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ACTIVE SURFACE SITES AND DEACTIVATION OF CHROMOSORB 102

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SUMMARY

A combined infrared spectroscopic and chromatographic study was undertaken in order to determine the adsorption properties of Chromosorb 102. This study shows that the unreacted vinyl groups in Chromosorb 102 are the active sites which give rise to extreme tailing of amine peaks when the material is used as a support material. A method was devised for removing these groups chemically by addition of HF to the double bond of the vinyl group. This method of deactivation is not dependent on the surface area of the support or on the amount of reagent used, as is the case in the deposition methods. The spectra obtained allow one to observe the interactions with the surface and enable one to predict which compounds give rise to extreme tailing in a chromatographic column. The predictions made were confirmed by running the test substances in a gas chromatograph containing support materials treated with HF, coated with Carbowax 20M, and untreated.

INTRODUCTION

In deactivating gas chromatographic (GC) support materials, empirical methods are usually tried until one obtains a support which gives satisfactory separations without too much tailing. It is desirable to identify the specific adsorption sites on a given support which lead to tailing of chromatographic peaks, because the identification of the active sites should allow one to devise effective means of deactivating these sites.

A few empirical studies have been reported in the literature using Chromosorb 102 as a support material. DAVE[1] made an extensive study of retention indices for a large number of porous polymers. Of interest to the study carried out here was that with Chromosorb 102, amines showed severe tailing and anilines excessive retention times. SUPINA AND ROSE[2] reported that acids tail on Chromosorb 102, but gave no data for amines. Various coatings have been tried in an attempt to improve separations on these porous polymers. On Porapak Q, which has a similar chemical structure to that of Chromosorb 102, the use of a 2% Carbowax 20M coating has been reported to give shorter retention times[3] and longer retention times[4], while JANSSON *et al.*[5] obtained the best results without any coating, although their curve for HETP *vs.* %

Carbowax 20M applied showed a minimum at 2%. In view of these discrepancies, it is clear that there is much to be learned about the surface properties of these porous polymers.

IR spectroscopy is eminently suited for a study to determine specific adsorption sites, since one can observe not only molecules adsorbed on a surface, but in many cases also the interaction between the adsorbed molecule and the surface sites. Most of the materials of interest as GC support materials (*e.g.* metal oxides, organic polymers) are sufficiently transparent in the IR region of the spectrum to be suitable for a study of this type. The main restriction of this method is that the surface to be studied must have a fairly high specific surface area.

In this paper, a study of this type is described in which Chromosorb 102, a porous styrene–divinylbenzene copolymer, with a specific surface area of 300–400 m^2/g was used. The spectroscopic study shows that vinyl groups are the active sites for adsorption. A method for chemically deactivating these sites was devised, rather than merely coating the particles with another substance. In order to confirm the results obtained spectroscopically, a series of test substances was run in a gas chromatograph containing the treated and untreated Chromosorb 102 as supports.

EXPERIMENTAL

Spectroscopy

All spectra were recorded with a Perkin-Elmer Model 621 IR spectrophotometer. The Chromosorb 102 samples were prepared by lightly grinding in an agate mortar and then pressing 30 mg of the material at 18000 lb./in.^{2} in a 1-in. diameter circular die at 90°. The Chromosorb 102 disc obtained was mounted in a Pyrex cell with Irtran-2 windows. The cell was constructed so as to cover both the sample and reference beams of the spectrophotometer, thus eliminating any absorption bands due to the gas phase present. The cell was connected to a conventional vacuum rack by means of which the various vapours were introduced into the cell.

Owing to the low transmittance of the samples (about 10% or less at 4000 cm^{-1}), a reference beam attenuator was used. For closely observing intensity changes in a given band, a 5 × ordinate expansion was used. All spectra were recorded at room temperature.

Chromatography

The column materials were evaluated in a Varian Aerograph Model 1860 gas chromatograph equipped with thermal conductivity and flame ionization detectors. The support materials were packed in 1/4-in. O.D. aluminium columns with a length of 120 cm. The columns were pre-conditioned for 24 h at 250° with a nitrogen flow rate of 100 ml/min. For any given compound, a column temperature was used which gave a large amount of peak tailing on the Chromosorb 102. This was done in order to facilitate the comparisons of specific adsorption effects on the variously treated support materials. The operating conditions are given with the data. A 5-μl Hamilton syringe was used to deliver the liquid samples.

