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Chemoselective reduction of nitrobenzenes having other reducible groups over titanium(IV) oxide photocatalyst under protection-, gas-, and metal-free conditions

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ABSTRACT

m-Nitrostyrene was chemoselectively reduced to *m*-aminostyrene in an acetonitrile suspension containing a titanium(IV) oxide (TiO_2) photocatalyst and a suitable hole scavenger at room temperature under atmospheric pressure without the use of a precious metal or reducing gas. Addition of a small amount of water to acetonitrile increased the reaction rate, and the highest rate was obtained. Moreover, applicability of the photocatalytic system was investigated using various nitro compounds having other reducible groups (chloro, bromo, carboxyl, and acetyl groups), and only the nitro group of these compounds was chemoselectively reduced, resulting in the formation of corresponding amino compounds with high yields.

1. Introduction

Chemoselective conversion of a functional group is important for organic synthesis, especially synthesis of fine chemicals. Lithium aluminum hydride, a traditional reducing reagent in organic chemistry, non-selectively reduces various groups such as carbonyl, carboxyl, vinyl, and nitro groups. Therefore, a protecting group is introduced into a compound by chemical modification of a functional group in order to obtain chemoselectivity in a subsequent chemical reaction. However, the yield of the product is decreased due to introduction of the protecting group and the deprotection process gives much waste. Therefore, a protection-free and catalytic chemoselective reduction method is favorable in many reduction processes.

Aminobenzenes are important compounds as intermediates of agrochemicals, medicines, dyes, and various useful compounds, and they are synthesized by reduction of corresponding nitrobenzenes.[1] Therefore, selective conversion of the nitro group in compounds having other functional groups to an amino group is an important technique. For example, when nitrobenzenes have other reducible groups such as a vinyl group, it is difficult to selectively reduce the nitro group. Catalytic hydrogenation over a metal catalyst such as nickel (Ni) or copper (Cu) is the main method for reduction of a nitro group.[1] However, this method cannot be applied for selective reduction of the nitro group of nitrobenzenes having a vinyl group because both the nitro and vinyl groups are reduced. Chemoselective reduction of the nitro group is achieved by using a large excess of a reducing agent such as tin (Sn),[2] zinc (Zn),[3] iron (Fe)[4] or sodium hydrosulfite.[5] However, these reaction systems give harmful wastes containing metal ions, and a catalytic process without metal reducing agents is therefore favored. Although catalytic chemoselective reduction of nitrobenzenes is important, there have been only a few reports on chemoselective reduction of a nitro group in the presence of C=C bonds[6–8] and their yields were low. Recently, chemoselective reduction of *m*-nitrostyrene (NS) to *m*-aminostyrene (AS) has been achieved by many researchers.[1,9–19] However, these (thermo)catalytic systems require precious metals, high temperature, and high-pressure of reducing reagents such as H_2 and carbon monoxide (CO). Reduction of NS to AS would be more attractive if reducing reagents other than gaseous H_2 and CO are applied and the reaction is catalyzed by common elements having a simple component and structure under mild conditions such as room temperature and atmospheric pressure. Since electrochemical (or electrocatalytic) reduction of nitro compounds proceeds at room temperature and without high-pressure of H_2, electrochemical hydrogenation of nitrobenzenes has been studied. However, these methods need a noble metal and a large energy cost to apply sufficient voltage to the reaction

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systems. When a noble metal is used as an electrode, reduction of protons to H_2 occurs and competes with reduction of the substrate. In addition, an electrolyte is indispensable.

