1308 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 1308—1313 (1981) [Vol. 54, No. 5

Heterogeneous Reactions of Nitrogen Monoxide on Titanium Dioxide Photocatalysts in Solutions

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(Received August 28, 1980)

Heterogeneous reactions of nitrogen monoxide on illuminated TiO_2 catalysts in 1 mol dm^{-3} $HClO_4$ were studied by electrochemical analysis. Nitrogen monoxide was reduced to ammonia and hydrazine. The main reaction was found to be a chemical reaction of hydroxylamine as a reaction intermediate with nitrogen monoxide to give molecular nitrogen. Nitrate was detected as an oxidation product formed by the counterpart reaction of the reduction of nitrogen monoxide.

Heterogeneous reactions on semiconductor photocatalysts in solutions are of interest in view of solar energy utilization. Fundamental mechanisms of the photocatalysts have been elucidated,[1-6] and several reaction systems in line with the established view have recently been reported.[7-14]

According to Guth and Schrauzer,[15] the reduction of molecular nitrogen to ammonia and hydrazine takes place on illuminated moist TiO_2 powders with simultaneous evolution of oxygen. However, the yield was poor. Causes for this might be: (1) the reaction terminates in the gas phase, when adsorbed active water is consumed, and (2) the reaction requires large positive Gibbs energy changes.

$$1/2N_2 + 3/2H_2O \longrightarrow NH_3 + 3/4O_2 \quad (1)$$
$$\Delta G^0_{298} = 382.5 \text{ kJ/mol}$$

$$N_2 + 2H_2O \longrightarrow N_2H_4 + O_2 \quad (2)$$
$$\Delta G^0_{298} = 625.7 \text{ kJ/mol}$$

In view of thermodynamics, the reduction of nitrogen monoxide to ammonia and hydrazine should take place more easily.

$$NO + 3/2H_2O \longrightarrow NH_3 + 5/2O_2 \quad (3)$$
$$\Delta G^0_{298} = 292.6 \text{ kJ/mol}$$

$$2NO + 2H_2O \longrightarrow N_2H_4 + 2O_2 \quad (4)$$
$$\Delta G^0_{298} = 448.1 \text{ kJ/mol}$$

The present study was undertaken to investigate reactions of NO on illuminated TiO_2 photocatalysts in solution.

Experimental

A tank NO gas (99.9% purity) was passed through 5 mol dm^{-3} KOH and then through 5 mol dm^{-3} H_2SO_4 to remove N_2O and NO_2.

TiO_2 powder of the rutile modification (Fuji Titanium Co.) was used in a commercially available form and a partially reduced one. The powder was soaked in a dilute HCl solution overnight, washed with twice distilled water several times, and then dried in a drying oven. Partial reduction was carried out under a stream of H_2 at 700 °C for 30 min. Platinization of the powder was carried out by means of photodeposition.[16] The powder was suspended in a HCl solution containing H_2PtCl_6. Illumination with a 500 W xenon lamp was carried out under N_2 atmosphere until the yellow color of the solution completely faded. The amount of platinum deposited on the powder surface was 21.8 mg/g of TiO_2, its specific surface area being 14.2 m^2/g as determined by the BET method. The amount of deposited Pt was comparable to that required for a monolayer coverage of the powder when the surface exposed to solution is the (001) face.

A TiO_2 single crystal, reduced in a stream of H_2 at 600 °C for 30 min, was used as an electrode as well as a photocatalyst. The (001) face was chosen as the electrode surface. Platinization of the electrode surface was carried out by means of electrodeposition.[17] The amount of deposited platinum was estimated by measuring the charge passed during the course of deposition, and converted into equivalent monolayers.[17]

Polarization measurements were carried out in the usual beaker type cell or in a H type cell with a potentiostat (Hokuto Denko, model HA 101). Experiments of the heterogeneous reaction were carried out in a beaker cell of *ca.* 10 ml capacity equipped with a gas inlet in the side wall near the bottom and with a gas outlet in the top of the cell. Illumination was made with focusing light from a 500 W xenon lamp. The powder catalyst was agitated with a magnetic stirrer during the course of illumination, NO gas being continuously bubbled into the solution.

