

HETEROGENEOUS PHOTOREDUCTION OF NITROGEN TO AMMONIA ON CATALYST-LOADED TiO₂ POWDERS

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RÉSUMÉ. — Des suspensions de TiO₂ dopées par catalyseurs sont utilisées pour la réduction photochimique de N₂ en NH₃. Le rendement quantique augmente avec le dépôt de Pt ou de Pd sur TiO₂ et le meilleur rendement est obtenu avec un catalyseur du type TiO₂/RuO₂ qui produit 9 µg NH₃ après 5 heures d'irradiation.

ABSTRACT. — The photosynthetic reduction of N₂ to NH₃ in an aqueous medium on catalyst-loaded TiO₂ powders was investigated. The yield of NH₃ was increased by Pt- and Pd-loaded TiO₂ and was highest with a mixed TiO₂/RuO₂ catalyst, where about 9 µg of NH₃ were produced after 5 hours illumination.

Introduction

This letter deals with the photosynthetic reduction of N₂ to NH₃ on irradiated TiO₂ powders loaded with catalysts, and it demonstrates that the yield of NH₃ is increased by use of RuO₂/TiO₂. The photoreduction of N₂ to ammonia on semiconductor powders represents an attractive way to convert solar energy into a useful chemical product. For example, N₂ photofixation has been suggested as a possible method of producing fertilizer in place with the appropriate semiconductor powder. ¹ Schrauzer and Guth ² first reported the production of NH₃ on moist iron-doped TiO₂ powders. Other studies showed that TiO₂-iron oxide materials, ³ soil minerals, and desert sand containing Ti ⁴ and Ti(III) exchanged zeolites ⁵ can also be employed for N₂ photoreduction. Miyama *et al.*, ⁶ reported NH₃ synthesis from N₂-saturated water in the presence of semiconductor powders (TiO₂, ZnO, CdS, SrTiO₃, GaP) and in the form of a two-layer system composed of a wafer of a layer of semiconductor and a layer of platinum black. Tamaru *et al.*, ⁷ used SrTiO₃ doped with RuO₂ and NiO for gas phase NH₃ photoproduction. However, there has been no detailed comparison of the activity of catalyst-loaded semiconductor powders for NH₃ photosynthesis. Therefore, we have studied the effects of catalyst loading on semiconductor particles.

Experimental

PREPARATION OF CATALYST

Commercially available TiO₂ powders (Degussa P-25) were used without further purification. Metal loading on TiO₂ was carried out by adding TiO₂ powder into aqueous solutions of metal chlorides, obtained from Alfa Products (Danvers, MA) (H₂PtCl₆, PdCl₂, RhCl₃, RuCl₃, and H₂IrCl₆), respectively. The resulting slurries were

dried and reduced in flowing hydrogen at 600°C for 4 hours and cooled to room temperature in hydrogen. The amount of loaded metal was 5 mol % of TiO₂. Two types of RuO₂-TiO₂ powders were investigated. In Type A, RuO₂ or RuO₂-TiO₂ loaded powders were prepared by adding TiO₂ powder into n-butanol solutions that contained RuCl₃·nH₂O, HCl, and Ti(OBu)₄. The resulting slurries were dried at 100°C for 24 hours, powdered in an agate mortar, and fired in a furnace at 450°C for 30 minutes in air. In Type B powders, commercially available RuO₂ (Alfa Products, Danvers MA, 99.9%) was mixed with TiO₂ powder or metal-loaded TiO₂ powder in an agate mortar. The amount of RuO₂ was 5 wt% of TiO₂. No attempt was made to optimize the amount of RuO₂ for ammonia production.

PROCEDURE

The metal/TiO₂ catalyst (0.20 g as TiO₂) was dispersed in 50 mL water in a Pyrex cylindrical reactor. The water was Milli-Q grade (Millipore Continental Water Systems) in each experiment. The sample in the reactor was stirred magnetically during the experiment. The reactor was irradiated for 5 hours with a 1600 W ozone-free Xe lamp, operated at a power of 1400 W. A 10 cm Pyrex water jacket was placed between the reactor and the lamp to absorb the IR light. The light intensity at the reactor was about 250 mW/cm². The temperature of the solution was ca. 45°C under irradiation. During irradiation, H₂O-saturated N₂ gas, that was purified by a hot copper pellet column, chromic acid solution, and NaOH solution, was passed through the solution. In all cases, dark controls were run. After the reaction, the dispersion was centrifuged to remove essentially all of the catalyst. The analysis of NH₃ was done spectrophotometrically by the indophenol method. ⁸ The method is useful for ammonia in water at the 0.01 to 0.5 µg nitrogen per ml level. With our instrument Beer's law was followed over the 0.02 to 1 µg/ml ammonia concentration range.

