Influence of titania matrix on retention behaviour in reversed-phase liquid chromatography

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Abstract

Titania was synthesized on a laboratory scale by the sol–gel method. Titania-based reversed-phase packings were prepared by reaction with octadecyltriethoxysilane. The titania and octadecyl-modified titanias obtained were tested under normal- and reversed-phase conditions to assess the influence of the titania matrix on retention. In normal-phase chromatography, the titania showed basic properties and strongly retained an acidic analyte. The k' value of the acidic analyte decreased with increasing surface coverage because the influence of the titania matrix on retention was greatly reduced by octadecyl modification. In reversed-phase chromatography with the use of a mobile phase containing acetic acid–sodium acetate buffer, the titania behaved as an anion exchanger, and the influence of the titania matrix on retention was reduced because octadecyl modification decreased the number of anion-exchange sites. On the other hand, cation-exchange properties of titania were not detectable although benzylamine was retained. Octadecyl modification increased the retention of benzylamine by the formation of silanol and octadecyl groups.

1. Introduction

It is generally accepted that the nature of the support can affect the chromatographic properties of bonded stationary phases. It is also necessary to have a detailed knowledge of the support when investigating the retention mechanism in reversed-phase liquid chromatography. However, data on the supports cannot be obtained because no manufacturer provides full details. Therefore, we have started an attempt to synthesize supports on a laboratory scale in order to investigate the effect of the supports on the chromatographic retention behaviour.

Titania has recently attracted interest as a ceramic packing material; it possesses the desir-

able mechanical and physical properties of silica and a chemical stability superior to that of silica [1,2]. Titania is an amphoteric metal oxide and has anion-exchange properties at acidic pH and cation-exchange properties at alkaline pH [3,4], whereas silica behaves only as a cation exchanger [4]. This means that the influence of the support on retention is worth further consideration when titania is used as a support.

We have already obtained silica on a laboratory scale [5] from hydrolysis and polycondensation reactions of silicon alkoxide by the sol–gel method [6–8]. We have attempted to synthesize titania on basis of the same method. The titania obtained was converted into reversed-phase packings in order to evaluate the influence of the titania matrix.

This paper presents some results for the prepa-

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ration of titania and octadecyl-modified titanias in the laboratory and the resulting chromatographic retention behaviour under normal- and reversed-phase conditions.

2. Experimental

2.1. Preparation of octadecy-modified titania packings

Titania was synthesized by a modification of the method described previously [5], as follows: in a 3-l beaker were placed 900 g of glycerol, 1500 g of 2-propanol and 30 ml of dilute hydrochloric acid (diluted by a factor of 2×10^5), then 60 ml of titanium isopropylate were dropped into the stirred solution. The alkoxide solution was allowed to stand at room temperature for 3 days. After removal of the precipitate, which was in the form of small spherical particles, the turbid supernatant was allowed to stand at room temperature for 7 days. The precipitate was repeatedly centrifuged and washed with water until the supernatant was clear, and finally dried at 200°C.

The titania obtained (henceforth referred to as Titania) was converted into reversed-phase packings by making the spherical materials react with octadecyltriethoxysilane (Wako, Osaka, Japan), as follows. In a 10-ml volumetric flask was placed 1 ml of octadecyltriethoxysilane and then toluene (Kanto Chemical, Tokyo, Japan) was added to the mark. By diluting the solution by factors of 10, 100 and 1000, the reaction solutions were prepared. Prior to reaction, Titania treated with 0.1 M hydrochloric acid overnight was dried at 200°C for 5 h. Dry Titania (1 g) was suspended in 20 ml each of the reaction solutions and the mixture was then refluxed. After 3 h it was filtered, washed with toluene, methanol and distilled water and dried at room temperature. Octadecyl-modified titanias obtained from the solution diluted by factors of 10, 100 and 1000 are abbreviated as ODT-1, ODT-2 and ODT-3, respectively. The carbon content of modifying ligands was determined by elemental analysis. Titania and ODT-1, -2 and -3 were slurry packed in 30 × 4.6 mm I.D. stainless-steel tubes.

2.2. Characterization

The particle-size distribution was determined with a Coulter Multisizer II (Coulter Electronics, Luton, UK). The physical properties of particles were determined by nitrogen adsorption measurements (Fuji-Silysia Chemical, Kasugai, Japan) on a laboratory-made apparatus.

