Titanium Dioxide as a Packing Material for Micro-Packed Column in Gas Chromatography

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Abstract
A gas chromatographic micro-packed column prepared with titanium dioxide (TiO₂) particles was developed. This study reports the fundamental retention behavior of the column for several organic and inorganic gaseous compounds, and quantitatively analyzes the high-temperature degradation behavior of the injected organic compounds. The anatase TiO₂ particles were prepared by hydrolysis of titanium (IV) isopropoxide. The particle size was classified as 150 – 180 μm. The micro-packed column was prepared by packing the classified TiO₂ particles into a stainless steel capillary of inner diameter of 1.0 mm and length of 1.0 m. The TiO₂ micro-packed column was connected to a conventional gas chromatograph equipped with a flame ionization detector or a thermal conductivity detector. The column showed high retentivity for carbon dioxide and also for organic compounds, achieving a baseline separation of methane and ethane. The TiO₂ packed column was highly thermally stable, with a temperature limit above 400°C. Above 300°C, the analytes injected into the column were thermally degraded by catalytic combustion of TiO₂ under N₂ carrier gas. On the other hand, the degradation was obtained above 200°C using air as the carrier gas.

Keywords: Titanium dioxide; Micro-packed column; Gas chromatography

1. Introduction
Gas chromatography (GC) is used for the separation and determination of gaseous compounds and volatile organic compounds (VOCs) in several fields [1]. Recently, capillary columns have become popular for separating VOCs owing to their higher theoretical plates. However, in certain fields, packed columns are advantaged by a variety of stationary phases, high loading capacity, and retentivity [1]. Previously, our research group developed a micro-packed column [2,3] composed of a stainless steel capillary (1.0 mm i.d.) packed with particulate adsorbent. Both ends of the column were connected to stainless steel capillaries of 0.3 mm i.d. and 0.52 mm o.d., enabling connection of the micro-packed column to a conventional capillary GC system without specific attachments [4-6]. The micro-packed column was more compatible with rapid temperature program elution [2], and required fewer stationary phase particles, than the conventional packed column. Therefore, the micro-packed column is a suitable GC column for investigating the retention performances of new particulate stationary phases. A fibrous stationary phase can be evaluated by introducing fiber into a fused silica capillary [7-9].

Titanium dioxide (TiO₂) is a well-known photocatalyst with wide applicability [10]. Photocatalyst are typically formed with nanometer-size TiO₂ particles to enhance the surface area of the photocatalytic reaction. Metal oxides such as TiO₂ catalyze the combustion reaction that degrades organic compounds to CO or CO₂ at high temperature [11]. Adsorption of CO₂ onto surface of TiO₂ has been studying for reduction of CO₂ using infrared spectroscopy [12,13]. Sub-micrometer-size TiO₂ particles are also used as the stationary phase in liquid chromatography as they uniquely adsorb specific molecules such as phosphopptide and purine derivatives [14,15]. However, a GC column packed...
with TiO₂ particles has not been reported.

In this study, TiO₂ particles with approximate diameters of 200 μm were synthesized by the hydrolysis of titanium isopropoxide. The fundamental retention performance of TiO₂ particles as the stationary phase in GC was investigated in a micro-packed column. In addition, the degradation of organic compounds injected into the TiO₂ packed column was quantitatively evaluated.

2. Experimental

2.1. Chemicals

Titanium (IV) isopropoxide and acetaldehyde were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Methanol and naphthalene were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Standard gases of methane (C₁), ethane (C₂), propane (C₃), butane (C₄), carbon monoxide (CO) and carbon dioxide (CO₂) were obtained from GL Sciences (Tokyo, Japan). Standard n-alkane reagents (pentane (C₅) – tridecane (C₁₃)) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Toluene, ethylbenzene, and propylbenzene were obtained from Tokyo Chemical Industry Co., Ltd.

2.2. Preparation of TiO₂ particles

Approximately 10 mL of titanium isopropoxide was added to 100 mL of pure water, and left for approximately 10 min at room temperature. The obtained particles were rinsed with pure water and methanol, and dried at 120°C. The dried particles were classified through a 140 – 100 mesh (150 – 180 μm), and heated at 270°C for 24 h. The specific surface area of the TiO₂ particles, determined by the BET method, was 370 m²/g. As evidenced by the hysteresis loop in the adsorption isotherm, the particles were meso- and macro-porous (Fig. 1). A scanning electron microscope (SEM) image of the obtained anatase TiO₂ particles is shown in Fig. 2.

