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# PREPARATION OF CARBONEOUS ADSORBENTS BY CATALYTIC DECOMPOSITION OF HYDROCARBONS FOR CHROMATOGRAPHIC APPLICATION

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## SUMMARY

A method for the preparation of carbon adsorbents with highly ordered structures by hydrocarbon decomposition on a metallic catalyst supported on a silica gel surface is described. Structural, morphological and chromatographic studies of carbon adsorbents produced by pyrolysis of *n*-butane over a nickel catalyst at 400–700°C were carried out. The carbon obtained has graphite-like structure with a specific surface area ranging from 130 to 300 $m^2/g$. X-ray diffraction data yielded $c/2$ spacings of 3.414–3.453 Å, corresponding to 30% graphitization. Relatively good chromatographic separations of polar substances (alcohols, ketones) and light hydrocarbons were obtained using these adsorbents. The sorptive and desorptive properties of carbons prepared by catalytic decomposition of *n*-butane were tested for the extraction and concentration of phenol, its nitro and chloro derivatives and halomethanes from aqueous solution.

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## INTRODUCTION

The utilization of different catalytic processes to prepare chromatographic materials has been widely applied. For example, Unger and co-workers[1,2] utilized a well known process[3] of catalytic gasification of carbons to prepare carbon adsorbents for chromatographic purposes. This is an important method for the preparation of adsorbents with differentiated porous structures. The potential role of carbon adsorbents either in high-performance liquid chromatography (HPLC) and gas chromatography (GC) was described by Unger *et al.*[1,4], Knox *et al.*[5], Ciccioli[6] and Di Corcia and Liberti[7], and investigations on the preparation of such materials would be useful.

The paper discusses another advantageous method for the preparation of carbon adsorbents, consisting in the catalytic decomposition of hydrocarbons on the surface of a metal catalyst supported on a mineral adsorbent matrix (silica gel, alumina).

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## EXPERIMENTAL

### *Preparation of adsorbents*

Carbon adsorbents were prepared by the catalytic decomposition of *n*-butane on a nickel catalyst supported on the surface of silica gel. Silica gel Si-100 (Merck, Darmstadt, F.R.G.) of particle size 0.15–0.20 mm was used. The amount of nickel deposited was 10% (w/w). Commercial silica gel was washed with 3 *M* hydrochloric acid to remove metal ions and then impregnated with a methanollic or aqeuous solution of Ni $(NO_3)_2 \cdot 6H_2O$ (10% Ni–$SiO_2$). The silica support impregnated with the catalyst was dried at 120°C for 2 h heated at 400°C for 1 h and then introduced to the reactor in which the processes of reduction and carburization were being carried out. NiO was reduced with hydrogen at 500°C for 3 h at a flow-rate of 100 ml/min, and the carburization process was maintained at 400–700°C using a mixture of *n*-butane and hydrogen (flow-rates 120 and 80 ml/min, respectively).

Part of the prepared adsorbents was heated additionally at 700°C for 6 h so as to obtain ordering of the structure of the carbon deposit. Nickel was removed from the prepared adsorbents by washing it with 2 *M* hydrochloric acid. All reactions were carried out in a common fluid reactor[8].

### *Testing of adsorbents*

The specific surface area, $S$ ($m^2/g$), was determined by the BET method on the basis of low-temperature isotherms of nitrogen determined using an 1800 Sorptomat apparatus (Carlo Erba, Milan, Italy). The percentage of carbon was determined as the decrease in sample mass during thermalanalysis in air. A Paulik and Paulik Model 1000/1500 derivatograph (L. Erdley) was used for this purpose.

X-diffractograms were determined using a DRON-2-apparatus (U.S.S.R.). A lamp with a copper anticathode and nickel filter was used. The percentage graphitization ($g$) was calculated from the equation $g = (3.44 - c/2)/0.086$ (ref. 9). Transmission electron micrographs were obtained using a TESLA BS 613 electron microscope (Czechoslovakia).

