

Preparation of Titania-Zeolite Composite Thin Film Using Dip-Coating and Hydrothermal Treatment

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Recently, decompositions of hazardous gaseous substances like vapor organic compounds and NO_x indoors and in the atmosphere are investigated by using TiO_2 photocatalyst. For such purpose, a combination of a TiO_2 photocatalyst and an appropriate absorbent is very effective in promoting the photocatalytic reaction because the concentration of hazardous substances is very low indoors and in the atmosphere. In this study, first of all, thin films composed of TiO_2 and SiO_2 were prepared on glass substrates by a dip-coating method using titanium diisopropoxide bis(acetylacetonate) and silicon tetraethoxide in iso-propanol solution, and subsequent heat-treatment at 700°C for 8h. The TiO_2 phase in the obtained binary thin film crystallized into photocatalytic-active anatase phase by this treatment. Second, the SiO_2 phase in the film was converted into zeolite phase by a hydrothermal treatment in alkaline solution containing Al_2O_3 , Na_2O and SiO_2 components at various temperatures. The crystalline phases of zeolite in the film were zeolite-Y and zeolite-A that were representative zeolites as industrial absorbent.

Key words: photocatalyst, absorbent, zeolite, hydrothermal treatment

1. INTRODUCTION

TiO_2 is a remarkable material as photocatalyst that can decompose hazardous gaseous substances like vapor organic compounds and NO_x indoors and in the atmosphere under ultraviolet (UV) light irradiation. Mechanism of photodecomposition by TiO_2 is schematically shown in Fig.1. When the TiO_2 absorbs UV light of which energy is less than band gap of TiO_2 , photo-excited electrons and holes are generated. They change oxygen molecules into active oxygen species which have strong oxidation ability, so that they decompose hazardous gaseous substances.

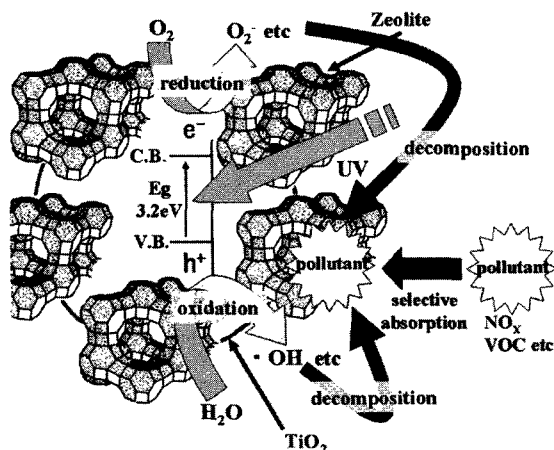


Fig.1 Mechanism of application of TiO_2 - Zeolite composite material[1]

As photocatalytic reaction proceeds at the surrounding close to TiO_2 surface, it is necessary to catch and concentrate the hazardous gaseous substances indoors and in the atmosphere near TiO_2 . Thus, in order to decompose the gaseous substances by TiO_2 photocatalyst, a combination of the TiO_2 photocatalyst and appropriate absorbents is very effective as shown in Fig.1. Therefore, there are various approaches of fabricating composite materials such as zeolite, silica gel, active carbon and apatite, etc [2-5]. Another advantage of such combination is removal of hazardous gaseous substances without light illumination like nighttime, because UV light irradiation is essential for the photocatalytic reaction.

Among porous materials as an absorbent which is mentioned above with the combination of a TiO_2 photocatalyst, zeolite which is basically alkaline aluminosilicate is very conventional adsorbent in industrial use. There are a lot of metastable phases of natural and synthesized zeolite. The absorption properties of especially synthesized zeolite are controllable due to the variety of their crystalline structures and compositions such as hydrophobicity or hydrophilicity, or acidity or basicity of the pore surface. This indicates that the composite of TiO_2 and zeolite is able to selectively decompose hazardous gaseous substances.

On the other hand, there is huge number of the studies on TiO_2 thin film photocatalyst coated on various materials by using various processes such as

sol-gel and sputtering methods [6-8]. When the thin film composite materials of a TiO_2 and an absorbent are fabricated, the two components should be mixed finely and homogeneously in the scale of at least several micrometers because of short life time and diffusion length of photo-induced active oxygen on TiO_2 .

TiO_2 and SiO_2 which is one of a source of zeolite have no compound in the whole range of their binary system. This suggests that a TiO_2 and zeolite composite thin film is synthesized by coating of TiO_2 and SiO_2 mixed thin film on appropriate substrates and subsequent conversion of SiO_2 component into zeolite phase by a hydrothermal treatment.