Quantitative analysis of NH_3, N_2H_4, NH_2OH, NO_3^-, and NO_2^- was carried out by colorimetry. Solutions in the heterogeneous reaction vessel were transferred to a volumetric flask and diluted to 25 ml. In the case of powder photocatalysts, the solution was separated from the catalyst by filtration, and then diluted to the same volume. The diluted solutions were used as the sample solutions. The amount of NH_3 was determined by the method of Kruse and Mellon.[18] 10 ml of the sample solution was subjected to distillation in a micro-Kjeldahl apparatus. The ammonia in the distillate was collected in 0.01 mol dm^{-3} H_2SO_4, and determined. N_2H_4 was determined in 10 ml of the sample solution with *p*-dimethylamminobenzaldehyde.[19] For the determination of NH_2OH,[20] 5 ml of the sample solution was mixed with 1 ml of 10% NaOH, and then with 0.25 ml ethyl acetate. After the color of the ester had faded the solution was acidified with 25% HNO_3 making the volume of solution 25 ml. 1 ml of a 8% $FeCl_3$ solution was then added and the absorbance was measured at 505 nm. NO_3^- was determined by the nitration of sodium salicylate in the presence of H_2SO_4.[21] In order to eliminate interference from NO_2^-, 1 ml of the sample solution was diluted to 10 ml, and 1 ml of a sulfanilamide solution (1 g of sulfanilamide/100 ml of 1% HCl) was added to it. After standing for 15 min, 1 ml of a *N*-(naphthyl)ethylenediamine solution (0.1 g of *N*-(naphthyl)ethylenediamine/100 ml of water) was added, and the absorbance was measured at 530 nm after shaking for 20 min.[22]

N_2 originated from NO was determined by gas chromatography with the use of a helium carrier and a 70 cm length molecular sieve 5 A column. In order to eliminate any error introduced by N_2 in air, experiments for collection of gases were carried out under Ar atmosphere. Since the chromatograms of N_2 and NO_2 overlapped at room temperature, the column was cooled down to −76 °C by dipping in a mixture of dry ice and acetone, the sample gas being then injected. After the chromatogram of Ar appeared, the coolant was removed to warm up the column to room temperature. During this time, N_2, NO, and NO_2 appeared successively in the chromatograms.[23,24]

Results and Discussion

Electrochemical Reactions of NO on TiO_2 Electrodes. According to the results obtained by Dutta and Landoldt on Pt electrodes in 4 mol dm^{-3} H_2SO_4,[25] the electrochemical reduction of NO occurs with two waves. The first wave starting at 0.6 V *vs.* SCE was postulated to be due to the formation of an intermediate having an oxidation state identical with that of N_2O such as $H_2N_2O_2$ or NO^-, and the second one to further reduction of the intermediate to NH_3OH^+. If the intermediate is assumed to be $H_2N_2O_2$, then the reactions are represented by

$$2NO + 2H^+ + 2e^- = H_2N_2O_2, \qquad (5)$$

$$E^0 = 0.71\ \text{V}\ \textit{vs.}\ \text{SHE}^{26)}$$

$$H_2N_2O_2 + 6H^+ + 4e^- = 2NH_3OH^+. \qquad (6)$$

$$E^0 = 0.39\ \text{V}\ \textit{vs.}\ \text{SHE}^{23)}$$

Figure 1 shows cyclic voltammograms for the reduction of NO in 1 mol dm^{-3} $HClO_4$ at a Pt electrode. Two waves appear by cathodic polarization up to 0.1 V *vs.* SCE. The formation of NH_3OH^+ is conceivable at potentials equal to or more negative than 0.1 V *vs.* SCE. The overall reaction for the reduction of NO is then represented by