Chromatographic tests were made using a Giede 18.3 gas chromatograph (G.D.R.) and columns of 400 × 3.2 mm and 1000 × 3.2 mm I.D. Detection was performed using a thermal conductivity detector. Hydrogen was used as the carrier gas at a flow-rate of 30 ml/min. Adsorption isotherms of the test substances and their isosteric of heat adsorption were determined by the standard chromatographic method[10].

In the sample preconcentration procedure, laboratory-made cartridges were used. Minicolumns constructed from 2-ml polypropylene syringes were packed with the investigated sorbents. Two porous polypropylene discs were used as stoppers for the packing. The packing weight of the sorbents was 200 mg.

Before the sampling, each column was conditioned with 10 ml of methanol using a vacuum manifold and water aspirator. The methanol was removed under vacuum. Doubly distilled water (5 ml) was then added to each column to prepare the packing material surface for adsorption. Fortified water samples were made from a methanolic stock solution containing 100 $\mu$g/ml of each substances by diluting it to 2 $\mu$g/ml with doubly distilled water. After the samples had passed through the column, the latter was installed in the manifold and 1 ml of doubly distilled water was flushed through it. Then the adsorbed substances were eluted to the collection tube with 2 ml of *n*-hexane (for halomethanes) or ethyl acetate (for phenol and its nitro and chloro derivatives).

Preconcentrated samples were injected into the chromatograph. Recoveries of the substances from the columns are expressed as percentages.

Quantitative analysis of halomethanes was carried out by GC with a column packed with Chromosorb W–10% SE-30 and electron-capture detection (ECD). Concentrations of phenol and its nitro and chloro derivatives were determined by HPLC. A LiChrosorb Si-60 column (250 × 4 mm I.D.) with *n*-hexane–ethyl acetate (80:20) as the mobile phase at a flow-rate of 1 ml/min was used with a UV–VIS detector (254 nm) (Laboratorní Přístroje, Prague, Czechoslovakia).

## RESULTS AND DISCUSSION

Fig. 1 shows the adsorption isotherm determined for adsorbent A as an example (Table I). The shape of the hysteresis loop suggests that this adsorbent does not contain micropores whereas the course of the curve of the differential distribution of pore volume *vs.* pore radius suggests that this adsorbent contains two types of pores for which the predominant radii are 47 and 310 Å. Asymmetry of the d*V*/d log *R* = f(log *R*) relationship unfortunately indicates geometric heterogeneity of the adsorbent pores.

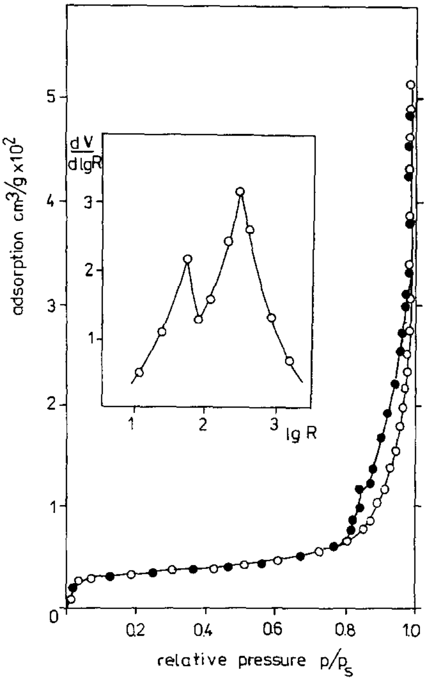

Fig. 1. Adsorption and desorption isotherms of nitrogen on adsorbent A (Table I). Inset: differential pore volume, *V*, size distribution as a function of pore radius, *R*.

