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Silica-Containing Mixed-Oxide Gels Prepared by a Coprecipitation Method as Novel Packing Materials for Liquid Chromatography

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The separation characteristics of silica-zirconia, silica-alumina, silica-titania, and silica-magnesia gels for benzene, dimethyl phthalate, and pyridine have been evaluated as column packing materials for liquid chromatography. Of these mixed-oxide gels, silica-magnesia had the best separation ability particularly for a basic compound, pyridine depending presumably on the reduction of the activity of silanol group on silica surface.

Liquid chromatography has become a useful method of separation and analysis of soluble compounds of higher volatilization temperature. It has further contributed to the development of the area of life science. A stationary phase for liquid chromatography should have not only good adsorption ability for the solute but also moderate desorption ability, because it is desirable that the interaction between the stationary phase and the solute is served effectively for the separation. Silica gel is a remarkable material for the stationary phase, of which the problems are the irreversible adsorption of a basic compound on the surface silanol group and the weak alkali-resistant properties. Therefore, silica packing materials have been mostly coated with silane-coupling agent, e.g., octadecylsilane as a reversed phase for the avoidance of the disadvantageous problems. Recently, other ceramic substances have been studied as column packing materials with regard to chemical stability and chromatographic selectivity. Kawahara et al. have reported that commercially available zirconia and titania were of interest, in which both these oxides have been possibly evaluated for the separation of organic phosphates, aromatic hydrocarbons, and nucleosides among diverse compounds examined.1,2) Porous zirconia and titania of the applicability for the separation of basic analytes and polycyclic aromatic hydrocarbon have also reported by Trüdinger et al.3) Rigney et al. have studied the physical and chemical characteristics of microporous zirconia which have exhibited the excellent properties as packing material.4) The mixed-oxide gels may open a new development in this field, because they are known to exhibit the different and interesting surface properties which are not observed in each component of the mixed-oxide, and appear the good adsorption abilities. We have already presented some interesting results of the surface properties of the mixed-oxide gels from the viewpoint of the removal of environmental pollutants,5) the recovery of trace valuable elements,6) and the separation of amino acids7) and so on. In this preliminary report, the mixed-oxide gels containing silica prepared by a coprecipitation method have been examined as novel ceramic packing materials for liquid chromatography.

An appropriate quantity of sodium *meta*-silicate enneahydrate was dissolved into 1 L of deionized water. After the pH of the solution was adjusted to 1 by adding hydrochloric acid, the metal (Zr, Al, Ti, or Mg) salt as another component in the binary gel was added to it. The total concentration of metal ions was kept to be 0.4 mol dm^{-3} (M). Under stirring the solution at room temperature, 3 M sodium hydroxide solution was added slowly to the solution until pH 7 to form gel. After further stirring the solution for 10 h, the gel was filtrated by suction and washed with deionized water until chloride ion was not detected in the filtrate. The gel obtained was dried at 110 ℃ in an air oven, and then ground and sieved to below 270 mesh. The surface area measurement of gel was carried out by applying the BET equation to adsorption isotherm of nitrogen at -196 ℃ (Table 1). The pore volume of gel was determined by a convenient water-titration method as described below. The granular sample (2-5 g) was transferred into a 50 mL glass bottle. A small amount of distilled water was dropped into the bottle from a buret. Then the bottle was stoppered tightly and shaken so that water added was adsorbed into the pore of sample entirely. Dropping of water and shaking of the bottle were repeated until all pores of sample were filled with water and the aggregation of granular sample occurred just as a result of the addition of excess water. The pore volume was obtained by dividing the total amount of dropped water by the sample weight. The pore size of gel was evaluated both from the pore volume and the surface area by means of the Cranston-Inkley method. The acidic properties of gel surface was determined by the amine titration method using dicinnamalacetone (*pKa*=-3.0), 4-benzeneazodiphenylamine (*pKa*=+1.5), 4-phenylazo-1-naphtylamine (*pKa*=+4.0), and methyl red (*pKa*=+4.8) as indicators. The gel sieved below 270 mesh was suspended into methanol. The very fine particles were decanted off. Then the gel was packed into a stainless steel column (4.6 mm i.d., 150 mm length) by a slurry method. Using benzene, dimethyl phthalate, and pyridine as test samples, the separation behavior of gel was chromatographically investigated under the conditions of mobile phase = 1% methanol / n-hexane, flow rate = 1 $mL\,min^{-1}$, and detection wavelength = 254 nm.

