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# Photocatalytic Reduction of Nitrobenzene to Aniline in an Aqueous Suspension of Titanium(IV) Oxide Particles in the Presence of Oxalic Acid as a Hole Scavenger and Promotive Effect of Dioxygen in the System

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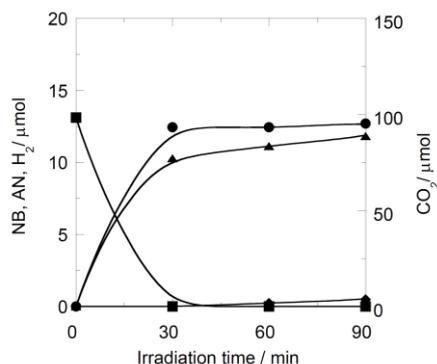
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Nitrobenzene was effectively and selectively reduced to aniline in an acidic aqueous suspension of titanium(IV) oxide photocatalyst in the presence of oxalic acid as a hole scavenger and the aniline yield was improved in the presence of a small amount of dioxygen.

One of the most promising applications of photocatalysis is mineralization (or degradation) of toxic organic compounds in air and water.<sup>1-3</sup> Since photocatalytic reaction satisfies several of the 15 proposed requirements for green chemistry,<sup>4</sup> organic synthesis of various compounds using photocatalysis has been studied by many researchers.<sup>2</sup> However, less attention has been paid to the photocatalytic reduction of organic compounds by photogenerated electrons ( $e^-$ ). Although  $e^-$  are potentially a useful reagent,  $e^-$  have been removed from the system using sacrificial electron acceptors such as silver ion and dioxygen ( $O_2$ ) in most photocatalysis studies. Photocatalytic reduction of organic acceptors such as nitroaromatics can be carried out in the presence of a large excess of an electron donor, such as methanol, and in the absence of  $O_2$ .<sup>5-8</sup> The purpose of the electron donor is to scavenge holes ( $h^+$ ), thereby reducing the degree of recombination within the particle. Removal of  $O_2$  from the system has been thought to improve reduction efficiency by removing this competitive electron scavenger. As far as we know, photocatalytic reductions have been carried out under deaerated conditions.

From the point of view of eco-friendly production of chemicals,<sup>4</sup> we should pay attention to the choice of solvent and sacrificial reagents. Methanol has been used as both a solvent and a sacrificial reagent for photocatalytic reduction of organic compounds such as nitrobenzene (NB). Since formaldehyde is formed as the oxidized species of methanol, a "greener" sacrificial reagent converting to a non-toxic compound is preferable. Oxalic acid (OA) is a "greener" sacrificial reagent because it is easily oxidized and converts into carbon dioxide ( $CO_2$ ), which is separated from the solvent under acidic conditions.<sup>9-11</sup> It is obvious that water ( $H_2O$ ) is the "greenest" among all solvents. Here we briefly describe the photocatalytic reduction of NB to aniline (AN) in an aqueous suspension of titanium(IV) oxide ( $TiO_2$ ) particles in the presence of OA as a hole scavenger and the improvement in yield of AN in the presence of a small amount of  $O_2$ .

Degussa P25  $TiO_2$  was used because it is known to be one of the most active photocatalysts. Bare  $TiO_2$  powder (50 mg) was suspended in an aqueous solution (5  $cm^3$ ) containing NB (13  $\mu mol$ ) and OA (100  $\mu mol$ ) in a test tube. Using a 3-



**Figure 1** Time courses of the amounts of NB (squares), AN (circles),  $H_2$  (diamonds) and  $CO_2$  (triangles) in photocatalytic reduction of NB in the presence of OA under 5%  $O_2$ -95%  $N_2$ .

mol  $L^{-1}$  HCl solution, pH of the suspension was adjusted to ca. 1. The tube was sealed with a rubber septum and then photoirradiated at a wavelength  $>300$  nm by a high-pressure mercury arc (400 W) under argon (Ar) or mixtures of dinitrogen ( $N_2$ ) and  $O_2$  with magnetic stirring at 298 K. The amounts of NB and product(s) were determined with a Shimadzu HPLC (ODS column). Quantitative analyses of the gas phase were performed using a Shimadzu GC-8A gas chromatograph equipped with Porapak QS ( $CO_2$ ) and MS-5A (dihydrogen ( $H_2$ ) and  $O_2$ ) columns. Blank reaction without  $TiO_2$  gave no product.

Figure 1 shows the time courses of yields of AN,  $H_2$  and  $CO_2$  in the photocatalytic reaction of the aqueous mixture of NB, OA and  $TiO_2$  powders under 5%  $O_2$ -95%  $N_2$ . After photoirradiation for 30 min, NB was almost completely consumed and AN was obtained in a high yield (95%), which was also identified by GC-MS [GC-17A, GCMS-QP5050 (Shimadzu); column = DB-1, 0.25 mm x 30 m (J&W), MS:  $m/z = 93$ ]. This result indicates that photocatalytic reduction of NB to AN occurred even in the presence of  $O_2$ . Reduction of NB to AN consists of several steps<sup>6</sup> (Eq. 1), and the probable stoichiometry of the reaction in the presence of OA is shown below (Eq. 2).