2.3. Micro-packed column

The TiO₂ particles (150 – 180 μm) were packed into a stainless steel capillary of 1.0 mm i.d., 1.27 mm o.d., and 1.0 m length (Shinwa Chemical Industries Ltd., Kyoto Japan). Two stainless steel capillaries of 0.3 mm i.d., 0.52 mm o.d., and length of 0.5 m were connected to both ends of the column. The reference column was an activated carbon micro-packed column (Micro-packed ST, 1.0 m length) obtained from Shinwa Chemical Industries Ltd.

2.4. GC measurements

The micro-packed column was connected to a GC system (Shimadzu, GC-2010 gas chromatograph, Kyoto, Japan) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The column head pressure and split ratio were set to 150 kPa and 10:1, respectively.

The GC system was injected with 1 μL of each compound dissolved in hexane (10 v/v%), or with 0.1 mL of each gaseous compound. The gases were directly injected into the GC.

3. Results and discussion

As C₁ was not retained in the TiO₂-packed micro column at temperature above 50°C, it was used as the t₀ (elution time of non-retained compound) marker of the TiO₂ column. The column showed a high retention power for investigated compounds, achieving a baseline separation of C₁ and C₂ at column temperatures of 50 to 100°C. As the peak symmetry factors for n-alkanes and alkylbenzenes are approximately 1.0, these nonpolar compounds exhibited symmetrical peaks. The theoretical plate numbers for the investigated alkanes ranged from 1800 to 1900. Figure 3 shows typical chromatogram for separation of alkanes. Conversely, formaldehyde and acetaldehyde yielded peaks with severe

Fig. 1. Nitrogen adsorption isotherm of the TiO₂ particles.

Fig. 2. Scanning electron microscope image of the TiO₂ particles.
Chromatography

tailings (with symmetry factors of 5.0 and 1.7, respectively). Methanol was not eluted from the TiO\(_2\) column. Figure 4 shows van't Hoff plots of C\(_2\) – C\(_7\), CO, and CO\(_2\). The \(\ln k\) values (where \(k\) is the retention factor) of all investigated analytes linearly decreased with column temperature over the investigated range (50 – 280°C). The slightly larger slopes (higher enthalpy change \(\Delta H\)) at higher molecular weights is a general trend and was also observed in an activated carbon-packed micro column. At 200°C, \(k\) on the TiO\(_2\) column was 3.30 for CO\(_2\), 2.19 for C\(_5\), and 3.27 for hexane (C\(_6\)). Conversely, on the activated carbon packed micro-packed column at 200°C, CO\(_2\) yielded a lower \(k\) (0.40) than C\(_1\). These results indicate the greater and more specific retention of CO\(_2\) on TiO\(_2\) than activated carbon. Although TiO\(_2\) particles used in this study are not pure TiO\(_2\) crystal, CO\(_2\) could adsorb on TiO\(_2\) because oxygen atoms of CO\(_2\) are weakly basic [16,17].

Previously our research group reported the decomposition of organic compounds on TiO\(_2\) particles (of diameter 3 – 4 \(\mu\)m) by thermal catalysis [18], which reduced several organic compounds to CO and CO\(_2\) at 200°C (in closed mode) or 250°C (in flow mode). In the present study, the chromatographic peak areas of the compounds injected into the TiO\(_2\) column with N\(_2\) carrier gas decreased at temperature above 300°C. Such a reduction in peak area was not observed in the activated carbon packed column. Therefore, it is probably attributed to catalytic combustion of the organic compounds on the TiO\(_2\) particles. Figure 5 shows the degradation ratios of the alkanes (decane (C\(_{10}\)) to C\(_{13}\)) and ethylbenzene at different temperatures under N\(_2\) carrier gas, derived from the reductions of their peak area. The higher molecular weight compounds remained longer in the column than the low molecular weight compounds, so their degradation ratios were higher. This degradation was not observed for the non-retained compounds such as C\(_6\) and toluene, whose peak area were unchanged as the column temperature increased from 250 to 350°C. Some small peaks were observed when alkylbenzenes were injected at earlier retention times of each compound. These peaks were not observed for alkanes. Therefore, they were considered as the peaks of degraded benzene. The retention time of naphthalene was similar to that of C\(_{12}\) on the TiO\(_2\) column, sufficiently long for degradation. However, the peak area of naphthalene was unchanged from 325 to 375°C, implying that the naphthalene molecule was stable against degradation. The degradation efficiency of the TiO\(_2\) packed