For the above-mentioned reasons, photocatalytic methods are preferable. When titanium(IV) oxide (TiO_2) is irradiated by UV light, charge separation occurs and thus-formed electrons in the conduction band and positive holes in the valence band cause reduction and oxidation, respectively. Titanium is a common and inexpensive element because it has the tenth largest Clarke number. Although various oxides of titanium exist, TiO_2, in which the oxidation state of titanium is +4, is most stable under the atmosphere and is easily formed without extra attention. Photocatalytic reaction proceeds at room temperature and under atmospheric pressure, and the TiO_2 photocatalyst is easily separated from the reaction mixture after the reaction. In addition, TiO_2 has been used for a long time as an indispensable inorganic material such as a pigment and UV absorber because it is inexpensive and not toxic for humans and the environment. Most of the applications of photocatalysis are mineralization (or degradation) of toxic organic compounds in air and water.[20–22] Since photocatalytic reaction satisfies almost all of the 12 proposed requirements for green chemistry,[23] organic synthesis of various compounds using photocatalysis has recently been studied by many researchers.[21,24,25] However, less attention has been paid to the photocatalytic reduction of organic compounds by photogenerated electrons because a deaerated condition is needed to achieve reduction of substrates.[21] Photocatalytic reduction for organic synthesis can be carried out in the presence of a large excess of an electron donor, such as methanol, and in the absence of dioxygen (O_2).[26–29] The purpose of the electron donor is to scavenge holes and to reduce recombination of holes and electrons in and/or on the particles. From the point of view of environmentally friendly production of chemicals, attention must be paid to the choice of sacrificial reagents for photocatalytic reduction of organic compounds. Alcohols such as methanol have been used as both a solvent and a hole scavenger.[26–29] However, since toxic aldehydes are formed as the oxidized species of alcohols, a sacrificial reagent converting to a non-toxic compound is preferable. We have reported photocatalytic reduction of nitrobenzenes to corresponding aminobenzenes in an aqueous suspension of TiO_2 in the presence of oxalic acid or formic acid as a hole scavenger.[30–32] These hole scavengers are 'greener' sacrificial reagents because they are easily oxidized into carbon dioxide (CO_2) and thus-formed CO_2 molecules are removed from the liquid phase in the presence of organic acids.

In this study, we examined the photocatalytic reduction of nitrobenzenes having other reducible groups using a simple photocatalyst, TiO_2, in the presence of oxalic acid as a hole scavenger at room temperature and atmospheric pressure, and we found that only the nitro group was chemoselectively reduced to an amino group and that aminobenzenes with reducible groups were obtained in high yields without using precious metals or high-pressure gaseous reducing reagents.

2. Results and discussion

2.1. Photocatalytic chemoselective reduction of NS to AS in an acetonitrile suspension of TiO_2

Fig. 1 shows time courses of the amounts of NS remaining and AS formed in the photocatalytic reduction of NS in an acetonitrile suspension of TiO_2 under deaerated conditions. The amount of NS monotonously decreased along with photoirradiation time and NS was almost completely consumed after 6 h, while AS was obtained in a high yield (86%). It is notable that there are few reports on photocatalytic chemoselective reduction of a nitro group having a C=C double bond. Scheme 1 shows the probable stoichiometry of photocatalytic chemoselective reduction of NS to AS in the presence of oxalic acid. The present photocatalytic reduction was achieved without precious metals, high-temperature or high-pressure of H_2 in contrast to (thermo)catalytic hydrogenation.

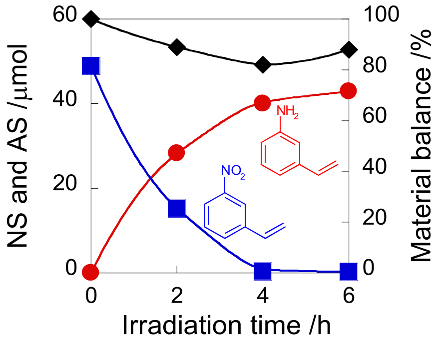
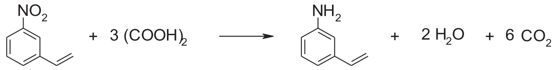


Fig. 1. Time courses of the amount of NS remaining (squares), AS formed (circles), and material balance (diamonds) in an acetonitrile suspension of TiO_2 (50 mg) in the presence of oxalic acid (200 µmol) as a hole scavenger under deaerated conditions.