In this study, nitrosobenzene and hydroxylamine intermediates were not detected, indicating that the rates of reduction of these species might be larger than that of NB or that these species are strongly adsorbed on the surface of  $TiO_2$ . As the oxidized product, 77  $\mu mol$  of  $CO_2$  was formed by photoirradiation for 30 min. Assuming that all of the  $CO_2$  originated from OA, efficiency of OA utilization as a hole scavenger (EOU) was calculated by using Eq. 3.

$$EOU = 6 \times (n_{AN} / n_{CO_2}) \times 100 \quad (3)$$

where  $n_{AN}$  and  $n_{CO_2}$  are amounts of AN and  $CO_2$  formed, respectively. Even in the presence of 5%  $O_2$ , EOU under these conditions was as high as 97%, indicating that OA worked effectively as a hole scavenger and fruitless mineralization of OA by  $O_2$  (Eq. 4) scarcely occurred.

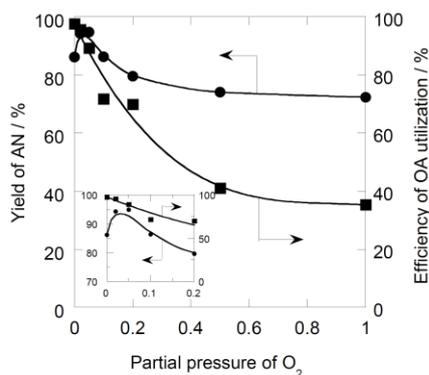


It should be noted that AN was not re-oxidized by further photoirradiation after 30 min, though a small amount of  $CO_2$  was formed due to mineralization of OA. Under acidic conditions, anilinium ion ( $AN^+$ ) was eliminated from the  $TiO_2$  surface. This mechanism for removal of the product from the surface of  $TiO_2$  also accounts for the high yield of AN.

Figure 2 shows the effects of content of  $O_2$  in the gas phase on AN yield and EOU in photocatalytic reduction of NB under the same conditions of photoirradiation for 60 min. When photocatalytic reaction was carried out in the absence of  $O_2$ , a high yield of AN (82%) and a high EOU (99%) were obtained. OA was almost quantitatively used as the hole scavenger for reduction of NB. The electrons have sufficient potential (flat band potential  $E_{fb} = -0.52$  V vs standard hydrogen potential (SHE) at pH = 6.8)<sup>12</sup> to reduce NB (half-peak potential  $E_{red/1/2} = +0.16$  V vs SHE).<sup>13</sup> Oxalate ions are oxidized by  $h^+$ , resulting in the formation of  $CO_2$  and  $CO_2^{\bullet-}$  (Eq. 5):



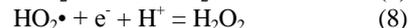
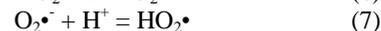
It has been reported that  $CO_2^{\bullet-}$  has a strong reducing ability ( $E^0(CO_2/CO_2^{\bullet-}) = -1.8$  V)<sup>14</sup> and is able to reduce NB. Therefore, NB might be reduced to AN by both  $e^-$  and  $CO_2^{\bullet-}$  in the present system.



**Figure 2** Effect of partial pressure of  $O_2$  on AN yield (circles) and EOU (squares) in photocatalytic reduction of NB in the presence of OA

It is interesting that the yield of AN in the presence of 2% and 5%  $O_2$  in the gas phase was larger than that in the absence of  $O_2$  as shown in Figure 2. The difference between the two reaction conditions is only whether a small amount of  $O_2$  is present or not. The results obtained indicate that a small amount of  $O_2$  caused rapid reduction of NB to AN in the presence of a sacrificial reagent. Photocatalytic oxidation (or mineralization) of organic compounds is generally carried out in the presence of  $O_2$  because  $O_2$  is a good electron-capturing reagent accelerating oxidation of organic compounds by  $h^+$  or hydroxyl radicals. In fact, further increase in  $O_2$  content in the gas phase decreased both AN yield and EOU (Figure 2). The decrease in AN yield was probably caused by re-oxidation of  $AN^+$  due to large consumption of OA under large  $O_2$  content. When  $O_2$  captures  $e^-$ , superoxide anion ( $O_2^{\bullet-}$ ) is formed under

neutral conditions (Eq. 6) and  $O_2^{\bullet-}$  is protonated, yielding  $HO_2^{\bullet}$  radicals, under acidic conditions (Eq. 7). Further reduction of these one-electron-reduced products of  $O_2$  yields hydrogen peroxide ( $H_2O_2$ ) (Eq. 8), which is believed to cause oxidation of organic compounds.



Active species other than  $e^-$  and  $CO_2^{\bullet-}$  should exist and cause rapid reduction of NB in the presence of  $O_2$ . It is well known that  $O_2^{\bullet-}$  (or  $HO_2^{\bullet}$ ) acts as a one-electron reductant.<sup>15</sup> Therefore,  $O_2^{\bullet-}$  (or  $HO_2^{\bullet}$ ) is a candidate for active species for reduction of NB in the presence of a small amount of  $O_2$ . Since  $H_2O_2$  has both reduction ability and oxidation ability depending on the type of target compound,  $H_2O_2$  formed in this reaction process may reduce NB. However, no homogeneous reduction of NB by  $H_2O_2$  in an aqueous solution (pH ca. 1) occurred. Therefore, all experimental results suggest an additional mechanism to increase the yield of AN in the presence of a small amount of  $O_2$ .  $O_2$  was reduced to  $O_2^{\bullet-}$  by  $e^-$  and then a part of NB was reduced by thus-formed  $O_2^{\bullet-}$ . Some mediators, such as  $IO_3^-I^{16}$  and  $Fe^{2+}-Fe^{3+}$ ,<sup>17</sup> have been reported to improve quantum efficiency in photocatalytic water splitting ( $H_2O$ ) to hydrogen and  $O_2$ .  $O_2$  works in the same manner as these mediators in an  $H_2O$  decomposition system, as a mediator in the photocatalytic reduction of BN to AN.

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