## Nitrogen Photoreduction by Coprecipitated Hydrous Oxides of Samarium(III) and Vanadium(III)

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An irradiated nitrogen-purged aqueous dispersion of a coprecipitate of samarium(III) and vanadium-(III) hydrous oxides is found to generate ammonia with oxidative sacrification of vanadium(III) hydrous oxide. The catalytic properties of the system and the reaction mechanisms are discussed.

## Introduction

Photocatalysis of chemical reactions by semiconductor particles continues to attract attention.<sup>1-6</sup> Although the quantum yields are small, there is evidence that semiconductor particles have the ability to photocatalyze important chemical reactions such as (a) photodecomposition of water, (b) photoreduction of nitrogen to ammonia, and (c) photoreduction of carbon dioxide to energy-rich compounds, e.g., methanol.<sup>5-7</sup> The factors that limit the quantum yields of the above reactions are (a) inefficient charge separation and transfer to the solvent, (b) the necessity of multielectron transfer, and (c) the presence of back-reactions and catalyst poisoning by the reaction products. It is also well known that the presence of a sacrificial electron donor (acceptor) in the solution greatly enhances the rate of the reaction associated with electron (hole) transfer to water. Here, the rapid consumption of holes (electrons) by the scavenger facilitates the multielectron (multihole) transfer needed to carry out the reduction (oxidation) reaction. Sacrificial electron donors enhance hydrogen photogeneration from water and to some extent the reduction of carbon dioxide. However, the same strategy is not generally helpful in improving the ammonia photoproduction rates in nitrogen-purged aqueous semiconductor dispersions. The presence of electron donors in solution (e.g., organic compounds and reducing ions) completely suppresses ammonia production. The explanation is that the dissolved sacrificial agent interferes with chemisorption of nitrogen on the surface of the catalyst (generally  $N_2$  is poorly chemisorbed and readily replaced by other species in the solution). One way to overcome this problem would be to have a waterinsoluble solid sacrificial agent "bonded" to the active catalyst, so that a part of the surface of the catalyst is not spoiled. If holes are transferred to the solid sacrificial agent, reduction of nitrogen will be enhanced.

Provided the conduction band position is favorable, the other essential factor for nitrogen reduction is chemisorption of nitrogen at the catalyst surface. After experimenting with a large number of materials, we have found

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Figure 1. Absorption spectrum of an aqueous suspension of  $Sm_2O_3 \cdot nH_2O$ .

that the hydrous oxides of iron(III) and samarium(III) are more effective photocatalysts for nitrogen reduction, when compared with titanium dioxide or its doped modifications. In the bare form, the hydrous oxide of Fe(III) is superior to that of Sm(III). Presumably, these hydrous oxides chemisorb nitrogen much more strongly than  $TiO_2$ . By a coprecipitation technique, it is possible to make composite catalyst particles consisting of two components, where one component is the sacrificial agent. A stable coprecipitate of titanium(IV) and iron(III) hydrous oxides has enhanced catalytic activity compared to the pure hydrous oxide of Fe(III). Here more efficient charge separation along is responsible for the more pronounced photocatalytic effect.<sup>18</sup> When hydrous ferric oxide  $(Fe_2O_3 \cdot nH_2O)$  is incorporated with a strong reducing agent, e.g., the hydrous oxide of V(III)  $(V_2O_3 nH_2O)$ ,  $Fe_2O_3 \cdot nH_2O$  gets partly reduced to iron(II) hydroxide, which inactivates the catalyst. However, samarium(III) hydrous oxide  $(Sm_2O_3 nH_2O)$  resists reduction by vanadium(III) hydrous oxide, and a coprecipitate containing hydrous oxides of V(III) and Sm(III) can be readily prepared. As expected, when a nitrogen-purged aqueous suspension of the composite dispersion is irradiated, ammonia production is observed to occur at a rate much higher than with other systems reported in the literature.<sup>8-20</sup> During this process V<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O gets oxidized as a result of hole consumption.

