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Study on Precursor of Visible-Light-Active Titanium Oxide Photocatalyst Characterized by Temperature-Programmed Desorption-Mass Spectroscopy (TPD-MS)

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Abstract

In this paper, we apply the temperature-programmed desorption (TPD) method combined with mass spectrometric (MS) analysis to characterize the hydrolysis products of $\text{Ti}(\text{SO}_4)_2$ (SHy-NH) and TTIP (AHy-NH) with an NH_3 aqueous solution, that can be vis-active photocatalysts when they are calcined at suitable temperatures in air. We find that H_2O is the only product that exists below 100°C . Beyond 100°C , however, NH_3 desorption begins and shows its maximum strength at approximately 200°C . This desorption continues to near 450°C ; we know this because NH^+ (m/z 15) can still be detected beyond 400°C . In the case of SHy-NH, desulfurization commences at approximately 400°C , since SO_2^+ (m/z 64), which cannot be removed by the washing process, is detected. Considering these results, the emergence of vis-activity during the process of hydrolysis product calcination appears to be concerned with the desorption of volatile species from the polycrystalline titanium oxide structure. We propose that this desorption leads to oxygen deficiency, as confirmed by XPS.

Key-words : *Visible-light-active titanium oxide photocatalyst, Temperature-programmed desorption-mass spectroscopy, Titanium sulfate, Titanium tetraisopropoxide*

1. Introduction

In our previous report¹⁾, we described a simple synthesizing process of a highly visible-light (vis)-active and vivid-yellow-colored anatase powder that contains trace amounts of nitrogen, and proposed the significance of oxygen-deficient stoichiometry to realize a vis-activity. We also discussed why polycrystalline structures with primary particle size in the nano-scale region, between several and 20 nm, and grain-boundaries (GBs) should be considered in the emergence of vis-activity. This photocatalyst exclusively absorbs light in the blue to bluish-green region in the vis range, which corresponds to the complementary color of yellow, and shows high photocatalytic activity when a monochromatic blue light-emitting diode (BLED) is used as a light source.

Preparing the anatase powder is quite a simple matter : the hydrolysis products of a $\text{Ti}(\text{SO}_4)_2$ and NH_3 aqueous solution are calcined using an ordinary electric

furnace in a dry-air atmosphere at 400°C . The crystallization and/or thermal transformation behavior that occurs at around 400°C could be the key for the emergence of vis-activity. As for a direct method of investigating these thermal behaviors, there are a variety of studies on titania hydrolysates prepared from titanium tetrachloride (IV), titanium sulfate (IV) and titaniumtetraisopropoxide (IV) using differential scanning calorimetry (DSC), TG/DTA, FT spectroscopy and X-ray diffraction (XRD)²⁻¹⁴⁾. However, there has been little work done on indirect methods for determining thermal behaviors such as detecting desorption species at increasing temperatures, despite the fact that the species are precisely detected when a mass spectrometer is used as detector. Furthermore, it might be worthwhile elucidating the thermal properties of the hydrolysis products to understand the structural changes that lead to the emergence of vis-activity in final product of the photocatalyst.

Temperature-programmed desorption (TPD) is a technique in which the sample is heated at a programmed rate in an inert atmosphere or under vacuum. In this way, information about the nature of chemisorbed species, volatile complexes and the decomposition of the sample can be detected. To investigate the thermal

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properties of the hydrolysis products, an apparatus consisting of a temperature-programmed furnace and a quadrupole mass spectrometer was connected together.

In this work, we apply the TPD method combined with mass spectrometric (MS) analysis to characterize the hydrolysis products of $\text{Ti}(\text{SO}_4)_2$ and titanium tetraisopropoxide (TTIP) with an NH_3 aqueous solution, which can be vis-active photocatalysts when these are calcined at suitable temperature in air.

