Separation behaviour of silica-containing mixed oxides as column packing materials for liquid chromatography

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Abstract

Four kinds of silica-containing mixed oxide gels (silica–zirconia, silica–alumina, silica–titania and silica–magnesia) were prepared by a coprecipitation method and studied as column packing materials for liquid chromatography. The physico-chemical characteristics of the gels such as the BET surface area and the acidity of the solid surface were determined. Further, the separation properties of these gels for benzene, dimethyl phthalate and pyridine were evaluated. It was found that silica–magnesia had the best separation ability for the basic compound pyridine, presumably owing to the decrease in the activity of the silanol group and the existence of only very weak acid sites on the surface.

1. Introduction

Liquid chromatography, HPLC in particular, has become a practical, useful method for the separation and analysis of various types of soluble compounds, including substances that are non-volatile or thermally decomposable. It has further contributed a great deal to developments in the life science field. The stationary phase for liquid chromatography should have not only adsorption ability for the solute, but also desorption ability, because it is desirable that the interaction between the stationary phase and solute serves effectively for a mutual separation. Although a wide variety of the column packing materials for liquid chromatography have been used, base silica and surface-modified silica are

the predominant materials at present. The disadvantages of silica and modified silica as stationary supports are instability in basic (pH > 8) and for surface-modified silica, acidic (pH < 2) mobile phases and the extremely strong adsorption ability for basic compounds.

Recently, new ceramics have been studied as packing materials with regard to chemical stability and chromatographic selectivity. Kawahara and co-workers [1–5] reported that commercially available zirconia and titania were of interest as packing materials for liquid chromatography. These two oxides were evaluated for the separation of organic phosphates, aromatic hydrocarbons and nucleosides. Rigney et al. [6] studied the physical and chemical characteristics of microporous zirconia, which exhibited excellent properties as a packing material. Further, the same group investigated polymer-coated zirconia

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as a reversed-phase chromatographic support [7]. Zirconia has also been studied in detail with regard to the relationships between the surface properties and the elution behaviour of various types of solutes by Blackwell and Carr [8,9]. Trüdinger *et al.* [10] used porous zirconia and titania for the separation of basic analyses and polycyclic aromatic hydrocarbons. These two porous oxides overcome the disadvantages of silica packing materials at high pH.

Mixed oxide gels may open up a new development in this field, because they are known to exhibit different and interesting surface properties that are not observed with the separate components of the mixed oxide, and appear to have good adsorption abilities. We have already reported some interesting results on the surface properties of mixed oxide gels from the point of view of the removal of environmental pollutants [11], the recovery of valuable trace elements [12,13], the adsorption and separation of amino acids [14–16], etc.

In this work, mixed oxide gels containing silica were prepared by a coprecipitation method and preliminarity examined as column packing materials for normal-phase liquid chromatography.

2. Experimental

2.1. Chemicals

Sodium metasilicate ennehydrate of purity >98% was purchased from Dai-ichi Kogyo. Other reagents, including metal chlorides ($ZrOCl_2 \cdot 8H_2O$, $AlCl_3 \cdot 6H_2O$, $TiCl_4$ and

$MgCl_2 \cdot 2H_2O$), were of analytical-reagent grade from Wako.

2.2. Preparation of mixed oxide gels [14]

An appropriate amount of sodium metasilicate ennehydrate was dissolved in 1 l of deionized water. After filtration, the pH of the solution was adjusted to 1 by adding hydrochloric acid. Then the metal (Zr, Al, Ti or Mg) salt as another component in the binary mixed oxide gel was added. The volume was made up to 2 l and the total concentration of metal ions was always kept at 0.4 *M*. With stirring of the solution at room temperature, 3 *M* sodium hydroxide solution was dropped in slowly until the pH reached 7–9 to precipitate the gel at room temperature. After ageing by further stirring the solution for 10 h, the gel was filtered by suction and washed with deionized water until chloride ions were not detected in the filtrate. The gel obtained was dried at 110°C in an air oven and ground and sieved to below 270 mesh.

Table 1 lists the preparation conditions for gels, *i.e.*, the initial mole ratio of the two metals on mixing and the pH of the source solution.