Surface treatments of Chromosorb 102

The 2% by weight of Carbowax 20M was applied to the surface by using the

standard technique of dissolving the Carbowax 20M in a solvent, methylene chloride, adding this solution to the Chromosorb 102, and evaporating to dryness.

The hydrofluorination was carried out by adding 150 ml of 50% HF to 15 g of Chromosorb 102 in a polyethylene vessel. The vessel containing the Chromosorb 102 and HF was heated gently on a hot-plate for three days, and agitated continuously with a magnetic stirrer. The material was filtered, washed with water and placed in an oven at 150° for several days. It was evacuated for 2 h to remove any residual traces of HF, prior to packing into a column.

RESULTS AND DISCUSSION

In Fig. 1, spectrum B represents the C–H stretching band region of Chromosorb 102, with an identification of the absorption bands. The relatively strong intensity of

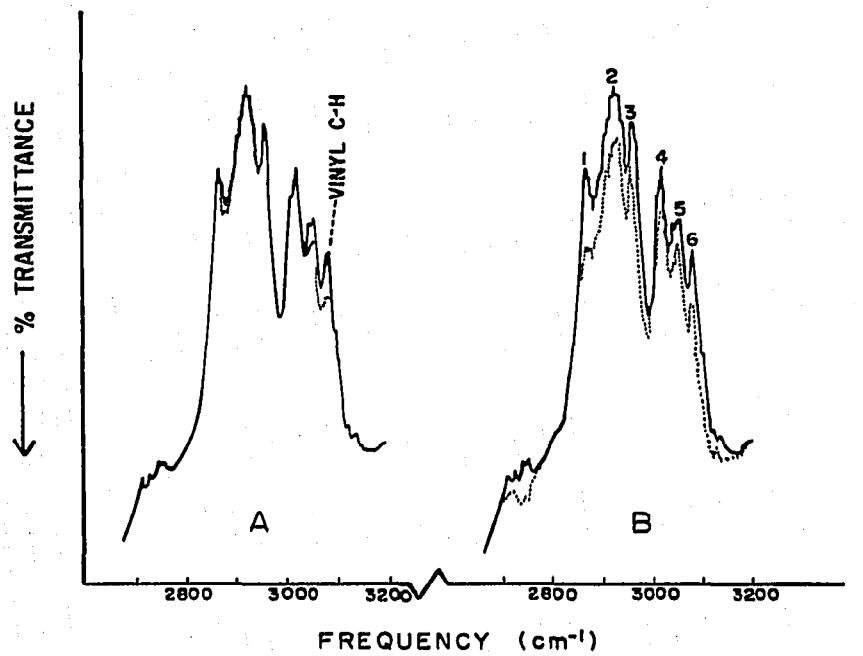


Fig. 1. Spectrum of C–H stretching band region of Chromosorb 102. The solid line is the spectrum of the evacuated sample. In B, the dotted line is the spectrum in the presence of gaseous diethylamine; in A, the dotted line is the spectrum of B after evacuating for a short time. The major bands shown are: 1,2,3=CH of CH_2/CH_3 groups; 4=CH of aromatic ring; 5,6=CH of vinyl groups.

the band at 3085 cm^{-1}, due to unreacted vinyl groups, is not surprising in view of the very large specific surface area. Calculation shows that a porous material with a surface area of about 350 m^2/g is equivalent to a sheet about 25 Å in thickness.

Various gases were introduced into the cell and the spectra recorded over a spectrum of the Chromosorb 102 in vacuum. A suitable absorption band due to the adsorbed molecules was chosen and the intensity change observed while the cell was evacuated. Some typical spectra are given in Fig. 2. For given pumping conditions, the time required to remove all the adsorbed material from the surface gives a rough estimate of how strongly adsorbed the molecule is on the surface. It should be

