

Native and stearic acid modified ceria–zirconia supports in normal and reversed-phase HPLC

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Abstract

Porous ceria–zirconia composite with narrow particle size distribution and large specific surface area was synthesized by a sol–gel process. Chromatographic properties of the native supports was investigated in normal phase mode for the separation of test mixtures of basic, neutral and acidic compounds. The new packing material exhibited polar and basic properties, which are suitable for the separation of basic compounds. Lypophilic packing has been obtained by the modification of the ceria–zirconia with stearic acid, which exhibited strong hydrophobicity relative to the native packing. Therefore, the modified ceria–zirconia behaves as a reversed-phase packing material. Different selectivity towards basic compounds was observed on the new packing compared to the native ceria–zirconia and conventional ODS stationary phase. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Column liquid chromatography; Ceria–zirconia composite; Stearic acid

1. Introduction

Column packing material is always a key factor in influencing the development of high-performance liquid chromatography (HPLC). However, it is obvious from the literature that currently available supports remain far from ideal. Although silica and modified silica have found wide application for separation of various compounds, it is well known that silica based stationary phases are not stable outside of the pH range of 2 to approximately 8 [1]. In addition, the separation of

basic solutes on the silica-based supports was undesirable owing to a strong interaction between the basic functional group and the residual silanol, leading to peak tailing and low selectivity.

Because of the problems mentioned above, many attempts have been undertaken to find alternative support materials with improved physical and chemical properties. Among these new supports, zirconia arouses much fascination owing to its remarkable mechanical, chemical and thermal stability [2–18]. Nawrocki et al. have given a comprehensive review concerning the physical and chemical properties of zirconia from a chromatographic point of view [2]. Unger and coworkers have compared the chromatographic performance of zirconia, silica, alumina and tita-

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nia in the normal-phase mode [3]. Their study indicated the promising prospect of zirconia as packing material. Since the surface of zirconia is highly heterogeneous, modification of zirconia on the surface to create ion-exchangable, hydrophobic and hydrophilic type phases has been investigated by other researchers. Carr and coworkers have thoroughly studied carbon [4–6] and polybutadiene-coated [7–11] zirconia as packing materials in various modes. The modification of zirconia with Lewis bases such as fluoride [12], phosphate [13] and ethylenediamine-*N,N'*-tetramethylphosphonic acid (EDTPA) was investigated by the same group [14,15]. Octadecylsilane bonded zirconia was synthesized as hydrophobic phases by Trudinger et al. [16] and Yu and Rassi [17]. A certain degree of success was achieved with these surface-modified zirconias. Although zirconia-based packing materials are quite attractive, some drawbacks still exist. 'Ink-bottle' shaped pores have been regularly found in porous zirconia according to the literature [18] and our work [19], leading to poor chromatographic efficiency for low mass transfer.

Mixed oxides have been used widely as catalysts, but very little attention has been paid to their application in chromatographic stationary phases. Recently, silica coated zirconia microspheres have been prepared by Shalliker et al. [20,21], and their physicochemical properties were evaluated. The surface area of the zirconia was increased significantly by doping with silica, which is ascribed to the silica as a stabilizer. However, the chromatographic application of the composite has not been reported. Other silica-containing mixed oxides were prepared by Kaneko's group by co-precipitation of silica with each of the corresponding oxides, ZrO_2 , Al_2O_3 , TiO_2 , MgO [22–24]. The chromatographic application of the mixed oxide to the separation of amino acids and other test solutes was discussed [22]. Their results showed that silica–magnesia had the best separation ability for the basic compound. [23,24]. Therefore, they pointed out the promising prospect of mixed oxides as a chromatographic stationary phase. The attention of our laboratory has been focused on modifying zirconia with inorganic oxides by using the sol–

gel technique for improvement of its physico-chemical properties. Recently, two kinds of zirconia-containing mixed oxide gels, zirconia–silica and zirconia–magnesia, were synthesized in our laboratory [25–27]. Both physicochemical and chromatographic properties show the mixed oxides are superior to the bare zirconia, and afforded satisfactory separation of basic compounds.

