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### 1. Introduction

Chlorinated aromatic compounds are organic waste products which are harmful to the human body, and are generally treated by incineration or biodegradation. Since these methods aim to mineralize the chlorinated aromatic compounds, a large amount of carbon dioxide  $(CO_2)$  is produced. In addition, it is not possible to recover and re-use the aromatic rings of the original chlorinated aromatic compounds by using these methods. Therefore, the recovery of aromatics by dechlorination of chlorinated aromatic compounds is one of the most promising methods for the treatment of chlorinated compounds from the viewpoints of the environment and chemical resources. Previous studies have shown that the effective removal of chloride ions from the reaction system is one of the key processes to enable the quantitative recovery of aromatics from chlorinated aromatic compounds.<sup>1-5</sup> In photocatalytic reactions, strong and selective electron injection into chlorinated aromatic compounds is also important to achieve efficient dechlorination.5-14

### Photocatalytic reductive dechlorination of chlorobenzene in alkali-free aqueous alcoholic suspensions of palladium-loaded titanium(IV) oxide particles in the absence or presence of oxygen

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Photocatalytic reductive dechlorination of chlorobenzene in aqueous 2-propanol suspensions of palladium-loaded titanium(IV) oxide (Pd–TiO<sub>2</sub>) particles was examined in a wide range of aerated and deaerated solutions with different water and NaOH contents. In water-free 2-propanol, the presence of dissolved NaOH and removal of oxygen (O<sub>2</sub>) were critical for the dechlorination of chlorobenzene at a sufficient reaction rate and a redox balance (stoichiometry with the oxidation of 2-propanol) close to unity. In 50 vol% water–2-propanol solvent, the yield of benzene under aerated conditions was the same as that under deaerated conditions and was very close to the yield of acetone under aerated conditions, indicating that photogenerated electrons were selectively used for the reduction of chlorobenzene in the water–2-propanol solvent even in the presence of O<sub>2</sub>. The low solubility of O<sub>2</sub> in the water–2-propanol solvent, NaOH was unnecessary when the reaction was performed under deaerated conditions, suggesting that water played a role in removing chloride ions from the reaction site (surface of TiO<sub>2</sub>) and in suppressing the consumption of chloride ions by another side-reaction even in the absence of NaOH. Under ideal conditions, *i.e.*, reaction in the absence of NaOH under aerated conditions, benzene was obtained in a 71% yield and a high material balance of benzene and chlorobenzene was recovered.

Based on the above considerations, we have examined the photocatalytic reductive dechlorination of chlorobenzene in a 2-propanol suspension of metal-loaded titanium(IV) oxide (TiO<sub>2</sub>) nanocrystals in the presence of dissolved NaOH and reported that benzene and chloride ions (as insoluble NaCl) were recovered quantitatively when palladium (Pd)-loaded TiO<sub>2</sub> nanocrystals were used as the photocatalyst.<sup>15,16</sup> The reaction is described in eqn (1).

$$PhCl + (CH_3)_2CHOH + NaOH \rightarrow PhH + (CH_3)_2CO + NaCl \downarrow + H_2O$$
(1)

In terms of its practical applications, photocatalytic dechlorination of chlorobenzene would be more attractive if the reaction could be applied to high concentration solutions. However, high concentration solutions, such as 0.2 mol dm<sup>-3</sup>, cannot be used because it is difficult to increase the NaOH concentration to 0.2 mol dm<sup>-3</sup> due to the limited solubility of NaOH in 2-propanol. One simple and plausible method to increase the solubility of NaOH is to add water to 2-propanol. In our previous paper, we reported that the addition of a small amount of water (1–5 vol%) to 2-propanol caused a drastic decrease in the reaction rate and yield of benzene.<sup>16</sup> It seems that addition of water to 2-propanol has both positive and

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negative effects on the photocatalytic dechlorination of chlorobenzene to benzene. In this study, we examined the photocatalytic dechlorination of chlorobenzene in aqueous alcoholic suspensions of Pd–TiO<sub>2</sub> particles with a wide range of water contents and compared the results with those obtained under water-free conditions. Here we report that the reaction rate and benzene yield were improved in aqueous alcoholic suspensions in the range 40–80 vol% water and that the photocatalytic dechlorination of chlorobenzene to benzene occurred even in the presence of oxygen (O<sub>2</sub>) and in the absence of NaOH in the 50 vol% water–2-propanol solvent.

