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The Effects of the Calcination Temperature of $SrTiO_3$ Powder on Photocatalytic Activities

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Photocatalytic activity of $SrTiO_3$ powder prepared by the alkoxide method was examined on the photodecomposition of water, the evolution of H_2 from aqueous methanol solution, and the evolution of O_2 from aqueous silver nitrate solution. The activity depends strongly on the calcination temperature of $SrTiO_3$ powder. The optimum calcination temperatures of $SrTiO_3$ for these reactions were different from each other. Several factors affecting the photocatalytic activity were discussed on the basis of the characterization of $SrTiO_3$ powder. © 1988 Academic Press, Inc.

INTRODUCTION

Recently, various kinds of semiconductor powder have been used as photocatalysts for many reactions. In particular, certain ones, e.g., TiO_2 (*1–3*), $SrTiO_3$ (*4, 5*), and $K_4Nb_6O_{17}$ (*6*), have been successfully applied to the photocatalytic decomposition of water into H_2 and O_2. $SrTiO_3$ photocatalysts loaded with NiO and noble metals can decompose distilled water stoichiometrically (*4, 5*), while TiO_2 can do so only under concentrated alkaline conditions (*1, 3*). The structure (*7*) and the photocatalytic activity (*5*) of the NiO–$SrTiO_3$ catalyst have been studied, and it was found that the properly treated NiO–$SrTiO_3$ catalyst exhibits the high and stable activity for the photocatalytic decomposition of water for a long period of time.

The activities of these photocatalysts, however, change markedly according to different preparations and/or pretreatment procedures. The particle size and the crystal form affected the activities of the H_2 evolution from aqueous solutions containing the sacrificial reagents on TiO_2 (*8, 9*) and CdS (*10*) photocatalysts. The activity of the O_2 evolution from aqueous silver nitrate solution increased with a decrease in the amount of surface hydroxyl group by the calcination of TiO_2 particle (*11*). The surface area and the adsorbed substrates influenced the activity of peroxide formation over the ZnO photocatalyst (*12*).

$SrTiO_3$ is usually prepared by heating a mixture of $SrCO_3$ and TiO_2 at high temperatures such as 900°C. In this case it is difficult to study the effect of the calcination temperature of $SrTiO_3$ on photocatalytic activity. Crespin and Hall (*13*) prepared $SrTiO_3$ powder by the coprecipitation method from aqueous $Sr(NO_3)_2$ and $TiCl_4$ solutions using $(C_2H_5)_4NOH$ as a base, followed by calcination at 550°C. They obtained $SrTiO_3$ powder with a high surface area (64 m^2/g) and examined in detail the surface chemistry of the powder as well as that of $BaTiO_3$ and $LaCoO_3$. On the other hand, when a mixture of alkoxides of strontium and titanium in alcohol solution is used as starting material (alkoxide method (*14, 15*)), $SrTiO_3$ powder can be obtained easily at low calcination temperatures.

In this paper we report the effect of the calcination temperature of $SrTiO_3$ prepared by the alkoxide method on photocatalytic activity.

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EXPERIMENTAL

1. *Preparation of Photocatalysts*

$SrTiO_3$ powder was prepared by the alkoxide method. Titanium isopropoxide (Wako Pure Chemicals, 99% purity) was purified by distillation. Strontium isopropoxide was prepared from strontium metal (Mitsuwa's Pure Chemicals, 99% purity) and isopropanol. H_2O was added into a mixed isopropanol solution of titanium and strontium isopropoxides (10 wt%) to hydrolyze at room temperature. A coprecipitate was washed with isopropanol, treated at varying calcination temperatures (CT) of 700, 900, 1100, 1300, 1400, and 1500°C for 10 h in air in a platinum crucible, and then cooled rapidly. A NiO(1.5 wt%)–$SrTiO_3$ photocatalyst was obtained by the impregnation method from nickel nitrate (Wako Pure Chemicals). The catalyst was reduced by H_2 (ca. 40 kPa) at 500°C for 2 h and reoxidized by O_2 (ca. 16 kPa) at 200° for 1 h as reported in previous papers (*5*). The Pt(0.5 wt%)–$SrTiO_3$ photocatalyst was prepared by the photodeposition method (*16*) from hexachloroplatinum acid (Koso Chemical Co., Ltd.) in aqueous methanol solution.