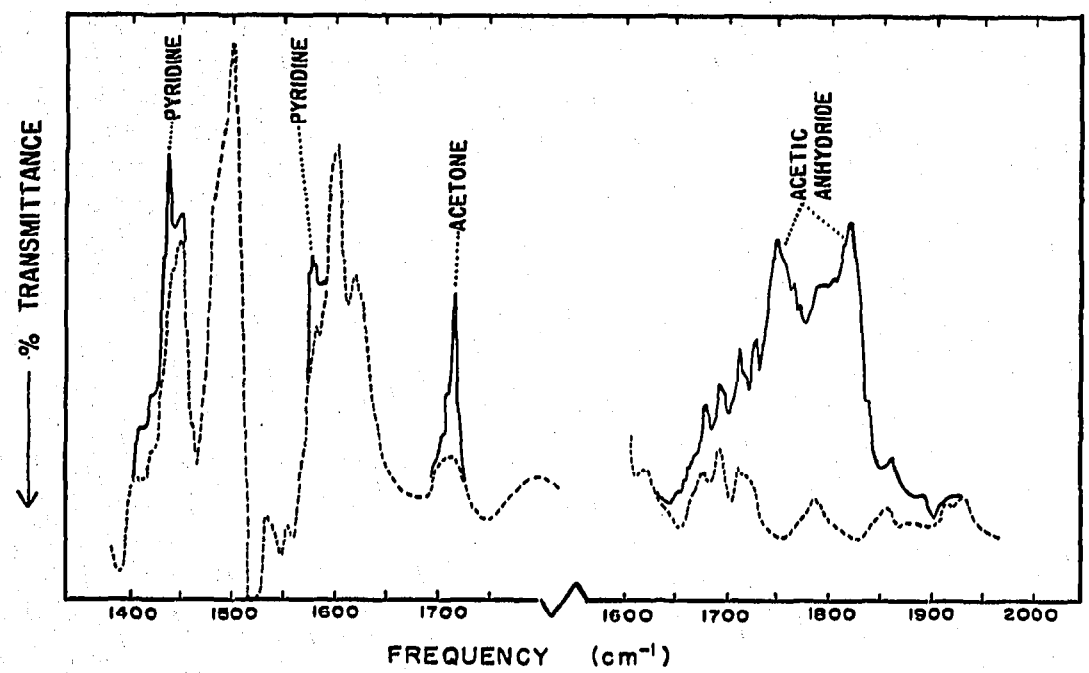


Fig. 2. Typical spectra showing bands due to adsorbed molecules. Dashed lines are the background spectra of the Chromosorb 102, and the solid lines are due to the adsorbed molecules.

mentioned here that the desorption times obtained will be different from those obtained in a chromatograph since the support material is only used at about 30° whereas most chromatographs are operated at higher temperatures. Also, the adsorbed molecules were removed by evacuation rather than by a flow of inert gas.

With the particular adsorbates and support materials used here, most of the adsorbed molecules were removed rapidly with pumping, but in some cases considerably more evacuation was required to remove the last traces of adsorbed material. Thus, the spectroscopic data will not give any indication of retention times but should indicate which adsorbates will give rise to extreme tailing in the chromatograph. For those compounds removed from the surface in less than about 30 sec, it is not possible to draw any conclusions regarding the strength of adsorption since the rate of desorption is faster than the rate at which the gas phase is removed from the cell by pumping.

Adsorption on untreated Chromosorb 102

The desorption times for the various gases adsorbed on untreated Chromosorb 102 are given in Table I. In all cases there was a general diminution in intensity of the C–H stretching bands (*i.e.* an interaction with the C–H groups) when the gas phase was present in the cell. A typical spectrum illustrating this is given in Fig. 1 (spectrum B). With sufficient pumping to remove the adsorbed molecules, these C–H bands were all restored to their original intensities.

In the case of diethylamine, all the C–H bands rapidly returned to their original intensity with pumping, with the exception of the band due to the C–H of the vinyl group (Fig. 1, spectrum A). This band only returned to its original intensity after about 1 h of pumping. This clearly shows that there is a specific and strong interaction between the amine and the vinyl group. The bulk of the amine was

TABLE I

SPECTROSCOPICALLY OBSERVED PUMPING TIMES REQUIRED TO REMOVE ADSORBATES AT ROOM TEMPERATURE

Compound	*Some of the IR absorption bands used (cm^{-1})*		*Support*		
			Untreated Chromosorb 102	*Chromosorb 102 coated with Carbowax 20M*	*Chromosorb 102 treated with HF*
Acetic acid	OH	3200	f[a]	2	>11
	C=O	1717			
Diethylamine	NH	1620	>30	15	1.5
n-Heptane	Perturbation of C–H		—	—	1.2
Acetic anhydride	C=O	1825, 1750	2	f	—
Water	OH	1595	13	5	—
Ethyl alcohol	OH	3330	5	1	—
Pyridine	Ring	1440, 1580	f	f	f
Aniline	NH	1615	4	—	—
Benzene	Perturbation of C–H		f	f	—
Acetone	C=O	1715	f	—	—

[a] f indicates too fast to measure (less than 30 sec).

removed rapidly and only a smaller portion much more slowly; this indicates that the amine will not be retained excessively in a chromatographic column, but that severe tailing will be observed.