TABLE I

PHYSICO-CHEMICAL PROPERTIES OF THE ADSORBENTS PREPARED BY CATALYTIC DECOMPOSITION OF *n*-BUTANE (10% Ni–$SiO_2$)

| *Adsorbent* | *Experimental conditions* | | | *C (%, w/w)* | *Specific surface area (m²/g)* | *C/2 (Å)* | *Graphitization (%, g)* | *Heat of adsorption (kcal/mol)* | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *Temperature (°C)* | *Time (h)* | *Additional modification* | | | | | *n-Hexane* | *Benzene* | *Chloroform* |
| A | 700 | 2 | – | 71.3 | 131 | 3.414 | 30.2 | 5.9 | 6.0 | 8.2 |
| B | 400 | 2 | – | 40.4 | 200 | 3.427 | 15.1 | 7.6 | 7.6 | 7.9 |
| C | 500 | 1 | 700°C 6 h | 88.1 | 147 | 3.414 | 30.2 | 5.3 | 5.8 | 5.1 |
| D | 500 | 3 | – | 76.3 | 292 | 3.453 | – | 9.8 | 8.7 | 8.5 |

The microcrystalline structure of the adsorbents was investigated by X-ray diffraction and high resulution electron microscopic methods. Fig. 2 shows the diffractograms of adsorbents A and B. The X-ray spectrum of adsorbent A possesses two sharp peaks, (002) and (004), indicating a typical two-dimensional graphite structure[11].

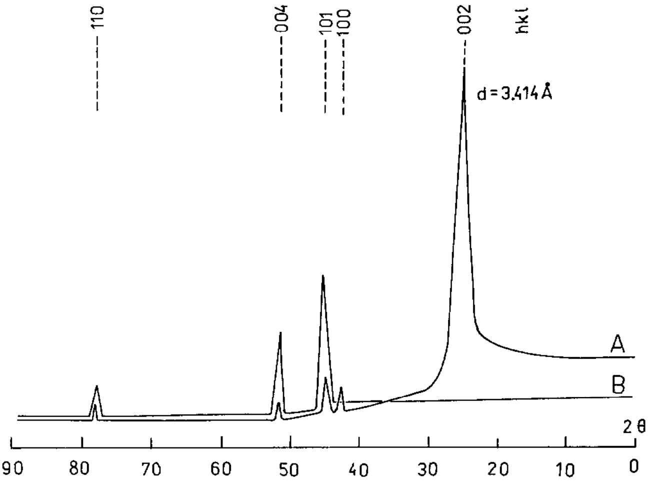

Fig. 2. X-ray diffractograms of adsorbents A and B (Table I).

In this spectrum the reflections (101) and (100), suggesting the existence of three-dimensional graphite structure in the carbon deposit, are also observed. The mean interplanar distance *c/2* for adsorbent A is equal to 3.414 Å, which indicates that 30.2% of this deposit is graphitized. This is a relatively high ordering of the structure of the carbon prepared at relatively low temperature, *i.e.*, 700°C (adsorbents A and C, Table I).

The spectrum of adsorbent B possesses the significant reflections (101) and (004). This points to a lower structural ordering of the adsorbent in comparision with adsorbent A. The interplanar distance for adsorbent B is $c/2 = 3.427$ Å, which suggests that only 15.1% of the adsorbent is graphitized (nevertheless, the two-dimensional and in some parts three-dimensional ordering is observed within the carbon deposit).

After measuring the half-width of the (100) reflection, the mean dimensions of graphite bands can be determined from Scherrer's equation. It has been calculated that within the investigated carbon deposits the crystallite dimensions are 80–120 Å. However, the heats of adsorption of the test substances are relatively low (Table I).

The topography of the adsorbent surfaces was examined by high-resolution electron microscopy. Fig. 3a and b show the micrographs of adsorbents A and B. It can be seen that two completely different structures of the carbon were obtained. These adsorbents differ mainly in the mode of suporting a nickel catalyst. Adsorbent A was impregnated before carburization with a methanolic solution of nickel nitrate whereas with adsorbent B the catalyst was supported from an aqueous solution of a