$SrTiO_3$ powder was characterized by X-ray diffraction (XRD; Rigaku), a scanning electron microscope (SEM; Akashi Seisakusyo, ISI-100B and Hitachi HFS-2), and BET measurement.

2. *Photocatalytic Reactions*

Reactions were carried out at room temperature in a closed gas circulation system attached to a vacuum line.

a. NiO–SrTiO$_3$. The photocatalytic decomposition of water (5 ml) into H_2 and O_2, the evolution of H_2 from aqueous methanol solution ($H_2O:CH_3OH = 1:1$ by volume, 10 ml), and the evolution of O_2 from aqueous silver nitrate solution (0.1 mol/liter) over NiO–$SrTiO_3$ (2 g) were performed in a flat bottom reaction quartz cell. Degassed solutions were introduced to the cell with the catalysts and irradiated by a high-pressure mercury lamp (USHIO, UM-452, 450 W) through the flat bottom of the reaction cell.

b. SrTiO$_3$ and Pt–SrTiO$_3$. The evolution of H_2 from aqueous methanol solution ($H_2O + CH_3OH = 4:1$ by volume, 250 ml) and the evolution of O_2 from aqueous silver nitrate solution (0.02 mol/liter, 250 ml) over $SrTiO_3$ and Pt–$SrTiO_3$ were carried out in a reaction cell of Pyrex with a flat window. The solutions with catalysts (0.3 g) were stirred during the reaction and irradiated by an Xe short arc lamp (USHIO, UXL-500D-O, 500 W).

The amounts of produced H_2 and O_2 were determined by gas chromatography (Ar carrier, MS-5A column). The rates of the steady-state reactions were obtained from the time courses for the evolution of H_2 from aqueous methanol solution and for the decomposition of water. For the evolution of O_2 from aqueous silver nitrate solution, the initial rate was regarded as the activity because the rate of the O_2 evolution decreased gradually with the reaction time. The efficiencies of two types of the reaction cells were compared and normalized using the reaction rates of the same catalyst.

RESULTS AND DISCUSSION

1. *Characterization of SrTiO$_3$ Powder Calcined at Varying Temperatures*

The crystallinities of $SrTiO_3$ powder calcined at varying temperatures were examined by XRD as shown in Fig. 1. The (211) diffraction peak of $SrTiO_3$ became sharper with the increase in calcination temperature up to CT 1100°C and above CT 1100°C the peak shape no longer changed. No peaks attributed to SrO and TiO_2 were observed. The broadening of XRD peaks at low calcination temperatures is probably due to the small sizes of the $SrTiO_3$ crystals in the catalyst.

SEM photographs of $SrTiO_3$ powder calcined at 700, 1100, and 1400°C are shown in Fig. 2. Primary particles (ca. 0.1–0.2 μm) were observed at CT 700 and CT 1100°C

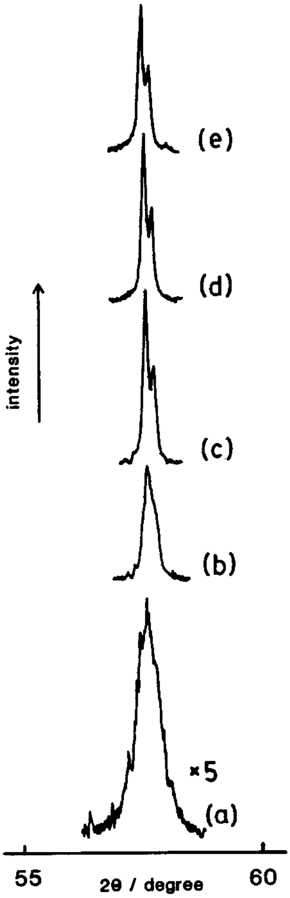

FIG. 1. XRD patterns of $SrTiO_3$ calcined at varying temperatures. (a) 700°C, (b) 900°C, (c) 1100°C, (d) 1300°C, (e) 1400°C.