#### 2. Experimental

All of the reagents were commercial materials of reagent grade and were used without further purification. Nanocrystalline TiO<sub>2</sub> powder was prepared at 573 K using the HyCOM method.<sup>17</sup> Titanium(IV) butoxide was used as the starting material and the product was calcined at 823 K. The HyCOM-TiO<sub>2</sub> powder (148.5 mg) was suspended in an 80 vol% aqueous solution of acetic acid containing palladium(II) acetate in a test tube. The test tube was sealed with a rubber septum under Ar and then photoirradiated at a wavelength,  $\lambda > 300$  nm using a 400 W high-pressure mercury arc (Eiko-sha, Osaka, Japan) with continuous magnetic stirring in a water bath kept at 298 K. The Pd source was reduced by photogenerated electrons and Pd metal was deposited on the HyCOM-TiO<sub>2</sub> particles, resulting in the formation of Pd-loaded HyCOM-TiO<sub>2</sub> (Pd- $TiO_2$ ). The resultant powder was washed with acetone and distilled water and then dried at 310 K overnight under air. The content of Pd was fixed at 1.0 wt% in this study.

Photocatalytic dechlorination of chlorobenzene in waterfree 2-propanol under deaerated conditions was carried out according to the method previously reported:15,16 Pd-loaded TiO<sub>2</sub> powder (50 mg) was suspended in 2-propanol (5 cm<sup>3</sup>) containing NaOH in a test tube. After the mixture had been bubbled with argon and sealed with a rubber septum, chlorobenzene (98 µmol) was injected into the mixture. The test tube was photoirradiated in the same way as for photodeposition. During photoirradiation, the test tube was placed in a water bath kept at 298 K to avoid thermal reactions. Water-2-propanol solvents having various water contents (shown in vol%) were used to examine the effect of the water content, and dechlorination of a high concentration of chlorobenzene (0.2 mol dm<sup>-3</sup>, 980 µmol in 5 cm<sup>3</sup>) was performed using 50 vol% water-2-propanol solvent. Photocatalytic reactions in air and O2 were also examined to determine the effect of O<sub>2</sub> on the reaction. The effect of the amount of NaOH on the photocatalytic dechlorination was also examined by reducing the amount of NaOH from 200  $\mu$ mol to 0  $\mu$ mol. The amount of hydrogen (H<sub>2</sub>) in the gas phase was measured using a Shimadzu GC-8A gas chromatograph equipped with an MS-5A column. The amounts of benzene and chlorobenzene in the liquid phase were determined with a Shimadzu GC-14B gas chromatograph equipped with a DB-1

capillary column (30 m × 0.25 mm). The amount of acetone in the liquid phase was determined with a Shimadzu GC-14A gas chromatograph equipped with a fused silica capillary column (HiCap-CBP20, 25 m × 0.22 mm). Toluene was used as an internal standard sample, and the amounts of benzene, chlorobenzene and acetone were determined using the ratios of the peak areas of benzene, chlorobenzene and acetone to the peak area of toluene. The reaction solution (1 cm<sup>3</sup>) was added to a diethyl ether–water mixture (2 : 1 v/v, 3 cm<sup>3</sup>). After the mixture had been stirred for 10 min, the amounts of benzene, chlorobenzene and acetone in the ether phase were analyzed. The amount of chloride ions in the liquid phase was determined with a Jasco PU-2800 plus ion chromatograph (IC) equipped with an ICNI-424 column (Shodex, Japan).

#### 3. Results and discussion

# 3.1 Effect of water content on the dechlorination of chlorobenzene in the presence of NaOH under deaerated conditions

In our previous study, the effect of adding water in the photocatalytic dechlorination of chlorobenzene to benzene was investigated in the range up to 5.0 vol%.<sup>16</sup> In this study, the water content was changed over a wide range (0-100 vol%) and the effects on photocatalytic dechlorination (98 µmol) in the presence of NaOH (200 µmol) under argon are shown in Fig. 1. Chlorobenzene was almost completely dechlorinated to benzene with a high stoichiometry in water-free 2-propanol after photoirradiation for 15 min. The yield of benzene drastically decreased in the presence of a small amount of water and most of the chlorobenzene was recovered with 3.0 and 5.0 vol% of water. The negative effect of water on the photocatalytic dechlorination of chlorobenzene in the range up to 5.0 vol% water was reconfirmed in this study. We noted that the conversion of chlorobenzene and the yield of benzene increased with a high mass balance when the content of water was further increased. Finally, the benzene yield reached 99% at 40 vol% water content and most of the chlorobenzene was dechlorinated to benzene with up to 90 vol% water content. Since water that has dissolved in 2-propanol would have various effects on the solubility and adsorption behavior of the