Scheme 1. Stoichiometry of photocatalytic reduction of NS to AS over TiO_2 in the presence of oxalic acid as a hole scavenger.

Reduction of a nitro group to an amino group consists of several steps as shown in Eq. 1, i.e., nitro compounds are reduced to amino compounds via nitroso compounds and hydroxylamines as intermediates.

$$R-NO_2\overset{2e^-}{\rightarrow}R-NO\overset{2e^-}{\rightarrow}R-NH(OH)\overset{2e^-}{\rightarrow}R-NH_2 \qquad (1)$$

Nitroso compounds and hydroxylamines were not detected under the present conditions, indicating that the rate of reduction of these intermediates was larger than that of NS or that intermediates were strongly adsorbed on the surface of TiO_2. The possibility of adsorption of intermediates can be discussed on the basis of the value of material balance calculated by Eq. 2.

$$\text{Material balance} = \frac{\text{Summation of NS and AS}}{\text{Initial amount of NS}} \times 100(\%) \qquad (2)$$

The time course of material balance is also shown in Fig. 1. The value of material balance was initially decreased by photoirradiation and then recovered with further photoirradiation, indicating that the reduction intermediate(s) was adsorbed on the TiO_2 surface and released when it was reduced to AS. Recently, photocatalytic cyanomethylation of aromatic compounds using acetonitrile as reagent, in which acetonitrile was activated by positive holes, has been reported.[33] However, cyanomethylation did not occur in the present system, indicating that hole scavenger reacted with holes much faster than acetonitrile.

2.2. Intermolecular chemoselective reduction of nitrobenzene and styrene

The high chemoselectivity of this method for reduction of NS was further investigated in the intermolecular competitive reaction of nitrobenzene and styrene. As expected, nitrobenzene (50 µmol) was reduced to give aniline (50 µmol) with over >99%yield, while no styrene (49 µmol) was reduced as shown in Scheme 2. These results clearly demonstrate that the photocatalytic system showed complete chemoselectivity for the nitro group in the presence of inter- and intra-molecular vinyl groups. The selectivity between

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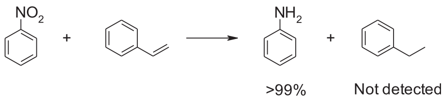
a nitro group and a vinyl group can be explained electrochemically, i.e., reduction potential of the conduction band of the TiO_2 and substrates. The half-wave reduction potential of styrene (−2.41 V)[34] is more negative than the potential of TiO_2 conduction band (−0.3 V), while the half-wave reduction potential of nitrobenzene (0.16 V)[35] is more positive.[36]



Scheme 2. Intermolecular competitive reaction of nitrobenzene and styrene in an acetonitrile suspension of TiO_2 in the presence of oxalic acid as a hole scavenger.

2.3. Blank reactions and effects of gaseous conditions and light intensity on photocatalytic reduction of NS to AS

Effects of various reaction conditions on photocatalytic reduction of NS to AS were investigated and the results are summarized in Table 1.

Table 1
Effects of various reaction conditions on photocatalytic chemoselective reduction of NS to AS[a]

Entries	TiO_2/mg	Light source	Reaction time/h	Gas phase	Conv./%	Sel./%
1	50	Mercury arc	6	Ar	99	87
2	50	Dark	5	Ar	Trace	—
3	—	Mercury arc	6	Ar	25	Trace
4	50	Mercury arc	5	Air	47	13
5	50	Black light	30	Ar	86	98
6	—	Black light	30	Ar	2	0

[a] Oxalic acid: 200 μmol.