When pyridine was adsorbed, strong bands were observed at 1440 and 1580 cm^{-1} and a weak band at 1455 cm^{-1} (Fig. 2). These bands are due to vibrations of the pyridine ring. The presence of these bands shows that the pyridine is principally physically adsorbed (1440, 1580 cm^{-1}) and that a small portion is also coordinately bound (1455 cm^{-1}), but that none of the pyridine is protonated (no band at 1540 cm^{-1}). Adsorption of pyridine and observation of the bands listed above is a common diagnostic test for coordinate bonding or the presence of surface acid sites[6].

Adsorption on Chromosorb 102 coated with Carbowax 20M

A spectrum of the C–H stretching band region of Chromosorb 102 coated with Carbowax 20M is shown in Fig. 3. The bands due to the presence of the Carbowax 20M on the surface are labelled in the figure.

The same series of experiments was carried out on this treated material as on the untreated material. The data for the pumping times required to remove the adsorbed molecules are given in Table I. The times required to remove the adsorbed molecules are in general somewhat less on this treated material. In some cases, but not all, the general interaction with the C–H bands was less than that on the untreated material. The greatest difference was noted with adsorbed diethylamine; pumping removed the adsorbed diethylamine from the surface much faster than on the untreated material and no specific interaction was observed with the vinyl C–H groups.

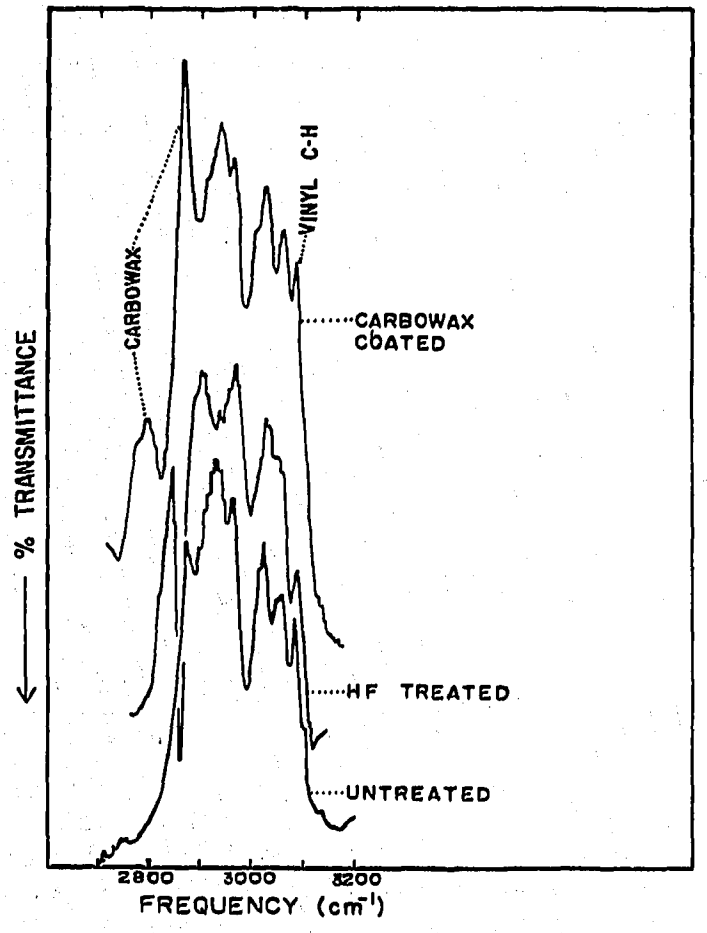


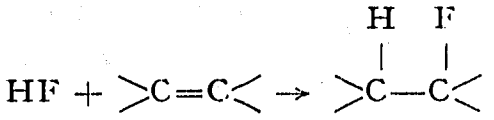
Fig. 3. Spectrum of C–H stretching band region of Chromosorb 102, showing the effect of various treatments. It should be noted that there is a decrease in the intensity of the vinyl C–H band in the HF-treated material, and that the presence of the Carbowax 20M can be seen by the presence of the bands at 2860 and 2800 cm^{-1}.