$$NO + 4H^+ + 3e^- = NH_3OH^+. \qquad (7)$$

Steady state current-potential curves obtained at the TiO_2 single crystal electrode are shown in Fig. 2, and those at a platinized electrode in Fig. 3. Measurements were carried out under both NO and N_2 atmosphere. The cathodic curves were obtained in the dark, while anodic ones under illumination. The cathodic current is enhanced by introduction of NO into the electrolyte, suggesting that the cathodic reaction is mainly due to the reduction of NO when it is present in the solution. The enhancement of the cathodic current is great when the electrode is platinized. On the other hand, a slight suppression of the anodic photocurrent is observed by introduction of NO. This seems to be due to the absorption of near-ultraviolet light in the electrolyte, causing a decrease in light quanta incident on the electrode. As shown in Fig. 4, NO-saturated 1 mol dm^{-3} $HClO_4$ shows relatively high absorption in wavelengths 340—400 nm which are effective for excitation of TiO_2.

In order to study the anodic photocurrents, constant

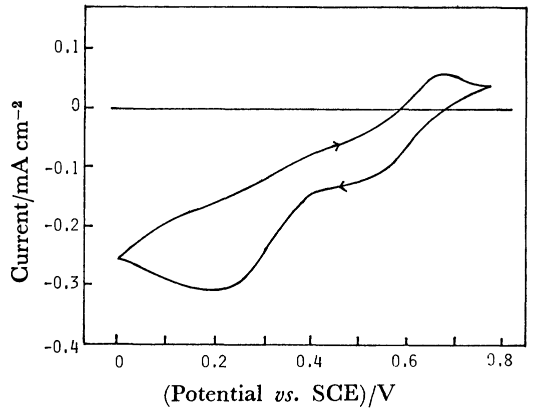

Fig. 1. Current-potential curves of a Pt electrode in 1 mol dm^{-3} $HClO_4$ under bubbling NO.
Sweep rate: 50 mV/s.

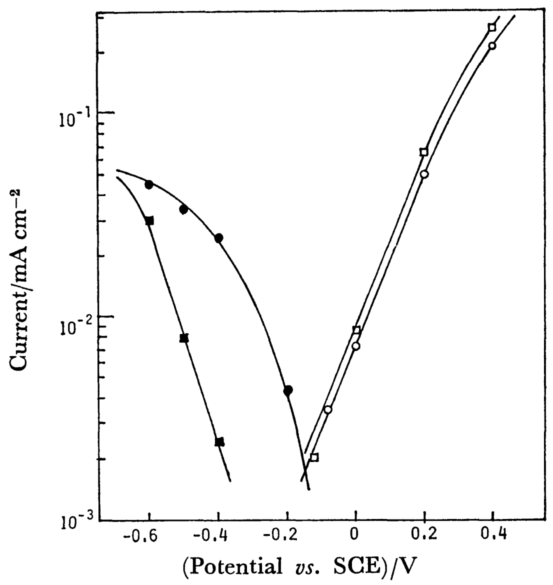

Fig. 2. Steady state current-potential curves of a single crystal TiO_2 electrode under illumination and in the dark.
Open symbols: under illumination, filled in symbols: in the dark. (○, ●): NO-bubbled 1 mol dm^{-3} $HClO_4$, (□, ■): 1 mol dm^{-3} $HClO_4$ under N_2 atmospheres.

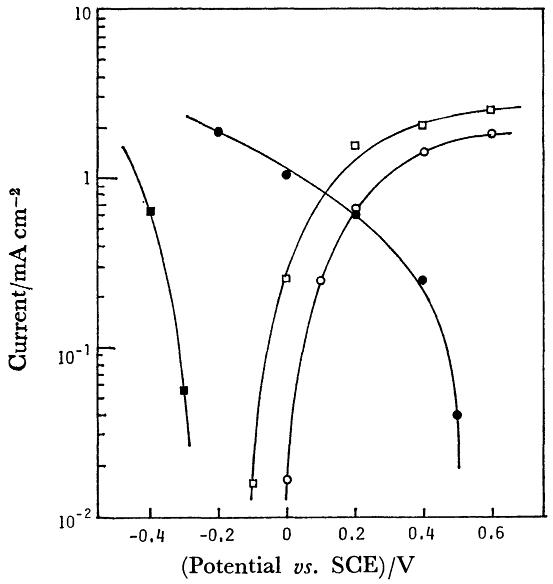

Fig. 3. As in Fig. 2, but for Pt(θ=100)/TiO_2 electrode.

