EFFECT OF THE STRUCTURE OF ACTIVATED CARBON ON ITS SATURATION BY HEXACHLOROPLATINIC ACID

Vladimír MACHEK, Marie ŠOURKOVÁ and Vlastimil RŮŽIČKA

Department of Organic Technology,
Prague Institute of Chemical Technology, 166 28 Prague 6

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The kinetics and equilibrium of adsorption of hexachloroplatinic acid on activated carbon was studied. The time course of saturation by chloroplatinic acid dissolved in water and in acetone, respectively, was examined on three types of activated carbon with different texture parameters. The effect of the support properties on the shape of the adsorption isotherm for the acid in solution was also investigated.

Hydrogenation catalysts of the type of platinum on carbon hold a important position among metallic supported catalysts. The catalysts can be successfully prepared if the relations between the preparation conditions, catalyst structure, and catalytic properties are solved. Generally, preparation of supported catalysts involves the following steps: impregnation of the support with the active component, its drying, thermal decomposition and reduction of the active component in the saturated support. Of these, the way of support impregnation with the active component is of crucial importance for the subsequent formation of the catalyst properties[1-5].

In the present work we have concerned ourselves with the pore structure of activated carbon and the course of their saturation by chloroplatinic acid from solutions.

EXPERIMENTAL

Chemicals. Hexachloroplatinic acid hexahydrate *p.a.* (Safina, Vestec). Acetone *p.a.* (Lachema Brno). Activated carbon Supersorbon H8-3 (Degussa, GFR), Norit RB 1 and Norit (without specification) (both Norit, The Netherlands); the samples were dried for 6 h at the temperature 95°C and pressure 2 kPa, and prior to use, boiled for 1 h in the solvent in question.

Saturation kinetics and equilibrium. The time course of the saturation and the adsorption isotherm were measured as described previously[6,7]. The chloroplatinic acid solution circulated through a fixed bed of the support, so that the process occurred in gradient less conditions and the active component was applied to the support in a defined way. The initial concentration of the acid solution for the saturation was chosen such that the content of platinum in the solution corresponded to 5% weight of the carrier. The acid concentration was determined colorimetrically at 400 nm by using a SPEKOL colorimeter (Zeiss, Jena).

The adsorption isotherms were examined in the concentration range of 2—100 g of chloroplatinic acid in 1 l solution. The adsorption isotherms were represented by the dependences of the adsorbed quantity of chloroplatinic acid (per unit weight of the support) on its equilibrium

concentration in the solution. The kinetics and equilibrium of the saturation were measured at 20°C.

Pore structure. The pore volumes were evaluated from the data of the desorption isotherm of benzene measured at 25°C on a flow-through sorption apparatus[8,9], and from the data of penetration of mercury, measured on a Carlo Erba-AG60 mercury penetrometer[10]. In view of the experimental conditions and physical limitations of the methods used, the pores measured by mercury porometry are referred to as macropores (pore diameter exceeding 15 nm), those measurable by the benzene sorption method and with diameter below 15 nm, as mesopores. The lower limit of the mesopore radius is given by the relative pressure of benzene at which capilalary condensation takes place (typically about 1·5 nm).

The heats of wetting were measured in the routine way in an adiabatic calorimeter[11,12].

RESULTS AND DISCUSSION

The texture parameters of the supports under study cover practically the entire region that comes into consideration for activated carbons employed as catalyst supports: the Degussa carbon is one with a large surface area, the Norit RB 1 and Norit samples represent carbon types with medium and relatively small surface areas, respectively. The parameters are given in Table I.

The course of adsorption of chloroplatinic acid on the supports was represented by the dependence of the concentration of the active component in the saturation solution on the saturation period. This dependence was converted to the dependence of the adsorbed quantity of the acid on time per unit size of the support grain.

The transfer of the dissolved substance from the solution into the porous grain is characterized by the diffusion equation[13], the solution of which is the dependence of the adsorbed quantity of the dissolved substance on the $(Dt/R^2)^{1/2}$ coordinate. The effective diffusion coefficient is dependent upon the nature of the diffusing matter, that of the medium, and the texture of the porous grain; it is usually defined by the relation[14] $D = D_0(\varepsilon/\tau)$, where D_0 is the bulk diffusion coefficient of the dis-

TABLE I

Texture parameters of the activated carbons used: specific surface area S, pore volume, porosity ε, mean pore radius R_p and mean particle size R

Activated carbon carbon	S m^2/g	Pore volume cm^3/g			ε	R_p nm	R mm
		total	meso	macro			
Degussa	1 513	0·98	0·63	0·35	0·66	1·3	2·2
Norit RB1	1 177	0·82	0·45	0·31	0·62	1·3	0·9
Norit	793	1·42	0·43	0·93	0·78	3·6	2·1

solved substance in the free solution, ε is the porosity, and τ the tortuosity of the porous support.