The presence of the Carbowax 20M has no effect on the intensity of the bands due to the vinyl C–H groups. This lack of interaction between the Carbowax 20M and the surface shows that the Carbowax 20M is merely resting on the surface, and its effect on the adsorption of other molecules is to mechanically block the active sites. That it does, indeed, block the active sites is shown by the lack of interaction between adsorbed diethylamine and the vinyl C–H groups, and the more rapid removal by pumping from this treated Chromosorb 102.

Adsorption on Chromosorb 102 treated with HF

With the exposed vinyl groups identified as the active sites (at least for the amine), it becomes possible to consider alternate methods for blocking or removing these active sites. Any method involving deposition on the surface will depend on the surface area of the support material; to find the amount of material that should be deposited in order to obtain optimum results one must use empirical methods. Clearly, it is desirable to use chemical reactions to remove these active vinyl groups, since chemical methods will be independent of the surface area of the support and also there will be no possibility of "bleeding". Hydrogenation of these vinyl groups

would be an attractive method, but owing to the small pore size, the reaction employed must not produce any reaction products which would remain within the pores and give rise to new active sites. Since there appear to be no simple, straightforward methods for accomplishing this, it was decided to add HF to the double bond of the vinyl group, *viz.*:



It is desirable, of course, that any chemical reaction employed should not be significantly more complicated to use than the deposition methods. A spectrum of the HF-treated Chromosorb 102 is given in Fig. 3. The intensity of the band due to the vinyl C–H group has been considerably reduced in intensity, showing that a large number of the vinyl groups have reacted with the HF. Also the relative intensities of some of the other C–H bands have changed.

The various gases were added to the treated sample in the cell. With the exception of acetic acid, the adsorbed molecules were removed by pumping at least as fast as on the Chromosorb 102 coated with Carbowax 20M (Table I). With added diethylamine, the adsorbed material was removed within 90 sec, compared to over 30 min on the untreated Chromosorb 102 and about 10 min on the Chromosorb 102 coated with Carbowax 20M. This is additional evidence that the surface vinyl groups give rise to the strong adsorption with the amine. With acetic acid, the required pumping time was considerably longer on the HF-treated surface than on the untreated or Carbowax 20M-coated support, showing that there is a strong specific interaction between the adsorbed acid and the HF-treated surface.

Gas chromatographic results

The untreated, Carbowax 20M-coated, and HF-treated supports were packed into columns and the various test substances run through them. The results are

TABLE II

CHROMATOGRAPHIC TAILING FACTORS (T_B)

T_B is the time for the elution peak to reach the baseline, as defined in the text. Nitrogen carrier gas, at a flow rate of 23 ± 2 ml/min, was used throughout.

Compound	*Column temperature (°C)*	*Support*		
		Untreated Chromosorb 102	*Chromosorb 102 coated with Carbowax 20M*	*Chromosorb 102 treated with HF*
Acetic acid	180	10.5	7	12
Diethylamine	180	100	30	40
n-Heptane	180	2.5	2.4	2.3
Water	95	5	5	—
Ethyl alcohol	150	4	3	3.5
Pyridine	220	>20	4	4
Benzene	150	~14	9	3.5
Acetone	150	4.0	4.0	1.8
Phenol	220	>35	18	8

summarized in Table II, which gives the times needed for the elution peak to reach the base line (T_B) measured from the peak maximum. This is the quantity which is most directly comparable with the spectroscopic results (*i.e.* pumping time required to remove the last trace of adsorbed material), and is a measure of the specific adsorptions causing the last part of the tailing. The correction to T_B due to the elution of the bulk of the material has not been taken into account as it is relatively short and does not significantly affect the results.

In most cases, the elution peaks obtained on the untreated Chromosorb 102 were less symmetric than those obtained on the two treated supports, even though the values of T_B were the same in some cases. The retention times for a given substance do not differ greatly on the various columns, but the amount of tailing, T_B, does vary over a large range. Some typical chromatograms are shown in Fig. 4.