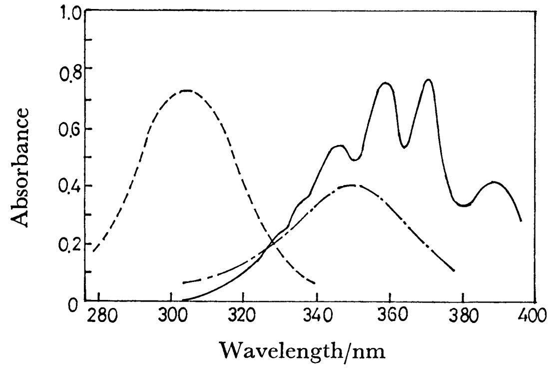

Fig. 4. Absorption spectra of 1 mol dm^{-3} $HClO_4$ containing oxide species of nitrogen.
(——): The solution bubbled NO for 5 min, (·——·): 0.01 mol dm^{-3} $NaNO_2$, (— —): 0.1 mol dm^{-3} KNO_3.

potential electrolysis at 0.5 V *vs.* SCE was carried out in 1 mol dm^{-3} $HClO_4$ in the presence and absence of NO, and the volume of gases evolved from the anodic compartment of an H type cell was compared with those predicted theoretically from the following equation on the basis of the consumed electrolytic charge.

$$2H_2O + 4p^+ \longrightarrow O_2 + 4H^+, \tag{8}$$

where p^+ denotes a photo-generated positive hole. The results are given in Table 1. When NO was dissolved in the electrolyte, gas evolution was appreciably suppressed, resulting in a low current efficiency for the oxygen evolution reaction. Not only water but also NO should participate in the photoanodic processes.

Reduction of NO gives rise to hydroxylamine.[25,26] However, by constant potential electrolysis of TiO_2 electrodes in the dark in NO-saturated solutions under various polarization conditions, ammonia and hydrazine, but not hydroxylamine, were produced regardless of whether or not the platinization of the electrode was made. The results are given in Table 2, in which the results obtained at Pt electrodes are also given. No formation of hydroxylamine was formed even by use of Pt electrode. If we assume that both ammonia and hydrazine are produced by the electrochemical reduction of hydroxylamine, then the reactions would be represented by Eqs. 9 and 10. We see from the

$$NH_3OH^+ + 2H^+ + 2e^- = NH_4^+ + H_2O, \tag{9}$$

$$E^0 = 1.35\ \text{V}\ vs.\ \text{SHE}^{26)}$$

$$2NH_3OH^+ + H^+ + 2e^- = N_2H_5^+ + 2H_2O. \tag{10}$$

$$E^0 = 1.41\ \text{V}\ vs.\ \text{SHE}^{26)}$$

results (Table 2) the following. (1) The ammonia production increases with a cathodic shift of the electrode potential. At the extreme of the shift of 0.5 V *vs.* SCE, however, hydrogen evolution seems to occur competitively, as judged from the onset potential of the cathodic current in alkaline solutions.[17] Even at 0.25 V *vs.* SCE, the same would be true for the platinized electrode, though the competition would occur to a much smaller extent. Adsorbed hydrogen on the electrode surface is essential for the production of ammonia and hydrazine in appreciable amounts. Theoretically, the reactions given by Eqs. 9 and 10 should occur easily, since the standard electrode potentials are positive. However, the actual rates of the reactions are so low[27] that a large overpotential is needed for the reactions to occur with appreciable rates. (2) The platinized TiO_2 is the most active for the conversion of NO to ammonia and hydrazine. Physical and chemical nature of the deposited platinum on TiO_2 has not so far been characterized. A high capability of sorbing hydrogen might be related to the observed high activity, since electrodeposited platinum has a high activity for the hydrogen electrode reaction.

