

Preparation of Zirconia Based Packing Material and Its Evaluation

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Abstract: A new reversed-phase packing (C_{18} -PBD- ZrO_2) was prepared by depositing and cross-linking 1-octadecene (ODE or C_{18}) and polybutadiene (PBD) onto the surface of porous zirconia microspheres (5~10 μm in diameter) which were synthesized by a sol-gel process. These novel column packings possess high mechanical and chemical stability, wider usable pH range and can be used to separate basic compounds with no observable peak tailing.

Keywords: Zirconia, C_{18} -modified polybutadiene-coatings, stationary phase, liquid chromatography.

Silica-based packing materials have two serious drawbacks: lackness of pH stability and severe peak tailing in separation of basic solutes^{1,2}. Recently, zirconia has been put much attention because of its high mechanical and chemical stability. Zirconia is completely stable from pH 1 to 14, even at temperature of 100°C³. The porous zirconia microspheres used as column packings can be synthesized by means of polymerization-induced colloid aggregation (PICA) method^{4,5} or a sol-gel process⁶. Modification of zirconia surface with PBD was reported by P. W. Carr⁷.

In this paper, C_{18} -PBD- ZrO_2 packings, which are useful in reversed-phase liquid chromatography, were prepared by depositing and crosslinking approach. The polymer coating immobilized on zirconia surface was confirmed by IR spectra, their hydrophobicity and chromatographic behavior were evaluated.

Experimental

Chemicals and Apparatus

PBD of average molecular weight 1000 was purchased from Beijing Yanshan Chemical Factory. All solvents used in liquid chromatography were HPLC-grade.

The infrared spectra of zirconia-based packings were measured by a Perkin-Elmer 983 IR spectrometer. Chromatogram was obtained with a Varian 5060 liquid chromatograph. Columns (150 × 4.6 mm) were slurry-packed.

Synthesis of C_{18} -PBD- ZrO_2

Zirconia microspheres were synthesized by sol-gel process as described in reference⁶.

The particle size of the porous zirconia was 5~10 μm , the surface area was 26.2 m^2/g , and the mesopore diameter was 3.4 nm.

Zirconia particulates were added to pentane solution containing PBD and ODE. The slurry was ultrasonicated under vacuum for 30 minutes, and then adding dicumyl peroxide (DCP). The slurry was then dried *in vacuo*. Cross-linking and immobilization of polymer on the zirconia surface was accomplished by heating to 130°C for 1 h and 200°C for 2 h under an argon purge. The zirconia particulates were then washed with dichloromethane, tetrahydrofuran, methanol and methanol-water (50/50, v/v).

Hydrophobicity

Hydrophobicity of packings was measured by particle wetting experiments⁸.

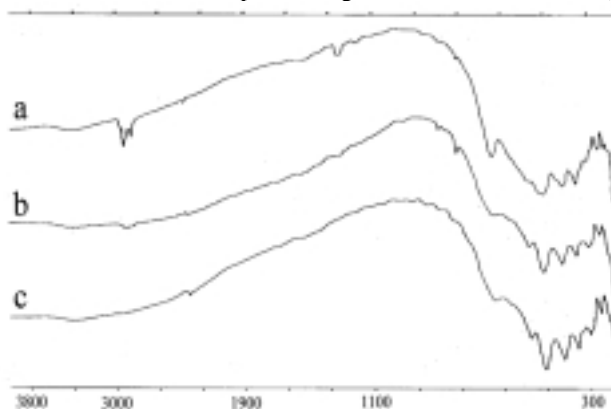
Result and discussion

In **Figure 1** were showed the infrared spectra of $\text{C}_{18}\text{-PBD-ZrO}_2$, PBD-ZrO_2 and bare ZrO_2 . The two C-H stretching modes are CH_2 *antisym* 2924 (or 2925) cm^{-1} and CH_2 *sym* 2852 cm^{-1} , respectively. The bands at 2860~2980 cm^{-1} are almost obscure because the terminal CH_3 in octadecyl is too less than CH_2 groups. There are more CH_2 groups in $\text{C}_{18}\text{-PBD-ZrO}_2$ than in PBD-ZrO_2 , even the carbon load of the former is lower than the latter. Therefore the absorption at 2924 (or 2925) cm^{-1} and 2852 cm^{-1} is stronger in the IR of $\text{C}_{18}\text{-PBD-ZrO}_2$ than in that of PBD-ZrO_2 . The C-H bending of methylene has absorption at 1458 cm^{-1} , which is clearly visible in the IR of $\text{C}_{18}\text{-PBD-ZrO}_2$, but almost invisible in that of PBD-ZrO_2 . The small peaks at 910 cm^{-1} can be interpreted as C-H wagging of C = C-H. Obviously, the absorption at 910 cm^{-1} is stronger in the IR of PBD-ZrO_2 than in that of $\text{C}_{18}\text{-PBD-ZrO}_2$. The absorption near 720 cm^{-1} is the in-phase CH_2 rocking of four or more methylene groups, which explains why the absorption at 744 cm^{-1} is very strong in the IR of $\text{C}_{18}\text{-PBD-ZrO}_2$. From all these facts, the conclusion can be made that ODE and PBD have been cross-linked onto the surface of zirconia microspheres with the preparation method used above.

A key measure of the hydrophobicity of the packings may be found in the methanol required in the particle wetting experiment. As shown in **Table 1**, for the same composition series, higher hydrophobicity is observed for the higher carbon load material. But for the packings with approximately the same carbon load, $\text{C}_{18}\text{-PBD-ZrO}_2$ has higher hydrophobicity than PBD-ZrO_2 .

The chromatographic performance of the $\text{C}_{18}\text{-PBD-ZrO}_2$ packing was documented by the separation of aniline derivatives in **Figure 2**. It is shown that the peak shape of basic compounds on the ZrO_2 -based stationary phase is quite symmetric, in contrast, the strong retention and peak tailing of basic compounds on the SiO_2 -based columns was reported frequently.

Figure 1 Comparison of IR spectra of the samples (with KBr diluting identical concentration, and KBr pellet being almost the same thickness)



The peaks of sample **a** and **b** with threshold 2 were **a**—2924(29.7), 2852(32.6), 1458(57.0), 744(27.1), 508(15.8), 421(18.2), 357(18.7), 256(29.3), 227(29.5)cm⁻¹(%T) and **b**—2925(27.3), 910(50.0), 424(16.5), 360(19.2), 303(21.8), 250(25.4) cm⁻¹(%T).

a: C₁₈-PBD-ZrO₂ (carbon load, 5.20%); **b**: PBD-ZrO₂ (carbon load, 7.30%); and **c**: bare ZrO₂ .

Table 1 Comparison of hydrophobicity of C₁₈-PBD-ZrO₂ and PBD-ZrO₂ packings

Packings	C ₁₈ -PBD-ZrO ₂		PBD-ZrO ₂	
Carbon load %	1.20	5.20	1.53	5.59
Methanol %	30	50	10	40

Figure 2 Chromatogram of the separation of aniline derivatives on C₁₈-PBD-ZrO₂



Mobile phase: methanol-water(50/50,v/v); Flow rate: 1 ml/ min; detection: 254 nm.

Peak identification: 1 = aniline, 2 = N-methylaniline, 3 = N,N-dimethylaniline

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