Entry 1 is the result at 6-h photoirradiation in Fig. 1. As shown in entries 2 and 3, photoirradiation and TiO_2 were indispensable for the formation of AS, indicating that NS was reduced to AS by TiO_2 photocatalysis. No AS was formed in the absence of TiO_2 (entry 3), although NS was consumed. We also observed colorization of the solution to light yellow after photoirradiation. This result indicates that photochemical reaction(s) occurred to give a by-product(s). The photochemical reaction(s) reduced the yield of AS in the present system. In the presence of O_2, the yield of AS was very low and many by-products were detected in the reaction mixture (entry 4). Over TiO_2 irradiated by UV light, electrons were injected into O_2 to give active oxygen species, and these species induced degradation of NS and/or the product(s). Thus, since active oxygen species decompose various organic compounds, almost all cases of photocatalytic reduction are carried out under deaerated conditions.[21,24,25]

Since the yield of AS was decreased by the photochemical reaction(s) in the absence of a TiO_2 photocatalyst under irradiation of strong light of a high-pressure mercury arc (entry 3), the effect of light source was investigated in detail by the use of a black light as another light source. Entries 5 and 6 show results when black light was used as the light source with small UV light intensity. Although longer photoirradiation was required, AS selectivity was much higher (98%, entry 5) than that obtained under photoirradiation of a high-pressure mercury arc (entry 1). Fruitless consumption of NS was avoided when black light was used as the light source (entries 3 and 6). Suppression of undesired photochemical reaction(s) of NS by using black light instead of a mercury arc as the light source is attributed to the high AS selectivity. Fig. 2 shows emission spectra of the high-pressure mercury arc and black light, the latter intensity being expanded 20-fold. A difference between the two emission spectra was observed under 350 nm, i.e., emission at around 300–350 nm (painted area) was observed in the high-pressure mercury arc, while there was almost no emission in the black light. Fig. 2 also shows the absorption spectrum of NS in an acetonitrile solution, in which strong photoabsorption was observed in the UV range, especially at wavelengths shorter than 350 nm. These results suggest that photochemical reaction(s) of NS is caused by UV light with strong energy emitted from a high-pressure mercury arc and can be avoided by using black light.

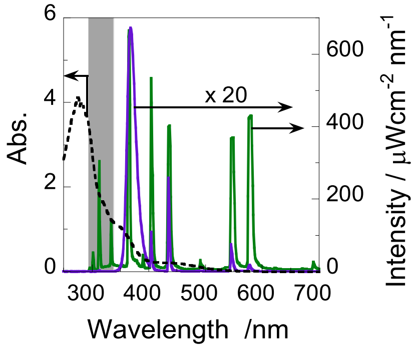


Fig. 2. Emission spectra of a high-pressure mercury arc (green line), black light (purple line), and absorption spectrum of NS in acetonitrile.

2.4. Effect of hole scavengers

When photocatalytic reduction is applied to organic conversions, hole scavengers are indispensable for donating electrons. In addition, frequency of recombination depends on the rate of oxidation of hole scavengers at holes. Therefore, a hole scavenger would strongly affect the yield in photocatalytic reduction. Table 2 shows the effects of various hole scavengers on yield of AS.

Table 2
Effect of hole scavenger on photocatalytic reduction of NS to AS under photoirradiation of a high-pressure mercury arc

Entries	Hole scavengers	Amounts of hole scavengers	Irradiation time/h	Conv./%	Sel./%	Material balance/%
1	—	—	6	39	9	56
2	Oxalic acid	200 μmol	6	>99	87	86
3	Oxalic acid	400 μmol	6	95	79	80
4	Formic acid	200 μmol	6	>99	17	17
5	Methanol	5 cm^3	2	>99	15	15
6	Ethanol	5 cm^3	2	>99	20	20