Judging from electrochemical analysis on the reduction of NO on Pt electrodes,[25,26] there is no doubt as to the formation of hydroxylamine. However, this is not the case in electrolyte solutions. The current efficiency for the production of ammonia and hydrazine, determined on the basis of Eqs. 7, 9, and 10,

TABLE 1. CURRENT EFFICIENCY FOR THE EVOLUTION OF OXYGEN AT ILLUMINATED TiO_2 ELECTRODE IN 1 mol dm^{-3} $HClO_4$ WITH AND WITHOUT DISSOLVED NO

Atmosphere	Volume of gas ml	Consumed charge C	Current efficiency %
N_2	0.82	14.1	100
NO	0.52	15.0	60.1

TABLE 2. ELECTROLYTIC REDUCTION OF NO AT TiO_2 ELECTRODES IN THE DARK IN 1 mol dm^{-3} $HClO_4$

Run No.	Electrode	Potential *vs.* SCE V	Consumed charge C	Produced substance NH_3 μmol	 N_2H_4 μmol	 N_2 μmol	Total current[a)] efficiency %
1	Pt	0.00	50.0	0.93	n.d.[b)]	n.d.	0.90
2	Pt	−0.50	12.5	2.1	0.66	n.d.	12.2
3	TiO_2	−0.25	12.4	0.60	0.12	n.d.	3.08
4	TiO_2	−0.50	12.5	2.8	0.11	n.d.	11.5
5	Pt(θ=100)/TiO_2[c)]	−0.25	12.7	0.76	1.87	n.d.	14.3
6	Pt(θ=100)/TiO_2	−0.50	12.5	5.13	1.87	n.d.	31.4
7	TiO_2	−0.20	12.7	0.55	0.08	34.1	80.3

a) Calculated on the basis of the determined substance. b) Not determined. c) TiO_2 electrode covered with deposited Pt the amount of which roughly corresponds to 100 monolayers coverage.

was found to be low, suggesting that a large fraction of the produced hydroxylamine is consumed in another reaction.

Gas bubbles stick to the electrode surface during the course of electrolysis even at potentials at which no hydrogen evolution is conceivable. The formation of N_2 was postulated as a principal reduction reaction. For the sake of confirmation determination of N_2 originating from NO was attempted. Electrolysis was carried out in a sealed cell with atmosphere of NO, the cell being kept in Ar during the course of electrolysis. After electrolysis at −0.2 V *vs.* SCE for 30 h, where the evolution of hydrogen is thermodynamically impossible, N_2 in the sealed cell was determined. As expected, N_2 was produced by electrolysis (Table 2). The reaction schemes for the formation of N_2 can be given by either one or both of the following equations.

$$NH_3OH^+ + 2NO = N_2 + HNO_2 + H_3O^+, \quad \Delta G^0 = -407.6\ \mathrm{kJ/mol} \tag{11}$$

$$4/3NH_3OH^+ + 2/3NO + 2/3H^+ = N_2 + 2H_3O^+. \quad \Delta G^0 = -214.6\ \mathrm{kJ/mol} \tag{12}$$

If the N_2 production is due to the reduction given by Eqs. 7 and 11, then the total current efficiency for the formation of ammonia, hydrazine and N_2 amounts to 80.3%. If Eqs. 7 and 12 are used, the value is 106%.

Table 3 shows the decrease in the amount of NH_3OH^+ by bubbling NO into the solution. The results show that even ammonia and hydrazine, when produced, are consumed to evolve N_2, causing a decrease in current efficiency for the formation of these substances. NO_2^- is formed by bubbling NO into 1 mol dm^{-3} $HClO_4$, possibly by the equation,