2. Experimental

2.1 Preparation

We synthesized hydrolysis products from $\text{Ti}(\text{SO}_4)_2$ as previously reported¹⁾ by adding 28% NH_3 to 100 g of its 20 wt% aqueous solution (both reagent grade, from Kanto Chemical Co.) until the pH of the mixture reached 7. The obtained hydrolysis product was rinsed with deionized water until the concentrations of SO_4^{2-} in 30 mL of rinsing water fell below 0.5 mg/L, then dried at 60°C (denoted as SHy-NH). For comparison, we additionally prepared a hydrolysis product from TTIP (> 99%, from Kanto Chemical Co.), similarly to SHy-NH. We added TTIP (0.09 mol) drop by drop to 200 mL of a 3.5 vol% NH_3 aqueous solution under vigorous stirring at room temperature. Subsequently, the precipitated hydrolysis product was separated from the solution by filtration without rinsing. Finally, the cake was dried at 60°C (denoted as AHy-NH).

2.2 TPD apparatus

We conducted the experiments using the apparatus presented in **Figure 1**.

For this experiment we employed a Double-Shot Pyrolyzer (Frontier Lab, PY-2020 D, Japan) with a cylindrical fused-silica desorption chamber (capacity of 0.98 cm³, 4.5 mm id and 62 mm long) placed in a

temperature-programmed furnace. The desorption chamber was connected to the gas-inlet interface of an gas chromatograph quadrupole mass spectrometer (Shimadzu, GCMS-QP 5050, Japan), and the gas-inlet interface and mass spectrometer were connected *via* a stainless steel column (2.5 m long). A 50 μL platinum cell with 1 mg of sample was inserted into the desorption chamber from the top. After introduction into the TPD system, we released helium carrier gas (99.9999%) into the desorption chamber and maintained the temperature at 50°C until all ion signals settled down to background levels before commencing the TPD run. This took less than 10 minutes in most cases.

To perform a TPD scan, the sample was heated by linearly increasing the temperature by 20°C/min between 50°C and 550°C. A PC with a GPIB/IEE 488 interface managed data acquisition during heating time so that the ion signals between m/z 11 to m/z 200 and the sample temperature were simultaneously recorded. Laminar flow was achieved from the furnace to the mass spectrometer and there were no dead volume products in the connection lines.

2.3 Characterization

The thermal analysis was carried out using DSC equipment (Shimadzu, DSC-60) in a helium atmosphere with flow rate of 50 ml(STP)/min.

We evaluated the vis-activity by photocatalytic oxidation of 540 ppm acetone in purified air using monochromatic BLED in the same manner as described elsewhere in our previous report¹⁾ and compared the quantities of CO_2 formed after 24 h of BLED illumination.

Using an X-ray diffractometer (Rigaku RINT 2000), we measured the powder's X-ray diffraction (XRD) pattern, and calculated the primary particle size D using the Scherrer equation¹⁵⁾.

The ESR spectra were measured at -196°C *in vacuo* (10⁻⁴ Pa) with Mn^{2+} as a marker with an ESR spectrometer (Nihon Denshi, JES-RE 2 X) operating in the X-band under irradiation with visible light.

3. Results and Discussion

The principle of the calcinations is to remove unbound and bound water, as well as sulfur compounds, from the hydrous hydrolysis product when it is prepared from $\text{Ti}(\text{SO}_4)_2$ ³⁾. As a result, various physico-chemical processes such as drying, dehydration, and desulfurization, transformation of amorphous to polymorphic anatase proceed during calcinations.

The TPD-MS spectra of AHy-NH are presented in **Figure 2**, which shows the relative intensities of the

Fig. 1 Schematic drawing of TPD-MS apparatus.

Fig. 2 TPD-MS spectra of ANH-Hy.

corresponding peaks presented as a function of TPD temperature. Total ion chromatogram (TIC) is also seen. The number multiplied in the parenthesis beside m/z indicates signal intensity.

The most significant products obtained by TPD were H_2O and NH_3 in the temperature range between $50^\circ C$ and $550^\circ C$, since H_2O^+ (m/z 18), NH_3^+ and OH^+ (m/z 17), NH_2^+ (m/z 16), and NH^+ (m/z 15) were the only signals detected in the measurements; moreover, these strength ratios corresponded closely to the fragment patterns of H_2O and NH_3 . We found that H_2O is the only product that exists below $100^\circ C$. Beyond $100^\circ C$, the onset of NH_3 desorption began and showed its maximum strength at about $200^\circ C$. It is said that this desorption continues to near $450^\circ C$, since we could still detect NH_2^+ (m/z 16) beyond $400^\circ C$. Signals detected between 200 and $250^\circ C$ were assigned to residual alkyl groups.