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Figure 2. Mott-Schottky plots  $(1/C^2 \text{ vs } V, C = \text{capacitance})$ (nF), V = potential for  $\text{Sm}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  ( $\Box$ , 1 kHz;  $\Box$ , 500 Hz) at pHs 7 and 8. Numbers indicated near the curves are the pH values.

## **Experimental Section**

To avoid ammonia contamination, all chemicals used were tested for ammonia, nitrite, and nitrate (photoreduction of nitrite and nitrate in the presence of semiconductor catalysts generates ammonia).

The composite system containing  $Sm_2O_3 \cdot nH_2O$  and  $V_2O_3 \cdot nH_2O$ was prepared as follows: Deaerated solutions of SmCl<sub>3</sub> and VCl<sub>3</sub> (0.1 M) were mixed in different proportions and made alkaline to a pH of 8, when a brown precipitate containing  $Sm_2O_3 nH_2O$ and  $V_2O_3 \cdot nH_2O$  is formed. The precipitate was washed with water, avoiding air contamination, and stored in deaerated water. Photolysis experiments were carried out in a water-cooled (26 °C) immersion well type photochemical reactor (Applied Photophysics) of volume 400 mL. The light source, a 400-W mediumpressure mercury lamp is mounted at the central axis of the inner doubled-walled quartz cylinder. As the precipitate cannot be dried (drying denatures the N2 reduction activity) for weighing, the amount used in each run was determined as moles of V + Sm present in the precipitate. In all experiments, the precipitate containing  $3.6 \times 10^{-2}$  mol of V + Sm was suspended placed inside the reactor was rapidly purged with nitrogen (99.99%) to remove any dissolved oxygen, the lamp was switched on, and the purging was maintained at a constant rate of 10 mL min<sup>-1</sup>. At different time intervals, aliquots of solution, drawn from the reactor, were tested for ammonia by the indophenol blue method.<sup>21</sup> Outgoing



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Figure 3. Time variation of the ammonia yield during photolysis: (curve 1)  $Sm_2O_3 \cdot nH_2O/V_2O_3 \cdot nH_2O$  precipitate, (curve 2) pure  $Sm_2O_3 \cdot nH_2O$  (initial pH of the solutions 8).



Figure 4. Variation of the optimum ammonia yield with the V/Sm molar ratio in the precipitate (photolysis carried out for 1 h).

gas was estimated for hydrogen by gas chromatography Shimadzu GC-9AM gas chromatograph, molecular sieves 5 Å column). Blank experiments were also conducted for 5 h by keeping the lamp switched off with  $N_2$  purging and with the lamp switched on under argon purging. Ammonia concentrations in the solutions obtained from the blank experiments were negligible (i.e., <11  $\mu$ mol L<sup>-1</sup>).

The flat-band potential of Sm<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O was determined by obtaining the Mott-Schottky plots. For this purpose, compacted pellets of Sm<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O (diameter 13 mm, pressure 40 MPa) were used (a Hewlett-Packard LCZ meter 4276A and Advantest Computing digital multimeter were used to measure capacitance and voltage, respectively).

## **Results and Discussion**

The absorption spectrum of an aqueous suspension of  $Sm_2O_3 nH_2O$  is shown in Figure 1, and the band gap derived



Figure 5. pH variation of the optimum ammonia yield when the composition of the precipitate is V/Sm = 1.

from the spectrum is ~3.6 eV. The position of the conduction band as determined from the Mott–Schottky plot (plot of (capacitance)<sup>-2</sup> vs applied potential (V)) shown in Figure 2 is -0.85 V vs SCE (standard calomel electrode) at pH 7. Clearly, the band position is sufficiently negative for reduction of water to hydrogen or dissolved nitrogen to ammonia. A nitrogen-purged aqueous suspension of  $Sm_2O_3 nH_2O^{22}$  generates detectable quantities of ammonia via the reactions