Ceria, as a common rare earth oxide, has comparable chromatographic advantages to zirconia, such as high mechanical strength, thermal and chemical stability [28]. Moreover, both ceria and zirconia are quadrivalent metal oxides, which affords the possibility for them to stoichiometrically match better, leading to homogeneity of the mixed oxide. Therefore, the purpose of this work was to prepare a ceria–zirconia composite by using the sol–gel process, which is expected to improve the chromatographic properties of zirconia. The physico-chemical parameters of the mixed oxide were measured and compared with that of zirconia. The chromatographic performance of the ceria–zirconia composite was investigated in normal phase mode and reversed phase mode after being dynamically modified with stearic acid.

2. Experimental

2.1. Chemicals

All reagents were obtained from commercial sources and were of reagent grade or better. Zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$), cerium nitrate, polyoxyethylenesorbitan trioleate (Tween 85), sorbitan monooleate (Span 80), light petroleum, methanol, ethanol, dichloromethane, chloroform and cyclohexane were all purchased from Shanghai Reagent Company. Distilled water, before use, was boiled for 15 min to remove dissolved carbon dioxide.

2.2. Preparation of mixed oxide gels

Ceria–zirconia spherical particles were synthesized according to procedures modified from our

previous method [23]. Briefly, zirconyl chloride and cerium nitrate were dissolved in distilled water and the mixture was then poured into light petroleum containing Span 80 and Tween 85 with stirring at the rate of 1800 rpm. After 10 min, the pH was adjusted to approximately ten by slowly introducing NH_3 . The reaction mixture was stirred for at least 48 h. To remove adhered light petroleum, surfactants and residual substances, the hydrogel particles of the mixed oxides obtained were subjected to a multi-stage washing procedure, with light petroleum, acetone, ethanol and water. The hydrogel was classified with water as solvent to remove the fine and the larger particles. The collection of the particles was heated at 120°C for 2 h to turn the hydrogels to xerogels. Thereafter the xerogels were calcinated at 600°C for 1h to remove the organic residues.

2.3. Physico-chemical properties

Nitrogen adsorption/desorption isotherms were measured on a model ST-03A specific surface area analyser (The Analytical Instrument Plant, Beijing, China). The specific surface area was calculated by using the BET equation in the range of linearity P/P_0 (0.05–0.30). Average pore diameter was calculated from desorption data by using the Barret–Joyner–Halenda (BJH) method. Element analysis of the bulk composite of the mixed oxide was measured by the chemical titration method: the mixed oxide was melted with Na_2O_2 at 650°C in a furnace, and then extracted with hot water. The pH of the solution was adjusted to approximately one by the addition of HCl. Then it was diluted to 250ml. The zirconia content was measured by complexometric titration with EDTA as complexon at a pH of about 1 to avoid interference from ceria. The ceria content was calculated by titration with $(\text{NH}_3)_2\text{Fe}(\text{SO}_4)_2$. Measurement of acid–base properties on the surface of the mixed oxides was performed according to the procedure proposed by Kita et al. [29].

Elemental analysis of the stearic acid modified ceria–zirconia was performed with a MOD-1106 elemental analyzer (Italy), and diffuse reflectance Fourier transform infrared (DRIFTS) spectra

analysis was carried out with a Shimadzu FTIR 8000 (Shimadzu, Kyoto, Japan).

2.4. Chromatography

Chromatographic tests were carried out with standard HPLC equipment, a Shimadzu 10A liquid chromatographic pump; a SPD-10A UV–Vis photometric detector; a Rheodyne 7125 injection system (sample loop, 20 μl); a Shimadzu C-R6A integrator (Shimadzu, Kyoto, Japan).

The native support, ceria–zirconia and zirconia were slurry-packed into 150×4.6 (i.d.) mm stainless-steel columns, respectively. Ethanol/cyclohexane, 50%-water-saturated dichloromethane–cyclohexane and 50%-water-saturated chloroform–cyclohexane were used as mobile phases. The flow rate of the mobile phase was set at 1.0 ml/min.

