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PHOTOCATALYTIC SYNTHESIS AND PHOTODECOMPOSITION OF AMMONIA OVER $SrTiO_3$ AND $BaTiO_3$ BASED CATALYSTS

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Photocatalytic synthesis of ammonia from N_2 and H_2O and its photodecomposition were investigated over $SrTiO_3$ and $BaTiO_3$ based catalysts. It was demonstrated that the yield of NH_3 formation increased markedly by the use of RuO_2 and NiO doped three component catalysts and that photodecomposition of NH_3 was coupled with photodecomposition of H_2O.

Although as early as 1941 it was reported that TiO_2 in soil could increase the velocity of N_2 fixation under sunlight[1)], no extensive attention has been received. Recently some photocatalytic systems which can produce ammonia from N_2 and H_2O under illumination have been reported by Schrauzer et al.[2)] and Miyama et al.[3)], though the efficiency of N_2 fixation is still low. On the other hand, we have reported that NiO doped $SrTiO_3$ catalyst is an efficient catalyst for the photodecomposition of water and examined the reaction mechanism in depth[4,5)]. In order to apply this system for the photocatalytic synthesis of ammonia $SrTiO_3$ and $BaTiO_3$ were chosen as bases, into which Ru and Ni were added in this study. It was thus revealed that the yield of photocatalytic formation of NH_3 increased markedly by the use of three component catalysts and that photodecomposition of NH_3 was coupled with photodecomposition of H_2O.

$SrTiO_3$ of 98.5% purity and a particle size of 2 micron was purchased from Alfa Products (Ventron) and was used without further purification except the heat treatment described below. Compressed gases (Ar, N_2, O_2, and H_2) were 99.9% pure. $BaTiO_3$ was provided by Zhang Zhong-Tai. RuO_2(0.8%)-NiO(1.5%)-$BaTiO_3$ catalyst was prepared by adding $BaTiO_3$ powder into aqueous solution of $Ni(NO_3)_2$ and $RuCl_3$. The resulting slurries were dried and calcinated in vaccum for one hour at 500°C. The catalyst was reduced by flowing H_2 (ca. 170 torr) at 500°C for one hour and oxidized by flowing O_2 (ca. 170 torr) at 200°C for half an hour before the reaction. The $SrTiO_3$ samples doped with other metals were prepared analogously.

All the experiments reported here were carried out in a closed gas circulation system equipped with a quartz reactor with a flat bottom (ca. 15 cm^2). The total volume of the system was 378 ml. The catalyst in the reactor was irradiated through the bottom by a 450W high-pressure mercury lamp covered with a water-cooling pyrex jacket at a distance of about 4 cm. The reactor was air-cooled by an electric fan to maintain temperature constant. The temperature of the catalyst, as measured by a thermometer placed in a hole on top of the reactor, was about 50°C. The reaction gas mixture after passing through a cold trap of solid CO_2 - methanol to remove H_2O was sampled at various reaction times and analyzed by gas chromatographic technique. An argon carrier gas and a molecular sieve 5A column were used for the analysis (detection limit for $H_2 = 0.1$ μmol and for $O_2 = 2$ μmol). After the reaction, a part of the aqueous mixture was filtrated to remove the catalyst and was analyzed by adding a given amount of Nessler's reagent. Amount of ammonia was determined by the absorbance at 425 nm with a HITACHI 430 Recording Spectrophotometer.

Table 1. Yields of NH_3 and H_2 over various catalysts (react. temp. = 40°C)
H_2O: 5ml, N_2: 0.9 atm, catalyst: 0.5g,

NO	Photocatalyst	Yields, μmol, 2h	
		NH_3	H_2
1	$SrTiO_3$	0.41	0
2	$BaTiO_3$	0.87	0
3	$NiO-SrTiO_3$	0.89	5.15
4	$RuO_2-SrTiO_3$	0.75	0.78
5	$RuO_2-NiO-SrTiO_3$	2.51	4.74
6	$RuO_2-NiO-BaTiO_3$	2.61	0.24

Photocatalytic activity for the synthesis of ammonia was tested for various catalysts. Table 1 summarizes a part of the experimental results. Undoped $SrTiO_3$ and $BaTiO_3$ produced a small amount of NH_3 but no H_2 was detected during 2h illumination. NiO-doping enhanced markedly the photocatalytic activity of $SrTiO_3$ for water photodecomposition, but the change in the yield of NH_3 was very small. When RuO_2 was doped in NiO - $SrTiO_3$ binary catalyst, the amount of NH_3 formation increased significantly. These are attributable to the increased activities of NiO for H_2 evolution and RuO_2 for N_2 activation. Although Kawai and Sakata[6] ascribed the effect of RuO_2 in RuO_2 - TiO_2 to enhance O_2 evolution, the catalytic promotion of O_2 evolution seems to be less important than that of N_2 activation in this system.