2.3. Physical properties

The nitrogen adsorption isotherms of the gels at 77 K were measured. From the results, the specific surface areas, pore volumes and pore-size distributions were determined. The specific surface area was calculated from the BET equation [17]. The pore volume was obtained by the liquid nitrogen volume evaluated from the nitrogen adsorption volume at $P/P_0 = 0.97$. The pore-

Table 1
Preparation of mixed oxides and silica gel

Mixed oxide	Materials	[Si]:[metal] mixing ratio	pH
Silica–zirconia	$Na_2SiO_3 \cdot 9H_2O$, $ZrOCl_2 \cdot 8H_2O$	50:50	7
Silica–alumina	$Na_2SiO_3 \cdot 9H_2O$, $AlCl_3 \cdot 6H_2O$	25:75	7
Silica–titania	$Na_2SiO_3 \cdot 9H_2O$, $TiCl_4$	75:25	9
Silica–magnesia	$Na_2SiO_3 \cdot 9H_2O$, $MgCl_2 \cdot 2H_2O$	50:50	7
Silica	$Na_2SiO_3 \cdot 9H_2O$	–	7

size distribution and the average pore size were determined using the Cranston–Inkley method [18]. The particle size distribution and the average particle size were measured with a Coulter Multisizer (Coulter Electronics).

2.4. Acidity of solid surface

The acidic properties of the gel surface were measured by amine titration [19]. The gel was degassed *in vacuo* at 90°C for 3 h, then 1 g of the gel and 5 ml of benzene were transferred into a 20-ml test-tube. The titration was carried out with 0.1 M *n*-butylamine with acid–base indicators for the measurement of solid acid strength such as dicinnamalacetone ($pK_a = -3.0$), 4-benzeneazodiphenylamine (+1.5), 4-phenylazo-1-naphthylamine (+4.0) and methyl red (+4.8).

2.5. Chromatographic test

The sieved gel was suspended in methanol. After decanting the very fine particles, the gel was packed into a stainless-steel column (250 mm × 4.6 mm I.D.) using a slurry method. Chromatographic tests were carried out using benzene, dimethyl phthalate and pyridine as test solutes, with an instrument composed of a Yanagimoto L-4000W pump, a Rheodyne Model 7125 injector and a Shodex M-315 UV detector. The mobile phase was *n*-hexane containing 1% of methanol at a flow-rate of 1 ml/min at room temperature. Detection was carried out at 254 nm with a UV detector.
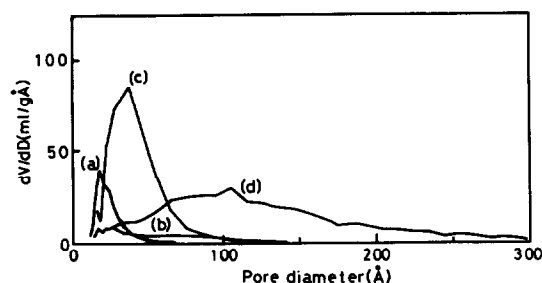

Fig. 1. Pore-diameter distributions of the mixed oxides: (a) silica–zirconia; (b) silica–alumina; (c) silica–titania; (d) silica–magnesia.

3. Results and discussion

3.1. Physical characteristics

The physical characteristics of the mixed oxide gels formed are summarized in Table 2. All the gels had sufficiently large specific surface areas to be porous. Silica–titania had the largest specific surface area and the largest pore volume and mean pore diameter were observed with silica-magnesia. The pore-size distributions of silica-zirconia and silica–titania were fairly narrow, as shown in Fig. 1. The average pore diameters of these two gels were about 20 and 40 Å, respectively. However, the pore diameter of silica-magnesia and silica–alumina were distributed over a very wide range. The particle size distributions of silica–magnesia sieved below 270 mesh are shown in Fig. 2.

The formation and microstructure of silica-containing mixed oxides are considered to occur as follows. Acidified sodium metasilicate solution contains silica sol at first, then the sol is converted into silica gel on addition of an alkaline

Table 2
Physical characteristics of mixed oxides and silica gel

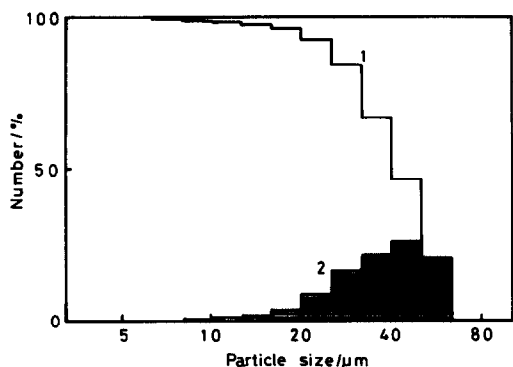| Mixed oxide	Specific surface area (m² g⁻¹)	Pore volume (ml g⁻¹)	Average pore diameter (Å)	Average particle size (μm)
Silica–zirconia	122	0.17	21	24
Silica–alumina	47	0.07	58	27
Silica–titania	357	0.38	37	(Coarse)
Silica–magnesia	212	0.69	112	36
Silica	280	0.75		

Fig. 2. Particle size distributions of silica–maganesia: (1) cumulative; (2) differential.

solution after being mixed with another metal chloride [20]. In addition, the mixed metal oxide gel is also precipitated from the mixed solution without too much delay. The resultant precipitate may be regarded as an intimate mixture of silica and the other metal oxide gels in which the silica framework is partly occupied with widely spread metal oxide, decreasing the surface area of the silica itself [21].