![Graph showing van't Hoff plots for alkanes, CO and CO\(_2\) using TiO\(_2\) packed column.](image1)

**Fig. 4.** van't Hoff plots for alkanes, CO and CO\(_2\) using TiO\(_2\) packed column.

![Graph showing degradation ratios of organic compounds in TiO\(_2\) packed column with N\(_2\) as the carrier gas.](image2)

**Fig. 5.** Thermal degradation of organic compounds in TiO\(_2\) packed column with N\(_2\) as the carrier gas.
column was retained for more than 100 h under the continuous N2 carrier flow.

Degradation of the injected organic compounds was further confirmed using TCD. When C11 (10% in hexane) was injected into the TiO2 packed column at a column temperature of 375°C, the baseline was significantly increased from the retention time of 0.5 min. This increase might be explained by degradation of the injected alkane to CO, CO2 or H2O. The baseline was not increased when hexane alone was injected.

Next, the catalytic degradation of the injected organic compounds with air carrier gas was investigated by FID. The degradation efficiency was significantly increased under the air carrier gas (Table 1). The degradation occurred above 200°C, and its efficiency was an increasing function of column temperature (Fig. 6). At column temperature above 300°C, the degradation ratios of C9 – C13 and toluene reached 100%. Under the air carrier gas, naphthalene was also completely degraded, and the benzene peak were not confirmed the degradation of alkylbenzenes in the TiO2 column. The retentions of C6 and C7 were decreased at column temperatures above 300°C, clarifying that their degradation ratios decreased with increasing column temperature. As shown in Table 1, the degradation ratio was related to both retention factor (k) and the column temperature.

4. Conclusion
The fundamental GC retention performance of TiO2 particles was confirmed in a TiO2 particle micro-packed column. The column achieved a high retention power for several organic compounds and CO2. The degradation of injected organic analytes by catalytic combustion was quantitatively evaluated at high column temperatures. The degradation efficiency was indicated by using air as the carrier gas. The micro-packed column is suitable for evaluating the retention performance of several volatile compounds and the catalytic activity of smaller amounts of adsorbent.

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Table 1. Degradation efficiency of organic compounds under air carrier gas.

| Temperature (°C) | C6 Degradation ratio (%) | k | C7 Degradation ratio (%) | k | C8 Degradation ratio (%) | k | Toluene Degradation ratio (%) | k |
|-----------------|--------------------------|---|--------------------------|---|--------------------------|---|-------------------------------|---|
| 175             | 0                        | 12.1 | 0                        | 32.5 | 0                        | 174 | 0                             | 70.3 |
| 200             | 2.79                     | 6.71 | 1.29                     | 22.9 | 51.7                     | 66.5 | 28.2                          | 33.8 |
| 225             | 8.16                     | 4.06 | 32.3                     | 9.51 | 95.1                     | 29.4 | 82.5                          | 19.8 |
| 250             | 21.0                     | 2.60 | 64.5                     | 5.11 | 99.6                     | 12.2 | 95.2                          | 10.0 |
| 275             | 60.7                     | 1.79 | 88.0                     | 2.98 | 100                      | 6.82 | 96.9                          | 5.99  |
| 300             | 78.3                     | 1.22 | 99.9                     | 2.12 | 100                      | 3.81 | 99.0                          | 4.43  |
| 325             | 58.5                     | 0.73 | 100                      | 1.28 | 100                      | 2.16 | 99.5                          | 2.13  |
| 350             | 38.0                     | 0.55 | 88.8                     | 0.96 | 100                      | 1.28 | 100                           | 1.47  |
| 375             | 35.9                     | 0.31 | 36.7                     | 0.71 | 100                      | 0.79 | 100                           | 1.00  |
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