**Fig. 1** Effect of water content on the photocatalytic dechlorination of chlorobenzene (98  $\mu$ mol) in water–2-propanol suspensions of Pd–TiO<sub>2</sub> in the presence of NaOH (200  $\mu$ mol) under argon for 15 min.

starting compounds and products, there are various possible reasons for the unusual water content dependency of the photocatalytic dechlorination of chlorobenzene. The addition of a small amount of water to 2-propanol might disturb the solidification (removal) of chloride ions as NaCl by sodium ions; however, the diffusion of chloride ions in the solvent (2propanol with a small amount of water) might be inhibited due to the low solubility of NaCl in the solvent, resulting in condensation of chloride ions on the hydrophilic surface of TiO<sub>2</sub> particles and a drastic decrease in reactivity. The solubility of NaCl sufficiently increased with the increase in water content, enabling Cl ions to diffuse in the solvents and minimize the negative effects of chloride ions on the dechlorination of chlorobenzene. Reaction in water again resulted in a low yield of benzene due to the poor solubility of chlorobenzene in water.

### 3.2 Photocatalytic dechlorination of chlorobenzene in 50 vol% water-2-propanol solvent under deaerated conditions

Since the photocatalytic dechlorination of chlorobenzene sufficiently occurred in the 50 vol% water-2-propanol solvent in the presence of NaOH, reactions in this solvent under various conditions were investigated. Table 1 shows the effects of UV light and the Pd/TiO2 photocatalyst on the dechlorination of chlorobenzene in the solvent under argon. Benzene was quantitatively obtained after 15 min irradiation when the reaction was carried out in the presence of a Pd/TiO<sub>2</sub> photocatalyst under UV irradiation (condition 1) as shown in section 3.1. No reaction occurred when the reaction system was irradiated in the absence of a Pd/TiO2 photocatalyst (condition 2), indicating that the photochemical dechlorination of chlorobenzene did not occur in the solvent. Benzene was not formed in an aqueous alcoholic solution of chlorobenzene and NaOH in the dark at room temperature (condition 3), indicating that thermochemical dechlorination of chlorobenzene by NaOH did not occur. In the fourth condition in a suspension of Pd/TiO<sub>2</sub> in the dark at room temperature, no benzene was detected, as in the cases of conditions 2 and 3. This result indicates that no thermocatalytic dechlorination of chlorobenzene occurred over Pd/ TiO<sub>2</sub> at room temperature. These results obtained in the 50 vol% water-2-propanol solvent under the four conditions show that Pd/TiO<sub>2</sub> and UV light are essential for the dechlorination of chlorobenzene, i.e., dechlorination of chlorobenzene occurs photocatalytically.

Since the amount of NaOH which can be dissolved in waterfree 2-propanol is limited, the amount of chlorobenzene to be dechlorinated is also limited because dechlorination of

Table 1 Results of photocatalytic dechlorination of chlorobenzene (98  $\mu mol)$  and blank reactions in 50 vol% water–2-propanol solvent in the presence of NaOH (200  $\mu mol)$  under argon for 15 min

Condition	UV light	1.0 wt% Pd-TiO <sub>2</sub> /mg	C <sub>6</sub> H <sub>5</sub> Cl/µmol	C <sub>6</sub> H <sub>6</sub> /µmol
1	on	50	<1	98
2	on	0	97	0
3	off (dark)	0	96	0
4	off (dark)	50	95	0



**Fig. 2** Time course diagrams for the photocatalytic dechlorination of chlorobenzene ((a) 98  $\mu$ mol and (b) 930  $\mu$ mol) in 50 vol% water–2-propanol solvent in the presence of Pd–TiO<sub>2</sub> and dissolved NaOH (200  $\mu$ mol and 930  $\mu$ mol, respectively) under argon.