In this study, therefore, as a candidate of absorbent with the combination of a TiO_2 photocatalyst, a zeolite was selected and the composite thin film was fabricated by using a sol-gel coating method and a hydrothermal treatment.

2. EXPERIMENTAL

2.1 Preparation of TiO_2 - SiO_2 thin films

In this study, first of all, thin films composed of TiO_2 and SiO_2 were prepared on glass substrates by a dip-coating method. The flowchart of preparation process is shown in Fig.2.

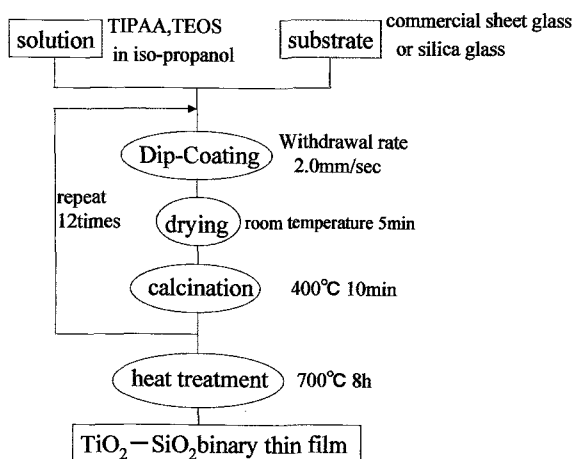


Fig.2 Preparation of thin films composed of TiO_2 and SiO_2

The raw materials of TiO_2 and SiO_2 in dip-coating process were titanium diisopropoxide bis(acetylacetonate) ($[\text{CH}_3\text{COCH}=\text{C}(\text{O}-)\text{CH}_3]_2\text{Ti}[\text{OCH}(\text{CH}_3)_2]_2$, TIPAA) and silicon tetraethoxide ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS) in iso-propanol solution. In the solution, the molar ratio of Ti to Si is 1 to 1. A commercial sheet glass (soda lime silicate glass) and a silica glass were used as substrates, of which surfaces were made uneven in order to suppress the peering of the thin film during subsequent hydrothermal treatment. Dip-coating was reciprocally carried out at the rate of 2.0 mm/sec with calcined at 400°C. The coated

substrates were subjected to heat-treatment at 700°C, finally.

2.2 Conversion of SiO_2 phase into zeolite phase

The SiO_2 phase in the coating film was converted into zeolite phase by a hydrothermal treatment in alkaline solution containing Al_2O_3 , Na_2O and SiO_2 components. That preparation flow is shown in Fig.3.

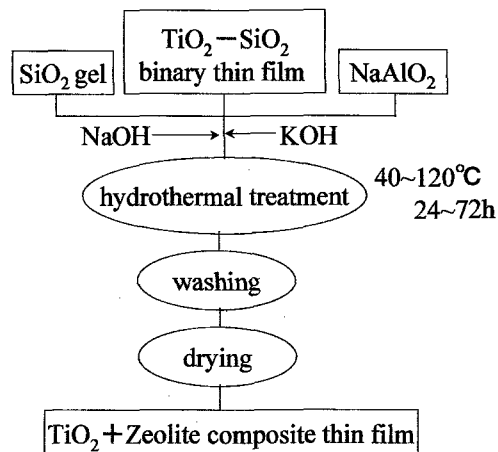


Fig.3 Conversion of SiO_2 phase in the film into zeolite phase

The 1-4M of NaOH and KOH mixed solution dissolved silica gel and NaAlO_2 as raw material of SiO_2 and Al_2O_3 components were prepared. The coated substrates were soaked into the solution in a sealed container, and hydrothermal treatment was carried out at the temperature, 40-120°C for 24-72h.

The crystalline phases of the obtained thin film were measured by X-ray diffraction (XRD, Shimadzu Labx XRD-6100) and their compositions are analyzed by electron probe micro analysis (EPMA, JEOL JXA-8900). The surface morphology of the thin film was observed by the scanning electron microscope (SEM, JEOL JSM-5800).

3. RESULTS & DISCUSSIONS

3.1 Crystallization behavior of TiO_2

XRD patterns of TiO_2 single phase thin film and TiO_2 and SiO_2 binary one with heat treatment are shown in Fig.4. The TiO_2 single phase thin film was crystallized at 400°C for 4h, however, the TiO_2 and SiO_2 binary thin film was not crystallized at the same condition but crystallized at 700°C for 8h. This is because the existence of amorphous SiO_2 phase surrounding TiO_2 phase disturbs the substance transfer and the restructuring of TiO_2 components [9-10].