The behaviour of the heptane elution peaks does not vary significantly on the differently treated support materials (Table II) and the peak shape is almost symmetrical in all cases (Fig. 4). This is to be expected, of course, for this relatively non-polar substance.

With diethylamine, very asymmetrically shaped peaks were obtained in all cases, even at temperatures above 200°. The amount of tailing, T_B, however, is considerably reduced on the treated columns for diethylamine and for pyridine. The improvement obtained with the HF-treated Chromosorb 102 suggests that a more complete hydrofluorination treatment, to remove all the residual vinyl groups, should result in even less tailing of the elution peak.

The acetic acid elution peak is improved on the support coated with Carbowax 20M, but shows greater tailing on the HF-treated support. This confirms

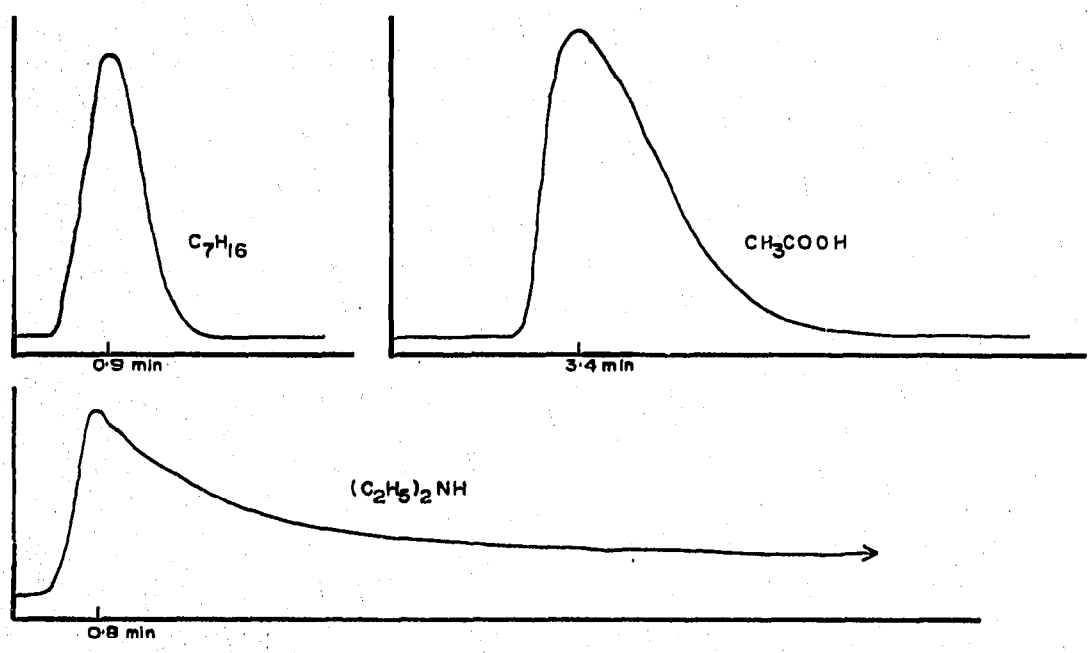


Fig. 4. Some typical chromatograms showing the shapes of the peaks obtained on the untreated Chromosorb 102 column (120 cm × 1/4 in. O.D.). Column temperature 180°; nitrogen carrier gas flow rate 23 ml/min; flame ionization detector.

that there is a stronger interaction between the acid and the surface fluoride group than between the acid and the vinyl group.

In view of the observed interaction of the amine and the surface vinyl group, it is of interest to recall that HOLLIS[7] used, among other compounds, a coating of tetraethylenepentamine for deactivating Porapak. Clearly, when a compound of this type adsorbs on the surface, it will interact preferentially with the vinyl groups and thus effectively deactivate them.

ZADO AND FABECIC[8], in a recent study of the heats of adsorption of alcohols, hydrocarbons, acetone and ether (but not nitrogen containing compounds) on Porapak Q and T, tentatively concluded that the specific interactions are most probably due to interactions of free electron pairs with the surface. Porapak Q is similar in structure to the Chromosorb 102 studied here. Thus, it seems likely that the specific adsorptions observed here are due to the interactions of the available electrons of the adsorbates with the surface vinyl groups.

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