EFFECT OF IMPREGNATION OF ACTIVATED CARBON WITH CHLOROPLATINIC ACID SOLUTION IN ACETONE AND SUBSEQUENT HEAT TREATMENT ON THE CARBON PORE STRUCTURE

Vladimír MACHEK[a], Vlastimil RŮŽIČKA[a] and Leoš JANÁČEK[b]

[a] *Department of Organic Technology,*
Prague Institute of Chemical Technology, 166 28 Prague 6, and
[b] *Research Institute for Chemical Utilization of Hydrocarbons,*
Czechoslovak-Soviet Friendship Chemical Works, 436 70 Litvínov

The effect of saturation of support with acetone and of subsequent heat treatment on the pore structure was studied for two types of activated carbon and platinum hydrogenation catalysts prepared from them. The observed distribution of the pore volumes with respect to the pore radii was compared with the initial pore structure of the untreated carbon. Changes in the pore distribution were found even in mild preparation conditions (calcination and reduction at 100 to 300°C). These changes are particularly pronounced in the region of bulkier macropores and depend on the carrier nature. Coating of support with platinum does not affect the support pore structure in the preparation conditions applied.

Activated carbon is frequently employed as support in the preparation of metallic hydrogenation catalysts. The commonest method of preparation of platinum support catalysts consists in saturation of the support with the active component solution and subsequent thermal decomposition and reduction of the saturated support in hydrogen gas stream. The various operations involved have been discussed in detail, *e.g.*, in refs[1-4]. The resulting catalyst properties are significantly affected by the kind and texture parameters of the carbon employed. During the catalyst preparation, the support is exposed to contact with solvent and subject to heat treatment, different according to the various preparation conditions. In the case of platinum catalysts, the heat treatment is usually conducted in nitrogen atmosphere and the reduction in hydrogen stream at temperatures 100—400°C (refs[1-5]). The preparation parameters then are related to the metal surface area, metal crystallite size, and activity of the catalyst prepared; information concerning the effect of the preparation conditions on the properties of the carrier itself is, however, usually lacking. Existing works, *e.g.*[5,6], largely deal with the effect of the carbon heat treatment on the course of oxidation and methanation studied at high temperatures (above 500°C), which, however, in catalyst preparation are applied only rarely.

In the present work, the texture properties (pore volume and size distribution) of activated carbons and platinum-on-carbon catalysts have been therefore studied and related to current preparation conditions.

EXPERIMENTAL

Chemicals. Hexachloroplatinic acid hexahydrate *p.a.* (Safina, Vestec). Acetone *p.a.*, benzene *p.a.* (both Lachema, Brno). Mercury for polarography. Hydrogen B grade, electrolytic, and nitrogen for bulbs (both Technoplyn, Prague). Activated carbon Supersorbon H8-3 (Degussa, GFR) and Norit (Norit, The Netherlands), surface (BET) 1 513 and 793 m^2/g, respectively, total pore volume V_p 0·98 and 1·42 cm^3/g, respectively, and grain size (length/diameter) 6/4·1 and 4·2/4 mm, respectively.

The catalyst preparation procedure has been described previously[2,3]. The metal was deposited on the carrier from chloroplatinic acid solution in acetone. The saturated support was dried for 2 h at temperature 75°C and pressure 3 kPa, and after drying, calcinated in nitrogen stream at the desired temperature (100, 200, 300°C). Subsequently, nitrogen was replaced by hydrogen and the sample was reduced at the same temperature. The appropriate calcination and reduction periods (3—8 h) have been discussed previously[2,3]. The pure carbon samples were treated likewise, only without using chloroplatinic acid in the saturating solution.

Determination of the pore structure. In fact, there are no unified procedures for classification and evaluation of pore structure of solids. Within the CMEA member countries, a collection of unified methods has been set up[7] for determination of the true densities, apparent densities, and pore distribution of catalysts and adsorbents; here, the pore volume distribution is recommeded to be determined based on the desorption isotherm of nitrogen (at —196°C), argon (at —196°C), or benzene (at 25°C). In our work, the pore volume distribution with respect to the pore radii was evaluated from the data of the adsorption isotherm of benzene measured at 25°C on a flow-through sorption apparatus[8], and from penetration of mercury measured on a Carlo Erba AG-60 mercury pressure porosimeter. The pore radii were calculated, in the case of the adsorption isotherm, from the relative pressure, employing Kelvin's equation with the shape factor in the range of 1—2 (refs[9—14]); in the case of mercury porosimetry, the pore radii were calculated from the mercury penetration pressure by using Washburn's equation for cylindrical pores[15]. The obtained integral dependence of the pore volume on the pore size was further differentiated by numerical central differentiation. The differential dependence corresponds basically to the frequency of pores of a radius in the pore system in question.