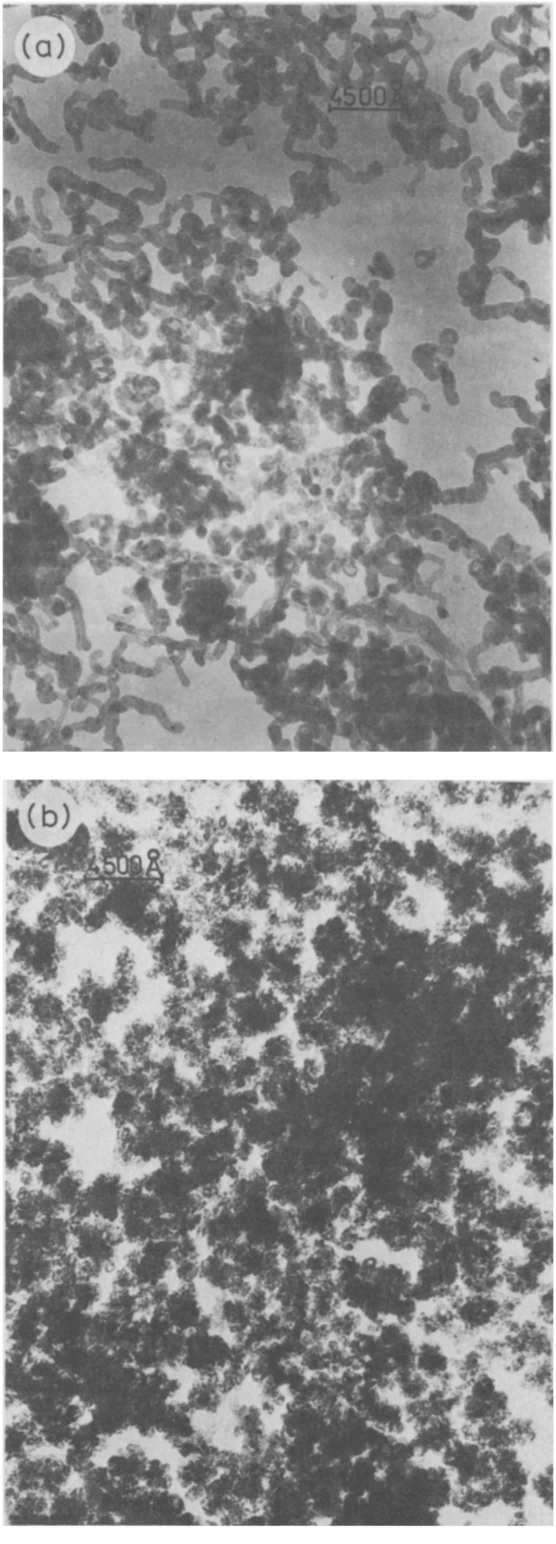

Fig. 3. Carbon layer deposited on (a) adsorbent A and (b) adsorbent B (magnification 22 000 × ).

nickel salt. The different methods of preparation of the $Ni(NO_3)_2 \cdot 6H_2O$ catalyst affect the sizes of the nickel crystallites after the reduction[12,13], which determines, in turn, the structure of the carbon deposit. When the catalyst is prepared from an aqueous solution, the nickel crystallites obtained after reduction are significantly smaller than those when an organic solvent is used[12,13]. As a result, the carbon deposit obtained on the surface of adsorbent A has the form of filamentous crystallites, the so-called "wiskers" (Fig. 3a). The wiskers formed on the adsorbent surface are composed of carbon tubes of different sizes, their diameters ranging from 350 to 800 Å and lengths from 3000 to 7000 Å. The thickness of the wisker walls varies from 120 to 300 Å and the inside diameter of the wiskers from 30 to 60 Å. This probably causes the poor mechanical properties of the carbon adsorbent and its opaque grains.

With adsorbent B, in which nickel dispersion is high, the carbon deposit containes compact agglomerates of a spherical shape (Fig. 3b). The adsorbent prepared in this way shows a slight lustre and significantly improved mechanical properties. Chromatographic measurements have shown that such a structure of the carbon deposit gives much better chromatographic properties.

Adsorption isotherms of *n*-hexane, benzene and chloroform (Fig. 4) determined with the prepared adsorbent suggest that in spite of the relatively low specific surface areas (Table I), the adsorbents are characterized by high sorption capacities for model substances in comparison with carbon–silica adsorbents obtained by carbonization of alcohols[14] or methylene chloride[15]. The adsorption values at a given pressure are significantly higher whereas the heats of adsorption of the test substances are relatively low (Table I).