chlorobenzene consumes an equivalent amount of NaOH, as shown in eqn (1). This means that photocatalytic dechlorination cannot be applied to high concentration chlorobenzene solutions. The increase of water content in 2-propanol improves the solubility of NaOH, and the amount of chlorobenzene can be increased in the water-2-propanol solvent system. Therefore, the photocatalytic dechlorination of larger amounts of chlorobenzene in 50 vol% water-2propanol solvent was examined. Fig. 2 shows time course diagrams for the photocatalytic dechlorination of 98 and 930 µmol chlorobenzene in 50 vol% water-2-propanol solvent in the presence of Pd/TiO<sub>2</sub> and NaOH under UV irradiation. In contrast to the results for the water-free system, chloride ions were observed in the liquid phase in the 50 vol% water-2propanol solvent. When 98 µmol of chlorobenzene was used, the chlorobenzene was almost completely consumed and benzene was obtained in a 97% yield within a short time (15 min) as shown in Fig. 2(a). After consumption of chlorobenzene,  $H_2$  was formed as a product of proton reduction (2H<sup>+</sup> +  $2e^- \rightarrow H_2$ ). This reaction can be expressed as the dehydrogenation of 2-propanol (eqn (2)).

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2$$
 (2)

2-Propanol was oxidized and acetone was formed in both reactions. As shown in Fig. 2(a), switching between the reduction processes (chlorobenzene dechlorination and  $H_2$  formation) was very quick. To understand the reaction in detail, the redox balance (ROB), *i.e.*, the ratio of the amount of

consumed photogenerated electrons to that of consumed holes, was defined as shown in eqn (3):

$$ROB = [n(benzene) + n(H_2)]/n(acetone)$$
(3)

where n(benzene),  $n(\text{H}_2)$  and n(acetone) are the yields of benzene, H<sub>2</sub> and acetone, respectively. The value of ROB at 15 min was determined to be 1.13. After 60 min reaction time, the value of ROB decreased to 1.0, although a large amount of H<sub>2</sub> was formed. The value of ROB close to unity indicates that both of the photocatalytic redox reactions, *i.e.*, dechlorination of chlorobenzene and formation of H<sub>2</sub>, occurred in a high stoichiometry without side reactions and formation of byproducts.

Fig. 2(b) shows that the photocatalytic dechlorination of chlorobenzene also occurred when the amount of chlorobenzene zene was increased to 930  $\mu$ mol. The amount of chlorobenzene linearly decreased, while the yields of benzene, acetone and chloride ions linearly increased with photoirradiation. Overlapping of the three yields within the experimental errors indicates that stoichiometric dechlorination of chlorobenzene occurred even in the *ca.* ten-times concentrated conditions in the 50 vol% water–2-propanol solvent.

### 3.3 Effect of water content on the dechlorination of chlorobenzene in the presence of NaOH in air

When a photocatalytic reaction is applied for the reduction of a substrate, O<sub>2</sub> is generally removed from the reaction system because O2 always acts as a strong acceptor of photogenerated electrons and decreases the efficiency of photocatalytic reduction of the target. To counteract the negative effect of O2, photocatalytic reduction has been performed under vacuum or under inert gases such as nitrogen and argon. However, removal of O<sub>2</sub> by vacuuming or replacement with these gases requires great care and consumes large amounts of energy. Reactions under air, *i.e.*, reactions free from any additional operations, are most favorable from the viewpoint of practical applications. In this study, the photocatalytic dechlorination of chlorobenzene in water-2-propanol solvents with various water contents under air was examined and the results after 15-min photoirradiation are shown in Fig. 3. The yield of benzene in water-free 2-propanol (at 0 vol%) drastically



**Fig. 3** Effect of water content on the photocatalytic dechlorination of chlorobenzene (98  $\mu$ mol) in aqueous 2-propanol suspensions of Pd–TiO<sub>2</sub> in the presence of NaOH (200  $\mu$ mol) under air for 15 min.

decreased to 30% in contrast to the reaction under deaerated conditions (>99%), indicating that the reductions of chlorobenzene and O<sub>2</sub> by photogenerated electrons competed in the solvent as predicted. A large amount of acetone was formed (368  $\mu$ mol), resulting in a very small value of ROB (0.08). This means that the unwanted partial oxidation of 2-propanol to acetone was the predominant reaction in water-free 2-propanol under air as shown in eqn (4).

$$(CH_3)_2 CHOH + 1/2O_2 \rightarrow (CH_3)_2 CO + H_2O$$

$$(4)$$

We noted that the yield of benzene increased with increasing water content in the water–2-propanol solvents even under air and reached >99% in the 50 vol% water–2propanol solvent after photoirradiation for 15 min. The yield of benzene was the same as the yield obtained in the 50 vol% water–2-propanol solvent under deaerated conditions as shown in Fig. 1. Surprisingly, the yield of acetone was 106 µmol, very close to that of benzene, and a small amount of H<sub>2</sub> (8 µmol) also formed in the solvent under air. The value of ROB was determined to be 1.01. These results indicate that the photogenerated electrons were selectively used for the reduction of chlorobenzene (and only partly for H<sup>+</sup> reduction) in the 50 vol% water–2-propanol solvent even in the presence of O<sub>2</sub>. The selective and quantitative dechlorination of chlorobenzene to benzene under air continued until 70 vol% water.

