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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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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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. Since photocatalytic reaction satisfies several of the 15 proposed requirements for green chemistry, organic synthesis of various compounds using photocatalysis has been studied by many researchers. 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 (O2) 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 O2. The purpose of the electron donor is to scavenge holes (h+), thereby reducing the degree of recombination within the particle. Removal of O2 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, 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 (CO2), which is separated from the solvent under acidic conditions. It is obvious that water (H2O) 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 (TiO2) 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 O2.

Degussa P25 TiO2 was used because it is known to be one of the most active photocatalysts. Bare TiO2 powder (50 mg) was suspended in an aqueous solution (5 cm3) containing NB (13 µmol) and OA (100 µmol) in a test tube. Using a 3-

Figure 1 Time courses of the amounts of NB (squares), AN (circles), H2 (diamonds) and CO2 (triangles) in photocatalytic reduction of NB in the presence of OA under 5%O2-95%N2.

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 (N2) and O2 with magnetic stirring at 298 K. The amounts of NB and product(s) were determined with a Shimadzu GC-8A gas chromatograph equipped with Porapak QS (CO2) and MS-5A (dihydrogen (H2) and O2) columns. Blank reaction without TiO2 gave no product.

Figure 1 shows the time courses of yields of AN, H2 and CO2 in the photocatalytic reaction of the aqueous mixture of NB, OA and TiO2 powders under 5%O2-95%N2. 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 O2. Reduction of NB to AN consists of several steps (Eq. 1), and the probable stoichiometry of the reaction in the presence of OA is shown below (Eq. 2).

\[
Pb-\text{NO}_2 \rightarrow \text{Ph-NO} \rightarrow [\text{Ph-NHOH}] \rightarrow \text{Ph-NH}_2 \quad \text{(1)}
\]

\[
Pb-\text{NO}_2 + 3(\text{COOH})_2 \rightarrow \text{Ph-NH}_2 + 6\text{CO}_2 + 2\text{H}_2\text{O} \quad \text{(2)}
\]

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 TiO2. As the oxidized product, 77 µmol of CO2 was formed by photoirradiation for 30 min. Assuming that all of the CO2 originated from OA, efficiency of OA utilization as a hole scavenger (EOU) was calculated by using Eq. 3.
The catalytic reduction of NB to AN by both e− and CO3•− radicals, under acidic conditions (Eq. 6) and O2•− is protonated, yielding HO2• radicals, under acidic conditions (Eq. 7). Further reduction of these one-electron-reduced products of O2 yields hydrogen peroxide (H2O2) (Eq. 8), which is believed to cause oxidation of organic compounds.

\[ \text{O}_2 + e^- = \text{O}_2\cdot^- \]  
\[ \text{O}_2\cdot^- + \text{H}^+ = \text{HO}_2\cdot^- \]  
\[ \text{HO}_2\cdot^- + e^- + \text{H}^+ = \text{H}_2\text{O}_2 \]  

Active species other than e− and CO3•− should exist and cause rapid reduction of NB in the presence of O2. It is well known that O2•− (or HO2•−) acts as a one-electron reductant. Therefore, O2•− (or HO2•−) is a candidate for active species for reduction of NB in the presence of a small amount of O2. Since H2O2 has both reduction ability and oxidation ability depending on the type of target compound, H2O2 formed in this reaction process may reduce NB. However, no homogeneous reduction of NB by H2O2 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 O2. O2 was reduced to O2•− by e− and then a part of NB was reduced by thus-formed O2•−. Some mediators, such as IO3− and Fe3+/Fe2+, have been reported to improve quantum efficiency in photocatalytic water splitting (H2O) to hydrogen and O2. O2 works in the same manner as these mediators in an H2O decomposition system, as a mediator in the photocatalytic reduction of BN to AN.

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References and Notes

Figure 2 Effect of partial pressure of O2 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% O2 in the gas phase was larger than that in the absence of O2 as shown in Figure 2. The difference between the two reaction conditions is only whether a small amount of O2 is present or not. The results obtained indicate that a small amount of O2 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 O2 because O2 is a good electron-capturing reagent accelerating oxidation of organic compounds by h+ or hydroxyl radicals. In fact, further increase in O2 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 O2 content. When O2 captures e−, superoxide anion (O2•−) is formed under neutral conditions (Eq. 6) and O2•− is protonated, yielding HO2• radicals, under acidic conditions (Eq. 7). Further reduction of these one-electron-reduced products of O2 yields hydrogen peroxide (H2O2) (Eq. 8), which is believed to cause oxidation of organic compounds.

\[ \text{O}_2 + e^- = \text{O}_2\cdot^- \]  
\[ \text{O}_2\cdot^- + \text{H}^+ = \text{HO}_2\cdot^- \]  
\[ \text{HO}_2\cdot^- + e^- + \text{H}^+ = \text{H}_2\text{O}_2 \]
**Graphical Abstract**

**Textual Information**

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**Graphical Information**

![Graphical Image](image-url)

Diagram showing the photocatalytic reduction of nitrobenzene to aniline with titanium oxide particles, oxalic acid as a hole scavenger, and the effect of dioxygen.