Figure 3 presents the TPD-MS spectra of SHy-NH. These data are similar data to those obtained for AHy-NH, except beyond $400^\circ C$. In the case of SHy-NH, it is

Fig. 3 TPD-MS spectra of SNH-Hy.

clear that the onset of desulfurization starts at about $400^\circ C$, since SO_2^+ (m/z 64), which could not be removed by the washing process, is detected in this figure.

Regarding the existence of the NH_3 species in the hydrolysis products, we have detected it as NH_4^+ by DRIFT spectra measurement¹⁾. Therefore, we consider that the NH_3 species exists as an ammonium salt.

In Figures 4 and 5, DSC curves and vis-activity (evaluated by CO_2 concentration formed from acetone) for AHy-NH and SHy-NH are plotted as a function of the calcination temperature. In AHy-NH (Figure 4), the DSC curve is characterized by an enhanced exothermic peak around $420^\circ C$. On the other hand, the vis-activity curve shows its maximum at $375^\circ C$, although a rapid decrease occurs with the onset of the DSC sharp exothermic reaction. A similar tendency is also observed in SHy-NH (Figures 5). The maximum vis-activity appears at $400^\circ C$, dropping when the DSC exothermic band with the peak at $420^\circ C$ emerges.

Fig. 4 Relationship between DSC curve and the vis-activity (CO_2 concentration: $\blacklozenge$) of ANH-Hy plotted as a function of the calcination temperature. Fig. 5 Relationship between DSC curve and the vis-activity (CO_2 concentration: $\blacklozenge$) of SNH-Hy plotted as a function of the calcination temperature.

The TPD-MS spectra of NH_2^+ (m/z 16), vis-activity and the average of primary particle size, D , calculated with the Scherrer equation, are superimposed in **Figures 6** and **7** as a function of TPD temperature. In Figures 6 and 7, m/z 16 signals can act as probes to monitor the NH_3 desorption level for AHy-NH and SHy-NH, respectively.

Q. Zhang et al. explains that the transformation heat of amorphous parts to the anatase phase and the discontinuous grain growth of the transformed anatase particles are most likely responsible for the appearance of the exothermic peaks of both samples at 375 to 400°C, as shown in Figures 4 and 5²⁾. Since many factors influence the crystallization of amorphous material into anatase, the position of the exothermic peak given in other literature is somewhat contradictory^{4,9–12)}. We also noticed the popcorn burst-like phenomenon when AHy-NH and SHy-NH were baked in an open crucible when the temperature was maintained at around 400°C.

Fig. 6 Superimposed profiles of TPD-MS desorption spectra of NH_3 for AHy-NH monitored as NH_2^+ (m/z 16), vis-activity (◆) and primary particle size, D (◇) as a function of the calcination temperature.

Fig. 7 Superimposed profiles of TPD-MS desorption spectra of NH_3 and SO_4 for SHy-NH monitored as NH_2^+ (m/z 16) and SO_2^+ (m/z 64), vis-activity (◆) and primary particle size, D (◇) as a function of the calcination temperature.

Considering this phenomenon, we assign responsibility for the exothermic bands to structural relaxation to eliminate inner distortion accumulated by desorption of NH_3 from the sample structure, since no TPD-MS signals are detected (Figures 2, 3). Furthermore, no remarkable changes are observed in the primary particle size D at this temperature range (Figures 6 and 7), and yet the onset of the crystallization of amorphous material into anatase is confirmed below the temperature at which respective peaks of exothermic bands are observed (Figures 6 and 7). These results and assumptions suggest that an adequate calcination temperature should emerge that would be considered suitable for vis-activity, i. e., slightly below the temperature at which DSC exothermic reactions occur. The greatest amount of internal distortion caused by NH_3 may be absorbed at this temperature.

We have already described elsewhere¹⁾ that the vis-activity is observed with the samples of which primary particle size D ranges from several to about 20 nm. Below this primary particle size range, that the crystallization speed in AHy-NH is higher than in SHy-NH is explained by SO_4^{2-} contamination, as mentioned above. At temperatures above 300°C in both cases, crystallization starts and NH_3 desorption still continues, suggesting that vacancies are forming and leading to an increase of inner distortion. However, at the peak of vis-activity, desorption of NH_3 is still occurs, indicating that NH_3 is not completely desorbed in these samples with the highest vis-activity. When we calculate the N content of the samples that showed the highest vis-activity from the TPD-MS spectra of m/z 16 in both samples, values of 0.19 and 0.2% N were obtained, respectively, these amounts agreeing well with the data obtained by XPS measurement reported previously¹⁾.