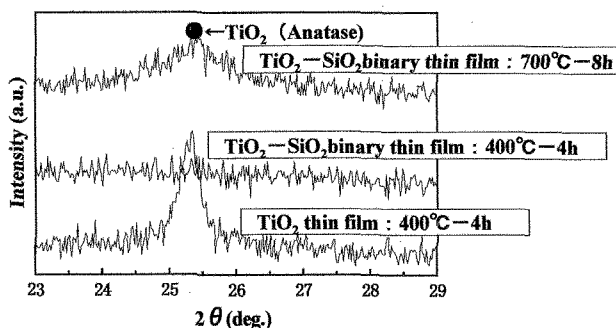


Fig.4 Relationship between crystallization of TiO₂ phase and heat-treatment

3.2 Domain Size of TiO₂ phase in the thin films

To investigate the domain size of the TiO₂ phase in the TiO₂-SiO₂ thin film, the SiO₂ phase was selectively leached by NaOH aqueous solution, and the leached thin film was observed by SEM. The result is shown in Fig.5. The size of TiO₂ phase in the film was about 10-100nm.

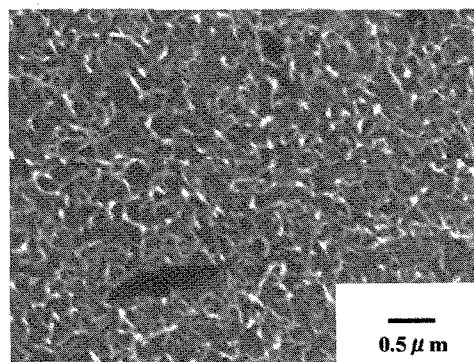


Fig.5 TiO₂ and SiO₂ binary thin film after SiO₂ phase selective leaching

3.3 Crystalline phase and morphology of zeolite synthesized by hydrothermal treatment

When the sheet glass substrates were utilized, zeolite phases were synthesized in the hydrothermal conditions of high temperature and high concentration of alkaline solution, and of low temperature and low concentration one. Those conditions are shown in Table 1, and the XRD patterns of the obtained samples in those conditions are shown in Fig.6.

In the hydrothermal condition of high temperature and high concentration of alkaline solution, zeolite-Y ($0.92\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 7\text{H}_2\text{O}$) was synthesized. In the condition of low temperature and low concentration one, the crystalline phase containing Mg ($\text{Mg}_6\text{Al}_2(\text{OH})_{18}\cdot 4.5\text{H}_2\text{O}$) was formed, which was confirmed by the result of semi-quantitative analysis by EPMA. In the preparation system, only a sheet glass substrate contains Mg. From those results, a glass substrate seemed to dissolve in the solution during

hydrothermal treatment.

The XRD patterns of the obtained samples on the silica glass substrate in the same conditions are shown in Fig.7. In the high temperature and high concentration hydrothermal condition, zeolite-Y was synthesized as same as that on the sheet glass substrate, but the synthesized zeolite layer peeled off during hydrothermal treatment in spite of using glass substrates of uneven surface. In the low temperature and low concentration condition, zeolite-A ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 1.85\text{SiO}_2\cdot 5.1\text{H}_2\text{O}$) was synthesized.

Table 1 Hydrothermal condition in which zeolite phase was formed

	(high temperature high concentration)	(low temperature low concentration)	Solution condition
SiO ₂ gel :	0.4g	0.04g	
NaAlO ₂ :	0.4g	0.12g	
NaOH :	3N,25ml	1N,25ml	
KOH :	4N,5ml	none	
temperature :	75°C	60°C	
time :	72h	72h	

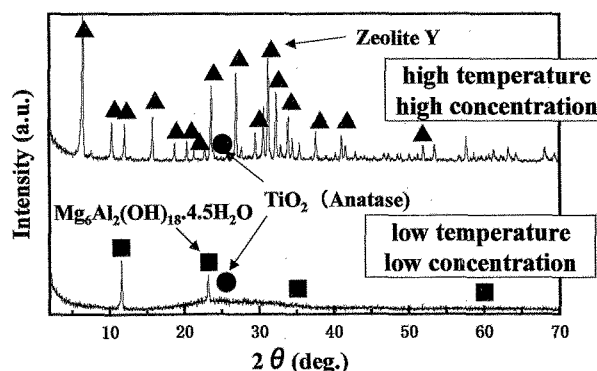


Fig.6 XRD patterns of the samples which formed on the sheet glass substrate in the hydrothermal condition of Table 1