In the case in question, the supports were saturated from the same solution, so that in a mutual comparison of the supports the effect of medium on the rate of adsorption is eliminated, and the differences in the course of the saturation are to be ascribed to the pore structure of the supports, characterized by the porosity and the tortuosity. The time courses of saturation of carbon by chloroplatinic acid from water and from acetone are shown in Figs 1 and 2, respectively. The rate of saturation from the two solvents increases in the carbon series Norit RB < Degussa < Norit. The total pore volume, or porosity, increases in the same order. It is apparent from Table I that decisive for the rate of adsorption is the occurrence of macropores; this has been observed[15] also for other types of activated carbon.

When the $\varepsilon(t/R^2)^{1/2}$ coordinate is introduced, the shape of the time course of saturation alters (Figs 3 and 4). The curves for the Norit and Degussa supports are nearly identical, indicating that the differences in the rates of saturation for the two supports are due to the different pore volumes; the complexity of the pore system, characterized by the tortuosity parameter, can be assumed to be similar for the two supports. The Norit RB 1 support, on the other hand, differs in the behaviour from two other ones: the course of saturation on this carbon type remains slower even

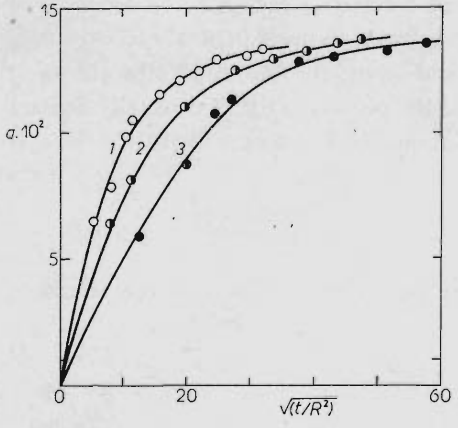

FIG. 1

Course of saturation of activated carbon samples by chloroplatinic acid dissolved in water. Activated carbon: *1* Norit, *2* Degussa, *3* Norit RB 1

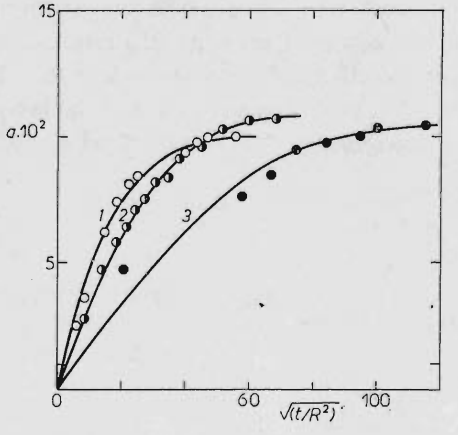

FIG. 2

Course of saturation of activated carbon samples by chloroplatinic acid dissolved in acetone. Activated carbon: *1* Norit, *2* Degussa, *3* Norit RB 1

if the porosity is included in the time coordinate (Figs 3 and 4). Apart from the smallest pore volume, the pore structure in this support is obviously more complex than in the Norit and Degussa supports.

The adsorption isotherms for the systems under study are shown in Figs 5 and 6. The effect of the solvent nature on the adsorbed quantity has been discussed previously[7].

As the results indicate, the decisive parameter affecting the adsorbed quantity is the specific surface area of the support. The maximum quantity of chloroplatinic acid adsorbed from the two solvents increases in the sequence Norit < Norit RB 1 < Degussa, which is also the order of the specific surface area values. Fig. 7 gives the correlation between the maximum adsorbed quantity of chloroplatinic acid and the surface area of the carbon for water and acetone as the solvents. It should be mentioned that all the considerations were made assuming that the chemical nature of the surface was the same for the three supports in question. In fact, various active functional groups (carboxy, carbonyl, hydroxy, lactone, *etc.*) are formed on the surface of activated carbon during its preparation[16,17], and their kind and amount can affect appreciably the adsorption ability of the carbon for adsorption of substances of different chemical nature (polarity). In view of the hydrophobic nature