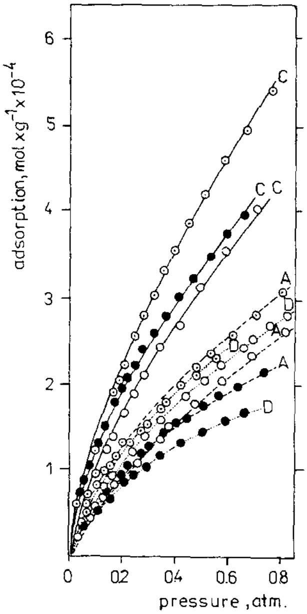

Fig. 4. Adsorption isotherms of (○) chloroform, (●) *n*-hexane and (⊙) benzene on the investigated adsorbents (Table I).

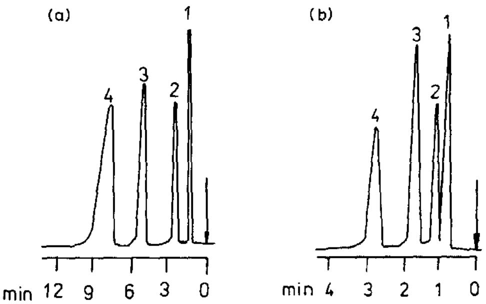

Fig. 5. GC separation of (a) aqueous solution of alcohols and (b) ketones on adsorbent B. Column, 400 × 3.2 mm I.D.; Column temperature, 120°C; flow-rate, 30 ml/min; detector, thermal conductivity. Peaks: (a) 1 = water, 2 = methanol, 3 = ethanol, 4 = *n*-propyl alcohol; (b) 1 = dimethyl ketone, 2 = methyl ethyl ketone, 3 = methyl *n*-propyl ketone, 4 = methyl *n*-butyl ketone.

The adsorbents characterized by a graphite-like structure show a non-specific nature of the surface which should be useful from a chromatographic viewpoint. They are used mainly in GC, especially to separate strongly polar substances (alcohols, fatty acids, etc.). Fig. 5a shows the chromatographic separation of an aqueous solution of light alcohols ($C_1$–$C_3$) on the adsorbent B as an example (Table I). The adsorbent surface is strongly non-polar, as confirmed by the fact that water is eluted before methanol. On this adsorbent we also obtained good separations of ketones (Fig. 5b), cyclichydrocarbons (Fig. 6a) and light hydrocarbons ($C_1$–$C_4$, Fig. 6b).

Carbon adsorbents possess very good selectivity, but unfortunately on this column no satisfactory separations of higher hydrocarbons and their derivatives were obtained. This is connected with the decrease in column efficiency and chromatographic peak broadening with increasing chain length or the presence of aromatic rings in the chromatographed substances. Knox *et al.*[11] suggested that deactivation of this very strong interaction between the carbon surface and chromatographed substances could be effected by prior adsorption of high-molecular-weight additives. This may influence the improvement in column efficiency for molecules of high molecular weight.

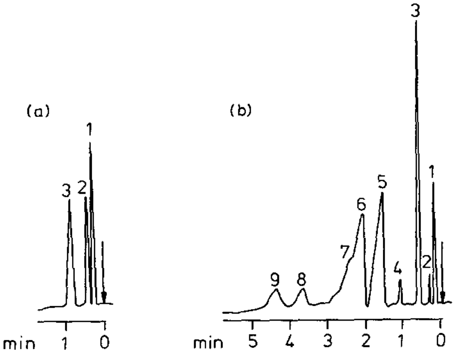

Fig. 6. GC separation of (a) cyclic hydrocarbons and (b) light hydrocarbons ($C_1$–$C_4$) on adsorbent B. Peaks: (a) 1 = cyclopentane, 2 = cyclohexane, 3 = cycloheptane. Column temperature = 150°C. Peaks in (b) are not identified.