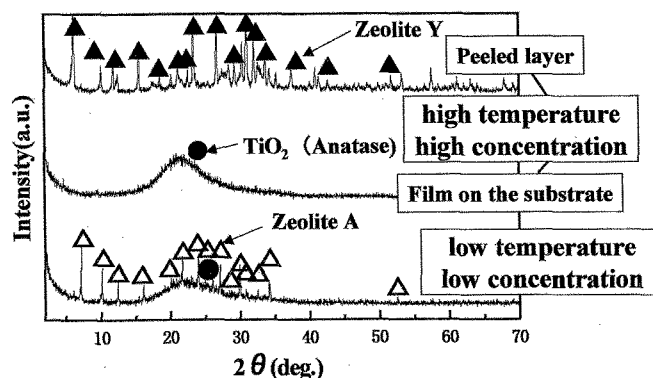


Fig.7 XRD patterns of the samples which formed on the silica glass substrate in the hydrothermal condition of Table 1

The size and morphology of zeolite synthesized on the sheet glass and the silica glass substrates were shown in Fig.8. The typical octahedral precipitates of zeolite-Y and the cubic ones of zeolite-A were observed, respectively. The size of synthesized zeolite was about 1-10 μ m. This size of zeolite phase is much larger than the size 10-100nm of TiO₂ phase in the thin films composed of TiO₂ and SiO₂.

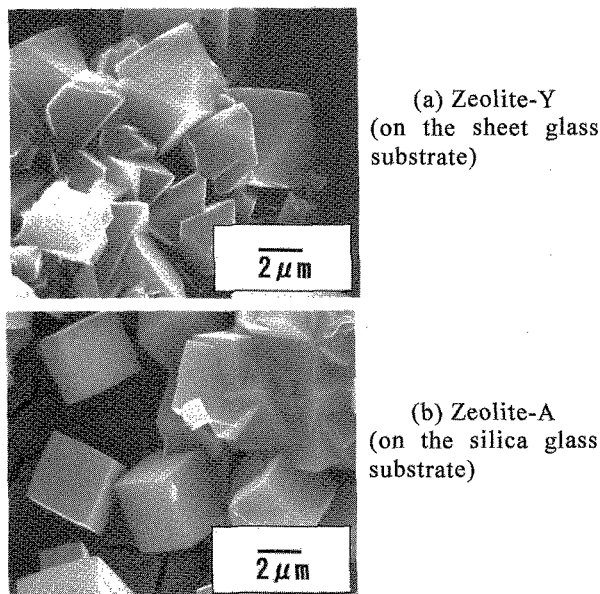


Fig.8 SEM photographs of the samples which formed on the sheet glass and silica glass substrate in the hydrothermal condition of Table1

3.4 Zeolitization process in the composite thin films

The results of various hydrothermal conditions indicates that the higher temperature and concentration of alkaline solution make synthesized zeolite have higher Si/Al ratio and poor alkali content, that is zeolite-Y, and the lower temperature and concentration make it oppositely, that is zeolite-A. Further, the compositions of glass substrates seem to affect the crystalline phase of the synthesized zeolite, that is, the zeolite containing higher silica and lower alkali components was synthesized on the substrate with relatively easy dissolution. On the other hand, the size of synthesized zeolite was much larger than that expected from the size of SiO₂ phase in the composite thin films.

From these behaviors of zeolite on the substrates, therefore, zeolite phase was not synthesized by conversion from SiO₂ phase in the binary thin film, but mainly precipitated from the mixed solution of raw material in hydrothermal treatment. However, in the early stage of the formation of zeolite, higher concentration of SiO₂ just close to the thin film surface, which is induced by the dissolution of the SiO₂ phase in

the composite thin film and the glass substrates, promoted the zeolitization. This first synthesized zeolite phases much affected the subsequently formed crystalline phase and morphology of the zeolite.

4. SUMMARY

In this study, subjecting the TiO₂-SiO₂ binary thin film prepared by dip-coating to the hydrothermal treatment, zeolite-Y and zeolite-A which are commercially utilized absorbents, were composed on photoactive anatase-phase TiO₂ in the thin film.

The size of synthesized zeolite was about 1-10 μ m. This size of zeolite phase is much larger than the size 10-100nm of TiO₂ phase in the thin films composed of TiO₂ and SiO₂. The zeolitization is much affected not only by the hydrothermal condition but also by the dissolution behavior of the SiO₂ component from the composite thin film and the substrates.

The prepared composite thin film is expected to show high absorption ability for vapor organic compounds and has a possibility to decompose the hazardous gaseous substances by photocatalytic process.

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