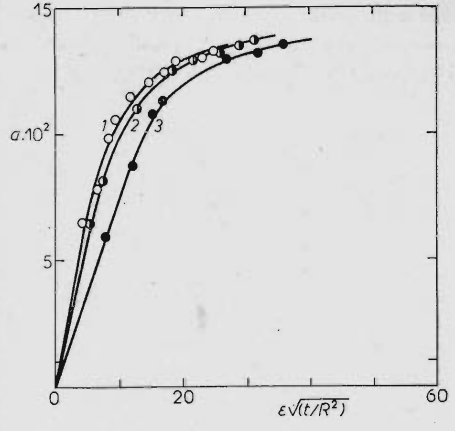

FIG. 3

Course of saturation of activated carbon samples by chloroplatinic acid dissolved in water. Activated carbon: *1* Norit, 2 Degussa, *3* Norit RB 1

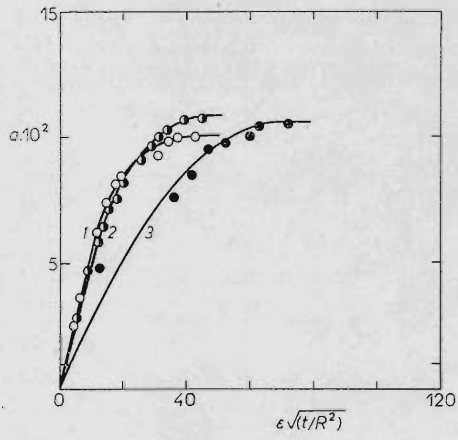

FIG. 4

Course of saturation of activated carbon samples by chloroplatinic acid dissolved in acetone. Activated carbon: *1* Norit, 2 Degussa, *3* Norit RB 1

of activated carbon, water and acetone represent media different enough for the possible differences in the surface composition of the carbons to show up in the adsorption of chloroplatinic acid. As Fig. 7 demonstrates, the dependence of the maximum adsorbed quantity of chloroplatinic acid (as obtained by extrapolation of the saturated part of the adsorption isotherm) on the specific surface area of the carbon is linear in both cases, which bears out the assumption of the same mechanism

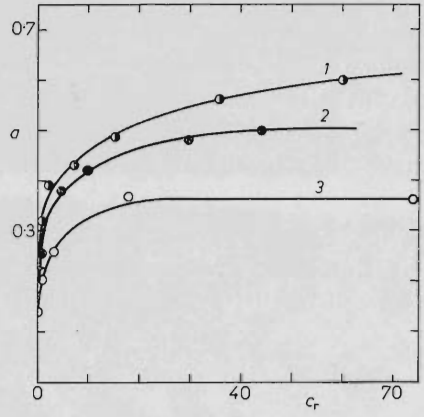

FIG. 5

Adsorption isotherms of chloroplatinic acid dissolved in water. Activated carbon: *1* Degussa, *2* Norit RB 1, *3* Norit

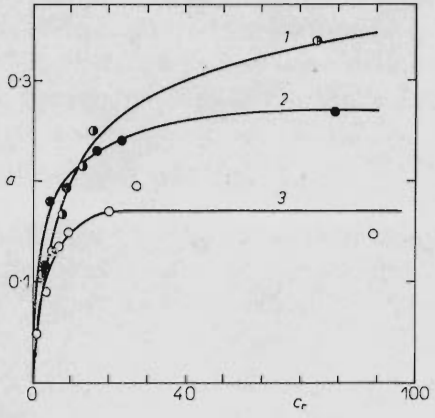

FIG. 6

Adsorption isotherms of chloroplatinic acid dissolved in acetone. Activated carbon: *1* Degussa, *2* Norit RB 1, *3* Norit

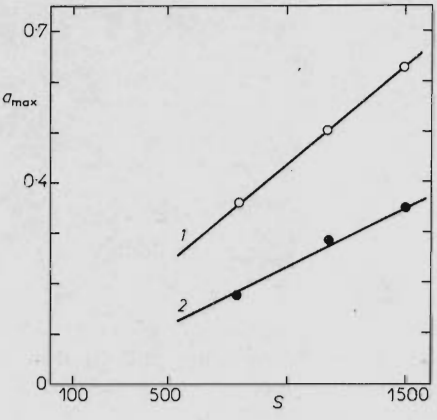

FIG. 7

Relation between the maximum adsorbed amount of chloroplatinic acid and surface area of the supports. *1* Saturation from water, *2* saturation from acetone