The stearic acid modified ceria–zirconia column was made by equilibration of the initial column with 800ml of 2.5mmol/l stearic acid solution, then washed thoroughly with methanol and distilled water to remove adsorbed stearic acid on the surface. Methanol/water in the presence or absence of stearic acid was used as mobile phases. Acetate or Tris buffers were used to control the pH of the mobile phase when investigating the influence of eluent pH on the capacity factor of solutes. The pH was measured in the aqueous buffer. The flow rate of the mobile phase was set at 0.5 ml/min.

All samples were dissolved in the mobile phase before injection. The retention time of the solvent peak was used as dead time for calculation of capacity factors. The column temperature was controlled at $24 \pm 1^\circ\text{C}$ with a CS501-SP water bath (Sida, Chongqing, China). The detection wavelength was set at 254 nm.

3. Results and discussion

3.1. Physicochemical characterization of the stationary phase

The molar ratio of ceria to zirconia of the bulk composition was determined as 31.5/68.5 by the titration method. Since the molar ratio of the

Table 1
physicochemical properties of supports

Supports	ZrO ₂	CeO ₂ /ZrO ₂ (native)	CeO ₂ /ZrO ₂ (stearic acid modified)
Average particle diameter, μm	5	5	5
Specific surface area, m ² /g	21	112	91
Average pore diameter, nm	24.3	6.3	5.5
Specific Pore Volume, cm ³ /g	0.128	0.136	0.122
Acidity at pH10, mmol/g	0.082	0.1784	–
Basicity at pH3.5, mmol/g	0.15	0.157	–

ultimate mixed oxide was approximate to that of the initial material, 39.4/60.6, it was considered that zirconia and ceria could co-precipitate favorably owing to their similarities. In contrast, a greater difference in the molar ratio between the initial material and the ultimate mixed oxide had been observed on SiO₂–ZrO₂ and MgO–ZrO₂ in our study [19]. This is possibly due to the difference in the formation rate of the oxides.

The physical and chemical characteristics of the native and the stearic acid modified ceria–zirconia are shown in Table 1. For comparison, corresponding parameters of zirconia are listed. It is apparent from the data that the specific surface area of the ceria–zirconia is much larger than that of the zirconia, while the average pore diameter is smaller. The adsorption/desorption isotherms (not shown) of the ceria/zirconia composite were measured by N₂ adsorption, which gives a narrow hysteresis loop with nearly parallel adsorption and desorption branches. The results show that good pore connectivity and fairly narrow pore size distribution was obtained for the ceria–zirconia. For the chromatographic separation of small molecules, satisfactory pore structure is more important than pore size because stagnant solutes in the pores with a narrow-neck and large body will significantly decrease chromatographic efficiency. From the data presented in Table 1, it can be seen that the specific surface area and pore volume of the support decreased slightly, but not significantly, after modification by stearic acid. Thus, ideal chromatographic properties can be maintained.

3.2. Behavior of native support in normal phase mode

The chromatographic performance of the native ceria–zirconia in the normal phase mode was investigated with ethanol/cyclohexane, chloroform/cyclohexane and dichloromethane/cyclohexane as mobile phases, and with neutral, basic and acidic compounds as test solutes.

As a result of our experiment, polycyclic aromatic hydrocarbons (PAHs) hardly retained on the native ceria–zirconia even with the mobile phase of 100% cyclohexane. However, the substituted PAHs with polar group compounds were retarded, to some extent, on the stationary phase. Their capacity factors obtained with ethanol/cyclohexane (1/99, v/v) as mobile phase are presented in Table 2.