In view of the experimental conditions and of the physical constraints inherent in the methods used, pores measurable by mercury porosimetry are termed macropores ($R > 15$ nm), and pores with radii below 15 nm but taking part in benzene sorption are referred to as mesopores. The lower limit of mesopore radii is determined by the relative pressure of benzene at which capillary condensation takes place, which is usually about 1·5 nm. Sorption procedures for mesopore measurements have been frequently combined with mercury porosimetry for macropore volume measurements[16,17]. The total pore volume was calculated in the usual manner from the sample apparent and true densities.

RESULTS AND DISCUSSION

The two activated carbon types used differ considerably in their texture parameters: the carbon of Degussa is one with exceedingly high specific surface area, in contrast to the Norit carbon with a comparatively small surface area. The supports saturated with acetone solution of chloroplatinic acid as well as those saturated with pure solvent were further treated in the same conditions, the pore volume distribution with respect to the pore radii was established for all of the samples. The pore volumes

of the fundamental pore types, *i.e.* mesopores and macropores, are given in Tables I and II. The pore frequency distribution with respect to pore radii (in the region of 2−6310 nm) for the various samples is shown in Figs 1 and 2.

The results indicate that the saturation of support and its subsequent heat treatment effect changes in the pore structure of both carbon types. The pore volume changes are in all cases highest in the macropore, or transport pore, region; the position of the maximum for mesopores as well as their volume, on the other hand, is practically constant. It should be noted that the micropore region was not the subject of this work; micropores (pore radii below 1·5 nm) are not readily accessible by common methods of pore structure study, and interpretation of results in this region is not unique[16,17]. In Tables I and II, the experimental and calculated volumes of mesopores are compared, the latter being obtained by employing a theoretical model of porous matter with slot-shaped pores[14], in which no allowance is made for micro-
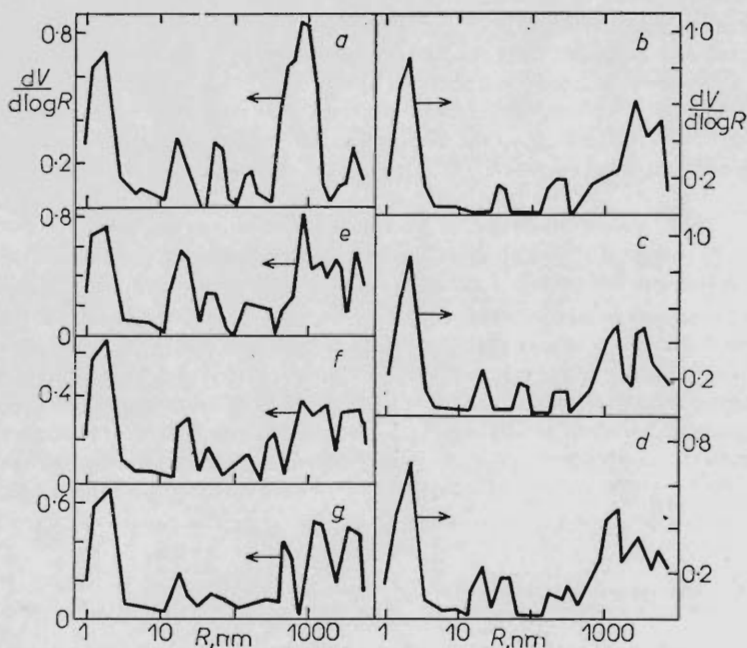

FIG. 1

Pore size distribution for activated carbon Degussa and for 5% Pt/Degussa carbon catalysts. *a* Untreated carbon, *b* carbon treated at 100°C, *c* at 200°C, *d* at 300°C; catalysts treated at *e* 100°C, *f* 200°C, *g* 300°C

pores. The high difference between the theoretical pore volumes, calculated for pores with radii lying in the $1-15$ nm region, and the experimental value, determined for pores with radii less than 15 nm, points to the presence of pores with radii below 1 nm, hence to occurrence of microporous structure.