2.3. Chromatographic use

The liquid chromatograph was constructed from a Model 880 PU pump (Jasco, Tokyo, Japan), a Reodyne Model 7125 injector and a UVIDEC-100-II detector (254 nm) (Jasco). A Model TM108M thermostat (Toyo, Tokyo, Japan) was used to maintain the column temperature at 30°C. The chromatograms were recorded on a Chromatopac CR1A (Shimadzu, Kyoto, Japan).

For comparison with C_{18} silica packing materials, ODT-1 was evaluated by the chromatographic characterization method [9]. This method is based on a few chromatographic runs in which k' values of test solutes are determined in 30% or 80% aqueous methanol.

Titania and ODT-1, -2 and -3 were tested under normal-phase conditions to examine their surface properties. The k' values of dimethyl phthalate, pyridine and phenol were determined in order to evaluate the chromatographic selectivity of these packings, with benzene as a t_0 marker.

Titania and ODT-1 were tested under reversed-phase conditions employing 80% aqueous methanol containing acetic acid–sodium acetate buffer as the mobile phase in order to investigate how Titania acts as an ion exchanger and the influence of the titania matrix on retention. The void volume was measured with methanol-d_4 in methanol.

3. Results and discussion

3.1. Characterization

The physical properties of Titania are summarized in Table 1. The value of d_{10} (the average

Table 1
Characteristics of Titania

Parameter	Value
Mean particle diameter (μm)	4.0
Particle size distribution:	
d_{10} (μm)	5.0
d_{90} (μm)	3.3
d_{10}/d_{90}	1.5
Surface area (m^2/g)	126
Mean pore diameter (nm)	11.1
Mean pore volume (ml/g)	0.3

value at 10% of the cumulative distribution)/d_{90} (the average value at 90% of the cumulative distribution) is used as a measure of the width of the particle size distribution for convenience, and it is preferable for the value to be as close as possible to unity. The values for commercial silica packings are estimated as 1.5–1.7 [10]. As shown in Table 1, the value for Titania is close to those for commercial silica packings. The other

Table 2
Carbon contents of octadecyl-modified Titania packings

Packing	Carbon content (%)
ODT-1	6.16
ODT-2	0.71
ODT-3	0.10

data also suggest that Titania can be useful as a packing and support.

Table 2 gives the carbon contents of ODT-1, -2 and -3 used in this study. It seems that the carbon content increases approximately in proportion to the increase in the amount of octadecyltriethoxysilane. The stationary phases with various surface coverages can be prepared by varying the dilution of octadecyltriethoxysilane. This means that the titania-based packings controlled by the properties of titania are available. As the surface area of Titania is smaller than that of standard silica, the carbon content of ODT-1 is expected to be comparable to that of a well modified silica packing material, as can be seen from Table 2.

Therefore, the chromatographic characterization method [9] was used to evaluate ODT-1 as a C_{18} packing material. Table 3 shows a comparison of ODT-1 with standard silica packing materials obtained from Ref. [9]. Kimata et al. [9] defined the parameters as follows. The separation factor, $k'_{amylbenzene}/k'_{butylbenzene}$ [$\alpha(CH_2)$] is a better measure of surface coverage than the carbon content when evaluating commercial packing materials prepared from various types of silica particles. The magnitude of the $\alpha_{T/O}(= k'_{triphenylene}/k'_{o\text{-terphenyl}})$ value is determined by the functionary of the silylating reagents. A higher $\alpha_{T/O}$ value is obtained with stationary phases prepared from the polyfunc-

Table 3
Comparison of ODT-1 with standard packing materials

Packing material[a]	Carbon content (%)	Surface coverage (μmol/m^2)	k'_{AB}[b]	$\alpha(CH_2)$	$\alpha_{T/O}$	$\alpha_{C/P}$
I-C$_{18}$-1	6.49	0.90	1.31	1.33	1.49	2.33
I-C$_{18}$-2	9.30	1.34	2.34	1.38	1.48	1.87
I-C$_{18}$-2-S			4.40	1.46	1.20	0.59
II-C$_{18}$-2			8.19	1.49	2.01	0.59
II-C$_{18}$-2-S			8.31	1.50	1.86	0.41
III-C$_{18}$-2			5.92	1.46	2.29	0.81
III-C$_{18}$-2-S			7.21	1.49	1.77	0.42
ODT-1	6.16		1.00	1.29	2.27	0.67