Entries 1–3 show the effect of amount of oxalic acid on photocatalytic chemoselective reduction of NS to AS. Oxalic acid was essential for effective reduction of NS. As shown in entry 1, NS was consumed and a small amount of AS was formed, while a large amount of by-products was obtained even in the absence of oxalic acid. In this case, NS probably worked as a hole scavenger, i.e., some NS was oxidized with positive holes and thus by-products were formed, while other NS was reduced by exited electrons. Excess of oxalic acid decreased the reaction rate (entry 3). The decrease in reaction rate may be caused by strong adsorption of oxalic acid because the carboxyl group of oxalic acid is strongly adsorbed on the TiO_2 surface. It has been reported that formic acid was an effective hole scavenger for photocatalytic reduction of

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nitro aromatics.[31] However, many by-products were produced and low selectivity was obtained in the present reaction (entry 4). Photocatalytic reduction of NS in some alcohols was examined because alcohols, mainly methanol, have often been used as solvents in photocatalytic reduction of nitrobenzenes. In the present reaction, alcohols also worked as hole scavengers as shown in entries 5 and 6. After 2-h photoirradiation, NS was almost completely consumed in alcohols; however, many unidentified by-products were formed probably due to side reaction(s) of amino and vinyl groups with alcohols. As a result, AS selectivities were much smaller than that obtained in the reaction system using acetonitrile and oxalic acid as a solvent and hole scavenger, respectively. These results indicate that the combination of acetonitrile and oxalic acid is essential for efficient photocatalytic reduction of NS.

2.5. Applicability

Applicability of the photocatalytic chemoselective reduction was investigated using various nitro compounds having other reducible groups (chloro, bromo, carboxyl, and acetyl groups), and Table 3 shows results of the photocatalytic chemoselective reduction of various nitrobenzenes in acetonitrile suspension of TiO_2 particles under deaerated conditions. Only the nitro group of these compounds was chemoselectively reduced even in the presence of chloro, bromo, carboxyl, and acetyl groups, resulting in the formation of corresponding amino compounds with high yields. These results indicate wide applicability of this photocatalytic method for chemoselective reduction of a nitro group to an amino group without using protecting process, precious metals and H_2. When *o*-acetylnitrobenzene was used as substrate (entry 8), the selectivity was low even at low conversion, suggesting that intermediate(s) and/or *o*-acetylaminobenzene easily converted to by-product(s) under photoirradiation.

2.6. Effect of amount of water contained in acetonitrile solvent

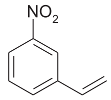
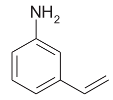
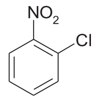
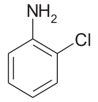
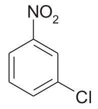
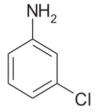
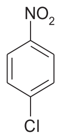
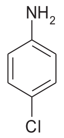
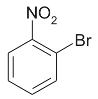
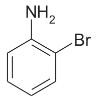
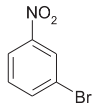
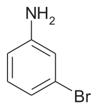
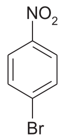
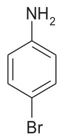
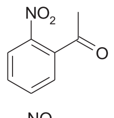
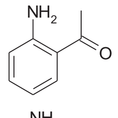
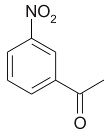
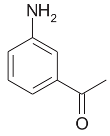
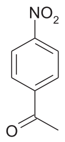
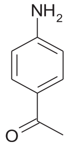
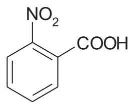
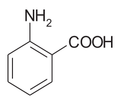
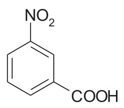
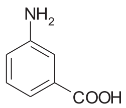
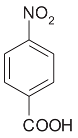
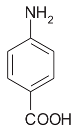
The effect of water addition to solvents on yields of AS was investigated and the results are shown in Fig. 3.

