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NOTES

Reduction of Nitrate Ions into Nitrite and Ammonia over Some Photocatalysts

Reduction of nitrogen oxides and oxyanions (NO, NO_2^-, NO_3^-, etc.) has been extensively studied electrochemically (using metal electrodes or electrocatalysts) (*1*), biochemically (using enzymes) (*2, 3*), catalytically (*4*), and so on. On catalysis, nitric oxide reduction has recently received considerable attention again for pollution control. Noble metal-supported catalysts are mainly employed for the thermal reaction.

The present authors have previously reported that nitrate was quantitatively reduced by Ti^{3+} to form ammonia on the surface of thermally reduced TiO_2 and Pt–TiO_2 powders (*5*) in the absence of light and that the photocatalytic reduction of nitrate to form ammonia proceeded on a Pt–TiO_2 catalyst (*6*) at room temperature. It is noteworthy that reduction of nitrate using water as a hydrogen source is an "up-hill" reaction, which has previously been successful in only a few systems, such as photodecomposition of water:

$$2HNO_{3(aq)} + H_2O_{(l)} \rightarrow NH_4NO_{3(aq)} + 2O_{2(g)} \quad \Delta G^\circ_{298} = 269 \text{ kJ}.$$

Nitrate is reduced to ammonia by hydrogen adsorbed on supported platinum even under dark conditions (*6*). The hydrogen absorbed on platinum in the present study is supplied by the photoreduction of water in the photocatalytic cycle. This process seems to be similar to those observed in ecological systems, where reduction of nitrate to ammonia proceeds in the dark phase of photosynthesis and the reducing power is supplied from substrates formed by the photoreduction (*3*).

Thus, the photocatalytic reduction of nitrate is important for energy conversion by artificial photosynthesis and pollution control. In this paper, the reduction of nitrate was studied over various photocatalysts (native and modified TiO_2, $SrTiO_3$, $K_4Nb_6O_{17}$, In_2O_3, and WO_3) under some different conditions, and the relationship between activity and reaction conditions (photocatalyst composition and solution acidity) was revealed.

TiO_2 and $K_4Nb_6O_{17}$ powders were prepared, as had been reported previously (*6, 7*). Proton-exchanged $K_4Nb_6O_{17}$ (H^+/$K_4Nb_6O_{17}$) (*8*) was also used. $SrTiO_3$ (Alfa-Products), WO_3, and In_2O_3 (Kanto Chemical) were used as received. Pt was photodeposited on catalysts at the beginning of reactions (*9*). NiO (1.5 wt%)-supported photocatalysts were prepared by an impregnation method and were activated by reduction at 773 K and subsequent oxidation at 473 K before use, as previously described (*7, 10, 11*). The procedure for photocatalytic reaction was as given previously (*6*).

Reduction of nitrate over various photocatalysts is summarized in Table 1. When aqueous nitric acid and sodium nitrate solutions were irradiated by a Xe arc lamp through a Pyrex window, only a small amount of nitrite was formed. TiO_2, $SrTiO_3$, and Pt–In_2O_3 powders gave similar amounts of nitrite. Although Pt–WO_3 enhanced nitrite formation slightly, ammonia was not formed. This is considered to be because they cannot supply hydrogen atoms to form ammonia, due to the lack of hydrogen evolution sites for Pt-free TiO_2 and $SrTiO_3$ or due to insufficient conduction band levels for Pt–In_2O_3 and Pt–WO_3. By contrast, Pt-supported TiO_2 and $SrTiO_3$ powders, which have potentials and sites for hydrogen evo-

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TABLE 1

Reduction of Nitrate over Various Photocatalysts Irradiated with a 500-W Xe Arc Lamp

Catalyst (0.2 g)	Solution (250–300 ml)	Rate of formation (μmol/h)			
		NH_3	NO_2^-	O_2	H_2
None	0.1 *M* HNO_3	0	0.3	0	0
None	1 *M* $NaNO_3$	0	0.3	0	0
TiO_2	0.1 *M* HNO_3	0	0.2	0	0
Pt–TiO_2	1 *M* HNO_3	2.4	0	2.2	—
	1 *M* $NaNO_3$	1.1	0.1	1.1	0
	1 *M* $NaNO_3$ + 0.1 *M* HCl	0.6	0	0	0.8
	1 *M* $NaNO_3$ + 0.1 *M* NaOH	0	2.8	0.8	0
NiO–TiO_2	1 *M* $NaNO_3$	trace	1.2	0.1	—
	1 *M* $NaNO_3$ + CH_3OH	—	2.9	0	0.03
$SrTiO_3$	0.1 *M* HNO_3	0	0.3	0	0
Pt–$SrTiO_3$	0.1 *M* HNO_3	1.4	0.4	0.3	0
NiO–$SrTiO_3$	1 *M* $NaNO_3$	0.1	1.4	0.9	0
$K_4Nb_6O_{17}$	0.1 *M* HNO_3	0	0.5	0	0
	1 *M* KNO_3	0	1.2	0	0
NiO–$K_4Nb_6O_{17}$	1 *M* KNO_3	0	1.2	0.5	0.2
$H^+/K_4Nb_6O_{17}$	1 *M* KNO_3	0	1.7	0	0.1
Pt–In_2O_3	0.1 *M* HNO_3	0	0.3	0	0
Pt–WO_3	0.1 *M* HNO_3	0	0.6	0	0

Note. Pt supported, 0.3 wt%; NiO supported, 1.5 wt%.

lution, formed ammonia as a main product. On the other hand, nitrite was produced over NiO–TiO_2, NiO–$SrTiO_3$, $K_4Nb_6O_{17}$, and NiO–$K_4Nb_6O_{17}$. The supported-platinum and -nickel oxide and $K_4Nb_6O_{17}$ provide sites for the reduction reaction. These results establish that nitrate can be reduced to ammonia on a metallic surface (Pt) but only to nitrite on oxide surfaces (NiO and $K_4Nb_6O_{17}$), since hydrogen generated on these oxide surfaces would not be active for the reduction of nitrate to ammonia.

