Photocatalytic Reduction of Se Ions Using Suspended Anatase Powders^{*1}

Sumiko Sanuki¹, Kazue Shako^{1,*2}, Shigeru Nagaoka² and Hiroshi Majima³

¹Department of Material Systems Engineering and Life Science, Faculty of Engineering, Toyama University, Toyama 930-8555

²Research and Development Department, Titan Kogyo K.K., Ube 755-8567

³Professor Emeritus, Kyoto University, and Special Advisor, Titan Kogyo K.K., Ube 755-8567

The photocatalytic reduction of aqueous Se(VI) solution was studied using two types of TiO₂ powders with different specific surface areas and dispersed particle sizes as a catalyst, and HCOOH as a reductant. The principal reduction products were Se⁰ and H₂Se; Se(IV) was not detected. The reduction rate of Se(VI) was mainly controlled by the amount of Se(VI) adsorbed onto each type of the TiO₂ powders. When different TiO₂ powders were used, the energy conversion ratio of TiO₂ played the more important role in the photocatalytic reduction of Se(VI) or Se⁰. Using a TiO₂ catalyst with a high conversion ratio, the time required for the reductions of Se(VI) to Se⁰ and of Se⁰ to H₂Se differed by a ratio of 3 : 1, as expected from reaction equations. The reduction rates for Se(VI) can be approximated from the amount of Se(VI) adsorbed onto TiO₂ powders and the energy conversion ratios. The pH of solution, amount of TiO₂ and concentrations of Se(VI) and HCOOH were additionally recognized as important factors.

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1. Introduction

It has been same time since the application of photocatalytic technology utilizing semiconductor powders to industrial and environmental problems has attracted public attention. Among the various photocatalysts, TiO₂ is a chemically stable material, which needs ultraviolet light to move electron from the valence band to conduction band,^{1,2)} and is certainly one of the most interesting photocatalysts to be studied.

Although the study of TiO₂ as a photocatalyst was initially aimed at the production of hydrogen through the decomposition of water³⁾ and the synthesis of various organic compounds through the reduction of carbon dioxide,⁴⁾ technological interest in recent years has been directed towards applications to clean and restore the environment. Photocatalytic decomposition of harmful organic matter,⁵⁾ photo-oxidation of air pollutants such as NO_x (nitrogen oxides) and SO₂,⁶⁾ and sterilization to MRSA and mold⁷⁾ are typical examples. In addition, fundamental studies on the decomposition reaction of harmful materials using photocatalysts, aiming at the control of soil contamination or water pollution caused by industrial discharge,^{8,9)} have been actively performed in recent years. Research into the utilization of photocatalysts in the treatment of industrial wastewater and sea water is mainly centered on the photocatalytic decomposition of organic chloride compounds and petroleum out-flow,⁵⁾ with no significant study having been conducted on the decomposition of harmful inorganic compounds.

Selenium is mainly contained in SO₂ gas generated from roaster of sulfidic ore, and thus treatment and recovery from the smelting process of sulfides and the production process of sulfuric acid provide problems to be solved. The re-

cent introduction of new regulations has made the disposal of wastewater containing selenate or selenite ions more difficult. For example, the effluent standard for Se in Japan is now 0.1 mg/cm³. In regard to this, Kikuchi¹⁰⁾ and Sanuki *et al.*¹¹⁾ examined the possibility of applying TiO₂ as a photocatalyst for Se treatment.

The purpose of the present work is to elucidate the role of various factors, including powder characteristics, amount of TiO₂ catalyst, pH of the solution, concentrations of Se ions and HCOOH.