To confirm the high selectivity for dechlorination of chlorobenzene in the 50 vol% water-2-propanol solvent even under air, reactions in water-free 2-propanol and in the 50 vol% water-2-propanol solvent under various partial pressures of O2 were examined, and the results are summarized in Table 2. The yield of benzene drastically decreased under air (in the presence of 20% O<sub>2</sub>) in water-free 2-propanol and no dechlorination of chlorobenzene occurred under 100% O2. On the other hand, the negative effect of the presence of  $20\% O_2$ on the dechlorination of chlorobenzene to benzene was negligible in the 50 vol% water-2-propanol solvent. Only a slight decrease in chlorobenzene conversion and benzene yield were observed under 100% O2. The results of these comparable experiments indicate that the negative effect of O2 on the photocatalytic dechlorination of chlorobenzene to benzene was greatly suppressed in the 50 vol% water-2-propanol solvent and that this reaction can be carried out even under air. The excellent non-sensitivity of the photocatalytic dechlorination towards O<sub>2</sub> in the 50 vol% water-2-propanol solvent is related to the solubility of O2 in the solvent. The solubility of a

**Table 2** Effect of O<sub>2</sub> on the photocatalytic dechlorination of chlorobenzene (98  $\mu$ mol) in suspensions of 1.0 wt% Pd–TiO<sub>2</sub> in the presence of dissolved NaOH (200  $\mu$ mol) under UV irradiation for 15 min

Solvent	$O_2/\%$	C <sub>6</sub> H <sub>6</sub> /µmol	C <sub>6</sub> H <sub>5</sub> Cl/µmol
2-propanol	0	98	<1
2-propanol	20	30	69
2-propanol	100	<1	97
50 vol% water-2-propanol	0	96	<1
50 vol% water-2-propanol	20	95	<1
50 vol% water-2-propanol	100	87	6

gas is expressed in terms of the Ostwald coefficient. The Ostwald coefficient (L) is defined as "the ratio of the volume of gas absorbed to the volume of the absorbing liquid". The L values of O2 in water and 2-propanol were reported to be 0.0347 and 0.246, respectively, at 293 K under standard pressure.<sup>18</sup> The mole fraction of 2-propanol  $(x_1)$  of the 50 vol% water-2-propanol solvent was 0.277. Since the L value of  $O_2$  in the water-2-propanol solvent with  $x_1 = 0.2985$  was reported to be 0.0917,<sup>18</sup> the L value of  $O_2$  in the 50 vol% water-2-propanol solvent should be smaller than 0.0917. Therefore, the low solubility of O<sub>2</sub> in water is attributable to the high selectivity of photocatalytic dechlorination in water-2-propanol solvents. Solubility of a gas in an aqueous electrolyte solution generally decreases due to the salting-out effect and it has been reported that the L value of  $O_2$  in an aqueous NaOH solution decreased with an increase in the concentration of NaOH,<sup>19</sup> suggesting that the L value of  $O_2$  in the 50 vol% water-2-propanol solvent in the presence of dissolved NaOH would be smaller than the L value in the absence of NaOH.