Figures 4 to 7 show that the temperature at which vis-activity peaks in SHy-NH is about 25°C higher than in AHy-NH, while the vis-activity drop shown in SHy-NH is not so rapid as in AHy-NH. This appears to be due to the existence of SO_4^{2-} , since the m/z 64 signal assigned to SO_2^+ signal is observed beyond 350°C. Moreover, the temperature range in which high vis-activity emerges is so narrow in the case of AHy-NH compared to SHy-NH where high vis-activity persists from 375°C to beyond 500°C. This expansion of the temperature range is thought to be due to the desorption of SO_4^{2-} from the sample; a similar mechanism as the one operating for NH_3 desorption in the samples. This means that SO_4^{2-} desorption can create vacancies that lead to the emergence of vis-activity when it is desorbed.

Considering these results, the emergence of vis-activ-

Fig. 8 ESR spectra of SNH-Hy_{cat} at -196°C in *vacuo* (10^{-4} Pa).

ity in the calcined hydrolysis products appears to be associated with the desorption of volatile species from the polycrystalline structure of titanium oxide. It is also thought that this desorption leads to oxygen deficiency, as confirmed by XPS described at previous report¹⁾.

ESR measurements were carried out for calcinated vis-active SHy-NH in air at 400°C (denoted as SHy-NH_{cat}) at -196°C in *vacuo* and the spectra are shown in Figure 8.

There were signals observed at $g=1.986$, 2.004 and 2.024 in the SHy-NH_{cat} when the vis illumination was applied. On the contrary, no signal was observed in the dark except the signals for the Mn^{2+} marker. As for the assignment of these signals, it seems to be due to O_2^- anion radicals formed by the transferred electrons that were trapped at the oxygen-deficient site^{16,17)}.

Assuming that the volatility of additives reflects the emergence of the vis-activity, the desorption energy, E_d , calculated using the peak-position method¹⁸⁾ as following, seems to be available to discuss the vis-activity emergence mechanism :

$$E_d = RT_m \ln(\nu/\beta)$$

where R is the gas constant, T_m is the peak temperature, *i.e.*, the temperature at which the desorption rate has a maximal value, β is the linear heating rate ($\beta = 20^{\circ}\text{C}/\text{min}$), and ν is a frequency factor of the chemisorption bond ($\nu = 10^{13}\text{s}^{-1}$). The desorption energies calculated from the position of the peak maxima are listed in Table 1.

All the calculated desorption energies are higher than 100 kJ/mol , indicating that chemisorption processes are involved. From these results, we suggest that chemical species with E_d values from approximately 100 to 170 kJ/mol are available to give a vis-activity on the titanium oxide when the chemical species are mixed in the hydrolysis product of titanium oxide.

Table 1 Desorption product and corresponding desorption energies, E_d

Desorption product	$E_d/\text{kJ mol}^{-1}$
NH_3	111.5
SO_2	170.8

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可視光応答型酸化チタン光触媒前駆体の TPD-MS による評価

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要 旨

大気雰囲気下、適切な温度で焼成すると可視光活性を示すことが確認されている硫酸チタンあるいはチタニウムイソプロポキシドとアンモニアとの反応によって合成した水酸化物 (SHy-NH, AHy-NH) について、昇温脱離-質量分析 (TPD-MS) を行った。SHy-NH, AHy-NH いずれの場合も 100°C 以下では水のための脱離が確認された。100°C を越えるとアンモニアの脱離が始まり、この脱離は 200°C 付近で極大となり、450°C 付近まで続くことがわかった。

SHy-NH では、洗浄工程で除去されなかった硫酸イオンの脱離に帰属される SO_2^+ (m/z 64) のシグナルが 400°C 付近から観察された。以上の結果と焼成温度と可視光活性の発現の関係から、可視光活性は水酸化物の焼成工程中に生じる揮発成分の脱離によって引き起こされる酸素欠陥が原因していると考察した。