Thermal Catalysis Reaction for Self-Surface-Modification of Titania and the Retention Behavior of Resulting Packing Materials in HPLC

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Abstract
The titania that was prepared as a packing material in our laboratory, which changed its color on heating, microwave irradiation, and heating under vacuum during nitrogen adsorption. We assumed that the compound adsorbed on titania was oxidized or oxidatively polymerized on heating, leading to the color change. The color faded on heating the sample at 270ºC. The catalytic ability of titania is assumed to accelerate its coloration and decoloration. We demonstrated the catalytic ability of titania using glycerol as an adsorbate; silica gel was used as an adsorbent for comparison with titania. Titania accelerated the oxidation or oxidative polymerization of the adsorbate and the decomposition of the oxidized or polymeric compound obtained. Furthermore, the catalysis of titania led to the modification of its surface by adsorbate oxidation or oxidative polymerization; also, surface modification was demonstrated by using glycerol as the adsorbate. Two different modified titania were prepared as packing material by heating the mixture of titania and glycerol at 120ºC and 200ºC for up to 2 h after coloration. The retention behavior of purine, allopurinol, hypoxanthine, and oxypurinol on these two modified titania and non-modified one was investigated. Oxypurinol eluted faster than hypoxanthine on titania modified at 120ºC although it was more strongly retained on non-modified titania than hypoxanthine. Thus, the retention site of oxypurinol is similar to that of glycerol on non-modified titania, that is, the surface modification by glycerol oxidation or oxidative polymerization blocked the site and accelerated its elution. The results could be used for explaining not only the modification of the surface but also the retention mechanism on titania.

Keywords: Thermal catalysis; Surface modification; Purine-related compounds; Titania

1. Introduction
Titania (titanium dioxide, TiO₂) is a novel attractive ceramic column-packing material used in high-performance liquid chromatography (HPLC). We have reported a laboratory-scale preparation of titania using hydrolysis and polycondensation reactions of titanium alkoxide by a sol-gel method [1] and the use of the titania as a packing material by examining its retention behavior [2-6] and found that the calcination temperature affected its chromatographic properties [7].

Titania turned into a slight beige color on microwave irradiation. The color of titania deepened as the irradiation time increased. We also observed coloration when titania was heated in the final treatment process during its preparation or when it was heated under vacuum during the nitrogen adsorption process. We assumed that the compound adsorbed on titania was polymerized on heating without desorbing, resulting in the coloration. The color faded on heating at 270ºC, which was the maximum temperature possible in the oven used. Titania was found to act as a metal oxide catalyst [8-11]; this process was hereinafter referred to as thermal catalysis to distinguish it...
from photocatalysis. Therefore, this phenomenon could be applicable to commercially available titania, as reported in some earlier studies by Mizuguchi et al. [12-15] and An et al. [16]. Allen et al. investigated the thermal catalytic activity of various titanium dioxide pigments with stabilizers in polymer films and reported that the catalytic activity was affected by the stabilizers [17-22].

We demonstrated that titania could act as a thermal catalyst and accelerate the oxidation or oxidative polymerization, and decomposition of an adsorbate by using glycerol as the adsorbate; silica gel was used as an alternative adsorbent for comparison. Furthermore, we presumed that the catalysis of titania could result in the modification of its surface by adsorbate oxidation or oxidative polymerization and attempted to demonstrate the modification using glycerol as the adsorbate. The retention behaviors of purine-related compounds on titania and the modified titania were compared.

2. Experimental

2.1. Chemicals

All chemicals were of analytical reagent grade quality and were used without further purification. Titanium isopropylate and 2-propanol were obtained from Nacalai Tesque, Inc. (Kyoto, Japan). Purine was obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Oxypurinol and allopurinol were obtained from Sigma-Aldrich, Inc. (Milwaukee, WI, USA). Other chemicals were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and Kanto Chemical Co., Inc. (Tokyo, Japan).

![Fig. 1. Chemical structure of the solutes used.](image)

The chemical structures of the solutes used are shown in Fig. 1. The numbers indicate the position of nitrogen atoms in the 2-ring heterocyclic skeleton of solutes based on the number of purine as that shown in Fig. 1 for expediency.

Additionally, the three most stable tautomeric forms of oxypurinol are numbered in the order of stability, as shown in Fig. 1.

2.2. Preparation and characterization of titania

Titania was prepared by modifying a previously described method [1] by hydrolysis and polycondensation of titanium isopropylate. The particle-size distribution, surface area, pore diameter, and pore volume of titania were examined. Particle-size distribution was determined with a SALD-2200 (Shimadzu Corporation, Kyoto, Japan). The surface area, pore diameter, and pore volume were determined with a micrometrics automatic surface area and porosimetry analyzer TriStar 3000 (Shimadzu).