2. Theoretical Considerations of Se(VI) Reduction

In an acidic solution, the state of selenium changes, in the sequence SeO₄²⁻ to HSeO₃⁻, Se⁰ and H₂Se, with the potential.¹²⁾

At a low pH, the reduction of selenate to selenite and continuously elemental selenium is expressed by eqs. (1) and (2).

$$E = 1.075 - 0.0886 \text{ pH} + 0.295 \log[\text{SeO}_4^{2-}]/[\text{HSeO}_3^-] \quad (1)$$

$$E = 0.0739 - 0.0739 \text{ pH} + 0.148 \log[\text{HSeO}_3^-] \quad (2)$$

As mentioned in a previous paper,¹¹⁾ in the reduction of selenate ions by a photocatalytic route, no formation of selenite is detected and selenate is directly reduced to elemental Se, as shown by eq. (3), and under low-pH conditions, Se⁰ is further reduced to H₂Se as given by eq. (4).

$$E = 0.876 - 0.0788 \text{ pH} + 0.0099 \log[\text{SeO}_4^{2-}] \quad (3)$$

$$E = -0.369 - 0.0591 \text{ pH} - 0.0295 \log p_{\text{H}_2\text{Se}} \quad (4)$$

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^{*2}Undergraduate Student, Toyama University.

TiO₂ powders are a typical *n*-type semiconductor, and its impurity level is determined either by an oxygen vacancy or an interstitial-impurity Ti atom. The energy band level of TiO₂ is determined by factors such as the particulate size of TiO₂ and the pH of the electrolyte used.¹⁰⁾ It is reported that the reduction potential at the edge of a conduction band of TiO₂ in an aqueous solution of pH 1 is 0 V vs NHE.¹⁰⁾ Therefore, Reactions (1) to (3) readily proceed on TiO₂ surface, whereas Reaction (4) is difficult to induce. With the use of a suitable reductant in the absence of any oxidizing agent, however, the value for conduction-band energy becomes negative. Product gas removal would be possible if an inert gas is bubbled through the reacting suspension and vented. And, as a result, Reaction (4) can proceed.

3. Experimental Procedures

3.1 Catalysts

In the present study, two different anatase-type TiO₂ powders having different specific surface areas and mean particle sizes were used. The BET specific surface area and mean dispersed particle size of sample A were 145 m²/g and 10.3 μm, respectively, while those of sample B, consisting of around 70% anatase and the rest rutile, were 47.6 m²/g and 0.20 μm, respectively. Figure 1 shows TEM photographs of TiO₂ samples used. Sample A is an aggregate of primary fine particles with a uniform size, while sample B comprises ultra fine particles with connections.

3.2 Reagents and preparation of test solutions

The reagents used were all of reagent grade and the water was deionized with a specific resistivity of $>5.0 \times 10^4 \Omega \cdot \text{m}$. Sodium selenate (Na₂SeO₄) and sodium selenite (Na₂SeO₃) were used as sources of Se, and HCOOH was used as a reductant. Na₂SeO₄ or Na₂SeO₃ was dissolved in deionized water to prepare solutions with suitable Se concentrations rang-

ing 50 ~ 200 ppm. The pH of test solutions was adjusted to 3, 4 and 5 with aqueous NaOH solution in case of need. Na₂SO₄ was used to examine the suppression effect on the reduction of Se(VI). The role of HCOOH is to prevent the re-oxidation of reduced material. The HCOOH concentration during the reaction was adjusted in the range 1.0×10^{-2} to $5.0 \times 10^{-2} \text{ kmol/m}^3$.

3.3 Photocatalytic reduction of test solutions

The assembly of the experimental apparatus, consisting of pure water reservoir to prevent the evaporation of the Se(VI) solution during the reaction, a photocatalytic reactor and traps for exhaust gas is schematically illustrated in Fig. 2. Ten 20 W BLB fluorescent lamps made by Toshiba were used as a source of ultraviolet (UV) light. Light was irradiated from the side of the reactor. The intensity of BLB fluorescence was strongest at a wavelength of 352 nm, and enough to excite TiO₂ catalyst. The experimental apparatus was set inside

Fig. 2 Schematic illustration of the experimental apparatus used for the photocatalytic reduction of Se(VI). L: BLB UV Lamps, R: Reactor, M: Magnetic stirrer, W: Water, T₁: Trap for H₂Se ($5 \times 10^{-3} \text{ kmol/m}^3 \text{ CuSO}_4$), T₂: Trap for H₂Se ($1 \times 10^{-3} \text{ kmol/m}^3 \text{ NaOH}$).