TABLE II

Initial rate of saturation of the support r_0, specific adsorbed amount of chloroplatinic acid $a_{max,s}$ and specific heat of wetting of the support Q_s

Activated carbon	r_0 mg/g $s^{1/2}$ mm	$a_{max,s}$ mg/g	Q_s mJ/m^2
	solvent: water		
Norit	17·1	0·45	34
Degussa	9·7	0·41	34
Norit RB1	5·7	0·42	26
	solvent: acetone		
Norit	6·3	0·23	104
Degussa	3·9	0·23	88
Norit RB1	1·8	0·24	97

of adsorption from water and from acetone. Also, the adsorbed quantity per unit surface area of the support does not vary substantially within the surface area region studied (Table II, column 3).

The heats of wetting the activated carbons by water and acetone, respectively, were also measured (Table II), as the values can be looked upon as a measure of the interaction between the activated carbon and the solvent. The specific (per 1 m^2 surface area of the support) heat of wetting for a solvent does not vary appreciably for the carbon samples examined. This fact, too, supports the assumption that the surface of the three samples is of similar nature.

LIST OF SYMBOLS

a	adsorbed quantity of chloroplatinic acid on activated carbon (g H_2PtCl_6/g support)
a_{max}	maximum adsorbed quantity of chloroplatinic acid on the support (g/g)
$a_{max,s}$	specific adsorbed quantity of chloroplatinic acid on activated carbon (g/m^2)
c_r	equilibrium concentration of chloroplatinic acid in solution (g/l)
Q_s	specific heat of wetting (J/m^2)
r_0	initial rate of saturation of the support by chloroplatinic acid (g H_2PtCl_6mm/g $s^{1/2}$)
R	mean radius of the support particles (mm)
R_p	mean radius of the pores (nm)
S	specific surface area of the support (m^2/g)
t	saturation period (s)
ε	porosity
τ	tortuosity

REFERENCES

1. Moss R. L. in the book: *Experimental Methods in Catalytic Research* (R. B. Anderson, Ed.), Vol. II, p. 43. Academic Press, London 1976.
2. Anderson J. R.: *Structure of Metallic Catalysts*, p. 164. Academic Press, London 1975.
3. Brunelle J. P., Sugier A., LePage J. F.: J. Catal. *43*, 273 (1976).
4. Brunelle J. P. in the book: *Preparation of Catalysts* (B. Delmon, Ed.), Vol. II, p. 211. Elsevier, Amsterdam 1979.
5. Delmon B., Houalla M. in the book: *Preparation of Catalysts* (B. Delmon, Ed.), Vol. II, p. 439. Elsevier, Amsterdam 1979.
6. Stunová M.: *Thesis*. Prague Institute of Chemical Technology, Prague 1979.
7. Machek V., Hanika J., Sporka K., Růžička V.: This Journal, in press.
8. Davies R. G.: Chem. Ind. (London) *23*, 160 (1962).
9. Innes W. B. in the book: *Experimental Methods in Catalytic Research* (R. B. Anderson, Ed.), Vol. I, p. 44. Academic Press, New York 1968.
10. Washburn E. W.: Proc. Nat. Acad. Sci. U.S.A. *7*, 115 (1921).
11. Juliš J., Hodek J., Jehlička V., Zábranský M.: *Návody pro laboratorní cvičení z fyzikální chemie*. Published by SNTL, Prague 1974.
12. Gravelle P. C.: Catal. Rev., Sci. Eng. *16*, 37 (1977).
13. Crank J.: *The Mathematics of Diffusion*, p. 84. University Press, Oxford 1964.
14. Kraus M., Schneider P., Beránek L.: *Chemická kinetika pro inženýry*, p. 315. Published by SNTL, Prague 1978.
15. Schnabel K. H., Parlitz B., Sacharov A. I., Dubinin M. M.: Z. Anorg. Allg. Chem. *389*, 43 (1972).
16. Cookson J. T. in the book: *Carbon Adsorption Handbook* (P. N. Cheremisinoff, Ed.), p. 249. Ann Arbor Science Publ., Ann Arbor 1978.
17. Kipling J. J. in the book: *Porous Carbon Solids* (R. L. Bond, Ed.), p. 65. Academic Press, London 1967.

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