Activated Carbon Degussa

In the case of the carbon of Degussa, the saturation of the support with pure solvent or with chloroplatinic acid solution followed by heat treatment results in the formation of supermacropores $(R > 6310$ nm), not present in the original carbon. On the support treatment the expressive maximum of macropores near 1000 nm diminishes, hence the original bidisperse structure of the carbon is less pronounced. On the other hand, there is no great difference in the pore structure of carbon saturated by pure solvent and of catalyst carbon + platinum); the coating of the carrier by the metal does not take part in the change in the carbon pore structure. As the
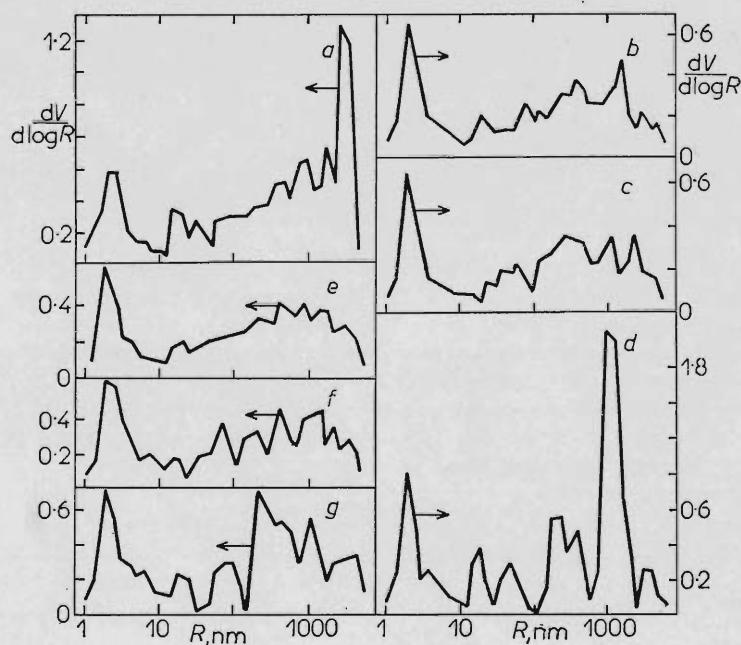

FIG. 2

Pore size distribution of activated carbon Norit and for 5% Pt/Norit carbon catalysts. *a* Untreated carbon, *b* carbon treated at 100°C, *c* at 200°C, *d* at 300°C; catalyts treated at *e* 100°C, *f* 200°C, *g* 300°C

total volume values demonstrate, the pore volume increases on the treatment. Thus the Degussa support does not change essentially under common conditions of preparation of platinum carrier catalyst; as far as the total pore volume is concerned, the pore structure is even improved.

TABLE I

Pore volume distribution with respect to pore radii for activated carbon Degussa and 5% Pt/Degussa carbon catalysts treated at 100, 200, and 300°C

Region of pore radii R nm	Pore volume V, cm^3/g						
	Degussa carbon				5% Pt/Degussa carbon catalyst		
	initial	100°C	200°C	300°C	100°C	200°C	300°C
<15 calc.	0·16	0·15	0·20	0·16	0·14	0·18	0·18
exp.	0·64	0·63	0·68	0·64	0·58	0·63	0·67
15—6 310	0·32	0·23	0·29	0·29	0·35	0·32	0·31
>6 310	0·03	0·23	0·27	0·20	0·14	0·17	0·23
Total pore volume V_p	0·98	1·20	1·18	1·02	1·43	1·01	1·12

TABLE II

Pore volume distribution with respect to pore radii for activated carbon Norit and 5% Pt/Norit carbon catalysts treated at 100, 200, and 300°C

Region of pore radii R nm	Pore volume V, cm^3/g						
	Norit carbon				5% Pt/Norit carbon catalyst		
	original	100°C	200°C	300°C	100°C	200°C	300°C
<15 calc.	0·22	0·27	0·26	0·26	0·24	0·30	0·28
exp.	0·43	0·46	0·46	0·46	0·41	0·49	0·47
15—6 310	0·88	0·62	0·56	0·80	0·65	0·57	0·63
>6 310	0·00	0·28	0·22	0·04	0·29	0·29	0·08
Total pore volume V_p	1·42	1·12	1·04	1·29	1·18	1·32	1·23

Activated Carbon Norit

In this case, too, saturation of the support with pure solvent or chloroplatinic acid solutions leads to a change in the volume of larger macropores $(R < 500\ nm)$, which is additionally dependent on the treatment temperature. In contrast to the Degussa carbon, temperature rise favours restoration of the pore structure of the initial carbon. In the case of samples calcinated and reduced at 100 or 200°C, the sharp maximum for pores near $R = 2500\ nm$, very marked in the untreated carbon, vanishes. The pore volume distribution spreads wider, as far as the supermacropore region. The pore volume and frequency distribution is similar for the support and the catalyst treated at 100 or 200°C. The fact is confirmed that at lower calcination and reduction temperatures the change in the support properties resulting from oxidation and methanation of carbon (platinum-catalyzed) is negligible; only calcination and reduction at 300°C restore to an extent the pore volumes found in the initial support. The maxima on the distribution curve are, however, shifted to lower pore radii (200, 1 000 nm). Nevertheless, the total pore volume in all of the Norit series samples is lower than in the untreated carbon. Thus after saturation of the support with pure solvent or chloroplatinic acid solution, part of the pore volume remains blocked. Obviously, then, the activated carbon Norit is more sensitive even to such mild preparation conditions. From this point of view, the activated carbon of Degussa is better suited for preparation of platinum-on-carbon type catalysts.

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