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Note

Coordination polymers as stationary phases and adsorbents for gas chromatography

VIII. An attempt to bind poly[chromium(III) diphenylphosphinate] to silica

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Chromium diphenylphosphinate (Cr-DPP) coated on Spherosil and a silica gel was previously used as a packing for gas chromatography (GC)[1,2]. The presence of Cr–OH groups in the structure of the polymer can be utilized for direct bonding between a silica surface and Cr-DPP.

Two general methods of bonding are currently used: organosilicone derivatives, used mainly to bind monomeric phases; thermal condensation of polymers with supports, *i.e.*, the method of Aue and co-workers[3,4] which can be realized by heating of a conventionally coated support in an inert gas atmosphere, or by refluxing the support with a polymeric phase in boiling hexadecane. The latter method was chosen to obtain a chemically bonded chromium diphenylphosphinate for the following reasons: an initial "cooking" of the silica in boiling hexadecane removes physically adsorbed water; a bubbling of an inert gas (argon) removes water formed as a side product of the condensation reaction; the method assures an uniform polymer layer on the silica surface. Surprisingly, considerable changes in the polymer structure were found after the cooking in hexadecane.

EXPERIMENTAL

Reagents and apparatus

Macherey-Nagel Kieselgel 60 was used. The silica was sieved and the particle fraction of 0.2–0.25 mm was extracted with 20% hydrochloric acid for several days. Subsequently the silica was rinsed with doubly distilled water until neutrality, dried in oven at 130°C and then in a vacuum over freshly dehydrated molecular sieves 3A and 4A.

Chromium(III) diphenylphosphinate was synthesized as described previously[1].

Hexadecane (Reachim, U.S.S.R.), purum grade, was purified by distillation in an argon atmosphere and then by passing through a silica–alumina column. Its purity was verified by UV spectroscopy. Reagent grade chloroform (POCh, Gliwice, Poland) was used.

IR spectra were recorded by means of a Perkin-Elmer 580 spectrophotometer.

TABLE I

CONDITIONS FOR BONDING OF Cr-DPP

Methods: A, a chloroform solution of Cr-DPP was slowly added dropwise to the boiling suspension of silica in hexadecane; B, the silica was conventionally coated with Cr-DPP from chloroform solution and subsequently the coated silica was refluxed in boiling hexadecane. Amount of silica: 1.0 g. Chloroform extraction time: 7 h.

Experiment	Amount of Cr-DPP (g)	Time of cooking (h)	Method
I	0.2	5	A
II	0.3	10	A
III	0.3	5	B
IV	0.3	10	B

Elemental analysis were carried out on Perkin-Elmer elemental analyzer. Chromium was determined by means of a Carl Zeiss atomic absorption spectrometer (G.D.R.).

Specific surface areas were determined on a Gravimat (Sartorius, F.R.G.).

Four experiments were carried out to establish the optimum conditions for bonding of the Cr-DPP. The conditions are given in Table I. After the refluxing in boiling hexadecane, the silica with bonded Cr-DPP was thoroughly extracted with chloroform in an extractor similar to that proposed by Aue et al.[5].

Determination of chromium

A 0.1-g amount of the modified silica was placed in a small pear-shaped flask and a mixture of 5 ml conc. nitric acid and 1 ml of conc. perchloric acid was added. The flask was connected to an all-glass rotary evaporator and was heated until the evolution of brown nitrogen oxides had ceased. A slow motion was applied to the flask to prevent overheating of the contents. Subsequently the silica was filtered off and the chromium was determined in the filtrate by atomic absorption spectrometry (AAS). This method was found to be superior over the reaction in a sand-bath where overheating caused a considerable loss of the chromium.

RESULTS AND DISCUSSION

Based on the chromium determination, the quantity of polymer bonded to the silica surface could be calculated. After carbon and hydrogen elemental analysis, the ratio Cr:C was calculated and found to be unexpectedly low. The results are presented in Table II. The important conclusions from the data of Table II are: 5 h of cooking

TABLE II

CHARACTERISTICS OF THE SILICA WITH BONDED Cr-DPP

Experiment	Amount of Cr-DPP bonded (%)	Specific surface area (m²/g)	Cr:C ratio
I	4.6	319	1:38
II	4.6	328	1:39
III	9.7	306	1:32
IV	9.9	309	1:29
Initial SiO$_2$	—	330	—

is sufficient; a higher polymer load can be obtained by cooking of the conventionally coated silica; higher contents of the polymer resulted in a decrease of the specific surface area.