(a) TiO₂ Sample A

(anatase, SSA:145 m²/g, d_{av} :1.0μm)

(b) TiO₂ Sample B

(anatase 70%, SSA:47.6 m²/g, d_{av} :0.2μm)

Fig. 1 TEM micrographs of the TiO₂ photocatalyst used.

an aluminum box, $50 \times 60 \times 80 \text{ cm}^3$, and the intensity of UV light was kept at 54 or 48 W/m^2 . A volume of 100 cm^3 of test solution was placed in a glass cylindrical reactor (a Muenck-type gas wash bottle was used for the photocatalytic reactor) with 250 cm^3 capacity, into which 0.11 g of TiO_2 powder was dispersed with the aid of a magnetic stirrer. The test solution was de-oxygenated by bubbling with N_2 gas for 1.8 ks. The photocatalytic reduction experiment was initiated by UV light irradiation. Exhaust gas was passed through two traps in series, containing $5 \times 10^{-3} \text{ kmol/m}^3$ CuSO_4 and 0.1 kmol/m^3 NaOH to remove H_2Se . After a predetermined period, a sample aliquot was taken to separate solution from TiO_2 and Se^0 by a centrifugal separator for quantitative analyses.

3.4 Adsorption isotherm determination of Se ions on TiO_2

Aqueous solutions containing Na_2SeO_4 or Na_2SeO_3 , with an Se concentration ranging from 5 to 100 ppm and a HCOOH concentration of $2.5 \times 10^{-2} \text{ kmol/m}^3$, were subjected to adsorption isotherm experiments. Twenty cm^3 of Se solution thus prepared was taken in a centrifugal tube, and 1.1 kg/m^3 of TiO_2 powder was added to it. Experiments were conducted at $293 \pm 1 \text{ K}$ by shaking the tube for 1.8 ks to attain a state of equilibrium. After removal of the TiO_2 powder from the solution with a centrifugal separator, the Se concentration of the resultant solution was determined. The amount of Se ions on the TiO_2 powder was calculated as the difference between the initial concentration of ions and the concentration in the state of equilibrium. In determination isotherms, blanks were used to ensure that there was no adsorption on the wall of the centrifugal tube.

3.5 Analysis

After irradiation with UV light, TiO_2 powders and precipitates were separated from the solutions by the centrifugal separator. The total Se remaining in solution was determined using a hydride generator and an atomic absorption spectrophotometer, and the selenate and selenite concentrations were analyzed by ion chromatography. The amount of H_2Se generated was determined from the amount of Cu(II) remaining in the CuSO_4 trap. Precipitates generated and the TiO_2 were filtered *in vacuo* and rinsed with water, then subjected to the analyses of elemental Se and Se ions adsorbed by TiO_2 powders. The Se ions adsorbed onto TiO_2 powders were washed with sodium carbonate solutions to desorb them from the TiO_2 surface, and the obtained solution was subjected to chemical analysis to estimate the amount of adsorbed Se. The elemental Se in the washing residue was dissolved with nitric acid¹³⁾ and the Se ion concentration was determined after removing the TiO_2 powders.

4. Experimental Results and Discussion

4.1 Effect of Se adsorbed onto TiO_2 catalyst on the photocatalytic reduction of Se ions

As mentioned previously,¹¹⁾ the photocatalytic reduction of Se(VI) or Se(IV) will not proceed without the addition of a suitable reductant for the prohibition of the re-oxidation of reduced products and the irradiation of UV light. In a pre-

vious paper, we mentioned that the decrease in concentration of Se(VI) or Se(IV) observed without UV irradiation is attributed to the adsorption of these ions onto TiO_2 powders.

On the other hand, it is considered that the mechanism of photocatalytic reaction is based on the delivery and receipt of electrons between excited TiO_2 and Se ions adsorbed onto TiO_2 catalyst.

Figure 3 shows the adsorption isotherm determined for Se(VI) or Se(IV) on anatase type TiO_2 powders without UV irradiation.