When a small amount of water was added to acetonitrile, yields of AS after 2-h photoirradiation increased and maximum yield was obtained at the ratio of 10 vol %. A positive effect of addition of water to acetonitrile was also reported in photocatalytic conversions.[37,33] Further addition of water, however, decreased the yield of AS. Recently, photocatalytic hydroxylation of aromatic compounds[38,39] and hydration of alkenes[40] in the presence of water over metal-loaded TiO_2 have been reported. However, these compounds were not formed in the present system because bare TiO_2 was used.

To understand the effect of water on reduction of NS in the presence of oxalic acid, another photocatalytic reaction using oxalic acid, i.e., photocatalytic decomposition of oxalic acid along with H_2 formation (Scheme 3) in a water/acetonitrile suspension of platinized TiO_2($Pt-TiO_2$) under deaerated conditions, was examined. This reaction system is simple because only oxalic acid is dissolved as a substrate in the liquid phase.

Since the oxalic acid decomposition was carried out under deaerated conditions as in the NS system, the effect of oxygen on the reaction can be eliminated. Therefore, hole trapping by oxalic acid would be important in the oxalic acid decomposition system, and the results are also shown in Fig. 3 (right axis). A tendency similar to that in the NS system was observed in the oxalic acid decomposition system and there was a clear correlation between them as shown in Fig. 4, indicating that water added to acetonitrile affected the two photocatalytic reactions in a similar way, though

Table 3
Photocatalytic chemoselective reduction of various nitrobenzenes to corresponding aminobenzenes

Entries	Substrates	Products	Time/h	Conv./%	Sel./%
1			6	>99	88
2			2	>99	>99
3			2	>99	95
4			2	>99	54
5			2	>99	>99
6			2	>99	>99
7			2	>99	88
8			2	>99	15
9			2	>99	91
10			2	>99	88
11			2	>99	98
12			2	>99	>99
13			2	>99	98

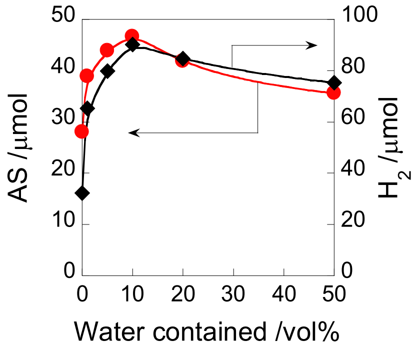
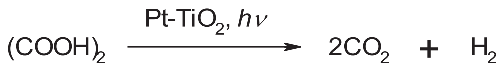


Fig. 3. Effect of water of solvents (water/acetonitrile) on yields of AS formed by photocatalytic reduction of NS over TiO_2 for 2 h and photocatalytic H_2 evolution from oxalic acid over 1 wt %Pt/TiO_2 for 0.5 h.



Scheme 3. Photocatalytic decomposition of oxalic acid along with H_2 formation in a suspension of Pt–TiO_2 under deaerated condition.

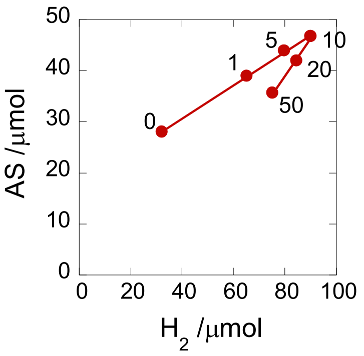


Fig. 4. Correlations between amount of AS formed and H_2 evolved after 2-h and 30-min photoirradiation. Values in the figure indicate the content of water in reaction mixtures.

the reduced products (AS and H_2) and photocatalysts (bare TiO_2 and platinized TiO_2) are different.