$$2NO + H_2O = NOH + HNO_2. \tag{13}$$

Heterogeneous Reactions on TiO_2 Single Crystal Photocatalysts. In heterogeneous reactions on n-type semiconductor photocatalysts, reduction process and photosensitized oxidation process proceed mainly on the non-illuminated and illuminated surfaces, respectively.[28,29] Electrochemical prediction of occurring heterogeneous reactions can be made by means of the current-potential curves of semiconductor photocatalysts in the photocatalytic reaction systems,[3,4] (Figs. 2 and 3). The current-potential curve due to the reduction of NO intersects with photoanodic curves, suggesting that heterogeneous reactions should occur on the illuminated TiO_2. By comparison of Figs. 2 and 3 we see that the platinization of TiO_2 photocatalysts mainly effects the reduction process. Experiments were carried out by illuminating the non-platinized surface, the platinized surface not being illuminated. Illumination was carried out for 15 h under bubbling NO into 5 ml of 1 mol dm^{-3} $HClO_4$, and the solution was analyzed for NO_3^- as an oxidation product, and for ammonia and hydrazine as reduced ones. The results are given in Table 4.

TABLE 3. DECREASE OF NH_2OH, NH_3 AND N_2H_4 BY CHEMICAL REACTIONS WITH NO

Substance[a)]	Amount[b)] Initial μmol	Final μmol	Decrease μmol	Produced NO_2^- μmol
NH_3	27.6	13.4	13.6	70.7
N_2H_4	112.0	0.7	111.3	59.9
NH_2OH	150.0	65.3	84.7	83.9
blank[c)]	—	—	—	55.1

a) Dissolved in the base solution 1 mol dm^{-3} $HClO_4$. b) Solution volume 5 ml, NO gas bubbled for 2 h. c) NO gas bubbled in 1 mol dm^{-3} $HClO_4$.

TABLE 4. HETEROGENEOUS REACTION OF NO ON SINGLE CRYSTAL TiO_2 PHOTOCATALYST[a)]

Pt coverage (monolayers)	Oxidation process Amount of NO_3^- μmol	Reduction process Amount of NH_3 μmol	Amount of N_2H_4 μmol
0	91.0	0.96	0.15
100	36.5	2.93	2.28
300	21.4	1.69	1.62

a) Experiments were carried out under illumination, made on the platinum-free surface, for 15 h for a solution volume of 5 ml.

The platinized photocatalysts give a lower amount of NO_3^- but higher amounts of ammonia and hydrazine than the non-platinized catalysts, in line with the results given in Table 2 when a comparison of results is made at the same potential.

Heterogeneous Reactions on Powder Photocatalysts. The formation of NO_3^- by oxidation and of NH_3 by reduction was investigated by using TiO_2 powder photocatalysts. As the photocatalysts, a commercially available powder, a partially reduced powder and a platinized powder subjected to no reduction were used. The degree of platinization was so low as to give a monolayer coverage, differing from the cases of single crystal catalysts. Photodeposition to give a much higher coverage was unsuccessful.

The results on the heterogeneous reactions on the powder photocatalysts are given in Table 5. The NO_3^- production was suppressed but NH_3 production seemed to increase with platinization as observed in single crystal photocatalysts. However, the effect of platinization was not so obvious as in the case of single crystal catalysts mainly due to the low coverage of deposited Pt. The effects of the partial reduction of the catalyst are not clear. The results obtained are greatly scattered, making it difficult to give conclusions on the effect of illumination time and the amount of catalyst loadings on the production of NO_3^- and NH_4^+. Since chemical reactions (Eqs. 11 to 13) are involved in the heterogeneous reaction, slight differences in bubbling conditions of NO might greatly influence the yield.

The results given in Figs. 4 and 5 indicate that the amount of ammonia produced is higher in the powder photocatalysts than in the single crystals. The ammonia production may require the adsorbed hydrogen on the catalysts surface. A large surface area of powder photocatalysts is advantageous. The attack

TABLE 5. HETEROGENEOUS REACTION OF NO ON TiO_2 POWDER PHOTOCATALYSTS[a)]

Catalyst	Sp. surface area $m^2\ g^{-1}$	Amount of powder g	Illumination time h	NO_3^- µmol	NH_3 µmol
Unreduced TiO_2	14.2	0.2	8	40.7	5.91
		0.2	15	43.9	6.22
		0.1	15	71.4	8.25
Reduced TiO_2[b)]	16.9	0.2	8	18.4	18.6
		0.2	15	26.3	7.66
		0.1	15	31.0	1.43
Platinized TiO_2[c)]	16.0	0.2	8	6.79	6.73
		0.2	15	8.04	9.31
		0.1	15	10.7	4.05
No catalyst			13.5		0.18

a) Solution: 5 ml of 1 mol dm^{-3} $HClO_4$. b) H_2 reduction at 700 °C for 30 min. c) Amount of Pt: 21.8 mg Pt/g of TiO_2, corresponding roughly to a monolayer coverage.

of NO on the ammonia produced would not take place with the same rate in the powder and single crystal catalyst systems, since experimental conditions differ.