TABLE 1

Surface Areas of $SrTiO_3$ Calcined at Varying Temperatures

Calcination temperature (°C)	Surface area (m^2/g)
700	27
900	14
1100	4
1300	2
1400	3
1500	3

although sintering of primary particles began partially at CT 1100°C. Above CT 1300°C primary particles disappeared completely to form large particles.

BET surface areas of $SrTiO_3$ powder calcined at varying temperatures are shown in Table 1. The surface area decreased remarkably with the increase in calcination temperature up to 1100°C. This result corresponds well with those obtained by XRD and SEM.

2. *Photocatalytic Activities*

a. H_2 evolution from aqueous methanol solution. The evolution of H_2 from aqueous methanol solutions with $SrTiO_3$, Pt–Sr TiO_3, and NiO–$SrTiO_3$ is shown in Fig. 3.

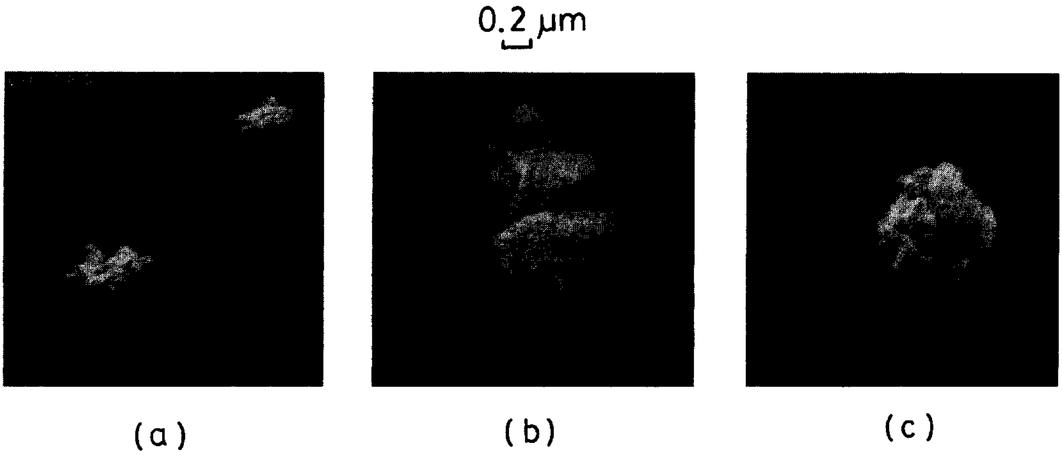

FIG. 2. SEM micrographs (×18500) of $SrTiO_3$ calcined at varying temperatures. (a) 700°C, (b) 1100°C, (c) 1400°C.

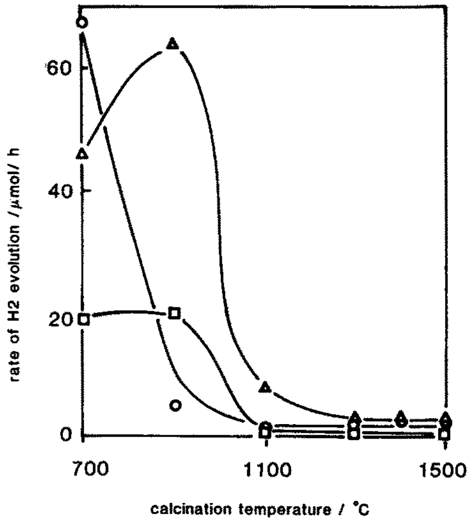

FIG. 3. Effects of the calcination temperature on the activity of the H_2 evolution from aqueous methanol solution over $SrTiO_3$, Pt(0.5 wt%)-$SrTiO_3$, and pretreated NiO(1.5 wt%)-$SrTiO_3$. (□) $SrTiO_3$, (△) Pt(0.5 wt%)-$SrTiO_3$, (○) pretreated NiO(1.5 wt%)-$SrTiO_3$.

All catalysts showed high activities at calcination temperatures around 900°C and the activities decreased remarkably above 1100°C. The decrease in activity seems to be due mainly to the decrease in the surface area of $SrTiO_3$. It is noteworthy that the $SrTiO_3$ powder at CT 700 and CT 900°C evolved H_2 steadily from aqueous methanol solution without Pt or NiO.