With sample A, adsorption of Se(VI) was saturated at about 10 mg/g , a value which decreased by around half on addition of $5 \times 10^{-3} \text{ kmol/m}^3$ Na_2SO_4 , the Se(VI) adsorption sites being replaced by SO_4^{2-} ions.

The adsorption isotherm of Se(IV) for sample A is also depicted on Fig. 3. As is clear from this figure, the amount of Se(IV) adsorbed is around 2.5 times that of Se(VI) . Figure 3 also shows that the adsorption isotherm of Se(VI) for sample B, was slightly less than half the value for sample A.

4.2 Photocatalytic reduction of Se(VI) and Se(IV) with sample A

Figure 4(a) shows the rate curves of photocatalytic reduction of Se(VI) with sample A. As is obvious from this figure, the time required to reach the peak, which corresponds to slightly more than 80% of elemental Se^0 formation, is 5.4 ks, and the time for the completion of H_2Se generation is about 9.0 ks. It is noteworthy that no Se(IV) was detected as an intermediate product. The color of the TiO_2 powders after the generation of H_2Se was slightly grayish. It is supposed that a small amount of elemental Se^0 precipitated inside the TiO_2 aggregate causes this color change.

Figure 4(c) shows the experimental results obtained for the reduction, which was performed under the same conditions as for Fig. 4(a), except that Se(IV) was replaced with Se(VI) . The maximum yield of elemental Se^0 was a little over 75%, and the time required to reach the peak position was 1.8 ks, which corresponds to only around 1/3 the time for Se(VI) . After 7.2 ks, the starting species was completely decomposed, but elemental Se^0 remained with a few percents in the solu-

Fig. 3 Adsorption isotherms of Se(VI) or Se(IV) onto TiO_2 powders without UV irradiation. Temperature: $293 \pm 1 \text{ K}$, TiO_2 : 1.1 kg/m^3 , agitation time: 1.8 ks, HCOOH : $2.5 \times 10^{-2} \text{ kmol/m}^3$, Na_2SO_4 : $5 \times 10^{-3} \text{ kmol/m}^3$.

Fig. 4 Rate curves of photocatalytic reduction of Se(VI) specify in the absence (a) and the presence of Na₂SO₄ (b) and those of Se(IV) (c). (a), (c) Total Se concentration: 100 ppm, reductant: 2.5×10^{-2} kmol/m³ HCOOH, catalyst sample A: 1.1 kg/m³ TiO₂, N₂ gas bubbling, UV irradiation: 54 W/m², ○: Se ions in solution, □: Se⁰, △: Se ions adsorbed on TiO₂, ◇: H₂Se (b) Na₂SO₄ added: 5×10^{-3} kmol/m³, ■: Se⁰ and Se ions adsorbed on TiO₂. Other experimental conditions and symbols used are the same as (a) and (c).

tion. However, red Se⁰ having characteristic of amorphous, was changed to gray. The time required to attain the stable state with no more reduction of Se⁰ was 5.4 ks from the time at the peak.

The reduction from elemental Se⁰ to H₂Se took longer than for Se(VI).

As can be seen from Fig. 3, the amount of Se(IV) adsorbed is about 2.5 times larger than that of Se(VI). Since the photocatalytic reaction proceeds on the surface of the catalyst, and 1.5 more electrons are required for the reduction of Se(IV) to Se⁰ than Se⁰ to H₂Se according to the reaction eqs. (2) and (4), it is reasonable that the time required for reduction would decrease. The fact that Se⁰ was not perfectly reduced to H₂Se may be attributed to less photocatalytic reduction on the catalyst surface due to a partial change in the Se⁰ structure.

If the reduction site on the catalyst is occupied by difficult-to-reduce species, the reaction rate should be decreased.