## 3.4 Effect of the amount of NaOH on the dechlorination of chlorobenzene under deaerated conditions

The effects of the amount of NaOH on the benzene yield in water-free 2-propanol were previously reported.<sup>15,16</sup> The results obtained in the reaction under argon for 30 min are shown in Fig. 4(a) and the features are briefly described for comparison with those obtained in the 50 vol% water-2-propanol solvent. Although dechlorination of chlorobenzene occurred in waterfree 2-propanol in the absence of NaOH, the yield of benzene was low. The benzene yield was improved by the maintenance of a high material balance by increasing the amount of NaOH up to ca. 100 µmol. The benzene yield was constant at higher concentrations of NaOH because almost 100% conversion of chlorobenzene had been achieved at ca. 100 µmol. From these results and the results of other additional experiments, it was concluded that the removal of chloride ions from the reaction system, *i.e.*, solidification of chloride ions, avoiding consumption of chloride by other reactions, is important for the effective recovery of benzene from chlorobenzene in water-free 2-propanol.<sup>15,16</sup> The effect of the amount of NaOH on the benzene yield in the 50 vol% water-2-propanol solvent was examined in this study, and the results obtained in the reactions under argon for 15 min are shown in Fig. 4(b). We found that dechlorination of chlorobenzene to benzene occurred in the 50 vol% water-2-propanol solvent only for 15 min even in the absence of NaOH, *i.e.*, the reaction yielded 92 µmol of benzene, which corresponds to a high conversion of chlorobenzene (94%) and almost complete selectivity (>99%). Since a small amount of  $H_2$  (7.2  $\mu mol)$  was formed, dehydrogenation of 2-propanol (eqn (2)) partly occurred. The value of ROB was determined to be 1.0 as shown in Fig. 4(b), indicating that only dehydrogenation of 2-propanol (eqn (2)) and dechlorination of chlorobenzene along with oxidation of 2-propanol to acetone occurred under these conditions. Therefore, most of the 2-propanol was consumed for the dechlorination of chlorobenzene and the reaction in the absence of NaOH is expressed as eqn (5).

$$PhCl + (CH_3)_2CHOH \rightarrow PhH + (CH_3)_2CO + HCl$$
 (5)



Fig. 4 Effect of the amount of dissolved NaOH on the photocatalytic dechlorination of chlorobenzene (98  $\mu$ mol) in (a) a 2-propanol suspension under argon for 30 min and (b) a 50 vol% water–2-propanol solvent under argon for 15 min. Photocatalyst: Pd–TiO<sub>2</sub>.

As discussed in section 3.1 (reactions in the presence of NaOH), the addition of water increased the solubility of the byproduct (NaCl), enabling Cl ions to diffuse in the solvents and minimize the negative effects of chloride ions on the dechlorination of chlorobenzene. The results obtained under the NaOH-free conditions support this explanation and also show that water played a role in removing chloride ions from the reaction site (surface of TiO<sub>2</sub>) even in the absence of NaOH and in suppressing the consumption of chloride ions by another side-reaction. Increasing the amount of NaOH added to the 50 vol% water-2-propanol solvent to 50 µmol, which was smaller than that required for the stoichiometric removal of chloride (98 µmol), resulted in an improved benzene yield (95 µmol), and almost quantitative conversion of chlorobenzene was achieved in the presence of 100 µmol of NaOH as well as in the reaction in water-free 2-propanol. As clearly shown by comparison of Fig. 4(a) and (b), a higher benzene yield was obtained in the 50 vol% water-2-propanol solvent. The use of the 50 vol% water-2-propanol solvent strongly contributes to "simple chemistry", i.e., reduction of the amounts of 2-propanol and NaOH. If the oxidized product (acetone) is regarded as a useful product, the atom efficiency of the reaction (eqn (5)) was calculated to be 79%. The value was larger than that of the reaction using NaOH (64%, eqn (1)).



**Fig. 5** Effect of the amount of dissolved NaOH on the photocatalytic dechlorination of chlorobenzene (98 µmol) in 50 vol% water–2-propanol solvent under air for 15 min. Photocatalyst: Pd–TiO<sub>2</sub>.