3.2. Acidity of mixed oxide surface

Table 3 shows the acidity of the four mixed oxides. Silica–alumina and silica–titania gave similar results. These two gels had large amounts of weak acid sites without the strongest acid sites ($pK \leqslant -3.0$). The amounts of weak acid sites in silica–zirconia were slightly smaller than those in silica–alumina and silica–titania. However, only silica–zirconia had the stronger acid sites ($pK_a \leqslant$

−3.0). Silica–magnesia differed considerably in the amounts of acid sites from other three mixed oxide gels: it has no stronger acid sites ($pK_a \leqslant -1.5$) and the amount of weak acid sites was the smallest among the mixed oxide gels examined. From these results, silica–magnesia was considered to have the weakest acidity of the solid surface.

It is noteworthy that all the mixed oxides exhibited stronger acidities of the solid surfaces than that of silica gel. The acidity of the solid surfaces of all the component oxides was strengthened by mixing with silica. Silica–zirconia has been reported to show very strong acidity with $pK_a \leqslant -8.2$ even when the zirconia content was only 0.1% [22]. Benesi [23] reported that silica–alumina had strong acid sites by complexing two oxides. Shiba et al. [24] clarified that the total acidity and Lewis acid sites of silica–alumina both increased with increase in the alumina content. The strong Lewis acid sites of silica–titania formed by mixing silica and titania was revealed by means of IR spectrometry [25,26]. Silica–magnesia, which had the weakest acidity of the solid surface of the four mixed oxides described above, was studied by Benesi [23] and Okamoto et al. [27]. Only very weak acid sites of silica–magnesia were formed by mixing these two oxides, and the total acidity increased considerably [22]. Okamoto et al. [27] showed that silica–magnesia with a 1:1 mole ratio had the highest acidity. Such an enhancement of the activity of the solid surface in the mixed oxides was considered to be due to the other metal entering the silica framework to

Table 3
Acidity of mixed oxides and silica

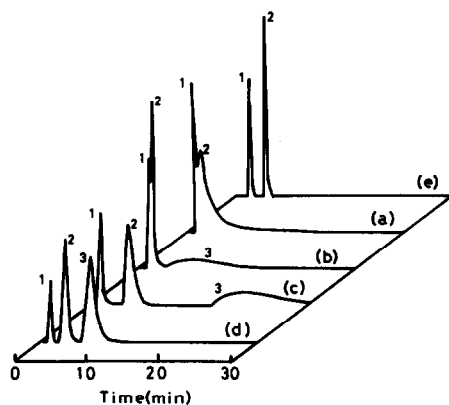| Mixed oxide	Acidity (mmol g^{-1})			
	$pK_a \leqslant -3.0$	$pK_a \leqslant +1.5$	$pK_a \leqslant +4.0$	$pK_a \leqslant +4.8$
Silica–zirconia	0.05	0.08	0.31	0.35
Silica–alumina	–	0.10	0.44	0.47
Silica–titania	–	0.05	0.40	0.49
Silica–magnesia	–	–	0.14	0.31
Silica	–	–	–	0.03

Fig. 3. Chromatograms obtained with the four mixed oxides as packing materials. Solute: 1 = benzene; 2 = dimethyl phthalate; 3 = pyridine. Column packing material: (a) silica–zirconia; (b) silica–alumina; (c) silica–titania; (d) silica–magnesia; (e) silica gel. Mobile phase, n-hexane containing 1% methanol; flow-rate 1 ml/min; column temperature, ambient; detection, UV at 254 nm.

coordinate incompletely, resulting in the formation of Lewis acid sites.

3.3. Chromatographic behaviour

Benzene, dimethyl phthalate and pyridine were used for chromatographic tests with the mixed oxides as column packing materials. The chromatograms obtained are shown in Fig. 3. Figure 3e shows the chromatogram with silica gel which was examined for comparison with the mixed oxide gels. The capacity factors were calculated from the retention data for these chromatograms, using the retention time of benzene as the dead time (Table 4).