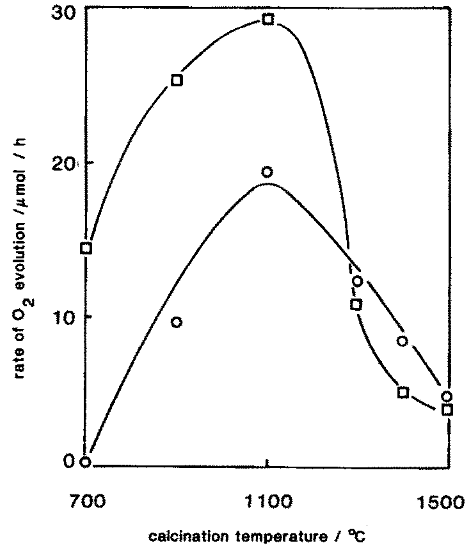

FIG. 4. Effects of the calcination temperature on the activity of O_2 evolution from aqueous silver nitrate solution over $SrTiO_3$ and pretreated NiO(1.5 wt%)-$SrTiO_3$. (□) $SrTiO_3$, (○) pretreated NiO(1.5 wt%)-$SrTiO_3$.

b. O_2 evolution from aqueous silver nitrate solution. Figure 4 shows the initial rates of the O_2 evolution from aqueous silver nitrate solution over $SrTiO_3$ and NiO–$SrTiO_3$. Both catalysts exhibited the highest activities at CT 1100°C. The $SrTiO_3$ catalyst shows higher activity than NiO-$SrTiO_3$ at low calcination temperatures (<1100°C). This behavior is markedly different from that of the H_2 evolution from aqueous methanol solution, especially at CT 700 and CT 900°C. The evolution of O_2, i.e., the oxidation of water, seems to proceed with difficulty over the $SrTiO_3$ surface calcined at low temperatures, while the oxidation of methanol by holes and/or OH radicals proceeds easily.

c. Photodecomposition of water. The dependence of the activity of photocatalytic decomposition of distilled water over NiO–$SrTiO_3$ upon the calcination temperature of $SrTiO_3$ is shown in Fig. 5. The evolution of H_2 and O_2 takes place steadily at CT 1400°C as shown in Fig. 6. The highest activity was obtained when $SrTiO_3$ was calcined at 1300–1400°C. The optimum calcination

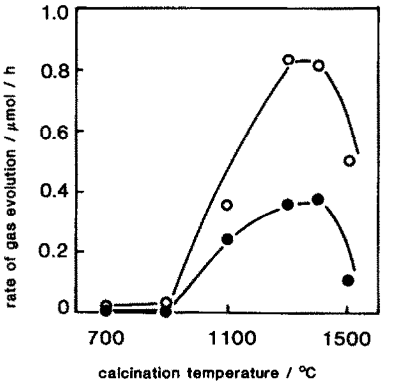

FIG. 5. Effects of calcination temperature on the activity of the photocatalytic decomposition of water over pretreated NiO(1.5 wt%)-$SrTiO_3$. (○) H_2, (●) O_2.

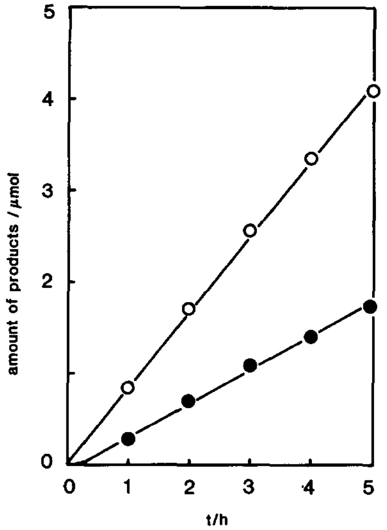

FIG. 6. Photodecomposition of water into H_2 and O_2 over NiO(1.5 wt%)–$SrTiO_3$ catalyst. (○) H_2, (●) O_2. $SrTiO_3$ catalyst was calcined at 1400°C.