Table 2

The capacity factors k' of substituted PAHs on the native and stearic acid modified CeO₂/ZrO₂ supports

Stationary phase	Native CeO ₂ /ZrO ₂	Modified CeO ₂ /ZrO ₂
Mobile phase	Ethanol/cyclohexane(v/v): 1/99	Methanol/water(v/v): 70/30
<i>o</i> -chlorotoluene	0.012	3.181
<i>p</i> -nitrotoluene	0.151	1.014
4-bromo-4-nitro-biphenyl	0.1744	9
anthraquinone	0.198	3.928
benzotrile	0.279	0.319
2,4-dinitrochlorobenzene	0.628	0.797
<i>m</i> -dinitrobenzene	0.942	0.630
aniline	5.116	0.304
3-phenylpropanol	6.814	0.616

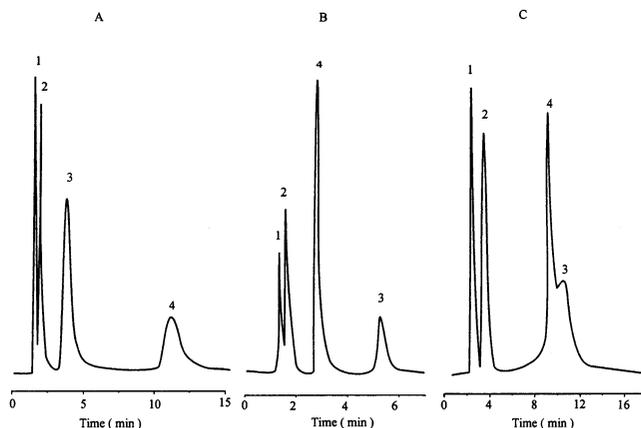


Fig. 1. Chromatogram of four basic compounds as test mixtures on ceria–zirconia: mobile phase: (A) ethanol/cyclohexane (1/99,v/v); (B) dichloromethane/cyclohexane (80/20, v/v); (C) chloroform/cyclohexane(50/50,v/v). Flow rate: 1.0ml/min. UV detection at 254nm. Peaks: 1, *N,N'*-dimethylaniline; 2, *N*-methylaniline; 3, pyridine; 4, aniline.

Fig. 1 gives typical chromatograms of four basic compounds with different mobile phases. It can be seen that the nature of the mobile phases plays an important role in the selectivity. Pyridine is eluted before aniline with ethanol/cyclohexane as mobile phase, whereas the elution order is reversed with dichloromethane/cyclohexane and chloroform/cyclohexane as mobile phases; chloroform/cyclohexane has the lowest selectivity for separation of the test mixtures.

The chromatographic behavior of phenols was also investigated on the native packing. Nitrophenols could not be eluted with the mobile phases used in this study; phenol eluted with a capacity factor of 10.07 when ethanol was used as the mobile phase. It should be noted that phenol exhibited a greater capacity factor on the ceria–zirconia than on the zirconia, but this was much smaller than on the magnesia–zirconia. The results can be related to the acid–base properties of the packing materials, because the basicity decreases in the order of magnesia–zirconia, ceria–zirconia, zirconia.

3.3. Behavior of stearic acid modified packing in reversed phase

The universal method of surface modification of silica is chemical bonding in the presence of silanizing agent. However, this method is not very

valid for other oxides with lower stability of M–O–Si bonds, which decrease as $\text{Si–O–Si–R} > \text{Si–O–Zr–R} > \text{Si–O–Ti–R} > \text{Si–O–Al–R}$ [30]. At present, the most promising method seems to be the coating of oxides by polymers. However, the coating conditions are not easy to control. Deposition of polymer into pores of the oxides always diminishes the surface area and pore volume [31]. Moreover, non-uniform coating of the polymer during an ill-controlled process will result in low column efficiency. As mentioned in the previous section, Lewis bases, such as nitrophenol, adsorbed strongly on the ceria–zirconia support even with a very strong eluent. This prompted us to modify ceria–zirconia with hard Lewis bases. In the present study, stearic acid, a long chain fatty acid, was chosen as the modifier due to its strong Lewis base site and hydrophobic properties comparable to octadecylsilane, commonly used in the silica-based stationary phase. The influence of the organic modifier, the concentration of stearic acid in the mobile phase and the eluent pH on the chromatographic behavior of solutes was investigated on the modified packing.