2.3. Coloration and decoloration of titania

We periodically captured images to examine the change in color with an increase in the heating temperature to investigate the relation between the coloration and heating temperature. 0.1 g of titania prepared in our laboratory and commercially available silica gel used as a packing material for HPLC (Super Micro Bead 150A-5, Fuji-Silysia Chemical Ltd., Kasugai, Japan) were added to two separate sample vials. Then, glycerol (0.17 g) was added to both sample vials containing the packing materials and to an empty vial. The amount of glycerol added to titania seemed to be too much but was enough for the silica gel because of its low wettability to glycerol. The three sample vials were heated in steps of 20°C increments from 60°C to 200°C. At each heating step, we examined the coloration time of the samples in the vials and changes in the color for up to 2 h after the coloration by capturing images of the samples.

The temperature was measured the area of the plate on which there were sample vials in the oven with an infrared thermometer (testo830-T2, TESTO Inc., Yokohama, Japan). For capturing images, the sample vials were quickly removed from the oven and immediately placed back after capturing images with a digital still camera (Cyber-shot DSC-F88, Sony Corporation, Tokyo, Japan) as it was difficult to capture images by keeping them inside the oven.

The samples heated to 200°C turned dark brown in color and were further heated to 270°C, which was the maximum temperature possible in the oven used, because of observing the samples and periodically capturing images to check the fading.

2.4. Surface modification of titania

We used a titania exhibiting the highest surface area (described as Titania-H) among the prepared titania for this experiment. Titania-H was modified using glycerol as follows: 0.20 g each of Titania-H was added to two 30 mL beakers, and glycerol (0.23 g each) was added to the beakers containing Titania-H. The beakers were heated to
120°C and 200°C for up to 2 h after coloration of the contents. The Titania-H samples modified at 120°C and 200°C (abbreviated to Ti-G120 and Ti-G200) were washed with water and methanol followed by drying at room temperature. The products and Titania-H were slurry packed into 50 mm × 2.1 mm i.d. stainless steel tube using 50% (w/w) aqueous methanol solution.

2.5. Thermal analysis of modified titania

Thermal analysis of Ti-G120 and Ti-G200 was conducted by thermogravimetry and differential thermal analysis (TG-DTA) using TG8101D (Rigaku Corporation, Tokyo, Japan). A portion of each sample was placed in a platinum crucible and heated in air from 30°C to 500°C at a heating rate of 10°C/min. Alumina was used as a reference in the DTA measurements.

2.6. Retention behavior of purine-related compounds on titania and modified titania

To demonstrate the effectiveness of the new modification method, the retention behavior of purine-related compounds on Titania-H, Ti-G120, and Ti-G200 was investigated. Purine-related compounds have been previously used as solutes for investigating the retention behavior and the effect of organic modifiers using titania as a packing material [21]. For further data collection, we used four molecules, namely, purine, oxypurinol, allopurinol, and hypoxanthine, as solutes and 70% and 80% aqueous methanol solutions as the mobile phase.

Chromatography was performed with an Alliance 2695 separation module and a 2996-photodiode array detector (Waters Corporation, Milford, MA, USA). Data were processed using the chromatography data software Empower (Waters). The column temperature was controlled at 40°C by a column heater (Waters). The retention data were recorded using 70% and 80% (w/w) aqueous methanol solutions with a flow rate of 0.2 mL/min. UV detection was at 254 nm for all measurements. All solutes were dissolved in water or methanol to obtain a concentration of approximately 100 mg/L, and the injection volume of these solutions was 5 µL.

Table 1. Physical properties of titania and silica gel.

|                      | Titania | Silica gel | Titania-H |
|----------------------|---------|------------|-----------|
| Mean particle diameter [µm] | 3.9     | 5.0        | 5.3       |
| Specific surface area [m²/g] | 87      | 202        | 226       |
| Mean pore diameter [nm]   | 9.0     | 14.7       | 5.8       |
| Mean pore volume [mL/g]   | 0.23    | 0.99       | 0.37      |

3. Results and discussion

3.1. Preparation and characterization of titania

The physical properties of the two titania obtained from the measurements are summarized in Table 1. Corresponding values of silica gel as provided by the manufacturer are also listed in Table 1 for comparison.