The rate of nitrite formation increased over the NiO (1.5 wt%)–TiO_2 photocatalyst when methanol was added as a reducing agent (Table 1). On this system, methanol works as a hole scavenger and the reduction reaction is enhanced by accumulated electrons,

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \quad \text{on NiO}$$

$$CH_3OH + nh^+ \rightarrow \text{Oxidized forms } (CO_2, \text{etc.}) \quad \text{on } TiO_2,$$

where h^+ denotes a hole. The rate of hydrogen evolution (0.03 μmol/h) was negligible, compared with that in the absence of nitrate (*10*), and has apparently been suppressed by the presence of nitrate, as observed for a Pt–TiO_2 photocatalyst (*6*).

When hydrochloric acid (0.1 *M*) was added to the sodium nitrate solution (1 *M*), hydrogen and ammonia were simultaneously formed as reduction products (Table 1), although oxygen was not detected, presumably because chloride is oxidized by holes. Contrarily, not ammonia but nitrite was formed from the solution containing sodium hydroxide (0.1 *M*), in this case, accompanied by oxygen as an oxidation product. Thus, the reduction products depend on the nitrate acidity. Ammonia formation is favored in acidic solution and nitrite in alkaline solution. This behavior corresponds to that of electrochemical reduction of nitrate on metal electrodes (*1*).

The amount of ammonia formed increased linearly with reaction time in aque-

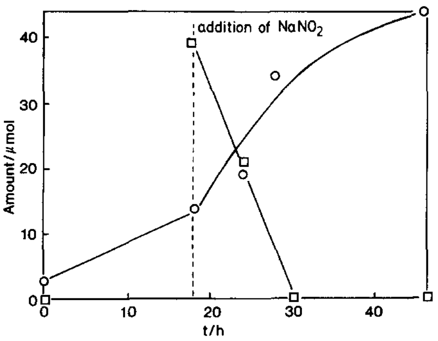

FIG. 1. Effect of NO_2^- addition on NH_3 formation from aqueous HNO_3 solution (300–250 ml) over Pt(0.3 wt%)-TiO_2 (0.2 g): ○, NH_3; □, NO_2^-.

ous nitric acid solution over a Pt–TiO_2 photocatalyst (*6*). When nitrite was added to the reactant solution, it was rapidly consumed and the rate of ammonia formation was enhanced markedly, as shown in Fig. 1. This result suggests that nitrite can be reduced easily to ammonia: i.e., the nitrite is an intermediate of the ammonia formation,

$$NO_3^- \rightarrow NO_2^- \xrightarrow[\text{fast}]{} NH_3$$

on a Pt–TiO_2 photocatalyst.

Ammonia, nitrite, and oxygen were evolved over a Pt–$SrTiO_3$ photocatalyst from aqueous nitric acid solution (0.1 *M*) (Table 1). In this case, the rate of ammonia formation decreased with reaction time and that of nitrite increased simultaneously. Figure 2 shows nitrite, nitrogen, and oxygen formation over Pt–$SrTiO_3$ from aqueous sodium nitrate solution (1 *M*). The main product was not ammonia but nitrite. These reduction products are different from those of Pt–TiO_2 and from those in aqueous nitric acid solution. The small amount of ammonia was also evolved only at an initial stage, and then the ammonia formed was consumed. This would be due to an oxidation reaction over $SrTiO_3$, because the reduction site must be a Pt surface in both the Pt–TiO_2 and Pt–$SrTiO_3$ cases, and the basic surface of $SrTiO_3$ is favored for nitrite formation. When NaOH was added to the solution nitrite and oxygen were evolved, as had also been observed in the case of a Pt–TiO_2 photocatalyst. On the other hand, $K_4Nb_6O_{17}$ photocatalysts, which are basic oxides, also formed nitrite (Table 1).

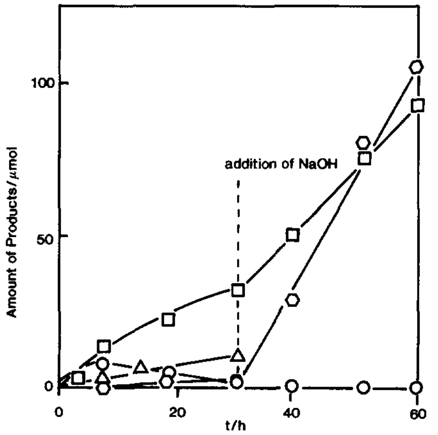

FIG. 2. Photocatalytic reaction of aqueous $NaNO_3$ solution (1 mol/l, 300–250 ml) over Pt(0.3 wt%)-$SrTiO_3$ (0.2 g): □; NO_2^-; ○, NH_3; △, N_2; ⬡, O_2.

In conclusion, Pt–TiO_2 and Pt–$SrTiO_3$ photocatalysts are active for the reduction of nitrate to form ammonia. Ammonia is evolved on metallic surfaces such as Pt, whereas nitrite formation is favored on oxide surfaces such as NiO. The products from aqueous nitrate solution over Pt–TiO_2 and Pt–$SrTiO_3$ are dependent on the pH of the solution. In acidic solution, ammonia is the main product and nitrite is easily reduced to ammonia. On the other hand, nitrite can be formed over both Pt–TiO_2 and Pt–$SrTiO_3$ photocatalysts under alkaline conditions.

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