# 3.5 Effect of the amount of NaOH on the dechlorination of chlorobenzene in 50 vol% water-2-propanol solvent under air

It was found that dechlorination of chlorobenzene occurred 1) even under air in the 50 vol% water-2-propanol solvent in the presence of NaOH (section 3.3) and 2) even in the absence of NaOH under deaerated conditions (section 3.4). In this study, the effect of the amount of NaOH on the benzene yield in the 50 vol% water-2-propanol solvent under air was examined and the results obtained in 15 min reactions are shown in Fig. 5. Under ideal conditions, i.e., in the absence of NaOH, 70 µmol of benzene was formed, while 26 µmol of chlorobenzene was recovered. These results indicate that the material balance of benzene and chlorobenzene was preserved even in the absence of NaOH under air. The yield of acetone (106 µmol) was larger than that of benzene and the value of ROB decreased to 0.67, indicating that O<sub>2</sub> reduction resulting in the unwanted partial oxidation of 2-propanol to acetone (eqn (4)) partly occurred under the conditions. The ratio of eqn (1) and (4) under these conditions was calculated to be 2:1 from the values of ROB, indicating that dechlorination of chlorobenzene was predominant even under air in the absence of NaOH. In the presence of 50 µmol of NaOH, which was smaller than the amount (98 µmol) required for stoichiometric dechlorination shown in eqn (1), the yield of benzene increased to 90 µmol, while the yield of acetone was almost unchanged, resulting in an increase in the value of ROB (0.84). This result indicates that the rate of 2-propanol oxidation (hole trapping by 2-propanol) was almost independent of the presence of NaOH and that the rate of dechlorination of chlorobenzene increased, in other words, the rate of  $O_2$  reduction (electron scavenging by  $O_2$ ) was suppressed in the presence of a small amount of NaOH. As discussed in section 3.3, the *L* value of  $O_2$ in an aqueous NaOH solution decreased with increasing concentration of NaOH.<sup>19</sup> Reduced solubility of  $O_2$  in the 50 vol% water–2-propanol solvent in the presence of dissolved NaOH is attributed to the decrease in the rate of  $O_2$  reduction, *i.e.*, an increase in the value of ROB. When NaOH (100 µmol) was added to the solvent, only dechlorination of chlorobenzene occurred as stated in section 3.3, indicating that the reduction of  $O_2$  was almost completely suppressed.

#### Conclusions

We examined the photocatalytic dechlorination of chlorobenzene in aqueous 2-propanol suspensions of Pd-TiO<sub>2</sub> particles over a wide range of water and NaOH contents under deaerated and aerated conditions and compared the results with results previously obtained in water-free 2-propanol with dissolved NaOH under deaerated conditions. The representative results are summarized in Table 3. The addition of a small amount of water drastically decreased the yield of benzene in the presence of dissolved NaOH. However, the yield of benzene increased with high mass balance when the content of water was further increased. Finally, the benzene yield reached 95% at 40 vol% water content and most of the chlorobenzene was dechlorinated to benzene until the water content reached 90 vol%. The yield of benzene under aerated conditions was the same as the yield obtained in the 50 vol% water-2-propanol solvent under deaerated conditions, and the yield of acetone was very close to that of benzene. Dechlorination of chlorobenzene to benzene occurred in the 50 vol% water-2propanol solvent only for 15 min even in the absence of NaOH under deaerated conditions and a high conversion of chlorobenzene (94%) and almost complete selectivity (>99%) were obtained. Under ideal conditions, i.e., reaction in the absence of NaOH under aerated conditions, benzene was obtained in a 71% yield, with the material balance of benzene obtained and chlorobenzene recovered being preserved.

The present study revealed that the use of the water–2propanol solvent has various advantages for the photocatalytic dechlorination of chlorobenzene to benzene. 1) Since the solubility of NaOH increased in the water–2-propanol solvent,

<b>Tuble 9</b> Results of the photocatalytic accilionnation of emotobelizene (50 $\mu$ mol/m suspensions of 1.0 wt/or a mol/anaci valious conditions and er ov madia
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Solvent	NaOH/µmol	Atmosphere	Time/min	C <sub>6</sub> H <sub>5</sub> Cl/µmol	C <sub>6</sub> H <sub>6</sub> /µmol	ROB <sup>a</sup>
2-propanol	200	Ar	15	<1	98	1.1
2-propanol	200	air	15	69	30	0.082
2-propanol	0	Ar	30	67	28	$ND^b$
50 vol% water-2-propanol	100	Ar	15	<1	98	1.0
50 vol% water-2-propanol	100	air	15	<1	95	0.96
50 vol% water-2-propanol	0	Ar	15	5	92	1.0
50 vol% water-2-propanol	0	air	15	26	70	0.67

<sup>*a*</sup> Redox balance determined by eqn (3). <sup>*b*</sup> Not determined.

the amount of chlorobenzene dissolved in the solvent can also be increased. 2) Dechlorination of chlorobenzene occurred while maintaining a high material balance and excellent ROB balance even in the presence of  $O_2$  if a small amount of NaOH was present in the water–2-propanol solvent system. 3) Dechlorination of chlorobenzene without the use of NaOH was achieved if the reaction was performed under deaerated conditions. 4) Alkali-free dechlorination of chlorobenzene with maintenance of a high material balance of benzene and chlorobenzene was achieved even under air, although one third of the photogenerated electrons were scavenged by  $O_2$ .

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