Figure 4(b) depicts the reduction rate curves for Se(VI) obtained in the presence of 5×10^{-3} kmol/m³ Na₂SO₄. In this figure, the mark ■ shows the value which calculated by subtracting the sum of residual Se(VI) concentration and the amount of H₂Se formed from the initial concentration of Se(VI); it corresponds to the Se⁰ formed including the several % of Se(VI) adsorbed. Under the experimental conditions, the

amount of Se(VI) adsorbed is around a half that in the absence of Na₂SO₄, as depicted in Fig. 3. The time required to reach the peak position for the reduction of Se(IV) to Se⁰ is doubled, 10.8 ks, as anticipated. When the adsorption of SeO₄²⁻ ions was controlled with SO₄²⁻ ions, the reduction of Se(VI) was terminated at 14.4 ks. Although the graphical presentation was omitted, several mass percent of Se⁰ remained in the reaction system without further reduction at 21.6 ks, after the reaction system reached a stable state. This phenomenon is also evident from the liberation of Se⁰ from the surface of the catalyst and the change in the color of Se⁰ to gray.

4.3 Photocatalytic reduction of Se(VI) with sample B TiO₂

Figures 5(a) and (b) show the respective rate curves of Se(VI) reduction using samples A and B under the same conditions listed in the caption. As can be seen in these figures, the peak position of Se⁰ at which yields were both 82% was observed when 7% of Se(VI) for sample A and 15% for sample B remain in the solutions. The time required to reach the peak position of Se⁰ formation was 5.4 ks with sample A and 4.5 ks with sample B. The time required for completion of the reaction of Se⁰ to H₂Se was 3.6 ks for the former case and 1.5 ks for the latter. As is indicated by eqs. (3) and (4), 6 electrons are required to reduce Se(VI) to Se⁰ and 2 electrons to reduce Se⁰ to H₂Se. When sample B was used as a catalyst, the time required for Se⁰ formation and that for the reduction of Se⁰ to H₂Se satisfied the requirement of the electron ratio for these reactions. As already mentioned, the time required for the reduction of Se(VI) and of Se(IV) to Se⁰ with sample A can be roughly anticipated from the adsorption amount and electron conversion ratio. From the adsorption isotherm curves for Se(VI), the amount of Se(VI) adsorbed on sample B is found to be around 50% less than that for sample A

Fig. 5 Rate curves of the photocatalytic reduction of Se(VI) using catalyst sample A (a) and B (b). [Se(VI)]: 100 ppm, [HCOOH]: 2.5×10^{-2} kmol/m³, TiO₂ used: 1.1 kg/m³, N₂ gas bubbling, UV irradiation: 54 W/m².

as shown in Fig. 3. This result differs from the finding that the photocatalytic reduction rate is determined by adsorption amount of reductant, which is the finding obtained with sample A.

Considering the time required for reduction using sample B under the present experimental conditions, the energy converted by UV irradiation is efficient for the formation of elemental Se, and that of H_2Se as well. Therefore, the energy conversion ratios for both reactions are the same.

Regarding the reduction of Se° to H_2Se , it is unnecessary to consider the adsorption of Se(VI) and Se(IV) onto TiO_2 . The peak percent values for the two samples are almost the same, so that the time required for the formation of H_2Se with sample A should be 1.5 ks, as with sample B. However, the actual time was 3.6 ks, which means that the energy conversion ratio is 42% of that with sample B.

Assuming that this finding is appropriate and considering the difference in amount of Se(VI) adsorbed by the sample catalysts, the time required for the reduction of Se(VI) to elemental Se with sample A can be estimated by dividing the product of the time required for the reduction of Se° to H_2Se with sample B (1.5 ks) and the electrons required for the reduction ($6/2 = 3$) with the product of energy conversion ratio (0.42) and the adsorption amount ratio with sample A against those with sample B (2.0).

The time required for the reduction of Se(VI) to Se° , thus calculated, is 5.36 ks, which coincides well with the value of 5.4 ks shown in Fig. 5(a).

The difference obtained using different samples of photocatalyst can be explained as follows.

The specific surface area of sample A is $145 \text{ m}^2/\text{g}$, which is around 3 times that of sample B, but the mean particle size of sample B is far smaller than that of sample A as can be seen from the photographs shown in Fig. 1. Judging from these values, we can assume that the porous structure of sample A results in an increase in specific surface area, and more Se(VI) is adsorbed than by sample B, and this finding is reasonable in view of the difference in specific surface area.