3.4. Stability study of the stationary phase

In order to investigate the stability of the stearic acid modified ceria–zirconia support, we have examined the retention of anthracene with

methanol/water (80/20,v/v) as mobile phases, after the column was continuously purged with different solutions. A plot of the capacity factor of anthracene against the volume of purge solution is shown in Fig. 2. Firstly, the stearic acid modified ceria–zirconia column was purged with a mixture of methanol and water. As shown in Fig. 2, after the column was purged with 5000 ml of the methanol/water solution, the retention of the probe solute decreased little. This result suggests that the stearic acid-modified stationary phase had acceptable stability, provided a methanol/water mixture was used as the mobile phase. Thereafter, the column was subjected to acetate buffers of pH 6 and 2 in sequence. Although the retention of the solute decreased slightly after the column was purged with about 500 ml of the acetate buffer, henceforth it changed little with increasing volume of the purge solution. This result may be interpreted by assuming that the surface of the ceria–zirconia consisted of two different sites interacting with stearic acid: one a strong site, and another relatively weak. The stearic acid adsorbed on the weaker sites would be displaced by acetate, leading to the

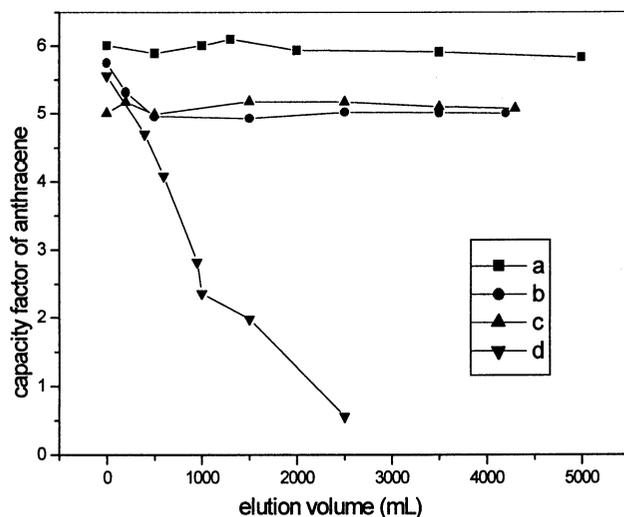


Fig. 2. Investigation of stability for stearic acid modified ceria–zirconia composite. Purge solution: (a) methanol/water (60/40,v/v); (b) acetate buffer, pH 6, [HAc] = 5mM; (c) acetate buffer pH 2, [HAc] = 5mM; (d) 10mM NaOH solution. Test solutes: anthracene. Mobile phase for test of solute: methanol/water (80/20, v/v).

decrease in the concentration of stearic acid on the surface of the stationary phase, and thus decrease in the retention of anthracene. However, the stearic acid adsorbed on the stronger sites could not be displaced by acetate, because the stearic acid has stronger interaction with the adsorption sites than acetate. Finally, the column was challenged with 5mM NaOH purge solution. The retention of anthracene, unfortunately, decreased significantly, suggesting the stationary phase is not stable under extreme basic conditions.

3.5. Characterization of the stearic acid modified ceria–zirconia

The stearic acid modified ceria–zirconia was washed thoroughly with methanol and water, and dried in a vacuum before characterization. The surface coverage of the stearic acid on the ceria–zirconia composite was calculated from elemental analysis data (carbon content). It was found to be 2.9 $\mu\text{mol/g}$. The IR spectra of the stearic acid modified ceria–zirconia and the native one are shown in Fig. 3. The spectra of the modified support show C–H stretching bands between 3000 and 2800 cm^{-1} . A small peak in the same region is also observed in the spectrum of the bare ceria–zirconia, which is a result of the residual organics introduced during the sol–gel process. The bands at 1458 and 1541 cm^{-1} were assigned to the asymmetric and symmetric stretch modes of the carboxylate groups [32].