All mixed-oxide gels had the large specific surface areas, then these were considered to be porous, as represented in Table 1. Silica-titania gel had the largest specific area, however, the largest pore volume and mean pore diameter were observed in silica-magnesia gel. The structure of these silica-containing mixed-oxide gels may be regarded as the intimate mixture of silica and other metal oxide in which the framework of silica particles is partly stuffed by widely spreaded metal oxide particles, reducing the surface area of silica gel itself.[8)] Meanwhile, silica-alumina and silica-titania gels had large amounts of weak acid sites without the strongest acid sites (*pKa*≦ -3.0). The amounts of weak acid sites in silica-zirconia gel were slightly smaller than those in silica-alumina and silica-titania gels. However, only silica-zirconia gel had the strongest acid sites (*pKa*≦-3.0). Silica-magnesia gel was considerably different in the amounts of acid sites from other three mixed-oxide gels : It has no stronger

Table 1. Surface characteristics of mixed-oxide gel

Mixed-oxide	Mixing ratio of Si:metal	Specific surface area $m^2 g^{-1}$	Pore volume $mL\,g^{-1}$	Average pore diameter Å	Acid amount / $mmol\,g^{-1}$ pKa≦-3.0	pKa≦+1.5	pKa≦+4.0	pKa≦+4.8
Silica-zirconia	50:50	260	0.20	31	0.05	0.08	0.31	0.35
Silica-alumina	25:75	131	0.29	89	—	0.10	0.44	0.47
Silica-titania	75:25	438	0.44	40	—	0.05	0.40	0.49
Silica-magnesia	50:50	274	0.92	134	—	—	0.14	0.31
Silica	100:0	279	1.23	—	—	—	—	0.03

acid sites ($pKa \leqq +1.5$) and the amount of weak acid sites were the smallest in the mixed-oxide gels examined. From these results, silica-magnesia gel was considered to have the weakest solid acidity. The mixed-oxide gels including silica-magnesia gel exhibited stronger solid acidities than silica gel. This tendency agreed with the fact that the solid acidity of the binary oxide, in general, is strengthened in comparison with that of the component oxide. Odenbrand et al. studied this phenomenon in silica-titania, and they concluded that Ti entered in small amounts into the silica framework, and consequently the incomplete tetrahedral coordination of Ti^{4+} ion exposed on the surface caused the formation of very strong Lewis acid sites.[9)]