TABLE II

RECOVERIES OF THE PHENOL AND NITRO- AND CHLOROPHENOLS ON ADSORBENTS A AND B, RP-18 AND RP-6 FOR 100-ml SAMPLES OF FORTIFIED WATER AND EXTRACTION WITH 2 ml OF ETHYL ACETATE

| *Substance* | *Recovery %* | | | |
|---|---|---|---|---|
| | *A* | *B* | *RP-6* | *RP-18* |
| Phenol | 17.1 | 29.3 | 2.2 | 4.2 |
| 2-Nitrophenol | 53.5 | 69.7 | – | – |
| 3-Nitrophenol | 51.2 | 90.7 | – | – |
| 4-Nitrophenol | 38.9 | 22.2 | – | – |
| 2-Chlorophenol | 85.7 | 85.2 | 6.8 | 14.2 |
| 3-Chlorophenol | 41.5 | 34.0 | 10.0 | 17.8 |
| 4-Chlorophenol | 30.8 | 30.8 | – | – |

The adsorbents obtained were tested for adsorption and concentration of polar compounds from aqueous solution. Tables II and III give some results for the preconcentration of phenol, its nitro and chloro derivatives and halomethanes on adsorbent A and B (Table I).

Problems with the preconcentration of polar compounds from water solution are connected with its adsorption from the water on the extraction packing and elution (desorption) of substances from the adsorbent surface by an appropriate solvent. Depending on this, the adsorbent used has to undergo a greater interaction with molecules of sorbed substances than with compounds of the water. Water is weakly retained by the carbon adsorbents presented here and is eluted before polar organic compounds (in contrast to adsorbents of the RP-8 and RP-18 type).

Chlorophenols were successfully preconcentrated with porous polymers[16,17], whereas Supelco[18] proposed the use of purge–trap samples with Carbopack B covered with 1% SP-1000 for the preconcentration of halomethanes from drinking water.

TABLE III

RECOVERIES OF THE HALOMETHANES ON ADSORBENTS A AND B, SILICA GEL AND RP-18 FOR 100-ml SAMPLES OF FORTIFIED WATER AND EXTRACTION WITH 2 ml OF *n*-HEXANE

| *Substance* | *Recovery (%)* | | | |
|---|---|---|---|---|
| | *A* | *B* | *Si-100* | *RP-18* |
| Chloroform | 47.7 | 48.4 | 34.2 | 36.0 |
| Bromoform | 12.2 | 3.6 | 3.7 | 16.5 |
| Carbon tetrachloride | 37.7 | 25.1 | 8.8 | 24.5 |

The carbon sorbents presented here do not give quantitative recoveries of tested substances, which may be due to the silica gel matrix or polar functional groups present on the carbon surface. This give a weakly polar character to the sorbents, which is reflected in specific interactions between the sorbent and polar benzene derivatives. This is a similar problem to that observed during the application of these sorbents to the separation of polar substances by GC.

The recoveries of the substances tested on these carbon sorbents were better than those with standard sorbents of the silica gel type such as RP-18 or RP-6. Pure carbon adsorbents are attractive as precolumn packings owing to their completely non-polar character and also because of their stability over a wide pH range.

## CONCLUSION

From the data obtained, there appears to be a possibility of preparing carbon or carbon-like adsorbents with a graphite-like structure characterized by good mechanical properties. The production of such carbon deposits is not difficult from the technological point of view. They can be obtained at relatively low temperatures (400–700°C). The method described here permits adsorbents with differentiated specific surface areas to be produced. The well known process of hydrogenolysis of hydrocarbons on a nickel catalyst has been applied to prepare the adsorbents. The catalyst must be carefully removed from the silica surface after its carburization because it badly affects the chromatographic separation of substances. The structure and properties of the prepared adsorbents depend on the mode of catalyst impregnation (size of the catalyst crystallites) and on the carburization process parameters. Appropriate conditions of the process (temperature, time, amount of the substance carbonized) will permit the preparation of adsorbents with any carbon content and different degrees of graphitization. The carbon deposit can be substantially graphitized without high-temperature graphitization processes.

The adsorbents prepared allow the separation of strongly polar substances and the extraction and concentration of phenol, its nitro and chloro derivatives and halomethanes from aqueous solution. Although the adsorbents described here consist of silica covered with a layer of carbon, they are called carbon adsorbents in view of the high content of the carbon deposit characterized by properties independent of the inorganic matrix.

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