3.6. Chromatography

A mixture of methanol and water was taken as the mobile phase to investigate the effect of the organic modifier on the chromatographic behavior of solutes. It was observed that the logarithmic capacity factor of both neutral and basic compounds on the modified ceria–zirconia stationary phase decreased linearly with an increase of the content of methanol in the mobile phase. This result suggests that the stearic acid modified ceria–zirconia behaves as a typical reversed phase packing material. Fig. 4 shows the relationship between $\log k'$ and $\log P$, partition coefficients

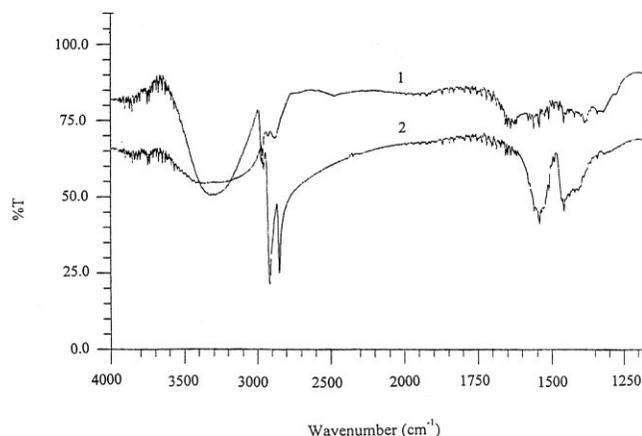


Fig. 3. DRIFT spectra of native ceria-zirconia and stearic acid modified ceria-zirconia. 1: native ceria-zirconia; 2: stearic acid modified ceria-zirconia.

between octanol and water, of PAHs. As can be seen, the $\log k'$ of PAHs increases linearly with their $\log P$, which further verifies the hydrophobic property of the stearic acid modified ceria-zirconia.

The effect of the concentration of stearic acid added to the mobile phase was tested in the range of 0–0.9 mmol/l. The retention of solutes increased slightly with the increase in the concentration of stearic acid, and reached a constant above 0.5 mmol/l. The results can be easily understood. The retention of solutes only depended on the density of stearic acid chemically adsorbed on the ceria-zirconia in the absence of stearic acid in the mobile phase, while physical adsorption of stearic acid on the support contributes to the increase in the retention by hydrophobic interaction when stearic acid occurs in the mobile phase. Furthermore, the increase of stearic acid did not increase physical adsorption significantly, so no change in the retention of solutes was observed.

The variation in capacity factors as a function of eluent pH was studied over the pH range from 2.07–9.33. In this experiment, stearic acid was added to the mobile phase in order to overcome the instability of the stationary phase at high pH. The volume percentage of methanol was held constant (60/40, v/v) and the stearic acid concentration was fixed at 0.1 mmol/l. The relationship between the retention of basic compounds and the eluent pH is presented in Fig. 5. As shown in Fig.

5, sigmoidal curves for the test solutes were obtained which are similar to the typical curve for pH dependence of basic compounds on nonpolar stationary phases [33]. The retention of ionizable solutes related to their chemical form. Most of the basic compounds are fully ionized at low pH, and hydrophobic interaction is not significant. More-