Curve 2 of Figure 3 shows the time variation of the ammonia yield during photolysis of a N<sub>2</sub>-purged aqueous suspension of  $Sm_2O_3 \cdot nH_2O$  at pH 8. Concomitant oxygen evolution was barely detectable, possibly because Sm<sub>2</sub>- $O_3 \cdot nH_2O$  adsorbs oxygen to form peroxo complexes (an o-anisidine test<sup>23</sup> suggests formation of bound peroxo complexes). Pure  $V_2O_3 \cdot nH_2O$  showed no activity toward  $N_2$  reduction, presumably because of the unfavorable band position (we did not succeed in measuring the band position of  $V_2O_3 \cdot nH_2O$ , owing to its instability toward atmospheric oxygen). However, with the composite precipitate  $Sm_2O_3 \cdot nH_2O/V_2O_3 \cdot nH_2O$ , the ammonia yield at the optimum is increased by a factor of more than 10 (Figure 3, curve 1). In the initial stages of photolysis, the ammonia concentration in the solution increases almost linearly with time for about 4 h and then begins to decrease rapidly. After about 8 h, the ammonia concentration remains nearly constant. The exact reason for the observed pattern of the decrease of the ammonia yield is not clear. Ammonia generated could also undergo direct and catalyst-assisted photodecomposition. The consumption of  $V_2O_3 \cdot nH_2O$  by



Figure 6. Hydrogen evolution during photolysis of the  $Sm_2O_3 \cdot nH_2O/V_2O_3 \cdot nH_2O$  precipitate: (curve 1) argon purging, (curve 2) nitrogen purging.

hole scavenging causes a progressive reduction in the rate of the nitrogen reduction reaction. An equilibrium between  $N_2$  reduction and  $NH_3$  photodecomposition could lead to a constant NH<sub>3</sub> concentration on prolonged irradiation. Figure 4 (plot of  $NH_3$  yield vs V/Sm ratio) shows the variation of the optimum ammonia yield with the V/Sm molar ratio in the precipitate, when the photolysis is carried out for 1 h. It is found that the maximum yield (as measured at the optimum point) is obtained when the V/Sm ratio is  $\sim 1$ . Insufficient capture of holes by the sacrificial agent and physical blocking of the absorption sites on  $Sm_2O_3 \cdot nH_2O$  are probably responsible for the existence of an optimum V/Sm ratio. The plot of the pH variation of the optimum NH<sub>3</sub> yield at the above precipitate composition is shown in Figure 5. Initially, the NH<sub>3</sub> yield increases with the increase of pH and reaches an optimum at a pH of  $\sim 8.5$ .

With the composite precipitate holes are effectively consumed via the reaction

$$V_2O_3 + 2h^+ \rightarrow 2VO(OH)_2 + 2H^+$$
 (3)

while electrons participate in (1), reducing nitrogen to ammonia.

Spectrophotometric analysis of the degraded precipitate suggests the presence of  $VO(OH)_2$ ; however, its qualitative estimation as the reaction progressed was found to be difficult.

If the photolysis is carried out at pH ~9, a pH change of ~0.5 is observed in ~4 h. However, when the initial pH is ~7, the pH change during photolysis is hardly detectable. The net reaction of (1) and (2), i.e.,  $N_2 + 3H_2O$  $\rightarrow 2NH_3 + 3/_2O_2$ , tends to increase the pH owing to hydrolysis of ammonia. However, at pH ~8, NH<sub>3</sub> has an insignificant effect on the change of pH and the influence of (3) becomes dominant.

The observed pH variation of the ammonia yield can be understood qualitatively as follows: Kinetically, the  $N_2$ reduction reaction (eq 1) is favored at low pHs. However, the flat-band potential of  $Sm_2O_3 \cdot nH_2O$  becomes more

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negative at higher pHs (Figure 2), again favoring nitrogen reduction. Two opposing effects give rise to an optimum pH. It is interesting to compare the rates of hydrogen photogeneration from nitrogen (Figure 6, curve 2) and argon (Figure 6, curve 1) dispersions of the composite precipitate. Argon-purged solutions give higher yields of hydrogen as expected. Such significant differences in the yields of hydrogen from argon- and nitrogen-purged solutions is not seen in the cases of  $TiO_2$ ,  $Fe_2O_3 \cdot nH_2O$ , or  $Sm_2O_3 \cdot nH_2O$ .