On the other hand, the mass transfer of reactant and reaction product from inside the pore of particles to the bulk phase is anticipated to be small, and furthermore, the transmission ability of UV light to the inside of the pore is poor. Thus the energy conversion of sample B, which has finer particles than sample A, is thought to proceed effectively under the experimental conditions of this study.

Photocatalytic particles are sometimes fixed in a binder. In such cases, it is necessary to expose the photocatalytic particles. However, this is difficult with extremely fine particles. It is important to select a suitable photocatalyst.

4.4 Effect of various factors on the photocatalytic reduction of Se(VI) to Se°

In Section 3, we mentioned that the reduction effect is more remarkable with sample B than sample A under the present experimental conditions, and this phenomenon is attributable to the difference in energy conversion ratio due to the difference in mean particle size of the photocatalyst. As another reason, we should consider the change in the level of the energy band of TiO_2 caused by the pH of the solution, and the re-

combination of positive holes and adjacent electrons on TiO_2 particles under the excited conditions. Thus, the effects of solution pH, concentrations of HCOOH and Se(VI) and amount of photocatalysts upon reduction of Se(VI) ions were also investigated.

4.4.1 Effect of initial pH of Se(VI) solution

Figures 6 and 7 show the time variations of photocatalytic reduction of Se(VI) with UV irradiation duration at pH values of 3, 4 and 5, with samples A and B, respectively. The ordinate of these figures is the difference of initial concentration of Se(VI) and that after the reaction. This value corresponds to the amount Se° formed. However, it actually includes the amount of Se(VI) adsorbed onto TiO_2 . In the present study, each factor was evaluated without subtracting adsorption amount.

In all cases, red Se° was formed on irradiation with UV light, and the amount of Se° increased with the increase in irradiation period, while the reaction amount also increased. In contrast, the pH of the test solution was raised with the increase in irradiation time and reaction amount. For the Se(VI) solution whose initial pH was 5 the reaction stopped at 30 ppm Se(VI) with sample A, compared with 10 ppm Se(VI) with sample B, raising the pH value for both solutions above 7. From these findings, it was concluded that the reduction of Se(VI) to Se results in the increase in pH, indicating that the reaction proceeded according to eq. (3), which is eqs. (1) and (2) combined. Also, we know that no reduction of Se(VI) to Se can occur above pH 7. When the solution pH with sample A is compared at the same reduction level to that with sample B, the latter's pH is higher.

To compare the reduction rates with both sample catalysts, the invert of the time taken for the reaction amount to reach

Fig. 6 Effect of initial pH on rate curves for the photocatalytic reduction of Se(VI) using sample A catalyst. $[\text{Se(VI)}]$: 100 ppm, $[\text{HCOOH}]$: $2.5 \times 10^{-2} \text{ kmol/m}^3$, TiO_2 used: 1.1 kg/m^3 , N_2 gas bubbling, UV irradiation: 48 W/m^2 .

Fig. 7 Effect of initial pH on rate curves for the photocatalytic reduction of Se(VI) using sample B catalyst. [Se(VI)]: 100 ppm, [HCOOH]: 2.5×10^{-2} kmol/m³, TiO₂ used: 1.1 kg/m³, N₂ gas bubbling, UV irradiation: 48 W/m².

50 ppm was employed to calculate their mean reaction rate $\bar{R}_{50}$, and the relationship between $\bar{R}_{50}$ and pH was examined. With sample B, the reaction rate stayed a constant value of 5.6×10^{-4} s⁻¹ even when the solution pH changed from 3 to 4, whereas the reaction rate at pH 3 with sample A was 4.7×10^{-4} s⁻¹ and that at pH 4 was 6.7×10^{-4} s⁻¹. However, the difference between samples A and B is not significant.

Figure 8 illustrates the effect of pH on Se(VI) adsorption by TiO₂ catalyst. The amount of Se(VI) adsorbed by sample A, whose specific surface area is greater than that of sample B, is larger than that by sample B. However, this amount decreases with the increase in pH regardless of which sample catalyst was used.