With the column packed with silica–zirconia, the elution of pyridine was not observed and the peaks of benzene and dimethyl phthalate overlapped, as shown in Fig. 3a. With the silica–alumina column, the peaks of benzene and dimethyl phthalate almost overlapped and a broad and tailing peak of pyridine was obtained. With the silica–titania and silica–magnesia columns, the three compounds were completely separated. However, with the silica–titania column considerable tailing of the pyridine peak appeared. Only the silica–magnesia column exhibited a good separation ability and symmetrical peaks for these three compounds.

These results show that there is a relationship between the acidity of the solid surface and the chromatographic behaviour of the basic compound pyridine. Only silica–zirconia with the strongest acid sites could not elute it. Silica–titania and silica–alumina with the strongest acid sites could elute pyridine, but with both columns the pyridine peaks were broad and tailing. Further, silica–magnesia with only weaker acid sites gave a good separation and a symmetrical peak for pyridine. Hence with the four mixed oxides the elution behaviour of pyridine is affected by the acidity of the solid surface of the gels.

However, silica gel could not elute pyridine, at least not within 30 min, in spite of having only the weakest acid sites. It is generally known that silica gel possesses some types of silanol groups on the surface, and the type and the concen-

Table 4
Retention characteristics of mixed oxides and silica gel

Mixed oxide	Capacity factor[a]		$\alpha(k'_{PY}/k'_{DMP})$
	Dimethyl phthalate (k'_{DMP})	Pyridine (k'_{PY})	
Silica–zirconia	0.52	–	–
Silica–alumina	0.18	3.19	17.8
Silica–titania	2.58	12.62	4.89
Silica–magnesia	1.10	3.06	2.87
Silica	0.97	–	–

[a] Capacity factors were evaluated using the retention time of benzene as the dead time.

tration affect the hydrogen bonding and acid-base interactions with solutes. Strong interactions with amines such as pyridine are especially known.

By mixing the metal oxide and silica, both the type and the concentration of surface silanol groups would be changed. Stout and DeStefano [28] determined by NMR that the number of silanol groups on a silica surface treated with zirconium was greatly diminished. With the four mixed oxides examined here, the silanol groups are considered to decrease similarly in the silica–zirconia. Consequently, it is considered that the specific interaction between silanol groups and pyridine on the surface of the mixed oxides decreases. However, the acid–base interaction with the Lewis acid sites formed by mixing affects the elution behaviour of pyridine. Blackwell and Carr [8,9] studied in detail the separation behaviours of different types of substances with diverse eluents on a zirconia support, and clarified the interaction between basic substances and the Lewis acid sites on the zirconia surface. Also, the interaction between pyridine and the very strong Lewis acid sites of silica–titania was reported by Odenbrand et al. [25]. The good separation ability of silica–magnesia for pyridine would depend on the very weak interactions, i.e., hydrogen bonding or Lewis acid effects, because it has no stronger acid sites and the number of silanol groups would be decreased.

The retention data obtained made these interactions clear semi-quantitatively. The ratios of the capacity factor of pyridine to that of dimethyl phthalate, α, are presented in Table 4. These α values demonstrate generally the adsorption ability for pyridine, because the capacity factor of the neutral compound, dimethyl phthalate, is proportional to the total surface area of the packing material in column. From these α values, the specific interactions of the mixed oxide gels with pyridine are considered to decrease in the order silica–zirconia > silica–alumina > silica–titania > silica–magnesia. These results suggest again that silica–magnesia would have the lowest activities of silanol groups and acid sites, and show a good separation ability for basic compounds such as pyridine. Therefore,

silica–magnesia gel might become a promising column packing material for liquid chromatography.

4. Conclusions

We have preliminarily investigated the surface properties and separation behaviours of silica-containing mixed oxide gels as column packing materials for normal-phase liquid chromatography. The gels were prepared from mixtures of sodium metasilicate and metal (Zr, Al, Ti or Mg) chloride solutions by a coprecipitation method.

Of four mixed oxide gels examined, it was found that silica–magnesia was effective for the separation of pyridine, which is relatively difficult to separate by liquid chromatography using silica gel as a stationary phase.

We consider that the ability of silica–magnesia to separate pyridine depends mainly on the very weak acid sites and a decrease in the silanol groups on the surface. However, the four mixed oxides examined exhibited very different physico-chemical properties such as surface area, particle size and acidity of the solid surface, and the characteristics greatly affect the chromatographic behaviour. Further research to clarify the effects of the method of preparation on the physico-chemical characteristics and the influence of these properties on the separation behaviour is in progress.

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