These results suggest that hole trapping by oxalic acid was important in the NS reduction as well as in the oxalic acid decomposition. Addition of water seems to have various effects on the surface properties and suspending state (stability) of TiO_2 particles as well as on the stabilities, solubilities, and adsorption behaviors of NS, AS, and oxalic acid. These factors would affect each other and would change complexly depending on the amount of water added. For example, a small amount of water would increase the stability of TiO_2 particles and the surfaces of TiO_2 particles would become more hydrophilic. Adsorption behavior of oxalic acid on the TiO_2 surface was also investigated, and Fig. 5 shows the effect of water on the amount of oxalic acid adsorbed on the TiO_2 surface. The amount of oxalic acid adsorbed on TiO_2 decreased with increase in water ratio of solvents. This tendency was different from that of the reaction rate shown in Fig. 3. Even when pH of the reaction mixture was changed, the reaction rate was not affected (Fig. 6). The experimental results suggest that various factors affecting photocatalytic efficiency including hole trapping by oxalic acid were balanced most efficiently when water was added at the ratio of 10 vol % water containing acetonitrile, though the reason(s) for this is not clear.

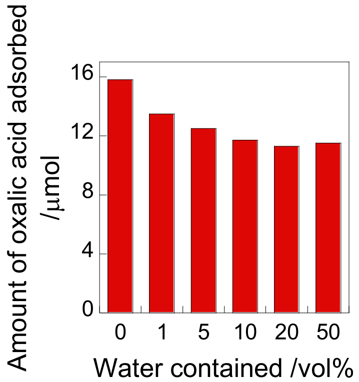


Fig. 5. Effect of water added in acetonitrile (50 cm^3) on the amount of oxalic acid (initially 200 μmol) adsorbed on TiO_2 (1 g).

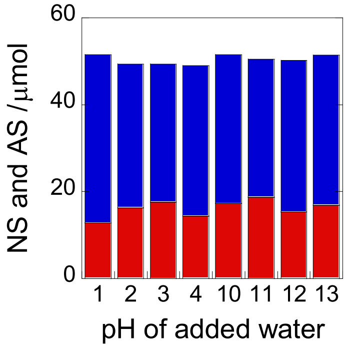


Fig. 6. Effect of pH on photocatalytic chemoselective reduction of NS to AS in water/acetonitrile suspensions (water/acetonitrile ratio=0.1) of TiO_2 for 30-min photoirradiation. NS: blue, AS: red. Other conditions were same for those described in Fig. 5.

2.7. AQE, durability, and effects of different kinds of TiO_2 photocatalyst

The value of apparent quantum efficiency (AQE) at 366 nm calculated from the ratio of the amount of AS and amount of photons irradiated using Eq. 3 reached 15%.

$$AQE = \frac{6 \times \text{amount of AS}}{\text{number of incident photons}} \times 100. \tag{3}$$

For comparison, AQE for photocatalytic H_2 formation from 2-propanol (200 μmol) in an aqueous suspension of platinized TiO_2 was also examined and was determined to be 4.1% under the same irradiation conditions. This reaction has often been used as a model reaction to evaluate the activity of a photocatalyst for H_2 evolution. The lager value of AQE in the present reaction than that of 2-propanol dehydrogenation indicates that oxalic acid efficiently works as a hole scavenger for photocatalytic reduction of NS to AS. These results indicate that the combination of water/acetonitrile and oxalic acid is effective for photocatalytic reduction of NS.

To examine the durability of the TiO_2 photocatalyst in this reaction system, TiO_2 was used repeatedly. After reaction in 10 vol % water containing acetonitrile for 2 h, TiO_2 particles were recovered by simple filtration from the reaction mixture and were re-used. As summarized in Fig. 7, TiO_2 photocatalysts were reusable without notable loss of activity.

Table 4 shows effects of different kinds of TiO_2 photocatalysts on photocatalytic chemoselective reduction of NS to AS in water/acetonitrile, and physical properties of TiO_2 are shown in Table 4.