Figure 1 shows the chromatogram on silica gel which was examined in order to compare with the mixed-oxide gels in addition to that on silica-magnesia gel resulting in the most appropriate separation behavior here. With the silica-zirconia packed column, the elution of pyridine was not observed at all, and the peaks of benzene and dimethyl phthalate overlapped. With silica-alumina packed column, the peaks almost of benzene and dimethyl phthalate overlapped, and the broad and tailing peak of pyridine were obtained. With the silica-titania or silica-magnesia packed column, these three organic compounds were eluted in complete separation. However, with the silica-titania column the considerable peak tailing by pyridine appeared. Although the peak of pyridine could not be detected with silica gel packed column (Fig. 1(a)), only the silica-magnesia packed column exhibited the good separation abilities and the symmetrical peaks for these compounds, as shown in Fig. 1(b). The capacity factors were calculated from the retention data in these chromatograms by using the retention time of benzene as dead time (Table 2). These results show that the chromatographic behavior of the basic compound is related to the solid acidity of the gels. Only silica-zirconia gel with the strongest acid site could not elute pyridine. While, silica-titania and silica-alumina gels with not the strongest acid site but stronger acid sites on the surface could elute pyridine, nevertheless the pyridine peaks in both the columns were broad and tailing. Furthermore, silica-magnesia gel with only the weaker acid sites gave the good separation and symmetrical peak for pyridine to be basic depending on the solid acidity of mixed-oxide gels. With silica gel, pyridine was not eluted at all, although the gel likely prepared by the coprecipitation method had only the weakest acid site. Silica gel, in general, has been known to possess the large adsorption ability for the basic compounds by hydrogen bonding with silanol groups located on the surface, which causes the peak tailing. Furthermore, it has been also considered that the ion-exchange-like adsorption on silica gel as the specific interaction would form. It may be supported from the fact that pyridine can be changed to produce pyridinium ion on the surface of silica-titania.[10)] If the intensely specific interactions described above occur, the basic compounds would not elute at all or result in considerable peak tailing.

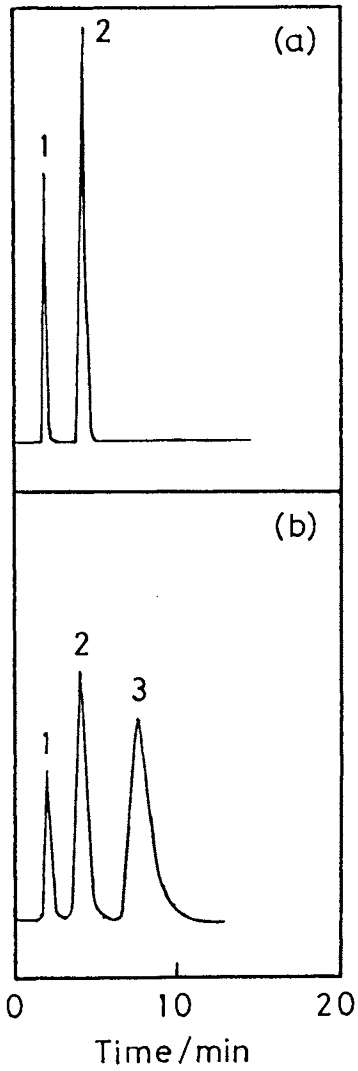

Fig. 1. Chromatograms on (a)SiO_2 and (b)SiO_2-MgO.

1: Benzene; 2: Dimethyl phtalate;
3: Pyridine.

Table 2. Retention characteristics of mixed-oxide gel

Mixed-oxide	Capacity factor[a)]		$\alpha(k'_{PY}/k'_{DMP})$
	Dimethyl phtalate(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	2.78
Silica	0.97	—	—

a) Capacity factor was evaluated by using the retention time of benzene as dead time.

The retention data obtained made semiquantitatively these considerations clear. The ratio of the capacity factor of pyridine to that of dimethyl phthalate, α, is presented in Table 2. This α suggests generally the adsorption ability for basic compounds, because the capacity factor of the neutral compound, dimethyl phthalate, is to be proportional to the total surface area of packing material in column. Also, this α would be considered as the measure of the intensity for the specific adsorption such as the ion-exchange-like described above. Therefore, it is presumed that the packing materials with the lager α possesses the stronger specific adsorption abilities. From these α values, the order of the specific ability of the mixed-oxide gels for the basic compounds are considered as follows:

silica ≈ silica-zirconia > silica-alumina > silica-titania > silica-magnesia

The α value of silica-magnesia gel was much smaller than those of the others. Consequently, the elution of pyridine on silica-magnesia column gave the symmetrical peak with little tailing, as shown in Fig. 2. These results suggests that the activity of the hydroxy group on silica-magnesia surface for basic compounds would be lower, therefore, this silica-magnesia gel would become a promising column packing material for liquid chromatography.

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