temperature for the photodecomposition of water is different from those for H_2 evolution from aqueous methanol solution and O_2 evolution from aqueous silver nitrate solution.

d. Comparison of three reactions over NiO–$SrTiO_3$. As the pretreated NiO–$SrTiO_3$ was able to photocatalyze all three reactions examined in this study, those reaction rates are compared, as shown in Fig. 7. It is clear that the optimum calcination temperatures are different even over catalysts pretreated in the same way. For each reaction the optimum calcination temperature is as follows:

(a) H_2 evolution from CH_3OH_{aq}, below 900°C,

(b) O_2 evolution from $AgNO_{3aq}$, ca. 1100°C, and

(c) photodecomposition of water into H_2 and O_2, ca. 1300°C.

It is not clear at present why such a high calcination temperature is necessary for the photocatalytic decomposition of water. The water decomposition reaction is accompanied by a large increase in free energy (ΔG°_{298} = 237 kJ/mol), while the other two reactions are not. In the case of the uphill reaction, separation of the reduction and oxidation sites would be a crucial condition for accomplishing the reaction because it avoids the reverse reaction between intermediates such as hydrogen atoms, hydroxyl radicals, and so on. Thus, the high calcination temperature for the optimum condition suggests the long-range migration of an electron and a hole produced in the bulk of $SrTiO_3$ powder. The amount of defects such as a boundary, which works as a recombination site between electrons and holes, decreases with the increase in calcination temperature above 1100°C. In the NiO–$SrTiO_3$ system an electron must migrate to the NiO surface and a hole to the $SrTiO_3$ surface where both sites are well separated (*7*). In the case of the H_2 evolution from aqueous methanol solution, holes are consumed irreversibly by reaction with methanol, and electrons are enriched in the catalyst. On the other hand, electrons are consumed irreversibly by Ag^+, and holes are enriched in the catalyst in the case of O_2 evolution. Thus, the small amount of defects would not play an important role in

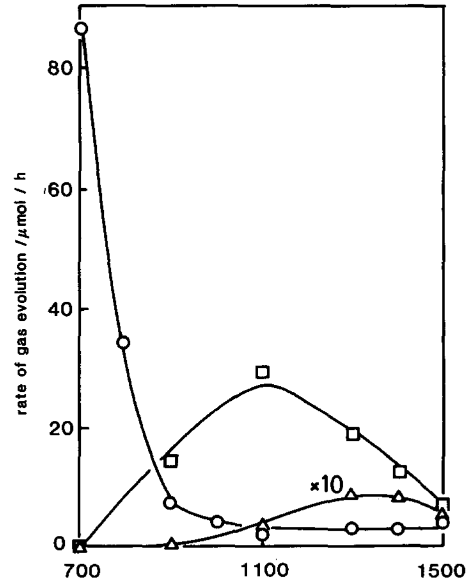

FIG. 7. Comparison of photocatalytic activities over NiO(1.5 wt%)–$SrTiO_3$. (○) H_2 from CH_3OH_{aq}, (□) O_2 from $AgNO_{3aq}$, (△) H_2 from distilled water.

those reactions, which is the case for the decomposition of water.

The amount and nature of surface hydroxyl groups also seem to have an effect on photocatalytic activities, as has been pointed out previously (*11, 13*). As the $SrTiO_3$ powder used in this study was calcined in air at varying temperatures, those properties were not well controlled. To understand the characteristic behavior of each reaction, a detailed mechanistic study including surface chemistry will be necessary.

CONCLUSION

The photocatalytic activities of three kinds of reactions, i.e., photodecomposition of water to form H_2 and O_2, evolution of H_2 from aqueous methanol solution, and evolution of O_2 from aqueous silver nitrate solution, were examined over the catalysts in which $SrTiO_3$ powder was calcined at varying temperatures. It was found that the optimum heat treatment conditions on $SrTiO_3$ varied with the reactions. This fact suggests that the optimum treatment conditions which were obtained by examining the evolution of H_2 from the solution containing a reducing agent and the evolution of O_2 from that containing an oxidizing agent will not always provide the best environment for decomposition of water into H_2 and O_2 in a small particle system.

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