysts, but its large bandgap ( $E_g=3.2\text{ eV}$ ) reduces enormously the fraction of solar radiation that can be utilized. Recent studies<sup>1,2</sup> revealed that the photocatalytic activity toward the decomposition of phenol is improved with a mixed oxide of  $\text{TiO}_2/\text{SiO}_2$  relative to  $\text{TiO}_2$ . The enhancement of the decomposition is attributed to the presence of a Ti-O-Si phase at the  $\text{TiO}_2/\text{SiO}_2$  interface with the  $\text{SiO}_2$  providing better adsorption sites in the vicinity of the  $\text{TiO}_2$ . Furthermore, titanium silicates are reported to exhibit photocatalytic reactivities in the reduction of NO and aromatic pollutants with aqueous hydrogen peroxide.<sup>3-5</sup> The nature of the environment of the cavity in TS-2 regarding its reactivity as a catalyst, however, needs to be further investigated. This paper aims to elucidate the relation between the photodecomposition rate of 4-CP and its adsorptivity to the TS-2 catalyst, based on a comparative investigation using TS-2 and  $\text{TiO}_2$  (Degussa, P25). 4-CP is a common pollutant in industrial wastewater originating from the production of dyes, drugs, and fungicides.

TS-2 was crystallized by hydrolysis of tetraethylorthosilicate and tetrabutylorthotitanate using tetrabutylammonium hydroxide (TBAOH) as a template, followed by washing, drying, and calcining at 500 °C for 5 h.<sup>6</sup> The chemical composition of the TS-2 initial gel was 0.03  $\text{TiO}_2$  :  $\text{SiO}_2$  : 0.36 TBAOH : 20  $\text{H}_2\text{O}$ . The degradation of  $2.0 \times 10^{-4}$  M 4-CP was monitored by measuring absorption spectra of the irradiated solutions in the presence of 1 g/L catalyst using a Hewlett Packard 8453 diode array spectrophotometer. Irradiation was carried out through a quartz window with a 250 W xenon lamp (Iltec Co.) in the presence of air after the adsorption equilibrium was reached. After the irradiation, the powder catalysts were filtered at 3500 rpm with a Hanshin Medical HC-16A centrifuge. The BET surface areas of TS-2 and  $\text{TiO}_2$ , determined from  $\text{N}_2$  adsorption data at 77 K, were  $360 \text{ m}^2/\text{g}$  and  $56 \text{ m}^2/\text{g}$ , respectively.

Figure 1 compares the variation of the relative concentration of 4-CP versus the irradiation time in the initial stage of the photochemical reaction. Under dark condition, virtually no change in the concentration of 4-CP was detected. It shows that the decomposition of the reagent proceeds faster with TS-2 than with  $\text{TiO}_2$ . Despite the lower surface  $\text{TiO}_2$  concentration of about 20% and the larger bandgap<sup>6</sup> in the TS-2 catalyst relative to the  $\text{TiO}_2$  catalyst, the enhancement of the photodecomposition rate is remarkable. The larger photoreactivity can be attributed to the increased adsorption of 4-CP due to the more hydrophobic



**Figure 1.** (a) Relative concentration of 4-CP and (b) absorbance of HQ at 300 nm vs irradiation time with the powdered catalysts in  $2.0 \times 10^{-4}$  M 4-CP aqueous solution.

**Table 1.** Distribution coefficients (D), solubilities in water (g/100g) and the logarithm of partition coefficients in octanol/ $\text{H}_2\text{O}$  ( $\log P_{\text{oct}}$ ) of some aromatic hydrocarbons

Aromatic hydrocarbon	D	Solubility	$\log P_{\text{oct}}$
Hydroquinone	0	7	0.59
Salicylic acid	0.04	0.2	2.26
Phenol	0.13	6.7	1.46
3,4-Dichlorophenol	0.31		
2,4-Dichlorophenol	0.39		
o-Cresol	0.42	3.1 <sup>a</sup>	1.95
2-Chlorophenol	0.52		2.15
3-Chlorophenol	0.60		2.50
m-Cresol	0.62	2.5 <sup>a</sup>	1.96
Aniline	0.62	3.5	0.90
p-Cresol	0.87	2.3 <sup>a</sup>	1.94
Benzylalcohol	0.98	0.08	1.10
4-Chlorophenol	1.08		2.39
2-Chlorobenzoquinone	1.21		
1,4-Benzoquinone	1.36		0.20
Benzoic acid	1.42	0.29	1.87
p-Toluidic acid	1.48	0.01	2.27
4-Chlorobenzoic acid	2.10	0.02	2.65

<sup>a</sup> at 40 °C.

environment of the TS-2 catalyst. It is found that more than half of 4-CP is adsorbed on TS-2, whereas less than 1% of 4-CP is adsorbed on  $\text{TiO}_2$ .