[a] I, II and III represent the functionality of silanes: mono-, di- and trichlorosilane, respectively. S indicates that the packing material was end-capped.
[b] $k'_{AB} = k'$ of amylbenzene.

tional silanes. The $\alpha_{C/P}(= k'_{caffeine}/k'_{phenol})$ value shows the effect of hydrogen bonding by cancelling the difference in hydrophobic properties among the packing materials. A smaller $\alpha_{C/P}$ value is obtained with the stationary phases that are trimethylsilylated compared with those not trimethylsilylated.

As shown in Table 3, the $\alpha(CH_2)$ value of ODT-1 indicates that the surface coverage is poor. It seems that highly polymerized octadecyl groups are localized on the Titania surface. The higher $\alpha_{T/0}$ value of ODT-1 is reasonable because ODT-1 was prepared from a trifunctional silane. The smaller $\alpha_{C/P}$ value of ODT-1 without trimetylsilylation suggests that the hydrogen bonding between caffeine and the surface titania is weak. The evaluation of ODT-2 and -3 by the method showed that they were not worth using as reversed-phase packings, as expected from their carbon contents.

3.2. Normal-phase chromatography

Dimethyl phthalate, pyridine and phenol were used as test solutes. Titania has a strong affinity for phenol as an acidic analyte, as shown for 1% (w/w) methanol in hexane as the eluent in Table 4. It is well known that the acidic properties of silica are responsible for the strong retention of basic analytes, which is often accompanied by severe tailing. Pyridine as a basic analyte showed good peak symmetry (Fig. 1). This chromatographic retention behaviour demonstrates that the surface of Titania has basic properties, in contrast to those of silica. This is borne out by the small $\alpha_{C/P}$ value of ODT-1 described above. The decrease in the k' value of phenol with
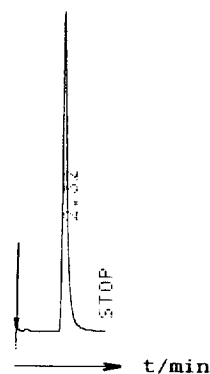
Table 4
Retention data for dimethyl phthalate, pyridine and phenol

Column	Capacity factor (k')		
	Dimethyl phthalate	Pyridine	Phenol
ODT-1	0.05	3.42	11.8
ODT-2	0.22	4.34	36.4
ODT-3	0.22	4.34	42.6
Titania	0.21	4.45	56.5

Fig. 1. Chromatogram of pyridine with Titania. Column, Titania, 30 × 4.6 mm I.D.; mobile phase, 1% methanol in hexane; flow-rate, 1.5 ml/min.

increasing surface coverage indicates that the influence of the titania matrix on retention is greatly reduced by octadecyl modification.

3.3. Reversed-phase chromatography

In order to account for the presence of anion- and cation-exchange sites on Titania and the influence of the titania matrix on retention, tetraethylammonium p-toluenesulfonate and trimethylphenylammonium chloride were used as anionic and cationic test solutes, respectively. Benzoic acid ($pK_a = 4.22$) and benzylamine ($pK_a = 9.38$) were used as acidic and basic test solutes.

As can be seen in Fig. 2, the retention of tetraethylammonium p-toluenesulfonate decreases steeply as the pH of the mobile phase is increased. The retention data suggest that Titania behaves as an anion exchanger. However, even at pH 8 there is still a slight retention of trimethylphenylammonium chloride. This retention of a cationic solute gives no indication of cation-exchange properties. The retention behaviours of the two solutes on ODT-1 are similar to those on Titania. The retention of an anionic solute on ODT-1 is smaller than that on Titania because the anion-exchange capacity of ODT-1 decreases with octadecyl modification.