The abnormally high contents of carbon in relation to chromium was surprising. To investigate this we recorded an IR reflectance spectrum of the bonded phase. This indicated the presence of some aliphatic radicals in the polymer. Additional experiments were therefore carried out.

Two samples of Cr-DPP were refluxed in hexadecane for 5 and 15 h respectively. The first sample was thoroughly extracted in a Soxhlet apparatus with hexane, then dried in a vacuum over molecular sieves for 24 h (sample R). The second sample was extracted with hexane, then dried and extracted again with chloroform. This extraction divided the sample into two parts, soluble (S) and insoluble (T) in chloroform.

IR spectra of all the Cr-DPP samples were recorded and they are shown over the range 2800–3200 cm^{-1} in Fig. 1. The initial Cr-DPP does not show any absorp-
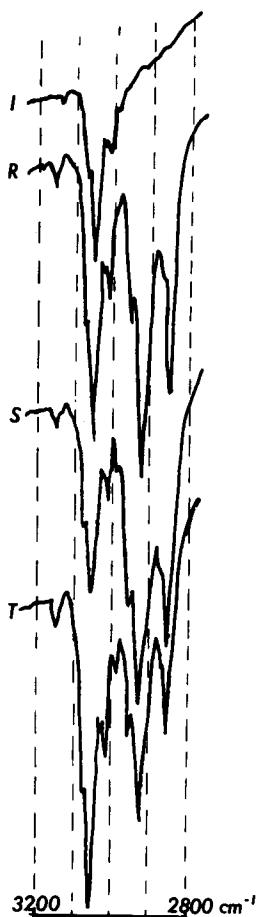

Fig. 1. IR spectra (3200–2800 cm^{-1}) of initial Cr-DPP (I) and the polymer refluxed in boiling hexadecane (samples R, S and T) (2 mg per 300 mg KBr as pellet).

TABLE III

ELEMENTAL ANALYSIS OF Cr-DPP REFLUXED IN HEXADECANE

Sample	Theoretical		Found*	
	% C	% H	% C	% H
Cr-DPP initial	55.29	4.45	55.40	4.30
Sample R			58.38	4.67
Sample S			59.46	6.09
Sample T			53.29	4.55
Cr-DPP-DHPP**	58.10	6.00		
Cr-DHPP***	60.95	7.68		

   * Average from three determinations.
  ** In every second monomer unit the phenyl is replaced by hexadecyl.
*** In every monomer unit the phenyl is replaced by hexadecyl.

tion which could be assigned to the aliphatic C–H vibrations. The cooking of the polymer in hexadecane obviously changes the polymer structure, yielding new absorption bands observed in the region 2800–3000 cm^{-1}. Absorption bands at 2855, 2926, 2958 and 2990 cm^{-1} can be assigned to CH_2 symmetric, CH_2 asymmetric, CH_3 asymmetric and CH_3 symmetric stretching bands respectively. Quantitative conclusions can be drawn on the basis of the relative intensity of the aromatic and the aliphatic C–H bands.

All the samples were analysed for carbon and hydrogen contents and the results are presented in Table III. Also given are the theoretical carbon and hydrogen contents for polymers with phenyl radicals partially replaced by hexadecyl ones. A comparison of the data with the elemental analysis of samples R and S indicates the possibility of such a replacement. The carbon contents of samples R and S considerably increased as a result of the cooking in hexadecane. Sample T had lost part of its carbon, although all three samples exhibited aliphatic C–H stretching bands. For sample T the loss of phenyls is probably greater than their replacement with alkyls. It has already been known that heating of chromium diphenylphosphinate causes dehydration and partial cross-linking of the polymer[6], which seems to be responsible for the insolubility.

The results of elemental analyses in Table II indicate that the replacement proceeds more easily when the polymer is suspended in the solvent than when it is coated on a support.

CONCLUSIONS

(1) Refluxing in hexadecane can be applied for binding the polymer to a silica surface.

(2) Very careful interpretation of the results is advised since at least some possibility of side reactions was found.

(3) The side reactions can be explained by the presence of impurities in the hexadecane or by a catalytic action of the polymer. Much attention should therefore be paid to purification of the hexadecane.

(4) The case described above cannot be generalized for all modifications performed in boiling hexadecane since, *e.g.*, Daniewski and Aue[4] studied the spent solvent and found unchanged octaphenyltetrasiloxane used for silica modification.

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