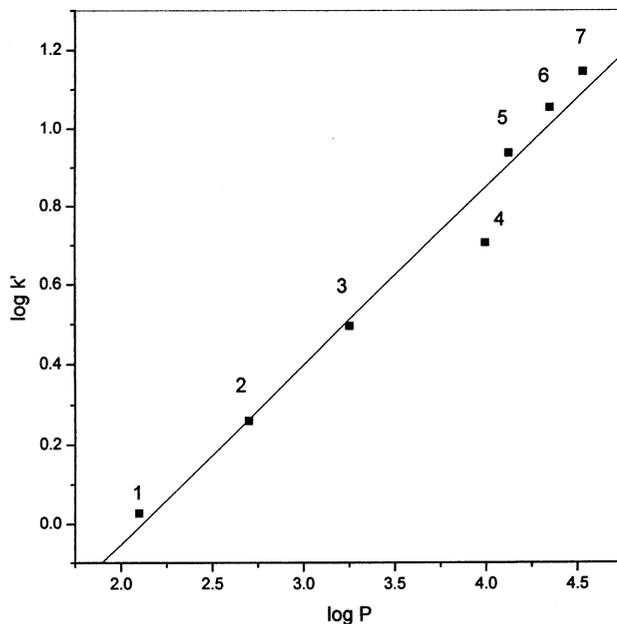


Fig. 4. Plots of $\log k'$ vs $\log P$ [34] of PAHs. Mobile phase: methanol/water (70/30, v/v). 1, benzene; 2, toluene; 3, naphthalene; 4, biphenyl; 5, fluorene; 6, phenanthrene; 7, anthracene.

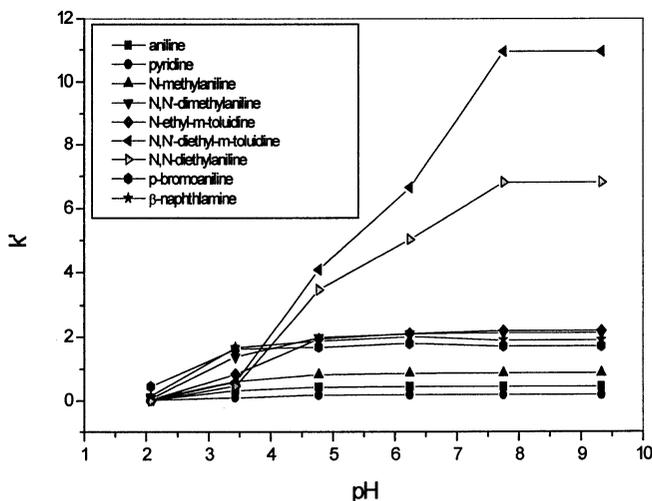


Fig. 5. Dependence of mobile phase pH on the capacity factors of basic compounds on the stearic acid modified ceria–zirconia. The mobile phase was methanol–buffer (60/40, v/v) containing 0.1mM stearic acid and 5mM acetate for pH 2.07, 3.43, 4.77, 6.24 and 5mM Tris for pH 7.75, 9.33.

over, the surface of the ceria–zirconia may possess anion-exchange property at low pH and basic compounds would undergo coulombic repulsion from the surface. This may explain why the basic compounds are weakly retained at low pH. As the pH increases, they are gradually deprotonated into the neutral form, so their retention increases by hydrophobic interaction, and reaches at a maxima at pH greater than their pK_a . The retention behavior of the neutral compounds such as PAHs was also investigated under the same chromatographic conditions. No obvious variation in their retention was observed over a wide pH range from 2.07 to 9.33. It suggests that hydrophobic interaction between the neutral compounds and the stationary phase is almost constant.

3.7. Separation

The separation of polycyclic aromatic hydrocarbons and their derivatives was carried out on the stearic acid modified ceria–zirconia with a mixture of methanol and water as the mobile phases. As shown in Fig. 6, satisfactory separation was achieved. It should be pointed out that the elution order of the derived PAHs on the

modified stationary phase was the reverse of that on the bare ceria–zirconia stationary phase (see Table 2) due to the difference in the retention mechanism. Separation of basic compounds has also been obtained by using the modified stationary phase. The elution order, as shown in Fig. 7A, is pyridine < aniline < *N*-methylaniline < *N,N'*-dimethylaniline, which depends on their hydrophobic properties. It can also be observed from Fig. 7A and B, that the elution order of basic compounds is not in complete accordance with that on a conventional ODS column, even if the hydrophobic interaction is the dominant mechanism on both columns. The difference can be assigned to different properties of the silica matrix and ceria–zirconia matrix. In addition, better selectivity of basic compounds was obtained on the stearic acid modified ceria–zirconia column than the ODS column.