Fig. 1 shows the rates of H_2 and NH_3 formation. The yields of H_2 increase with time almost linearly, which is quite different from the resultes of Schrauzer and Guth[2], that is, molecular nitrogen at 1 atm of pressure completely inhibits the H_2 formation. The yield of O_2 was not plotted in Fig. 1 because of its detection limits. But at the later stage of the reaction, almost stoichiometric amount of O_2 could be detected, which suggests that this reaction is proceeding catalytically. The rates of NH_3 formation were initially high but rapidly dropped. This decrease in the rate may partly be due to a loss of the

Fig. 1. Time courses of NH_3 and H_2 formations

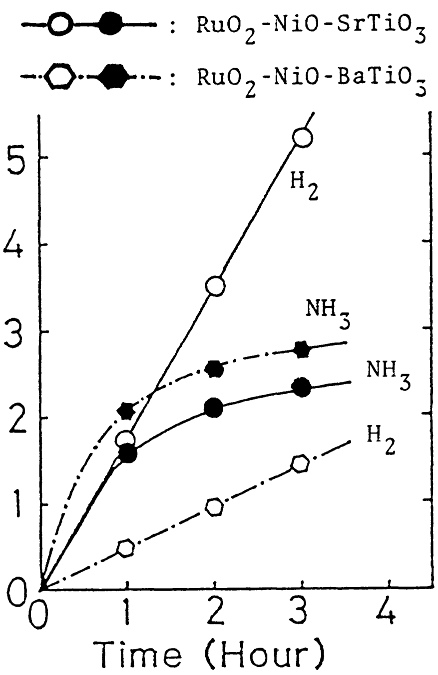


Fig 2. Photodecomposition of ammonia over various catalysts (0.5 g, 40°C)

○ : RuO_2-NiO-$SrTiO_3$, ⬡ : RuO_2-NiO-$BaTiO_3$

△ : NiO-$SrTiO_3$

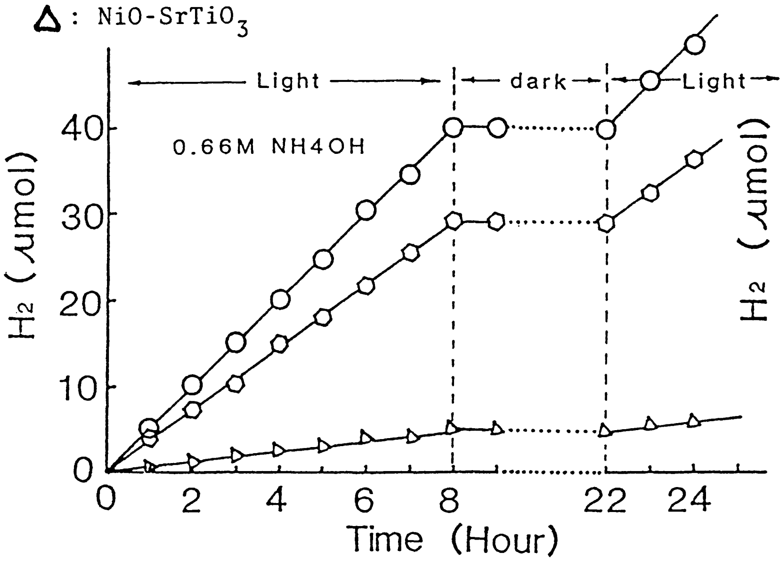
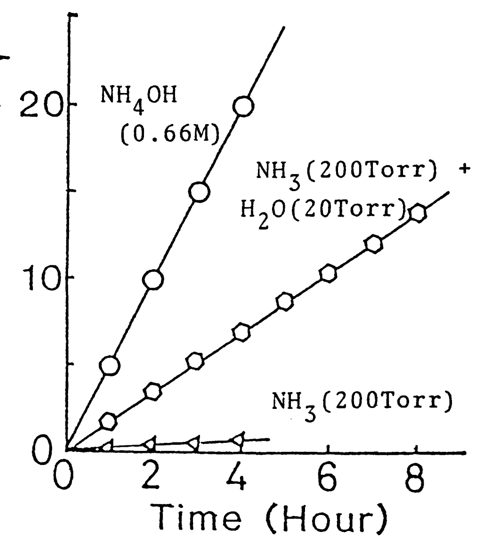


Fig. 3. Photodocomposition of NH_3 over RuO_2-NiO-$SrTiO_3$ (0.5 g, 40°C)



photocatalytic activity, but also due to the reverse reaction (photodecomposition of NH_3).

In order to examine this point more clearly, the photocatalytic decomposition of NH_3 over RuO_2-NiO-$SrTiO_3$ catalyst was tested. Fig. 2 shows the time dependence of 0.66M NH_4OH decomposition over various catalysts, where only formed H_2 were protted. The molar ratio of H_2 and N_2 obtained was the stoichiometric value of 3 and no O_2 was detected during 12h illumination in these systems. But for lower NH_4OH concentration, both the N_2 and O_2 could be meantime detected. No decomposition was observed without illumination as shown in the figure. On the other hand, the rates of photocatalytic decomposition of ammonia markedly depends on the reaction conditions conducted. Fig. 3 shows comparison of rates of photocatalytic decomposition of NH_3 in different states. The rate of photocatalytic decomposition of ammonia in aqueous solution is faster than that in gaseous phase water and ammonia. Also, the rate of photocatalytic decomposition of gas phase ammonia alone was very small, which suggests that the photocatalytic decomposition of NH_3 over RuO_2-NiO-$SrTiO_3$ is coupled with that of water (for example, oxidation of ammonia by OH radical).

These findings demonstrate that the thermodynamically unfavorable reaction to form NH_3 from N_2 and H_2O can proceed at 50°C using band-gap illumination of a RuO_2-NiO-$SrTiO_3$ or RuO_2-NiO-$BatiO_3$ powder covered with liquid water. As ammonia is accumulated, the photodecomposition of ammonia becomes important correspondingly.

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