Fig. 3 indicates that the retention behaviours of the acidic and basic solutes are different from those of the anionic and cationic solutes. The
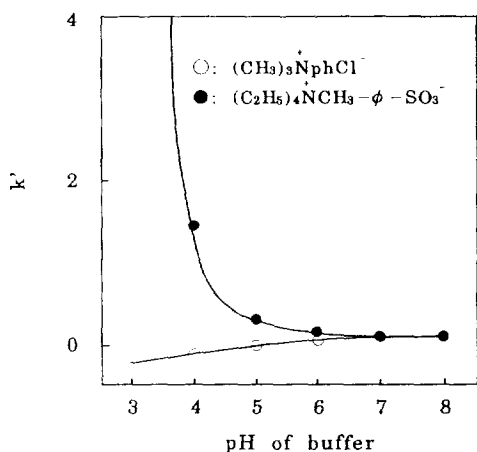
Fig. 2. Retention behaviours of (●) tetraethylammonium *p*-toluenesulfonate and (○) trimethylphenylammonium chloride versus the pH of the mobile phase on Titania. Column, Titania, 30 × 4.6 mm I.D.; mobile phase, 80% methanol containing acetic acid–sodium acetate buffer; flow-rate, 1.0 ml/min.

retention of benzoic acid decreases slowly with increasing pH of the mobile phase. This retention behaviour is largely due to the anion-exchange properties of Titania. The decrease of the retention of benzoic acid on ODT-1 can be explained by the decrease in the number of anion-exchange sites for octadecyl modification. The retention of benzylamine increases slowly
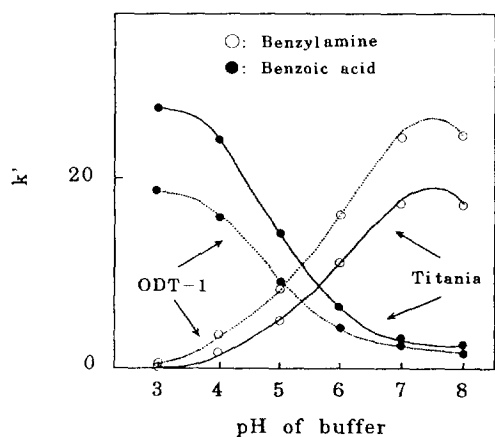

Fig. 3. Retention behaviours of (●) benzoic acid and (○) benzylamine versus the pH of the mobile phase on (solid lines) Titania and (dotted lines) ODT-1. Columns, 30 × 4.6 mm I.D.; mobile phase, 80% methanol containing acetic acid–sodium acetate buffer; flow-rate, 1.0 ml/min.

with increase in the pH of the mobile phase. This retention implies that Titania has cation-exchange properties if the increase in retention of benzylamine on ODT-1 is due to cation exchange with silanol groups formed by silylation. This is because the retention of benzylamine on ODT-1 should decrease owing to the decrease in the number of cation-exchange sites for octadecyl modification as well as the anion-exchange sites. If the retention of benzylamine on Titania is attributed to cation exchange, the slight retention of the cationic solute in Fig. 2 is not explicable. However, if the retention of benzylamine is attributable to interaction with adsorbates from the buffer on Titania, the slight retention can be explained by the retention of the cationic solute being inhibited by the strong adsorption of buffer components on Titania. Therefore, the increase in the retention of benzylamine on ODT-1 seems to be due to hydrophobic interaction with octadecyl groups. Of course, the occurrence of cation exchange with silanol groups formed by silylation cannot be eliminated. In this respect, it is necessary to compare ODT-1 with octadecyl-modified titania prepared from monofunctional silane. It has been reported with respect to zirconia, which is another new ceramic packing material, that the ion exchange shows both anion- and cation-exchange properties depending on the solution pH and the nature of the buffer [11]. For the purpose of elucidation of the cation-exchange properties of Titania, it is necessary to evaluate the retention behaviours by use of different buffers and alkaline pH.

4. Conclusions

The preparation of titania and octadecyl-modified titanias and the chromatographic investigation of their properties have been reported. Titania was found to be basic by a normal-phase chromatographic test. The influence of the titania matrix in normal-phase liquid chromatography is reduced by octadecyl modification. Under reversed-phase conditions using acetic acid–sodium acetate buffer, Titania behaves as

an anion exchanger. The influence of the titania matrix is reduced because octadecyl modification decreases the number of anion-exchange sites. On the other hand, cation-exchange properties of Titania are not detectable although a basic solute is retained on Titania. The increase in the retention of the basic solute with octadecyl modification suggests that silanol groups formed by silylation behave as a cation exchanger, and/ or that octadecyl groups produce a hydrophobic interaction with a basic solute.

Acknowledgements

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