Summary of the Heterogeneous Reactions of NO. It was confirmed that NO dissolved in 1 mol dm^{-3} $HClO_4$ undergoes heterogeneous reactions on TiO_2 photocatalysts, the reaction schemes being complicated. From the current-potential curves of TiO_2 single crystal electrodes (Figs. 2 and 3), we see that heterogeneous reaction takes place on single crystal catalysts following electrochemical mechanism. This might be the case also for powder photocatalysts, since as regards ZnO[30)] and TiO_2[17,31)] there is close similarity in photoelectrochemical properties of semiconducting powders to those of single crystals. The reaction schemes can be estimated on the basis of anodic and cathodic reactions at TiO_2 electrodes.

The oxygen evolution occurs as the main anodic reaction (Table 1). The oxygen evolved would easily react with NO to give NO_2, and the resulting NO_2 would dissolve into solutions to give NO_3^- with a disproportionation reaction. The current efficiency for the oxygen evolution decreases in the presence of NO. This is partly attributable to the contribution of the chemical reaction with NO. The electrochemical oxidation of NO to finally give NO_3^- should also be taken into consideration. NO is oxidized to NO_3^- at high anodic potentials on Pt electrodes.[32)]

The oxidation processes are postulated on the basis of the electrolysis experiments. The main difference expected between the electrolysis experiments and photocatalytic experiments would result from the difference in the magnitude of the electric field built in the semiconductor surface, the magnitude being usually small in the cases of heterogeneous reaction systems. The weak electric field enhances the recombination of photo-generated positive holes with electrons as majority charge carriers, resulting in a low utilization efficiency of light quanta as demonstrated by Ohnishi *et al.*[33)] To our present knowledge this effect is the only one expected for the change of surface electric field. No change would be predicted in the nature of electrochemical reactions when variation arises in the electric field of semiconductor surfaces.

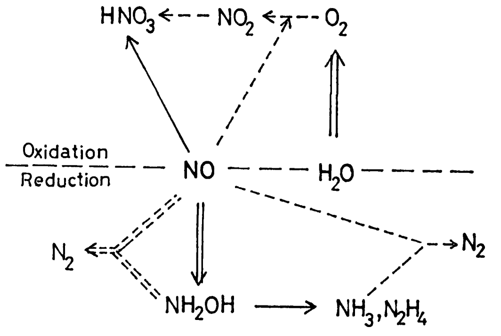

Fig. 5. Schematic illustrations of heterogeneous reactions of NO on illuminated TiO_2 in 1 mol dm^{-3} $HClO_4$.
Double lines stand for the main reaction path. Solid line: electrochemical reaction path, dashed line: chemical reaction path.

If there were any change the proposed reaction schemes would then become invalid.

As a cathodic process which should occur to keep the electrical neutrality of the photocatalysts, the reduction of NO to hydroxylamine would take place. A fraction of the hydroxylamine produced escapes from the chemical reaction with NO, and is subjected to further reduction to ammonia and hydrazine. A part of the produced ammonia and hydrazine would be decomposed into N_2 by the chemical reaction of NO. These routes are illustrated in Fig. 5.

In view of electrochemistry, the production of ammonia and hydrazine from NO seems promising in the heterogeneous reaction systems on illuminated TiO_2 if the entire processes are governed by electrochemical mechanisms. Actually, however, several chemical reactions are involved, and as a result N_2 is produced as the main substance.

The present study was supported by Grant-in-Aid for Scientific Research No. 505008 from the Ministry of Education, Science and Culture.

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