In all cases, NS was consumed and AS was obtained. Among these samples, the anatase-type TiO_2 sample (ST-01) and anatase-rutile mixed TiO_2 (P 25) exhibited higher conversion of NS. When P 25

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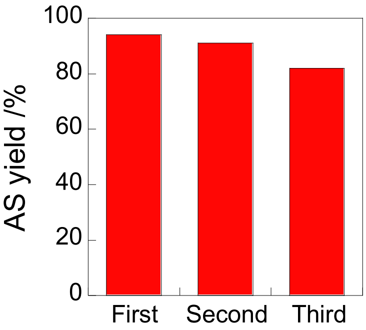

Fig. 7. Durability of TiO_2 in photocatalytic chemoselective reduction of NS to AS in 10 vol % water/acetonitrile solution for 2-h irradiation.

Table 4
Effects of kinds of TiO_2 on photocatalytic chemoselective reduction of NS to AS

TiO_2	S_{BET}/m^2 g^{-1}	Crystal phase	Conv./%	Sel./%
P 25	50	Anatase/rutile	>99	94
ST-01	338	Anatase	62	61
MT-150A	97	Rutile	50	99

was used, 99% of material balance was obtained, indicating that NS was reduced to AS selectively. Lower material balance (76%) was observed with formation of an unknown by-product when ST-01 was used. In addition, the color of ST-01 became light pale-yellow after the reaction. As mentioned in Section 2.1 (about Fig. 1), the intermediate(s) of reduction of NS may be strongly adsorbed on the TiO_2 surface. Using TiO_2 with a large surface area, ST-01, the intermediate(s) that accumulated on the TiO_2 surface may react to give by-products, and thus the color of TiO_2 surface was changed. When rutile-type MT-150A was used as the TiO_2 photocatalyst, good material balance (>99%) was obtained as in the case of using P 25. Conversion of NS, however, was lower than that of P 25.

3. Conclusions

We succeeded in a photocatalytic chemoselective reduction of various nitro compounds having other reducible groups to corresponding aminobenzenes in an acetonitrile suspension of TiO_2 in the presence of oxalic acid as a hole scavenger. Addition of water to acetonitrile increased the reduction rate and improved the yield of AS. This photocatalytic chemoselective method was applied to reduction of nitrobenzenes having halogen atoms, carboxyl groups, and carbonyl groups, producing corresponding aminobenzenes. This study should enhance the potential of photocatalytic reaction for advanced conversion.

4. Experimental section

4.1. General

Three kinds of commercial TiO_2 samples were used as photocatalyst, i.e., P 25 (Degussa), ST-01 (Ishihara), and MT-150A (Tayca). Bare TiO_2 powder (50 mg) was suspended in a mixture of acetonitrile (Wako Pure Chemical Industries, Osaka) and water (5 cm^3) containing NS (50 µmol, Sigma–Aldrich Japan, Tokyo) and oxalic acid (200 µmol, Wako Pure Chemical Industries, Osaka) in a test tube. The tube was sealed with a rubber septum and then photoirradiated at a wavelength >300 nm by a high-pressure mercury arc (Eiko-sha, 400 W) under argon (Ar) with magnetic stirring at 298 K. After the reaction, the gas phase was analyzed by a gas chromatograph (Shimadzu, GC-8A equipped with MS-5A columns). After the suspension had been filtered to remove the particles, the amounts of NS and product(s) were determined by high-performance liquid chromatography (Jasco, UV-2075Plus detector, PU-2089Plus pump, equipped with an Inertsil ODS-3 column, eluent: aqueous sodium borate buffer/acetonitrile=50:50, flow rate: 0.5 cm^3 min^{-1} at room temperature) and GC–MS (GC-17A, GCMS-QP5050 (Shimadzu); column: DB-1, 0.25 mm, 30m (J&W)).

To obtain apparent quantum efficiency (AQE), an UV light-emitting diode (UV-LED, PJ-1505-2CA, CCS Inc, Kyoto, 927 µW cm^{-2}, maximum energy at λ=366 nm) was also used as a light source. A spectrum and light intensity of the UV-LED were determined using a spectroradiometer USR-45D (Ushio, Tokyo).

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