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-
$EOU = 6 \times (n_{\infty} / n_{0\infty}) \times 100$  

(3)

where $n_{\infty}$ and $n_{0\infty}$ 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.

(COOH)$_2$ + 1/2O$_2$ = 2CO$_2$ + H$_2$O  

(4)

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 hydrogen potential (SHE) at pH = 6.8) to reduce NB (half-peak potential $E^{1/2}_{\text{Ox/Red}}$ = +0.16 V vs SHE). Oxalate ions are oxidized by h$, resulting in the formation of CO$_2$ and CO$_2$ (Eq. 5):

$\text{C}_2\text{O}_4^{2-} + \text{h}^+ = \text{CO}_2 + \text{CO}_2$  

(5)

It has been reported that CO$_2$ has a strong reducing ability ($E^{1/2}_{\text{CO}_2/\text{CO}_2}$) = -1.8 V) and is able to reduce NB. Therefore, NB might be reduced to AN by both e$^-$ and CO$_2$ 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^-$) is formed under neutral conditions (Eq. 6) and O$_2^-$ is protonated, yielding HO$_2^+$ radicals, under acidic conditions (Eq. 7). Further reduction of these one-electron-reduced products of O$_2$ yields hydrogen peroxide (H$_2$O$_2$) (Eq. 8), which is believed to cause oxidation of organic compounds.

$O_2 + e^- = O_2^-$  

(6)

$O_2^- + H^+ = HO_2^-$  

(7)

$HO_2^- + e^- + H^+ = H_2O_2$  

(8)

Active species other than e$^-$ and CO$_2^-$ should exist and cause rapid reduction of NB in the presence of O$_2$. It is well known that O$_2^-$(or HO$_2^-$) acts as a one-electron reductant. Therefore, O$_2^-$ (or HO$_2^-$) is a candidate for active species for reduction of NB in the presence of a small amount of O$_2$. Since H$_2$O$_2$ has both reduction ability and oxidation ability depending on the type of target compound, H$_2$O$_2$ formed in this reaction process may reduce NB. However, no homogeneous reduction of NB by H$_2$O$_2$ 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$_2^-$ by e$^-$ and then part of NB was reduced by thus-formed O$_2^-$. Some mediators, such as IO$_3^-$ and Fe$^{2+}$, have been reported to improve quantum efficiency in photocatalytic water splitting (H$_2$O) to hydrogen and O$_2$. O$_2$ works in the same manner as these mediators in an H$_2$O decomposition system, as a mediator in the photocatalytic reduction of BN to AN.

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References and Notes

Graphical Abstract

Textual Information

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[Diagram showing the photocatalytic reduction process with TiO₂, CO₂, O₂, and NH₂ reactions]