To understand the nature of the environment in the TS-2

catalyst, the distribution coefficients (D) of a variety of aromatic hydrocarbons between TS-2 and aqueous medium were measured by UV absorption spectroscopy using  $1.0 \times 10^{-4}$  M 4-CP and 1 g/L TS-2. Table 1 summarizes the results, listing the data on solubility in water (g/100g water)<sup>7</sup> and the logarithm of the partition coefficient,  $\log P_{\text{oct}}$ .<sup>8,9</sup>  $P_{\text{oct}}$  is the partition coefficient for octanol-water system. Upon examining the D values in Table 1, we find the following list of substituents arranged in the order of decreasing D : -COH > -Cl > -COOH > -CH<sub>3</sub> > -NH<sub>2</sub> > -H > -OH. Among isomers with a -OH group, the D values decreases in the order : para > meta > ortho.

The D values apparently correlate well with the available solubility. Since salicylic acid is a relatively strong acid, with  $pK_a = 2.97$ , more than 90% of the acid in  $1.0 \times 10^{-4}$  M solution exist as the deprotonated species. Assuming the deprotonated species have limited access to TS-2, the D of the protonated form is calculated to be about 0.52, which is consistent with the general trend. A similar relationship is obtained from Table 1 with  $\log P_{\text{oct}}$ . The deviations of aniline, benzyl alcohol, and benzoquinone (BQ) are noteworthy. Aniline appears to have a much lower  $\log P_{\text{oct}}$ , presumably because of forming an extra hydrogen bond. Benzyl alcohol apparently behaves like an aliphatic alcohol, which is more hydrophobic than an aromatic alcohol. It is surprising to find that BQ has a very low  $\log P_{\text{oct}}$ , since the result implies that ethylenic carbon is actually hydrophilic. BQ appears to behave differently, since its electronic structure is different from the other aromatics. With a few exceptions, it may be concluded the environment of the TS-2 cavity is indeed hydrophobic. That is, the higher the hydrophobicity of the solute, the larger the D.

To confirm the notion that the photocatalytic reactivity of TS-2 is linked to its hydrophobicity, a comparison of the reactivity was made with phenol, 2-CP, 4-CP, and p-chlorobenzoic acid (4-

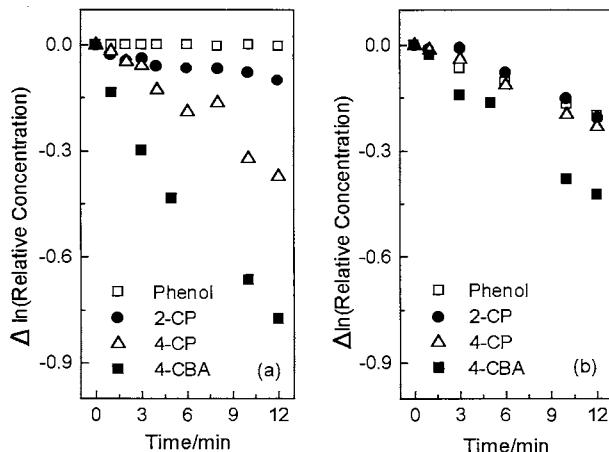
CBA) having the D values of 0.13, 0.52, 1.08, and 2.10, respectively. The differences in the relative concentration of the aromatics in the presence of TS-2 with respect to those in the absence of the respective catalysts are plotted in Figure 2(a). The result indeed demonstrates that the larger the D, the faster the initial reaction rate. That is, an aromatic hydrocarbon having a stronger adsorption on TS-2, decays faster. A similar data with TiO<sub>2</sub> is plotted in Figure 2(b). The results from Figure 2(a) and Figure 2(b) reveal that the larger the D, the larger the difference in the initial reaction rate on TS-2 and that on TiO<sub>2</sub>.

It is interesting to find that the D of hydroquinone (HQ) is nearly zero, with BQ having a relatively large D. In the initial stage of the reaction, BQ and HQ are spectroscopically identified to be two major photodecomposition intermediate of 4-CP.<sup>10</sup> The rates of appearance of HQ shown in Figure 1(b), support the result in Figure 1(a). The amounts of the produced HQ at 10 min are calculated to be  $8.8 \times 10^{-5}$  M and  $5.9 \times 10^{-5}$  M, respectively, using  $1700 \text{ M}^{-1} \text{ cm}^{-1}$  as the molar absorptivity of HQ at 300 nm. The non-accessibility of HQ to TS-2 implies that HQ is excluded from TS-2 upon formation, which subsequently increases the decomposition of 4-CP in accordance with Le Châtelier's principle. This is consistent with the faster rate of decomposition for 4-CP with the TS-2 catalyst in Figure 1(a). After irradiation for 2 h, no characteristic peaks were observed suggesting that the species containing aromatic rings are absent. It appears desirable to develop catalysts having larger D values for the photodegradation of aqueous aromatic pollutants than that used in this study.

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**Figure 2.** Relative concentrations of aromatics with (a) TS-2 and (b) TiO<sub>2</sub> corrected for photodegradation in the absence of the respective catalysts vs illumination time. Initial concentration of the aromatics :  $2.0 \times 10^{-4}$  M.