Results and discussion

The experimental results are shown in Table I. Under our conditions the yields on untreated or H₂-reduced TiO₂ alone were no higher than the dark controls. Platinum- and

Table I

Catalyst	NH ₃ yield (μg) (5 hours)		Remarks
	Irradiation	Dark (control)	
TiO ₂	≤1.0	<1.0	Untreated
TiO ₂	<1.0	-	Reduced in H ₂ 600°C × 4 hours
Pt/TiO ₂	3.6	<1.0	Reduced in H ₂ 600°C × 4 hours
Ir/TiO ₂	2.1	<1.0	Reduced in H ₂ 600°C × 4 hours
Ru/TiO ₂	2.1	<1.0	Reduced in H ₂ 600°C × 4 hours
Rh/TiO ₂	<1.0	-	Reduced in H ₂ 600°C × 4 hours
Pd/TiO ₂	3.6	<1.0	Reduced in H ₂ 600°C × 4 hours
RuO ₂ (100%) / TiO ₂ (A)	<1.0	-	Impregnation of RuCl ₃ fired in air
RuO ₂ (90)-TiO ₂ (10) / TiO ₂ (A)	<1.0	-	Impregnation of RuCl ₃ and Ti(OBu) ₄ fired in air
RuO ₂ (80)-TiO ₂ (20) / TiO ₂ (A)	<1.0	-	Impregnation of RuCl ₃ and Ti(OBu) ₄ fired in air
RuO ₂ (60)-TiO ₂ (40) / TiO ₂ (A)	<1.0	-	Impregnation of RuCl ₃ and Ti(OBu) ₄ fired in air
RuO ₂ (33)-TiO ₂ (67) / TiO ₂ (A)	<1.0	-	Impregnation of RuCl ₃ and Ti(OBu) ₄ fired in air
RuO ₂ + TiO ₂ (B)	9.1	<1.0	Ground in mortar
RuO ₂ + Pt / TiO ₂ (B)	<1.0	-	Ground in mortar
RuO ₂ + Ru / TiO ₂ (B)	<1.0	-	Ground in mortar

palladium-loaded TiO₂ powders were found to be active catalysts, while RuO₂-loaded TiO₂, prepared by grinding a mixture of RuO₂ and TiO₂ powders in an agate mortar, was the most active catalyst. The photosynthesis of NH₃ on the semiconductor particles, based on the photoelectrochemical cell model,¹ requires anodic and cathodic reactions at appropriate sites. In this system, the anodic reaction is probably the oxidation of water (although oxidation of impurities in the system is also possible) and NH₃ while the overall cathodic one is N₂ reduction, probably via hydrogen production followed by NH₃ production. Thus, the overall reaction would be favored by promotion of the H₂O oxidation reaction, the hydrogen evolution reaction, and the reaction of N₂ with hydrogen. RuO₂ is a good oxygen evolution catalyst, but in some cases, it can also function as a hydrogen catalyst.⁹ However, Type A RuO₂-TiO₂ catalysts, which are solid solutions of RuO₂ and TiO₂, show high oxygen evolution activity, and low hydrogen evolution activity.¹⁰ These Type A RuO₂-TiO₂ catalysts show poor activity for NH₃ production. Because hydrogen atoms, which are necessary in the synthesis of ammonia, are considered to be formed by the photoelectrochemical reduction of water molecules, hydrogen evolution activity of metal-loaded semiconductor powders is probably required to effect NH₃ synthesis. For photosynthetic hydrogen evolution on metal-loaded TiO₂ powders, Pt- and Pd-loaded TiO₂ were the most active catalysts of the precious metal-loaded powders.⁹ With the Pt- and Pd-loaded TiO₂ catalysts, the increased ammonia yields can be attributed to the higher hydrogen evolution activities. Note that the order of photocatalytic hydrogen evolution rate for metal-loaded TiO₂ is Pt > Pd > Rh > Ru for aqueous,⁹ as well as 1 : 1 ethanol-water mixtures.¹¹ For NH₃ synthesis from H₂ and N₂ in the gas phase¹² the order of catalytic activity is Ru > Rh > Ir > Pt. The Type B RuO₂/TiO₂ mixture showed the highest ammonia yields, implying that in this case, RuO₂ plays a dual role as oxidation and reduction

catalyst. However, RuO₂-loaded Pt/TiO₂ showed poor photochemical ammonia yields, although it is known to show a high activity for photocatalytic hydrogen evolution.¹¹ Perhaps this combination of RuO₂ and Pt enhances H₂ evolution compared with nitrogen reduction, yielding low competitive use of the photogenerated electrons for ammonia synthesis. The role of the catalysts in promoting photooxidation of the NH₃ formed at reduction sites, which is known to occur at TiO₂ powders,^{3a, 13} must also be considered.

Conclusion

Catalytic activities of metal-loaded TiO₂ powders in the photochemical reduction of nitrogen have been studied. While Pt- and Pd-loaded TiO₂ were more active than TiO₂ alone, a RuO₂/TiO₂ mixture showed the highest activity.

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