By raising the solution pH from 3 to 4, the amount of Se(VI) adsorbed on the catalysts was reduced significantly, but the rate of reduction showed no significant change when sample B was used. In contrast, the rate with sample A increased slightly. Therefore, it is suggested that not only adsorption in the control catalytic reaction, but also the driving force is increased by the shift in the energy band level of TiO₂ in the minus direction due to the increase of pH of the test solution.

4.4.2 Effect of the amount of catalyst

Next, the effect of catalyst amount on reduction of Se(VI) to Se⁰ was examined. The amount of Se(VI) reacted and pH variation were determined by changing the amount of catalyst under the conditions of a HCOOH concentration of 2.5×10^{-2} kmol/m³, initial Se(VI) concentration of 100 ppm, initial pH of 4, and UV light irradiation period of 1.8 ks. The amount reacted increased with catalyst amount up to 1.5 kg/m³, but no further, with sample B. By contrast, the re-

Fig. 8 Effect of pH on adsorption of Se(VI). Room temperature, TiO₂ used: 1.1 kg/m³, agitation time: 1.8 ks, [Se(VI)]: 100 ppm, [HCOOH]: 2.5×10^{-2} kmol/m³, pH control: NaOH.

action amount increased with catalyst amount up to 1.1 kg/m³ but then decreased slightly, with sample A. On the other hand, the pH was raised more with sample B which brought a larger reduction in the amount than that with sample A, and increased with the increase in reduction amount for both catalyst samples. The effect of the amount of catalyst on the reaction rate may also be influenced by the dispersibility of catalyst.

4.4.3 Effect of formic acid concentration

The variation in amount reacted and solution pH with time were determined by changing the formic acid concentration in the test Se(VI) solution to 1.0, 2.5 and 5.0×10^{-2} kmol/m³ using both catalysts A and B. With both catalysts, the rate of decrease in Se(VI) concentration was smaller when 1.0×10^{-2} kmol/m³ rather than 2.5×10^{-2} kmol/m³ or more HCOOH was used. On the other hand, the tendency for the pH to increase was more remarkable with sample B than A, when the formic acid concentration was low.

Figure 9 shows the plots of mean reduction rate vs formic acid concentration. The reductive rate was calculated from the time required for Se(VI) to be reduced to 50 ppm. The rate increases with the HCOOH concentration, showing a constant value above 2.5×10^{-1} kmol/m³ HCOOH. Initial pH values of Se(VI) solutions were adjusted to 3, at which pH the rate of reduction is slightly larger with sample B than A.

4.4.4 Effect of initial Se(VI) concentration

Using both sample catalysts, reduction rates for Se(VI) solution were measured by changing initial Se(VI) concentrations to 50, 100 and 200 ppm. With sample A, the rate tended to decrease in the sequence of the initial Se(VI) concentration of 100, 50 and 200 ppm. With sample B, these solutions whose initial Se(VI) concentrations were 50 and 100 ppm, showed a similar rate of reduction until the reaction amount reached 50 ppm, but the reduction of Se(VI), whose concentration was 200 ppm was slow. Also, the reduction of Se(VI)

Fig. 9 Effect of HCOOH on $\bar{R}_{50}$ for the photocatalytic reduction of Se(VI). [Se(VI)]: 100 ppm, initial pH: 3.0, TiO_2 used: 1.1 kg/m^3 , N_2 gas bubbling, UV irradiation: 48 W/m^2 .

Fig. 10 Effect of initial Se(VI) concentration on $\bar{R}_{40}$ for the photocatalytic reduction of Se(VI). [HCOOH]: $2.5 \times 10^{-2} \text{ kmol/m}^3$, initial pH: 3.0, TiO_2 used: 1.1 kg/m^3 , N_2 gas bubbling, UV irradiation: 48 W/m^2 .

solution, whose initial Se(VI) concentration was 200 ppm, proceeded slowly up to 1.8 ks with both catalysts, and accelerated later on.