4. Conclusion

Ceria–zirconia was successfully synthesized by the sol–gel process as a new packing material. Physico–chemical properties of the mixed oxide

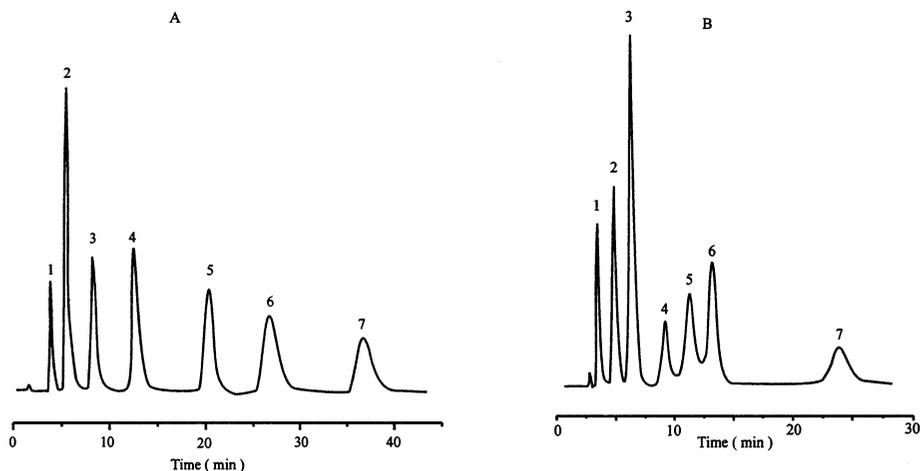


Fig. 6. Chromatogram of PAHs and substituted PAHs on the stearic acid modified ceria–zirconia. Mobile phase: methanol/water (70/30,v/v). Flow rate: 0.5ml/min. UV detection at 254nm. Peak: (A) 1, benzene; 2, toluene; 3, naphthalene; 4, biphenyl; 5, fluorene; 6, phenanthrene; 7, anthracene. (B) 1, benzonitrile; 2, *p*-nitrotoluene; 3, toluene; 4, *o*-chlorotoluene; 5, antraquinone; 6, biphenyl; 7, 4-bromo-4-nitro-biphenyl.

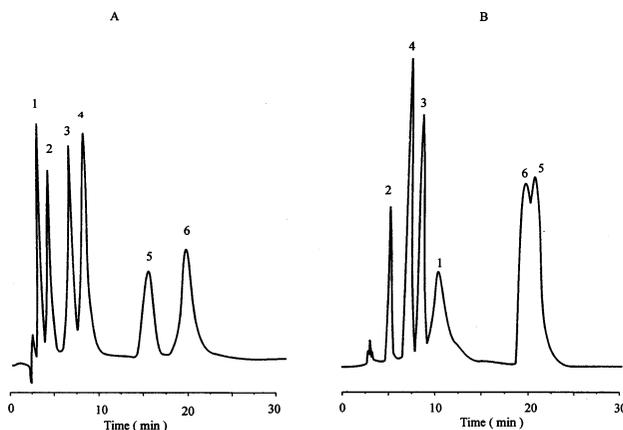


Fig. 7. Chromatogram of basic compounds on stearic acid modified ceria-zirconia (A) and ODS stationary phases (B). Mobile phase: methanol/water(40/60, v/v). For other conditions see Fig. 6. Peak: 1, pyridine; 2, aniline; 3, *N*-methylaniline; 4, *p*-toluidine; 5, *N,N'*-dimethylaniline; 6, *N*-ethyl-*m*-toluidine.

were characterized. In comparison with zirconia, ceria–zirconia composite has a higher specific surface area and appropriate pore structure. The chromatographic properties of the native support were evaluated in normal phase mode. Results show the stationary phase is promising for the separation of basic compounds. The new packing material of reversed-phase performance can be prepared by modification of ceria–zirconia with

stearic acid, which is available for separation of neutral and basic compounds.

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