3.2. Coloration and decoloration of titania

Plots of the coloration time of the three samples versus the heating temperature are shown in Fig. 2. Titania sample started to color after heating at 60°C for 45 min, but the silica sample and glycerol blank maintained their color up to 160°C. The images of the samples heated at 120°C and 160°C for 2 h after coloration are shown in Fig. 3. The coloration time shortened and the color deepened as the heating temperature elevated. The deepening of the color indicated increasing amount and type of reaction products on heating. Heating up to 200°C did not cause decoloration of the samples. Titania accelerated the coloration as can be seen in Figs. 2 and 3. Titania acted as a thermal catalyst in the adsorbate oxidation or oxidative polymerization because we presumed that the coloration resulted from the oxidation or oxidative polymerization. Titania was modified along with the adsorbate oxidation or oxidative polymerization, resulting in changes in the retention behavior of titania depending on the degree of oxidation or oxidative polymerization, which could be controlled by the heating temperature, as seen in Fig. 3. The coloration on titania indicated the possibility of reforming of titania.

![Fig. 2. Plots of coloration time of the samples against the heating temperature.](image-url)

Images captured at different times during heating the samples at 270°C are shown in Fig. 4. The coloration of the samples deepened soon after starting to heat at 270°C.
However, titania sample became brownish-red after 2 h of heating and the color faded as the time increases. The color of the titania sample turned white after 6 h of heating, as seen in Fig. 4. The other samples remained colored after 6 h of heating. Thus, it was evident that titania accelerated the decoloration. Titania caused decoloration by acting as a thermal catalyst in the decomposition of oxidized or polymeric compounds prepared from the adsorbate. The decoloration of titania indicated the possibility of reusing it because few changes in the physical properties of titania were observed on calcining it at a temperature of up to 400°C for 1 h, as we previously reported [7]. Therefore, this attempt to heat at 270°C for decoloration resulted from the idea that even long time heating titania could keep the physical properties before coloring.

3.3. Thermal analysis of modified titania

Simultaneously recorded TG and DTA curves of Ti-G120 and Ti-G200 are shown in Figs. 5(A) and 5(B), respectively. The oxidized or polymeric compounds obtained from glycerol at 120°C considerably differed from those obtained at 200°C, as can be seen in Fig. 5. Ti-G120 and Ti-G200 exhibited remarkable exothermic DTA peaks around 235°C and 265°C respectively, and wide-ranging peaks from 300°C to 400°C regardless of the magnitude.

The DTA curve analysis and the weight loss measured from the TG curve indicated that the oxidation or oxidative polymerization of glycerol was enhanced with an increase in heating temperature, implying that titania accelerated the oxidation or oxidative polymerization of glycerol.
3.4. Retention behavior of purine related compounds on titania and modified titania

Chromatograms of purine-related compounds on Titania-H, Ti-G120, and Ti-G200 using 70% aqueous methanol solution as the mobile phase are shown in Figs. 6(A)-(C). The case of 80% aqueous methanol solution, all solutes eluted more slowly in the same elution order, and oxypurinol did not elute after 120 min on Titania-H.

As can be seen in Fig. 6(B), oxypurinol eluted faster than hypoxanthine on Ti-G120 although it more strongly retained on Titania-H than hypoxanthine. The fast elution indicated that the surface modification at 120°C was effective, and the retention site of oxypurinol was similar to that of glycerol on titania. Thus, the surface modification by glycerol oxidation or oxidative polymerization blocked the sites of oxypurinol and accelerated its elution. This result was in agreement with our previous prediction [23] that oxypurinol retained on titania as an enolic tautomer wherein C(2)=O and N(3)H were converted to C(2)-OH and N(3) on the oxypurinol skeleton (please refer to Fig. 1, Oxy-3).

Thus, oxypurinol would exist in the enolic form in the mobile phase, although keto forms of oxypurinol and their structural isomers were presumed to be more stable.

Additionally, the peak shape of oxypurinol was sharper than that of purine and hypoxanthine. On the contrary, the surface modification at 200°C seemed to be ineffective since purine-related compounds eluted slower than those on Ti-G120 and their peaks were broadened. The increase in the degree of oxidation or oxidative polymerization of Ti-G200 resulted in an increase in the interaction of solutes and its surface.

4. Conclusions

We demonstrated the ability of titania to act as a thermal catalyst for accelerating the oxidation or oxidative polymerization and decomposition of adsorbates by means of visual examinations although a clear analysis of the process could not be carried out. The metal-oxide catalysis of titania resulted in the modification of its surface along with the oxidation or oxidative polymerization of the adsorbate. We also explained the retention mechanism on titania. Additionally, decomposition of the oxidized or polymeric compound obtained from the adsorbate by titania indicated that titania could be repeatedly used as a packing material.

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