To compare photocatalytic reductions with sample A to these with sample B, mean reduction rates were calculated from the inverse of the time required to reach a Se(VI) concentration of 40 ppm, $\bar{R}_{40}$, and plotted against initial Se(VI) concentration as shown in Fig. 10. As is clear from this figure, the rate of Se(VI) reduction was maximal at an initial Se(VI) concentration of 100 ppm when sample A was used. A similar tendency was observed with sample B, at below 100 ppm Se(VI), but the reduction was greatly suppressed at an initial Se(VI) concentration of 200 ppm. With both sample catalysts, the reduction rates decreased markedly when initial Se(VI) concentrations were high. This may be caused by the slow mass transfer of the product of reduction onto the TiO_2 catalyst, and thus the progress of the inverse reaction, re-oxidation of the product, was significant. On the other hand, the decrease of reduction rate observed with the initial Se(VI) concentration of 50 ppm for sample A is considered to be caused by the decrease of adsorption amount.

5. Summary

Suspensions of the fine particles of two anatase-type TiO_2 catalysts with different specific surface areas and particle sizes were used to study the photocatalytic reduction of Se(VI) in aqueous Se(VI) solutions. The effects of various factors on reduction rates were elucidated. The main results obtained are as follows:

(1) Se° and H_2Se were detected during the photocatalytic reduction of Se(VI), whereas Se(IV) was not.

(2) The rate of reduction of Se(VI) was controlled by the amount adsorbed onto each type of TiO_2 .

(3) Less Se(VI) was adsorbed on sample B with smaller dispersed particle size in comparison with sample A. Nevertheless, the rate of reduction was slightly larger with sample B than that with A. The energy conversion ratio of the irradiation of UV light, which is calculated from the reduction rate from Se° to H_2Se , is greatly affected by particle size, thus the value is larger for sample B than A.

(4) The time required for the reduction of Se(VI) to Se° and of Se° to H_2Se with sample B are proportional to the electrons required for these reactions.

(5) The values of relative energy conversion ratio for sample A, estimated from the time required for the reduction of Se° to H_2Se with samples A and B, and the amount of Se(VI) adsorbed, were used to calculate the theoretical time required for the formation of Se° from Se(VI), which is consistent with the experimental value.

(6) The effects of solution pH, amount of catalyst, formic acid concentration and initial Se(VI) concentration upon the reduction rate of Se(VI) were examined. It was found that the solution pH as well as dispersibility of the catalyst powder are important factors affecting reduction in the catalytic reaction of suspension type used in the present study.

REFERENCES

- 1) Y. Isshihashi, H. Yamashita and M. Anpo: *Kinouzairyo*, **16** (1996), 12–22.
- 2) H. Kubokawa, K. Honda and Y. Saito: *Hikarishokubai*, Asakurashoten, Tokyo, (1988), pp. 53–55.
- 3) A. Fujishima and K. Honda: *Bull. Chem. Soc. Japan*, **44** (1971), 1148–1150.
- 4) T. Inoue, A. Fujishima, S. Konishi and K. Honda: *Nature*, **277** (1979), 637–638.
- 5) A. L. Pruden and D. F. Ollis: *J. Catal.*, **81** (1983), 404–417.
- 6) H. Takeuti and S. Nishikata: *Kankyokanri*, **32** (1996), 915–928.
- 7) A. Fujishima, K. Hashimoto and Y. Kubota: *J. Surface Sci. Soc. Japan*, **16** (1995), 188–193.
- 8) K. Tanaka: *Kankyokanri*, **32** (1996), 923–928.
- 9) K. Tanaka: *Ceramics Japan*, **31** (1996), 825–828.
- 10) E. Kikuchi: *Shigen-to-Kankyo*, **6**(2) (1997), 173–177.
- 11) S. Sanuki, T. Kojima, K. Arai, S. Nagaoka and H. Majima: *Metall. Trans. B*: **30B** (1999), 15–20.
- 12) M. J. N. Pourbaix, J. Van Muylden and N. de Zoubov: *Atlas d'Equilibres Electrochimiques a 25°C*, Gautier Villard, Paris, (1963), 554–559.
- 13) I. Iwasaki, A. Kishioka and Y. Yoshida: *Bunsekikagaku*, **10** (1961), 479–482.